

Library of Processes

Nanopatterning, Production and Applications
based on Nanoimprint Lithography

Third edition with results of the NaPANIL-project, August 2014

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NaPANIL – Library of Processes

Nanopatterning, Production and Applications based on Nanoimprint Lithography

Third edition of the NaPa Library of Processes

with results from the NaPa-project, 2004 – 2008,
and from the NaPANIL-project, 2008 – 2012
revised and updated, August 2014



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The content of this work is the sole responsibility of the authors. However, the authors of the processes are not liable for errors in the descriptions or for improper use of processes that use dangerous or poisonous media. We are not liable for any misuse; the recipes are not error proof.

This library intends to be of help for a researcher, engineer or technician experienced in basic chemical and lithographic processes. It is intended for a person who is familiar with basic cleanroom and chemical process knowledge. The processes described in this library do not have the same level of maturity. Some of the recipes cannot be used without significant own further development. Therefore, the user should make a distinction between processes which are ready to use or which are still in development.

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NaPANIL - Library of Processes

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NaPa and NaPANIL – and the “NaPa Library of Processes”

From 2004 to 2008, the EU Integrated Project “Emerging Nanopatterning Methods” (NaPa) brought together 35 leading academic and industrial European institutions with a vast amount of expertise in nanofabrication. The NaPa consortium integrated the new patterning methods, **Nanoimprint Lithography**, **Soft Lithography & Self-assembly** and **MEMS-based based Nanopatterning**, into one project, both anticipating and responding to the increasing need for technologies, standards and metrology required to harness the new application-relevant properties of engineered structures with nm-scale features. In addition to the further development of process technology, including processes, tools, and materials, a range of applications was an intrinsic part of NaPa. This went far beyond the development of next generation nanolithography for chip manufacturing. While at the beginning of the project many processes were still at an embryonic stage, towards the end of the project many processes have gone through a phase of consolidation. An example for this is that during the last last years many applications have emerged. The research in the three overarching themes was supported by developments in the subprojects **Materials**, **Tools** and **Simulation**, and **Dissemination** activities towards the public.

The project **NaPANIL**, from 2008 to 2012, can be considered as the natural follow-up to NaPa. Although different in the range of processes and the orientation towards industrial applications, it takes up the impetus generated by NaPa and adds some essential ingredients in terms of the **value chain of manufacturing**, which goes further than the original NaPa subproject “Nanoimprint Lithography” with its workpackages **Stamps**, **Processes** and **Applications**. In NaPaNIL, a Large Scale Integrating Collaborative Project on “Nanopatterning, Production and Applications based on Nanolithography”, the focus is on applications, with three industrial applications stemming from different fields as the drivers for process development. In this library, we will nevertheless focus on contributions of **Manufacturing Technology**, the largest subproject within the project, and add contributions from more research oriented applications. The main reason is that we do not want to disclose the entire value chains of the industrial applications, since – although each protected by intellectual property – we are aware that much knowhow does not lie in the “what?” but also “how?”

One of the main outputs of NaPa was the **NaPa Library of Processes** (NaPa LoP) which included processes for scalable and cost-efficient manufacturing of e.g. polymer-based optical elements, organic LEDs and lab-on-a-chip systems among others. The NaPa library consisted of 27 processes, which was a small fraction of the process developed during the project. Originally, it was planned that this library would be a “living document”, which would constantly grow with contribution from former NaPa members or others. This is now possible within the **NaPANIL**-project, in its role as a successor of NaPa, since most of the research partners in NaPANIL were already participating in the NIL-related workpackages in NaPa.

Although NaPANIL is focused mainly on process chains leading to selected industrial applications, a range of processes have been developed, from which some were selected for this LoP. Furthermore, we included many of the processes from NaPa (related to ongoing work from partners in NaPa), in order to make the NaPANIL LoP the successor of the NaPa LoP, which found their way into students’ education and as a resource for researchers and engineers interested in NIL processes. Thus, NaPANIL, as NaPa, offers a unique opportunity to unleash the potentials of nanotechnology in Europe.

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The NaPANIL project

The concept of the NaPANIL project is based on application fields with very high potential impact but with no mature production processes developed yet. The NaPANIL consortium has identified potential target applications for large-scale implementation and upscaling to industrial production of tools, materials, processes and know-how developed in the **nanoimprinting lithography (NIL)** workpackages of the project. The applications chosen are based on the idea of controlling light at surfaces using **nanoscale 3-dimensional surface structures**. In the moment, there is no efficient production method available for this kind of surfaces and the aim in this project is to develop and qualify processes that can produce such surfaces in small scale production environments. The focus of this project is driven by our end-user partners, on applications with surface areas in the range from a few mm to tens of cm. These include mobile applications, automotive applications, housing and spot lighting. Additionally to the Polymer Diffractive Optical Element (PDOE), Light DIrectional Device (LDIR), emissive Head Up Display (eHUD), a range of more exploratory research devices were chosen to complement the industrial applications.

The central part of the NaPANIL project is **nanoimprint lithography (NIL)**, a replication process, which makes a difference to state-of-the-art manufacturing techniques. It is a moulding process, if based on heating and cooling also called (hot) embossing, which uses mechanical means to shape a mouldable material instead of patterning with very advanced photolithographic steps. The main step is therefore the displacement of material by force and capillary action. The big advantages of moulding are:

Throughput: Processes such as injection moulding and roll embossing are considered as fabrication proved high volume production processes with a high degree of market penetration. This means that small and medium sized enterprises can use these techniques for their own in-house fabrication. Furthermore, companies are available which offer replication services, i.e. pharmaceutical enterprises that do not want to be involved in fabrication use the expertise of specialized enterprises. Back up and redundancy is more important than proprietary processes.

Parallel: In Compact Disc (CD) moulding, many data pits are transferred from a master to the moulded part by filling a cavity with a polymer. This data transfer rate is unmatched by other techniques. Scaling up can be done by using larger formats (cavities), but mostly by enhancing the resolution.

Resolution: sub-10nm replication has to be proven, and because NIL is a mechanical process, the limitation of the process is given by the availability of the masters rather than by restrictions of the process.

Low-cost: It is valid as long as low-cost polymers are used instead of expensive metals, glass and silicon. However, as always, low cost has to be referred to the entire process chain, and apart from materials, the energy consumption and the number of copies possible with one master stamp are becoming important inputs for the Cost of Ownership (CoO). In many applications, the materials used for replication are considered as low-cost, i.e. in the case of PDOE, standard polymer foils (PMMA) will be used, in the case of LDIR glass and sol-gel materials from standard original materials and in the case of eHUD standard glass and polymers. The interesting thing about these applications is that the cost criteria are quite different. While an eHUD can be sold for a few hundreds of EUR, the illumination device for PDOE should not be more expensive than a few cent. This is also the price tag for the LDIR application, where larger areas have to be replicated with more requirements on lifetime and durability.

Apart from throughput, low-cost, high-resolution parallel fabrication, replication offers more than this:

Freedom of materials: Because NIL is a mechanical process, almost every material can be processed. The main prerequisite is that the mechanical properties of stamp and mouldable material are sufficiently different during the process (e.g. by heating up) that the mouldable material can be patterned while the stamp can be retrieved without damage and reused. This is way apart from a range of polymers and sol-gels can be used as a template.

3D patterning and moulding of complex shapes: If you need to mould 3D instead of 2D surface structures, as needed for saw-tooth, multi-level, lens-like structures, in most cases you need a more complex stamp and continue as used in 2D patterning. But you need also a way to fabricate the stamp – in a reproducible way. Often there is only a limited set of processes suitable for 3D patterning, and they are less reproducible than the more established 2D processes. If 3D stamps are saw-tooth like (symmetric or asymmetric), i.e. with sloped walls, there are a few ways to do this, by gray tone lithography, ion-beam etching or lithography with inclined beam. Often these techniques do not allow a var-

iation of the slope within the pattern. Multilevel structures are fabricated by multiple, aligned lithography. With each level, overlay issues will become more prominent. A stamp with a defined 3D shape with different levels is self-aligning, i.e. all levels are fixed and every replication will mould exactly the same shape as the previous one. Tolerances are therefore more relaxed. Lens-like structures are fabricated using reflow or isotropic etching processes. Large areas are often not possible because the initial structures have to be fabricated by high-resolution techniques. In addition, here, a mould with a defined structure needs to be replicated in S&R for devices.

Small and big structures in one step: As in patterned media, small bits can only be detected if there are large structures as border or for orientation. Large structures often also allow the handling and are used for process validation. Although most lithography techniques allow for the patterning of large and small patterns, too, often this is not economically or the writing strategy for mask patterns are not optimized for both kind of patterns. In NIL this is a question of the amount of material to be displaced.

Advances in with respect to the state of the art in 2007: The former development in the worldwide community was marked by the following convictions:

Thermal NIL was considered as useful for large area because of its ability to use large stamps. However, because of thermal expansion and high thermal capacities, high throughput is only achieved in a parallel way. UV-NIL was considered as more appropriate by using the step and repeat (S&R) approach for CMOS with repeated dies on one substrate. Transparent substrates enable easy alignment of patterns if multiple levels are needed.

Today, these rules are only partly valid: Thermal NIL has developed hybrid strategies, with thermoplastic resists which can be cured by heat or UV-light. UV-NIL has expanded to large area by using thin flexible stamps. Both techniques use more and more stamp copying processes to ensure lifetime of the original mould.

CMOS was still considered as one of the major application fields for nanoimprint lithography (NIL). Because CMOS is only linked to a few centres in Europe, and major players are from US and Asia, Europe was always stressing the fact, that other applications than CMOS would be important, if not dominant for the introduction of NIL into the production lines.

In 2009, the major industrial players pointed out that they deliver more machines to patterned media and optical devices. This is large area, while at the same time the complexity of the processes was reduced. CMOS was mostly aiming for replacing single lithographic process steps based on DUV by NIL, i.e. many lithographic levels are exposed as before, and for the first with highest resolution requirement, NIL would be used for resist patterning. One example to reduce the number of lithographic levels was the introduction of the dual-damascene process, which reduces the number of lithographic steps per level from 20 to 7 by using a multilevel (multi-tier) stamp. However, there is still a number of levels and the main problem is overlay remains the same. Pattern media, in contrast, needs one level to be patterned, with a rather simple (uniform) dot pattern over the entire disk surface. Here the introduction of microstructures for alignment causes most of the complexity, as well as the fabrication of the large area master in good quality. This is the reason why most of the enterprises testing NIL for patterned media are favouring a stamp copying strategy for higher throughput and reliability. One very expensive master is copied into many daughters, and these daughters further processed are used in a production environment.

The processes used in NaPANIL will be mostly taken for a toolbox already available by different partners. This includes a range of nanoimprint lithography variants, but also processes for upscaling in area and speed, large area imprint (embossing), roll-to-roll (R2R) embossing, step&repeat NIL and injection molding. These are proved manufacturing techniques, which are „upscalable“.

The unique thing about NaPANIL is that NIL is used not only as a low-cost replication process, but also as a means for stamp manufacturing. This makes it necessary that many partners with sound experience in NIL, including stamp manufacturing, will cooperate in order to find process flows which lead to the desired results. We have established a data base / tool box in NaPa. Now we have to employ it to specific applications. The strategies for that are:

- Make stamp originals with simple 3D geometries with known litho/etching techniques
- Use Step&Repeat machines for surface enlargement
- Use multi-level embossing for building up complex geometries
- Use stamp copies (working stamps) instead of originals
- Test them in high throughput manufacturing

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PART I : INTRODUCTION – A GUIDE TO NANOPATTERNING

1. Summary

This library is not an *introduction to nanopatterning*, with long introductions into the fundamentals of different processes and explanations about the limitations of processes. Nor is it presenting the state-of-the-art, i.e. the newest developments and shippings around the world. It is also not complete; therefore, many nanopatterning methods are missing. This is subject of publications, reviews and books. What is it then?

This introduction is like a *cookbook*, and a cookbook should be simple. It also requires a certain amount of familiarity with the subject. As in cookbooks, it will rather be a collection of processes, recipes, references, which can be selected without reading the entire book. It is the result of the European Integrated Project *NaPa*, and continued and enlarged with processes from European Large Scale Project *NaPANIL*, which during a total of 8 years period gathered scientists and engineers to develop a range of nanopatterning method, with the aim that they become enabling techniques for a range of institutes and applications.

In this library of processes (LoP) the need of applied scientists and process engineers in research and industry for reliable patterning processes is addressed. It is an introduction into basic nanopatterning processes from a practical point of view, and complements the reviews and publications already published in books and journals in a unique way only possible by a collective approach. This is done for the parallel patterning methods developed in the *NaPa* project, with a focus on thermal nanoimprint lithography (NIL), but it also takes up the input from the two other main processes for parallel processing from the *NaPa* project, soft lithography (SL) and stencil lithography (STEN). The aim is to enable researchers and engineers to choose from different processes depending on the specific challenges of a new application. Three different approaches are provided, ordered in two parts. In the first section of this *Part I* we try to satisfy the beginners' needs for practical advice, with easy-to-go recipes in a cookbook fashion. A second section gives more information about general processing issues, by presenting standard lithographic processes with emphasis on single layer pattern transfer. In addition to the *NaPa* Library of Processes, the reader will also find hybrid manufacturing processes and value chains. *Part II* - an appendix – is a collection of more elaborate processes, which – depending on equipment and application – can vary to a large extend. This collection of recipes is intended for the experienced user, and has to be complemented by the technological literature in publications and patents. The library does not have the ambition to cover every aspect of the processes used. It could serve as the basis for a living document, which – depending on its way of dissemination – can be an integral part of the nanofabrication community.

2. To Whom this Library is Addressed

Alternative nanopatterning methods are needed both by research institutes and by industry. This library is aimed on these different users, with the idea in mind that the *comparison of processes*, rather than the *description of single processes*, helps to step into the manufacturing. The library, however, is not meant to be a buyers' guide for building up a new nanoimprint laboratory or production site. Real comparisons of processes can only be made by benchmarking with defined rules and boundary conditions. In the last four years several rounds of benchmarking were performed on NIL within *NaPa* and *NaPANIL*. The main result can be described as the following: good results can be achieved with almost any kind of equipment currently on the market, and different applications may profit from the advantages of different equipment. The resulting machine is often a compromise. Restrictions of flexibility, alignment, speed, technological limitations can be overcome by further developing both, equipment and processes. The user will profit from the competition between manufactures. However, the lack of standards makes the comparison of tools difficult to the customer and demands a high level of knowledge about the state of the art.

3. Towards a Library of Processes for Alternative Lithography

3.1 Introduction

The vast number of publications, which describe complex processes and are often only valid for one application, overwhelms the user. Furthermore, in these publications, basic concepts are missing, which enable the beginner to become acquainted with the process in an easy-to-go manner. In this library, the need of process engineers in research and industry for reliable pattern processes is addressed.

The NaPa project was a unique platform for a collective approach to develop alternative processes for lithography, which now found its continuation in the NaPANIL project. It has advantages over the bilateral exchange of scientists and the dissemination during conferences, because:

- It united partners with different equipment to work on related issues – with a practical point of focus (e.g. an application or process issue), and gives more room for exchange.
- It created a platform for exchange of researchers and collaborations, which is flexible and adaptable during the project time. Researchers opened their labs to visitors from other labs. They jointly used equipment, exchanged tools, and samples.

All this is of benefit for the community, which currently grows steadily. While the number of research groups building up NIL processes is continuously increasing, nanoimprint is now moving into industry. Not all these people have a platform for comparison, or exchange.

3.2 How this library is structured

The reader often wants to get a simple ready-to-use process with a wide process window, or has an application that defines which process can be used. Most of the applications are based on simple pattern transfer: there the resist (one layer of polymer) is structured by an alternative patterning method and post-processing is similar to standard lithography. In this case, we have to note only the specific differences between conventional techniques and the NIL, i.e. steps or precautions that are necessary, have to introduce a new process step. E.g. for lift-off, undercuts have to be created, since the sidewalls in NIL are at best vertical. For more complex applications, e.g. when multilevel stamps are used, alignment is needed or pattern transfer is done via repeated reversal imprint, it is advisable to revise the entire traditional process route, which is a challenge to the thinking of a process engineer specialized and familiar with planar technology. While in the first case, generalities are needed, in the latter case there is an abundance of processes, which cannot be written down in a process library. It is by definition incomplete, and often – depending on specific equipment and materials – not easily transferable without a deep understanding of process characteristics and knowledge about the fabrication tools used.

A library of processes will enable people to get quickly into:

- In the first section, we try to satisfy the beginners' needs for practical advice, with a short presentation and comparison of processes and easy-to-go recipes in a cookbook fashion, for the processes nanoimprint, soft lithography and stencil lithography. It is a mixture of concepts and some initial process parameters for a quick start.
- A second section gives more information about general processing issues in nanoimprint lithography, by presenting standard lithographic processes with emphasis on single layer pattern transfer. In addition, tables and schemes are provided. Simple (basic) recipes are presented, which are modified depending on the application. Additionally, the reader will also find hybrid manufacturing processes and value chains.
- The third section, structured as an appendix to the introductory sections, is a collection of more elaborate processes, which – depending on equipment and application – can vary to a large extent. This collection of recipes is intended for the experienced user, and has to be complemented by the technological literature in publications and patents. The library is far from being complete and perfect, and does not have the ambition to cover every aspect of the processes used. It is a loose collection of processes rather than a book.

3.3 Mode of dissemination

The 2nd edition of the library was printed as a booklet in a limited number by the NaPANIL consortium and distributed by NaPANIL partners and *micro resist technology* GmbH. This 3rd edition is a reprint by *micro resist technology* GmbH and authorized by the former NaPANIL coordinator. The library's status is that of the end of the NaPANIL project (March 2012). This has practical reasons, because as in NaPa, the NaPANIL consortium does not meet any more as a whole as it did frequently during the active time of the NaPANIL project and other projects. All editions (1st to 3rd) of the NaPa LoP can be downloaded via the editor's website at Paul Scherrer Institute [1], to enable its use for teaching and further distribution.

The library is not published as a textbook with theory and overviews, about the state of the art of nanopatterning as it was done before the start of NaPa in [2], with contributions from several NaPa authors, for several reasons: First, time was too short at the end of the NaPa project to go through all the editing process for a book of this size and content. The lifetime of its recipes will be short and within a few years, many of them will be improved or obsolete. Second, the library is mainly the result of a collection of recipes from different researchers, and therefore not of same style and depth. Most recipes are not checked by independent sources, i.e. there is a chance that recipes do not work out if copied.

It can serve as the basis for lectures and courses on nanopatterning. The NaPa project organized a series of Summer Schools in Toulouse each year in July called PANAMA. The concept of this training was a "hands-on" approach of nanotechnologies focused on nanopatterning. PANAMA stands for "PAttering at the NANoscale – Methods and Applications". The concept of summer schools dedicated to nanopatterning and applications has been selected as the main tool for training actively young scientists in the domains relevant to NaPa project. Further training courses have evolved, like the course on nanolithography at the DTU in Denmark or the PSI in Switzerland. Meanwhile, a review was published on Nanoimprint [3] and a book on Lithography by Nanoimprint [4].

- [1] NaPa Library of Processes (NaPa LoP) [in print and online]. URL: <http://www.psi.ch/lmn/helmut-schift>
- [2] C. Sotomayor Torres: *Alternative Lithography – Unleashing the Potential of Nanotechnology*, book series on Nanostructure Science and Technology, book series on Nanostructure Science and Technology in Kluwer Academic/Plenum Publishers, Springer, editor D.J. Lockwood. Hardbound, ISBN 0-306-47858-7, Nov. 2003, 425 pp. (2003).
- [3] H. Schiff, *Nanoimprint lithography: An old story in modern times? A review*, J. Vac. Sci. Technol. B **26**(2), 458-480 (2008), doi: 10.1116/1.2890972
- [4] S. Landis, *Nano-lithography*, ed. S. Landis, John Wiley & Sons, London, UK: ISTE, Hoboken, NJ: Wiley, 2010, ISBN 1848212119.

3.4 Addresses for feedback

This library is compiled from a range of inputs from different partners. The current version is a direct result from activities of the NaPANIL project. The introduction and overview about nanoimprint lithography stems from lectures and articles written by H. Schiff, who is the library manager for this edition. Suggestions about new input and a possible update of the library should be addressed to J. Ahopelto, VTT and H. Schiff, Paul Scherrer Institut. Please do not contact the editor for copies of this library.

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3.5 Beyond the NaPANIL project (Update 2014)

After two editions, the first after the NaPa project (2004-2008) and the second after the NaPANIL project (2008-2012), the NaPa LoP has found its place within the nanofabrication community. It is a valuable tool as a printed version, but also as a download. It is still not the living document, which the authors hoped it would become, but it is now widely spread within the research participants of conferences but has also found wide interest by industrial partners, e.g. of micro resist technology GmbH.

In 2014, micro resist technology GmbH proposed to reprint the NaPa LoP. Two years after completion of NaPANIL, this is not an easy task, since the character of the NaPa LoP was mainly defined by the contributions of partners from the two large projects, which have finished in 2008 and 2012, respectively. Therefore, we decided to prepare a third edition of the NaPa LoP. For this, the Paul Scherrer Institute and micro resist technology GmbH have carefully revised and updated the second edition of the NaPa LoP. In order to preserve its character as the result of the NaPANIL project, only minor modifications and additions were done. The advantage of this is that the third edition is still the old NaPa LoP. A complete revision and update of details, e.g., confirmation of addresses in the second part, was avoided. The disadvantage is that new developments, machines and tools, are not included. However, as reference and for teaching, it is still a valuable resource. The main modifications are the following:

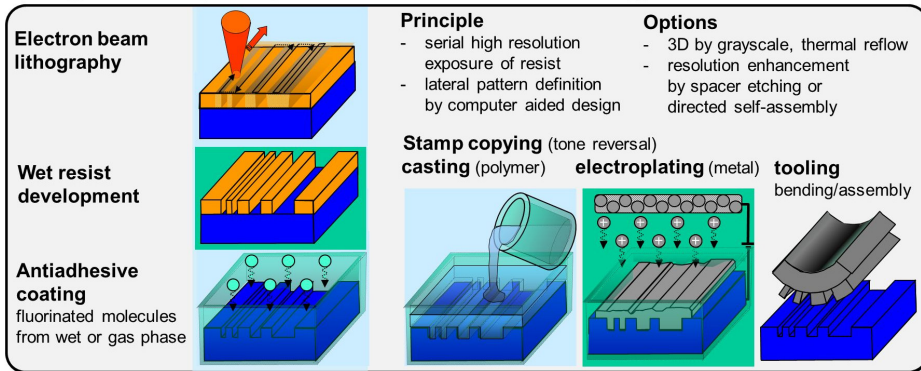
- In the first section, we have updated the process chains to facilitate the introduction into nanoimprint lithography. Additionally, the reader will find a short review of the state-of-the art (2014).
- In the second section, updates about materials from micro resist technology GmbH were included. This is particularly important because the LoP has found much interest from researchers and engineers who search for a quick introduction into nanoimprint processing.
- The third section is the part where the processes, which were prepared by the partners, are presented. These processes are still the essential backbone of the LoP, and even when they are not updated, they contain processes which can be both useful for the new and the experienced user.

Today, nanoimprint lithography can be considered as a mature technology taken up not only by many researchers, but also by industry. However, after nearly 20 years of development, NIL is rather a toolbox than a single process. While it exhibits a large potential as a manufacturing process for a range of nanoscale surface topographies, its definition as “lithography” is only valid for specific applications. The process chain is composed of *origination*, *replication* and *pattern transfer*, in which the last step is the transformation of the surface topography in the thin polymer film into a different material, e.g. by using it as a masking layer for etching into the substrate or for metallization. In Figure 3.1, the left column of processes depicts the standard NIL process (with its main replication variants thermal and UV-assisted NIL). While *stamp copying* and *tooling* are added to the origination, step&repeat and roller NIL variants are added to the replication section. Particularly interesting are resolution enhancement methods by using spacer etching techniques and directed self-assembly (DSA) of block copolymers. In pattern transfer, only the most prominent processes are displayed. As an example for DSA, particle self-assembly was chosen. Figure 3.2 presents the resulting process chain.

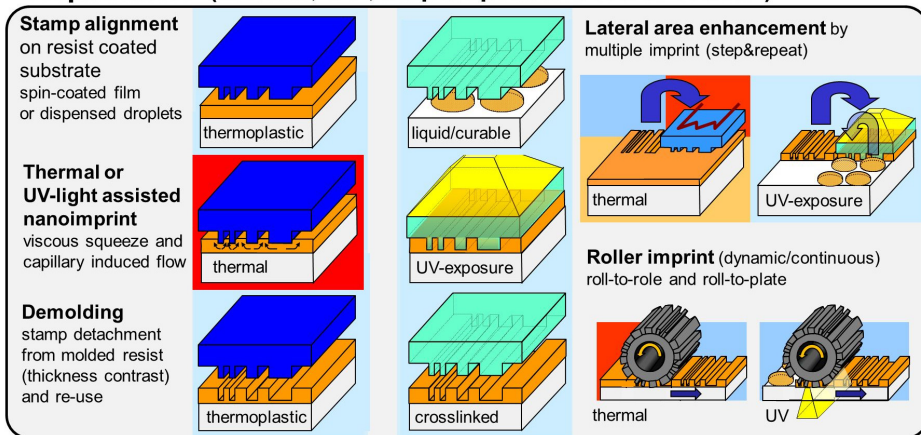
Which kind of these processes are currently evaluated or used in industry? With the transfer of part of Molecular Imprints' (MII) NIL business to Canon Inc. in 2014, NIL is now seen as a key process for the fabrication of flash memory, e.g. by Toshiba Inc. Most likely NIL will be also used in patterned magnetic media, by using high-resolution stamps made by electron beam lithography and block-copolymer based DSA. This combination of top-down and bottom-up techniques is unique for production, at least for the tool manufacturing. However, both applications are still in pre-production. Confirmed is the use of NIL for the fabrication of patterned sapphire substrates (PSS), which allows the increase of light extraction of LEDs. In addition, NIL for enhancement of the emission efficiency of LEDs by photonic crystals is also likely. Although this is still a moderate market (80'000 LED devices are patterned during a single wafer imprint), it is part of a growing business of photonic products as well as energy and lightning technology.

In conclusion, the most important factors for the success of NIL in production are throughput, defectivity and reliability – thus cost-efficiency. In this context, NIL gains maturity in all these fields. The basic requirements are still the same: stamps with high resolution and good surface quality, tools and materials that enable high volume fabrication and the use of NIL as a simple alternative to other costly lithographies. For these areas, the LoP will be a valuable tool.

Origination (stamp/mold fabrication and tooling)



Replication (thermal, UV-, step&repeat and roll-to-roll NIL)



Pattern transfer (window opening and substrate patterning)

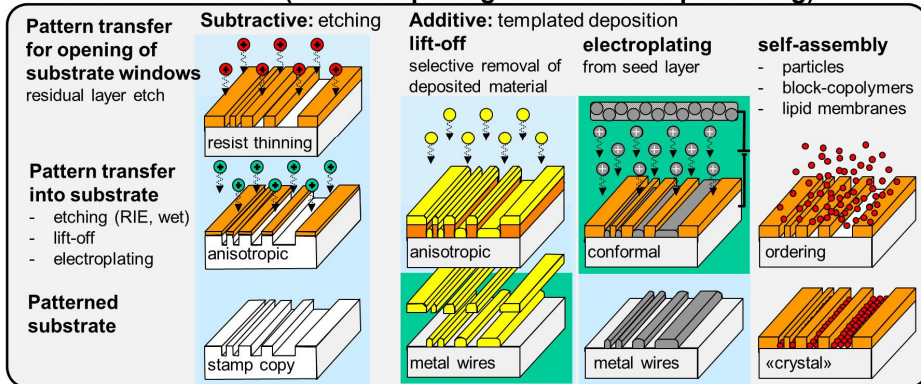


Figure 3.1: Nanoimprint lithography (NIL) consists of the three major steps origination, replication and pattern transfer.

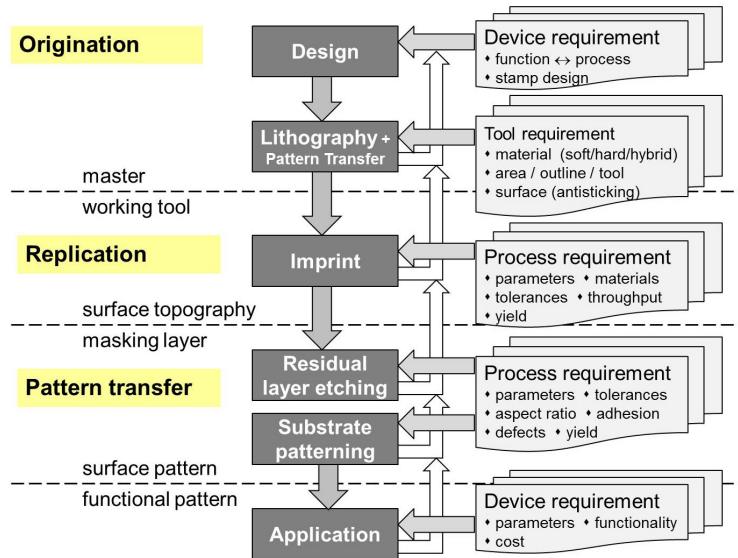


Figure 3.2: NIL process chain including feedback loops for process and device requirements.

Also from the view of a manufacturer and supplier of advanced NIL materials such as *micro resist technology* GmbH, NIL has gained momentum recently. Industry is now requesting resists and standardized solutions for production in larger quantities. The nanotechnology market is expanding very rapidly, which means material suppliers must constantly renew, add to and complement products and processes. This assumes individual solutions by specialist knowledge. Material suppliers are required to continue developing chemically and technically tailored answers to provide the market with complex system solutions with sufficient reliability and availability.

The research community learns that the industrial market is very different from that in research. While the research community is still working on new variants of processes, industry requires standards, often relying on processes that need to be simple and reliable. The imprint process is a single step in a process chain, and should not interfere with the preceding or with the following process steps. Although the market share of UV-NIL is growing, thermal NIL is still a much simpler process. Resists can be prepared in advance by spincoating and the coated substrates can be stored before imprint. Original resists have been further developed towards standardized solutions of defined viscosity and etching properties, but also inherent antiadhesive properties are requested to enable high throughput and stamp lifetime. Soft stamp solutions have been developed for UV-NIL, which enable the use of mask aligners with only minor modification. This is totally different from the step&repeat solutions developed for semiconductor lithography, where more expensive tool solutions can be tolerated.

For many partners the large network projects such as NaPa and NaPANIL were a “one-time” experience. However, the network is still continuing to grow and the take-up of NIL by industry will enable researchers and engineers to further develop solutions for the manufacturing of a variety of devices. These researchers will be trained “experts” with valuable knowledge, which may be useful in industry for future products. Many of them still contribute to conferences such as Nanoimprint and Nanoprint Technology (NNT, <http://www.nntconf.org>), but also on lithography conferences with research focus such as Micro- and Nanoengineering (MNE, <http://www.mne2014.org>) in Europe and their sister conferences Electron, Ion Photon Beam Technology and Nanofabrication (EIPBN, <http://eipbn.org>) in USA, Microprocesses and Nanotechnology (MNC, <http://imnc.jp>) in Asia, as well as SPIE Alternative Lithographic Technologies (SPIE AL, <http://spie.org/AL/>) in USA with a stronger industrial focus.

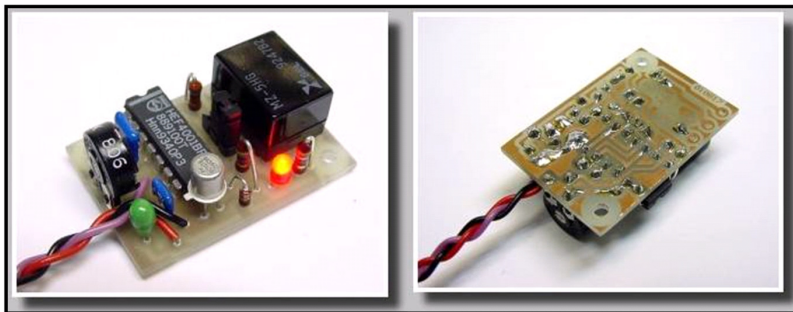
4. Guide to Alternative Nanopatterning

4.1 Processes and process chains

Either a cookbook contains easy-to-go recipes with thumb rules for the beginner, or more elaborate recipes for the professional. The latter will be able to develop basic recipes into an own set of recipes. In the world of nanopatterning, this means that a basic recipe is something that always works out, with a great tolerance range, while the success of a more elaborate recipe is dependent on the experience and the ability to adapt these experiences to a new situation with many (new) parameters. In this section, we try to do satisfy the beginners' needs for practical advice, however, without going into technological details. More elaborate recipes for the experienced engineer, are collected at the end of this report, without any claim on completeness. This cookbook is the part of the library, which may be used as an easy introduction for a beginner, with the aim, to enable him to get a fast hands-on experience with nanopatterning.

Printed circuit boards are a good example of how lithography is used for the patterning of metal wires on an insulating plastic substrate. The assembly of a variety of electronic elements is facilitated by this board, which served both as a mechanical support, and for the wiring between them. For simple circuits made from discrete elements, a single layer of metal lanes was often sufficient. The mounting is done by drilling holes into the board and soldering the discrete elements to the wires of the backside of the board. These wires were defined by an optical mask, and produced by photolithography and etching as pattern transfer.

Printed Boards for Electronic Circuits



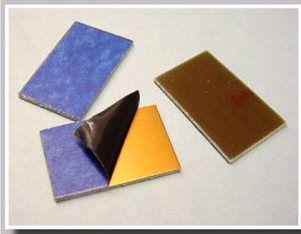
Printed board with mounted electronic elements

Backside with wires to connect electronic elements

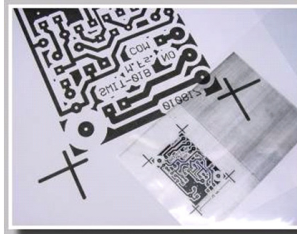
Figure 4.1: Photographs of a printed board after mounting of the discrete electronic elements (front and backside).

The methods of printed circuit board fabrication were much refined in photolithography and scaled down by many orders of magnitude. The mask fabrication, first by gluing patches of opaque tape on a transparent carrier, was then fabricated by plotters and photographic printers, and finally glass masks were fabricated by focused laser or electron beam lithography of resist with a thin opaque chromium layer as masking layer for UV light. Mask aligners for 100 to 300 mm glass mask and silicon substrates are now precision tools with sub- μm alignment and leveling. The pattern transfer processes have been equally developed, and apart from etching processes, electroplating and lift-off methods are now widely used. An overview is given in Fig. 4.3.

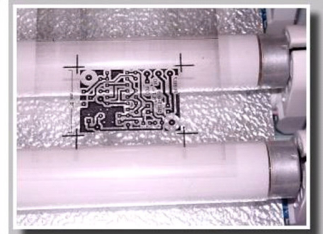
Printed Boards for Electronic Circuits - Lithography



Base material



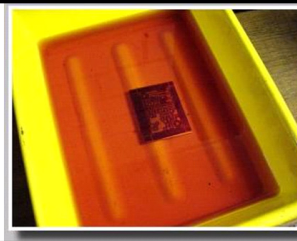
+ Mask foil



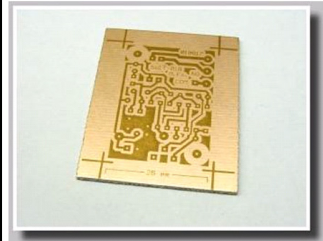
+ Exposure setup



⇒ Expose (UV-light)



⇒ Develop

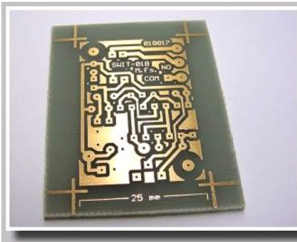


Developed Resist

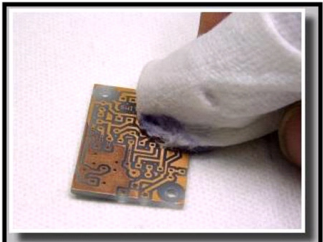
Printed Boards for Electronic Circuits – Pattern Transfer



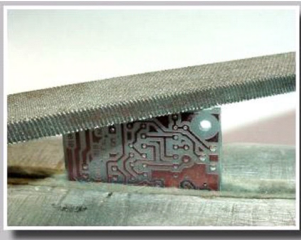
Copper etching



Conductor lines free



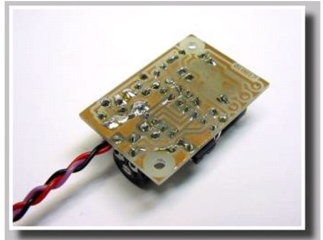
Remove protective coating



Drilling



Mounting

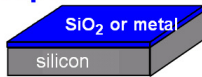


Soldering

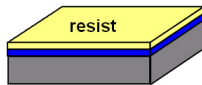
Figure 4.2: Photographs of printed board fabrication sequence: lithography and pattern transfer (<http://www.kap-man.de/pcb01.htm>).

Lithography : Exposure and Pattern Transfer

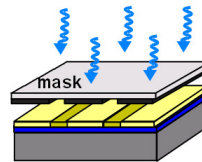
Preparation and exposure



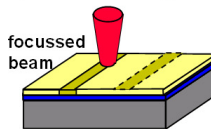
oxidation
or deposition
of seed layer



photoresist
coating

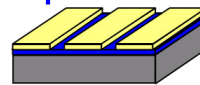


exposure
with mask
(parallel)



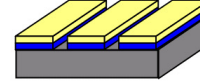
exposure
with scanning
beam
(sequential)

Development and pattern transfer

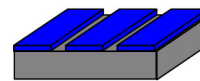


positive
resist:
exposed areas
removed

a) subtractive process (etching)

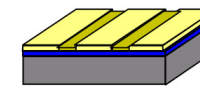


SiO₂
removed

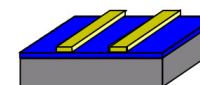


unexposed
photoresist
removed

b) additive process (plating, lift-off)



electroplating



unexposed
photoresist
removed

Figure 4.3: Example of standard photon and electron based lithography and pattern transfer.

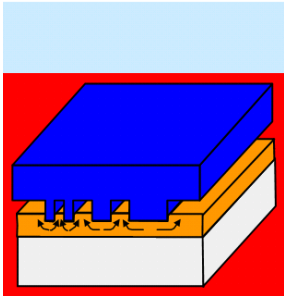
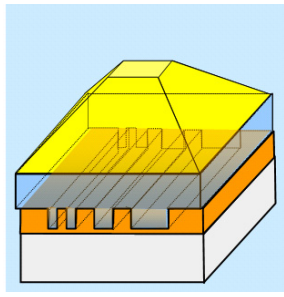
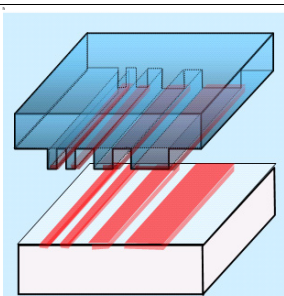
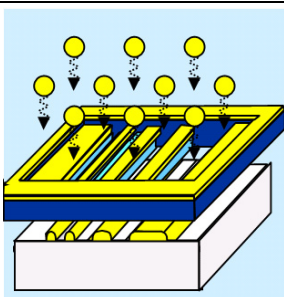
These schemes of lithography and pattern transfer are similar in the alternative patterning methods presented here, with some restrictions and variations.

4.2 Which process to choose?

Everybody having access to advanced photolithography (PL) and electron beam lithography (EBL) enjoys the benefit of these techniques. He or she will not easily switch to a different process, which is less mature than the standard lithographies. The change is often necessary if either mass fabrication aspects have to be met, or – more and more often – standard lithographies come to their limits, in terms of throughput, resolution, accessibility and reproducibility. In many cases, the decision for a different lithographic process is based on the needs of a specific pattern transfer process. The lithographic process is only complete when the resist pattern is transferred into another material. This process, in which the resist is transformed into a patterned masking layer, allows the substrate to be attacked by plasma, etching solvents, electroplating, deposition of materials and other substrate altering processes. E.g. in NIL, a unique advantage of molding instead of exposure is that complex stamp profiles, such as staircases, V-grooves, pyramids, both convex and concave, can be replicated. They can be used for the generation of 3D structures as for T-gate transistors or contact holes or serve for the step-wise etching of underlying layers with variation of the opening width. As long as undercuts and 3D patterning is not necessary, in most cases this pattern transfer is therefore similar to EBL.

The general (very simple) rule is the following: If a resist has to be structured with a three-dimensional sub-500 nm pattern, then nanoimprint should be employed, because it is nearest to the common lithography. If chemical patterning is needed, then soft lithography, based microcontact printing is of advantage, it is also low cost, and suitable for fabrication in a chemical lab without expensive clean-room facilities. In addition, if patterning has to be done over topography, a soft stamp or stencil method is predestined for use – stencil is very adapted to pattern different kinds of materials, too. However, there are many intersections where different techniques may be used with similar results. A first comparison can be seen in Tab. 4.1.

Table 4.1. Comparison of different alternative patterning methods.

Patterning Process	Patterning Scheme	Process	Specific advantages	Industrial Activity
Thermal Nanoimprint Lithography (NIL, T-NIL) – Hot Embossing Lithography (HEL)		<p>Stamp: hard, opaque (silicon wafers)</p> <p>Process: Thermoplastic molding at elevated temperature (100-200°C), demolding at low temperature (20-100°C)</p> <p>Tools: Hot presses (1-100 kN)</p>	<p>Similar to standard lithography (generating a thickness contrast of a resist)</p> <p>Maximum resolution: 2-5 nm</p> <p>Variety of thermoplastic materials</p> <p>Standard materials for stamps and substrates</p>	Very large research community, industry with increasing activity
UV-Nanoimprint Lithography (UV-NIL) a) Hard Stamp (Step and Flash) Lithography (SL) b) Soft Lithography (SL)		<p>Stamp: a) transparent (quartz) b) elastomer with hard backplate</p> <p>Process: Molding of liquid resin and hardening by UV-exposure</p> <p>Tools: a) step and repeat tool with UV-lamp b) modified mask aligner</p>	<p>Similar to standard lithography (thickness contrast of a resist, UV-exposure of negative resist)</p> <p>Maximum resolution: 2-5 nm</p> <p>Fast, no heating involved</p>	Fairly large research community with increasing activity, industry
Soft Lithography (SL) – Micro-contact Printing (μCP)		<p>Stamp: Elastomer, often backed by a hard plate</p> <p>Process: Transfer of an ink from the stamp surface (and from the bulk)</p> <p>Tools: chemical lab, modified mask aligner</p>	<p>Surface patterning of functional molecules possible (chemical contrast)</p> <p>Maximum resolution: 50 nm</p> <p>Easy stamp fabrication and printing</p> <p>Unexpensive</p>	Beginning, first professional tools available
Stencil Lithography (STEN)		<p>Template: hard, thin MEMS membrane (Si₃N₄)</p> <p>Process: Thermal evaporation in vacuum</p> <p>Tools: Physical vapor deposition combined with modified mask aligner</p>	<p>Patterning over topography possible (topological contrast)</p> <p>Maximum resolution: 50 nm</p>	Beginning, first professional tools available

In the next section, we are presenting the different methods in more detail. For a better comparison, we start by standard optical lithography, before giving an introduction on imprint and stencil lithography.

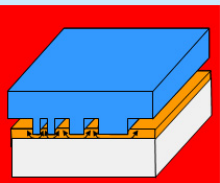
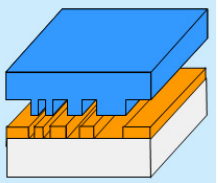
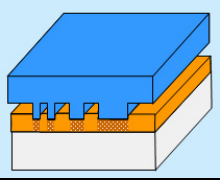
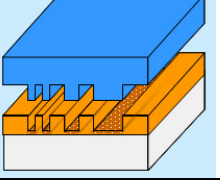
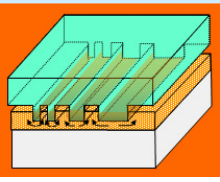
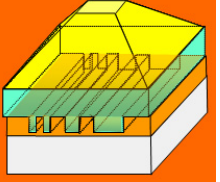
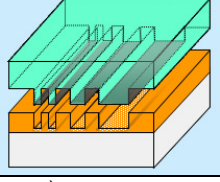
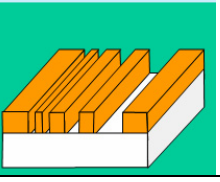
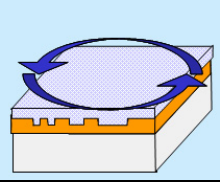
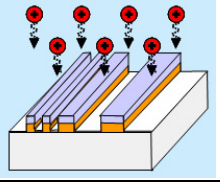
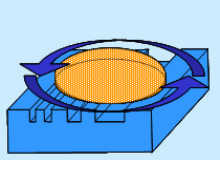
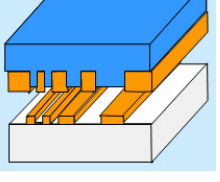
4.3 Combination of processes and hybrid processing

Process chains are normally composed of a sequence of single processes. In the fabrication of electronic circuits on silicon substrates, the lithographic sequences are typically composed of a resist coating, photolithography and specific pattern transfer step, which are often repeated with different masking patterns. These processes are often interlinked, and adaptations have to be made that the processes work properly within a narrow process window. E.g. for coating over topography, equilibration and antireflexion layers have to be used to reduce the influence of variation in surface height variations and reflectivity. In photolithography, the thickness of resist can be adapted to achieve high aspect ratio or high resolution. Pattern transfer processes such as lift-off or etching demand different resist heights, tones and profiles. In non-standard lithographies such as nanoimprint lithography, the photolithography step cannot be simply replaced by the imprint steps, but a range of trade-offs have to be made. This is not only due to the novelty of the process, but also because some of the characteristics are different. E.g. in after the imprint step, the residual layer has to be removed which means that an etching step has to be included into the process chains. Furthermore, lift-off processes are difficult because they need resist undercuts to interrupt the coated metal film. High aspect ratio trenches can achieve the same effect, but they are difficult to achieve due to high demolding forces.

Hybrid processes combine processes or materials in a way to circumvent obstacles given by standard processes or take advantage of single aspects of process. Therefore, "hybrid" basically means that two processes which are seen as different and incompatible, are used together or in immediate sequence, often on the same substrate or resist, and used as complementary rather than alternative processes:

- **Combined processes**, e.g. **combined nanoimprint and photolithography** (CNP). Basically, UV-light assisted NIL or UV-NIL is a combination of photolithography and nanoimprint lithography. Instead of heating to change the thermo-mechanical properties of the resist, a liquid resist is used which is cured and hardened by light before demolding. In CNP, additionally to the imprint of the surface profile a masking layer on or below the surface profile is used to block the light in UV-light assisted NIL from different areas.
 - a) Masking layer on the protrusions of the stamp: Then the resist area below the protrusions (the residual layer) is inhibited to crosslink and can be removed after demolding in a wet developer.
 - b) Masking layer around an area of interest of a stamp, either on top of all structures or behind them (e.g. on the backside of the stamp or buried below the surface relief): Then the resist in the area of interest is crosslinked while the other areas can be removed in a wet developer. This is typically done to generate waveguides or mesas.
 - c) Masking layer within an area of interest of a stamp, either on top of all structures or behind them (e.g. on the backside of the stamp or buried below the surface relief): Then the resist around the area of interest is crosslinked while the resist in the center of interest can be removed in a wet developer. This is only done if the structure below the resist (e.g. a grating) has to be replicated and the replica should act as generate waveguide or mesas.
- These processes, dealing with the same resist but using two different properties, are often called **mix and match**. They can be used:
 - a) To add **nanostructures onto microstructures**: E.g. by imprinting the top of the resist before photolithography a large area surface topography, e.g. an antireflective grating, can be patterned into the resist before exposing it with a masking structure. Only the remaining resist exhibits the surface pattern on top. However, care has to be taken that the imprint process (e.g. by temperature) does not interfere with the curing of the resist in the photolithography process.
 - b) To add **microstructures onto nanostructures**: Normally this is done by a two-step approach, i.e. by two lithography processes. However, if a foil with nanostructures is thermoformed, i.e. drawn over a microstructure, that it assumes this overall macroscopic shape, a hybrid process is defined.
- A very different concept of combined hybrid processes is the **postprocessing of structures**. Here the difference to normal stepwise processing is, that processes are combined, which are not "usually" used together, and a structure is modified before a pattern transfer process takes place. E.g. the **thermal reflow** of resist structures, i.e. a melting to box-type resist structures into spherical or cylindrical shapes by capillary action is an example where the resist is modified. The pattern transfer will then use this resist pattern and transfer it into the substrate either by proportional etching, or to replicate it by molding.

Table 4.2. Hybrid processes:

Process	(1) Pattern generation	(2) Curing or transfer	Status
Process schemes for optimized pattern transfer			
T-NIL Partial mold filling and zero residual NIL			<p>Process: Self-limiting flow of a thin resist</p> <p>Resolution: lateral 200 nm, h_f nearly zero</p>
RT-NIL Room temperature NIL (hard stamp)			<p>Process: Resist compaction by high pressure under protrusions</p> <p>Resolution: 80 nm line with 300 nm spacing (100 nm deep)</p>
Combined (hybrid) processes			
T+UV-NIL Simultaneous thermo-plastic and UV-NIL (e.g. STU)			<p>Process: Thermoplastic molding and UV curing</p> <p>Resolution: lateral <50 nm, h_f 20 nm</p>
NIL+PL Combined NIL and photo-lithography (e.g. CNP)			<p>Process: Exposure through semitransparent stamp and removal of unexposed residual layer</p> <p>Resolution: lateral 350 nm</p>
Pattern transfer (reverse) processes			
NIL / R Reverse tone NIL (e.g. SFIL / R) – Patterning over topography			<p>Process: Overcoating of Si-containing etch barrier on prepatterned organic transfer layer, etch back and dry developing (window opening)</p> <p>Resolution: lateral <100 nm</p>
R-NIL (T or UV) Reversal NIL – With complete resist pattern transfer or “inking” mode (partial transfer)			<p>Process: Spincoating of resist onto stamp, complete or partial transfer to substrate by thermal bonding</p> <p>Resolution: lateral <100 nm, h_f nearly zero</p>

- a) **Hybrid materials** are materials e.g. with organic and inorganic components. In NaPANIL ORMOCER[®] materials were extensively used, e.g. hybrid polymers with SiO₂ and carbon backbones.
- b) **Hybrid masks** or stamps are a combination of a stamp and a mask, i.e. exhibiting both a surface relief and an absorbing layer for local masking of a transparent substrate. This was shown in combined nanoimprint and photolithography (CNP) processes. **Hybrid molds** can also mean that molds are composed of different materials, where one material takes the mechanical part and the other the structuring. This is the case when an OrmoStamp[®] surface relief is placed on a flexible metal plate, which can serve as a flexible backbone for mounting and clamping.

Hybrid processing also contains all strategies of combining **top-down and bottom-up** manufacturing, such as **templated self-assembly**. In a similar way, ordered nanostructures such as graphene layers can be patterned using lithography. While the latter is rather a step-by-step patterning using conventional process steps, the first process includes several interesting variants:

- a) In templated self-assembly structural topographies in the micro- and nanorange serve as guiding lines for the self-assembly of smaller entities such as beads made from polymers (styrene or latex) or inorganic materials to form a 2-D or 3-D ordered semi-crystal (e.g. in opal shape). The frame serves as a starting boundary for the ordering and the main aim is to keep the order intact until the crystal frame is disrupted.
- b) In **directed self-assembly (DSA) of block-copolymers** (e.g. blocks consisting of a polymethyl-metacrylate (PMMA) and of polystyrene (PS)), templates of lithographically defined structures (e.g. a grating consisting of hydrophilic and hydrophobic lines with distances of several 10s of nm) enable the ordering of several blocks of the polymer chain between two lines of same property (i.e. the PMMA on the hydrophilic and the PS on the hydrophobic lines). Thus, the orientation of entire polymer chains can be achieved. The periodicity of the grating has to be chosen in a way that full numbers of blocks can order between two lines of same property. Thus a near-field ordering can be achieved and a doubling or tripling of periods. If one entity can be selectively etched away (e.g. the PS etches faster than the PMMA in oxygen plasma), the remaining PMMA can serve as a masking layer for the substrate. This process is used to enhance the density of patterned media. The original surface pattern is generated via the imprint of a stamp with dense nanopillars (e.g. with 100 nm period), and the resulting structure after block-copolymer coating will have half periods and thus four times density and dot numbers due to the ordering. The pattern is then transferred into the substrate and a stamp can be fabricated for high-density nanoimprint.
- c) Imprint of surfaces can also generate nodes or crystallization points for processes which are basically ordered in near-field, but will lose far-field ordering after a few periods. One example is the patterning **anodized aluminium oxide (alumina)**. The nodes will enable that a far-field ordering of holes with vertical sidewalls is achieved.

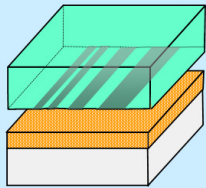
In NaPANIL a range of hybrid processes was used. Most of them are considered non-standard, not only because of the added complexity, but also because the geometries that are achieved by hybrid processing are different from those used in standard photolithography. Additional to this in NaPANIL replication techniques were not only used for manufacturing of large quantities, but for the fabrication of stamp copies. Once such a stamp copy is fabricated, it can be used in upscalable processes and reproduces the surface profile given by the manufacturing steps.

4.4 Process chains for industrial applications

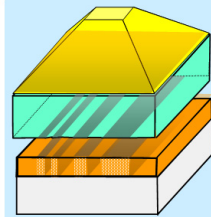
Three industrial NaPANIL applications were chosen to be the focus of the NaPANIL project, for which value chains were established. **Value chains** contain the full set of manufacturing steps and processes, but also the preparation steps from idea, design, data preparation, simulation to the process definition. This includes backup solutions and contingencies, and even strategies for the next generation devices (called "N+1"). At the back-end of the value chain, the upscaling up to a production line is linked. This includes measurement and assessment of quality issues in benchmarking and process validation. The **NaPANIL value chain** specifically involves the fabrication of stamp copies, e.g. by hybrid processes which to enlarge throughput and reduce defectivity. A specific issue of this is that stamp copies also assure, that different partners can participate in the setup of processes, since often not single solutions have to be pursued. Stamp copies are fabricated using replication, this means that the nanoimprint process is used for setting up tools for replication, either for small scale or for large scale production. Particularly important is the surface enlargement by step and repeat processes, a process well known in holography industry, where large area molds are fabricated using recombin-

Photolithography (through locally transparent Mask)

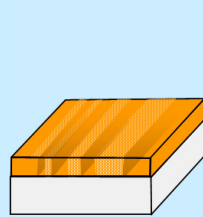
Negative resist



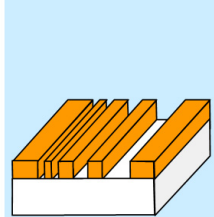
alignment of mask



exposure of negative resist

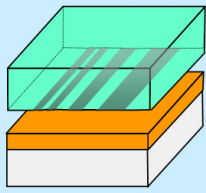


post-bake (curing of exposed areas)

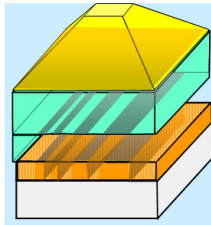


development (exposed resist)

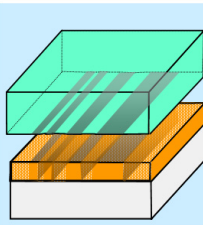
Positive resist



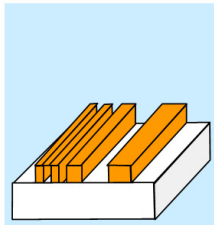
alignment of mask



exposure of positive resists



no post-bake



development (non-exposed resist)

Figure 4.5: Process sequence for photolithography for top: negative resist and bottom: positive resist

Short description

Photolithography is a standard method for resist patterning. It uses a semitransparent mask and exposes the resist locally. Depending on the type of resist (positive or negative tone), the exposed areas become soluble or are crosslinked. This contrast in solubility makes it possible to selectively remove one part of the resist. Both contact of mask to resist and proximity patterning is possible.

Main application

- Standard lithography method for many applications (in the microrange).

Advantages

- No residual layer.
- No mechanical contact during proximity patterning.
- Undercuts can be created for better lift-off

Disadvantages

- Locally transparent mask (shadow mask with absorber structure on transparent carrier) needed
- Yellow room needed

References:

- [1] M.J. Madou: *Fundamentals of Microfabrication*. Second edition, CRC-Press. ISBN: 0849308267, March 2002, 723 pp., (2002) 239-278.
- [2] T.A. Brunner, *Why optical lithography will live forever*, J. Vac. Sci. Technol. B 21(6) (2003) 2632-2637.

4.5 Nanoimprint Lithography (NIL) – for beginners

What is Nanoimprint Lithography ? – Short description

In Nanoimprint Lithography (NIL), the thermal version is also called Hot Embossing Lithography (HEL), a hard stamp with a surface relief is used to deform a softened polymer layer. The generated thickness contrast can be used as a mask for pattern transfer to the substrate.

Nanoimprint Lithography in daily life? – Examples

- Molding of waffles with a hot structured iron.
- Printing a seal into wax.

When do you use Nanoimprint Lithography ? – Main applications

- Resist based processes (replacement of e-beam lithography), 3D patterning of surfaces
- Mix- and match applications with resist based (optical) lithography

Advantages

- The resist can be prepared as a solid layer on silicon and glass substrates by spincoating before imprint.
- A crosslinkable resist is more stable in subsequent processes
- A photosensitive resist can be exposed by optical lithography after imprint (add microstructures)

Restrictions

- The main bottleneck is to provide suitable stamps, which normally are fabricated via electron beam lithography and etching. It is highly advisable to make stamp copies via NIL and use them instead of the original, which reduces the risk of damaging the original due to handling errors.
- Nickel stamps (by electroplating) are often not suitable because of the thermal expansion mismatch between stamp and substrate

How do you start Nanoimprint Lithography ? – Main tools, materials, processes

- Basic cleanroom facilities and processes (mask aligner, silicon cleaning, plasma processes for ashing, residual layer etching) are of advantage. Laminar flow is necessary to avoid contamination by dust.
- Antiadhesive coating setup (basically once the stamp is coated, this coating can last for a long time, but occasional re-coating might be of advantage)
- Hot press (pressure and heat which a parallel force, or a press on a pressurized membrane) with sufficient plate size, pressure, and the possibility to heat and cool these platens
- Optical microscope (stereo / high resolution) for quality control
- Beginners often break stamps because silicon is susceptible to notching due to contamination, scratches (due to handling errors) and bad alignment of stamp and substrate
- Use same size of stamp and substrate (e.g. 20x20mm² or entire wafers), or smaller stamps

Beginners' "kit" for Nanoimprint Lithography

- Manual hydraulic press with up to 1 tons force and heating platens. Temperature range up to 200 °C. Cost: > 1000 €. Simpler (for demonstration) is a metal clamp which is heated in an oven. However, efficient cooling (e.g. with nitrogen gas is beneficial) is needed.
- Resist (e.g. PMMA with molecular weight 25k-75k, or mr-I 8000R series). Thickness 300 nm. Cost: 50 € to 2000 € / liter
- Stamp with antiadhesive coating, regular pattern (grating) with largest features around 10 μm, depth around 200 nm, protrusion coverage around 50%.
- Antiadhesive coating. Cost of perfluorinated silane 100€ / 10 ml (for > 50 coatings)
- Rubber (PDMS), 1 mm thick, from the workshop
- Tweezers and doctor's blade for demolding.

Thermal-NIL (Hot Embossing)

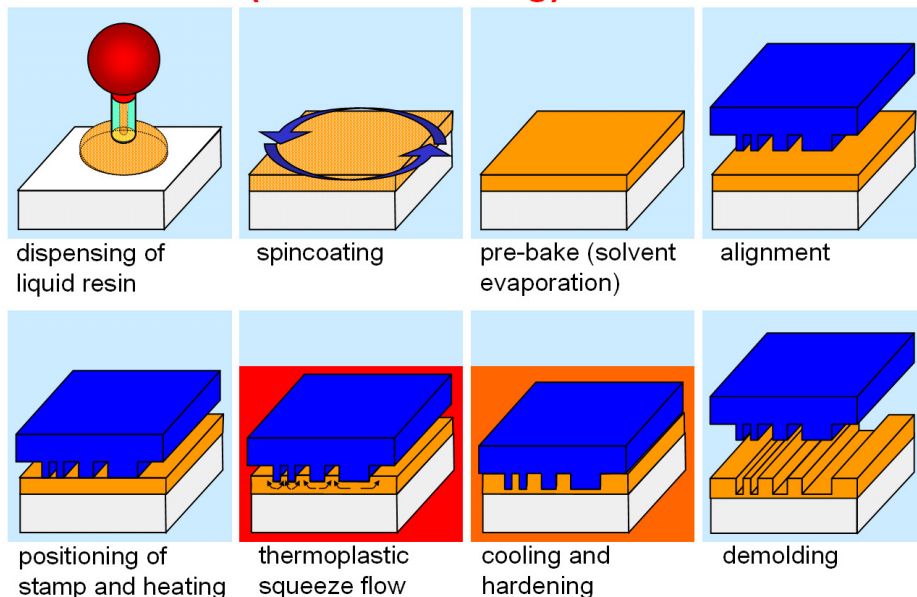


Figure 4.6: Process sequence for thermal nanoimprint lithography.

Nanoimprint : Process description

In a parallel press setup, the imprint is quite simple; apply heat and pressure in a controlled way

Stamp and materials

- Stack of stamp and substrate + compliance layer on top is assembled on press stamper
- Use stamp silicon with smooth vertical sidewalls, smaller or equal size than silicon substrate
- Antiadhesive coating needed

Process parameters

- Imprint in viscous state 50 – 70°C above the glass transition T_g . Demolding 20°C below T_g .
- Pressure between 10 – 100 bar, applied after imprint temp. is reached, maintained cooling
- Imprint time 1 min (without heating/cooling) up to 30 min, depending on structures and temperature; e.g. a stamp covered with a grating of dense micropillars will imprint in less than 1 min (without cooling)
- Evacuation before imprint is beneficial but not prerequisite (air is compressed and dissolves)
- Manual demolding using a doctor's blade – easier when substrates have a small wedge at the corner

Restrictions – and how to deal with them

- Avoid any kind of notch effect; furthermore reduce bending, shearing and local high pressures

References:

- [1] H. Schiff and A. Kristensen, *Nanoimprint lithography - patterning resists using molding*. Chapter (Part A/9) in "Handbook of nanotechnology", Volume editor B. Bhushan, third edition, revised and extended, 2010, Springer Verlag Berlin Heidelberg, Germany. ISBN: 978-3-642-02524-2, XLVIII, 1964 p. 1577 illus. in color, with DVD, Hardcover, 271-312 (2010).
- [2] C. Sotomayor Torres: *Alternative Lithography – Unleashing the Potential of Nanotechnology*, book series on Nanostructure Science and Technology, book series on Nanostructure Science and Technology in Kluwer Academic/Plenum Publishers, Springer, editor D.J. Lockwood. Hardbound, ISBN 0-306-47858-7, November 2003, 425 pp. (2003).
- [3] H. Schiff, *Nanoimprint lithography: An old story in modern times? A review*, J. Vac. Sci. Technol. B **26**(2), 458-480 (2008), doi: 10.1116/1.2890972.

4.6 Soft Lithography (SL) – for beginners

What is Soft Lithography ? – Short description

In Soft Lithography (SL) a patterned soft elastomer stamp is the key element. Instead of generating a surface profile in a resist by mechanical hard contact through rigid inorganic materials, the pattern is transferred to the substrate by soft, conformal contact using flexible materials.

Soft Lithography in daily life? – Examples

- Printing of ink by rubber stamp.
- Fingerprints

When do you use Soft Lithography ? – Main applications

- Microcontact Printing (μ -CP)
- Soft UV-NIL

Advantages

- Low-cost (precursor SYLGARD 184, 1 bottle 150 €).
- No cleanroom facilities necessary.
- Low pressure, the flexible stamp accommodates planar and non-planar surfaces by conformal contact.
- Large areas, the flexible stamp can make contact with and pattern large areas.

Restrictions

- Balanced stamp hardness is necessary (too soft: shallow structures difficult because of local bowing; too hard: conformal contact difficult)
- Stamp swelling by many organic solvents

How do you start Soft Lithography ? – Main tools, materials, processes

- Basic chemical lab (thiols, buffer solutions, vacuum, etch chemistry)
- Template (master) with antiadhesive coating
- Oven for curing
- (Fluorescence) Microscope
- Metal deposition capabilities
- UV-Light source (for Soft UV-NIL)

Beginners' "kit" for Soft Lithography

Stamp fabrication:

- Mix precursor SYLGARD 184 elastomer base with curing agent 10:1 and degas.
- Pour on master in Petri dish and let spread. Put into a vacuum bell jar to enhance outgassing.
- Cure at 60°C in oven.
- Cut and peel from master.

Pattern Transfer:

For μ -CP:

- Ink stamp with alkanethiol from solution or PDMS inks.
- Place gently on gold-coated surface.
- Detach.
- Wet etch.

For Soft UV-NIL:

- Spin-coat liquid resin onto substrate.
- Place stamp under moderate pressure and cure by UV-light exposure.
- Detach.
- Use residual layer etch and substrate etching techniques to transfer pattern into substrate.

Soft Lithography – Microcontact Printing

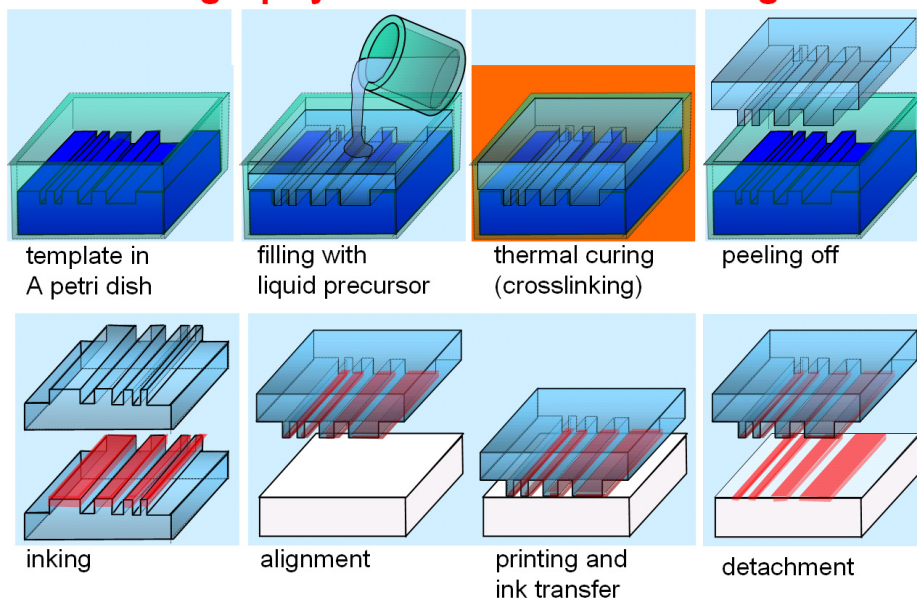


Figure 4.7: Process sequence for soft lithography – stamp manufacturing and microcontact printing.

Soft lithography / Microcontact Printing : Process description

For Microcontact Printing, one Soft Lithography technique, the soft elastomer stamp is fabricated by molding from a patterned template (master). Next, the stamp protrusions transfer the ink-like resist to the substrate by soft conformal contact.

Main application

- Printing of chemical patterns, alkanethiol SAMs on gold, biomolecules.

Advantages

- Applicable for a wide variety of inks.
- Possibilities for multiplexing.

Restrictions

- Pattern geometries: printing of very shallow structures is difficult (local bowing = sagging).
- Ink diffusion might limit resolution and sharpness of pattern.

References:

- [1] Y.N. Xia and G.M. Whitesides, *Soft lithography*, *Angew. Chem.-Int. Ed.* **37**, 551-575 (1998).
- [2] E. Menard and J.A. Rogers, *Stamping techniques for micro- and nanofabrication*: Chapter (Part A/9) in *“Handbook of nanotechnology”*, Volume editor B. Bhushan, second edition, rev. and extended, Springer Verlag, Berlin, Germany, Hardcover. ISBN: 978-3-540-29855-7, November 2006, XLIV, 1916 pp., 1593 illus, with CD-ROM, 279-297 (2007).
- [3] B. Michel, A. Bernard, A. Bietsch, E. Delamarche, M. Geissler, D. Juncker, H. Kind, J.-P. Renault, H. Rothuizen, H. Schmid, P. Schmidt-Winkel, R. Stutz, and H. Wolf: *Printing meets lithography: soft approaches to high-resolution*, *IBM J. Res. Dev.* **45**(5) (2001) 697-719.
- [4] H. Schmid and B. Michel, *Siloxane polymers for high-resolution, high-accuracy soft lithography*, *Macromolecules* **33**, 3042-3049 (2000).

Soft Lithography – UV-Nanoimprint

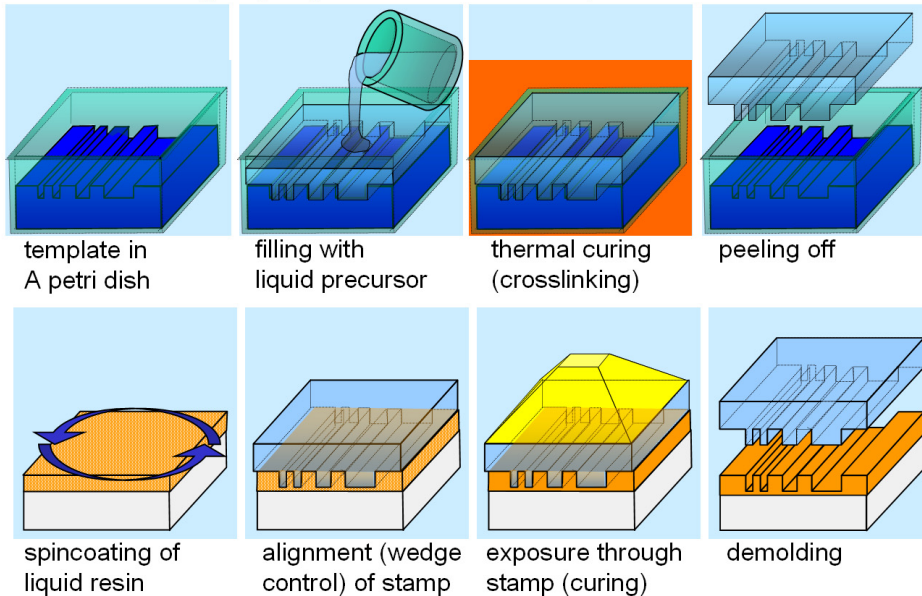


Figure 4.8: Process sequence for soft lithography – stamp manufacturing and UV-NIL.

Soft lithography / UV-Nanoimprint : Process description

Also for UV-NIL, another Soft Lithography technique, the soft elastomer stamp is fabricated by molding from a patterned template (master). Next, the soft stamp is used to generate a surface topography (resist thickness contrast) via molding of a liquid pre-polymer which is hardened by UV-exposure.

Main application

- Resist patterning
- 3D patterning

Advantages

- Low viscosity resist makes molding fast.
- Multilevel 3D geometries are accessible.
- Alignment through stamp is possible.
- Only low temperature and pressure required.
- Patterning of large areas possible.

Restrictions

- Liquid resist has to be applied before imprint by dispensing or spin-coating.
- Transparent stamps (elastomer and quartz backplane) are needed.
- Easy demolding requires controlled adhesion between stamp and resist

References:

- [1] Y. Xia and G. M. Whitesides: *Soft lithography*, *Angew. Chem. Int.* **37** (1998) 550-575.
- [2] U. Plachetka, M. Bender, A. Fuchs, B. Vratzov, T. Glinsner, F. Lindner, H. Kurz: *Wafer scale patterning by soft UV-Nanoimprint Lithography*, *Microelectron. Eng.* **73–74**, (2004) 167–171.
- [3] U. Plachetka, M. Bender, A. Fuchs, T. Wahlbrink, T. Glinsner, and H. Kurz, *Comparison of multilayer stamp concepts in UV-NIL*, *Microelectron. Eng.* **83** (2006) 944-947

4.7 Stencil Lithography (STEN) – for beginners

What is Stencil Lithography ? – Short description

Stencil lithography uses a pellicle instead of a stamp, and has much resemblance with optical proximity lithography, but uses particles instead of photons. Material is evaporated through the openings of the membrane in a shadow type way. In contrast to lift-off in optical lithography, the shadow mask is made for multiple use and either placed in a distance to the surface to be patterned or pressed against this surface. After evaporation the stencil has to be cleaned from material deposited on the stencil structures.

Stencil Lithography in daily life? – Examples

- Patterning sugar (icing / powdered sugar) by means of a pellicle onto a cake.
- Airbrush through mask (on cars or walls)

When do you use Stencil Lithography ? – Main applications

- Mix- and match applications by patterning on already patterned substrates.
- Dots

Advantages

- Coating on substrates which do not allow a resist process
- Patterning of a vast range of materials, which can be evaporated.
- Patterning over topography.

Restrictions

- Mask distortion due to material deposition and by heat.
- Possible clogging of openings.
- Design restrictions due to stability of mask (membrane openings).

How do you start Stencil Lithography ? – Main tools, materials, processes

- Basic cleanroom facilities and processes (mask aligner, silicon cleaning, plasma processes for ashing, residual layer etching) are of advantage. Laminar flow is necessary to avoid contamination by dust.
- Antiadhesive coating setup (basically once the stamp is coated, this coating can last for a long time, but occasional re-coating might be of advantage)
- Evaporation machine
- Optical microscope (stereo / high resolution) for quality control

Beginners' "kit" for Stencil Lithography

- Place stencil on substrate and clamp it
- Install it at the top of the evaporation chamber opposite to the evaporation source.
- Evaporate metal (no rotation)
- Detach stencil from substrate
- Clean stencil

Stencil Lithography (with Membrane Type Pellicle)

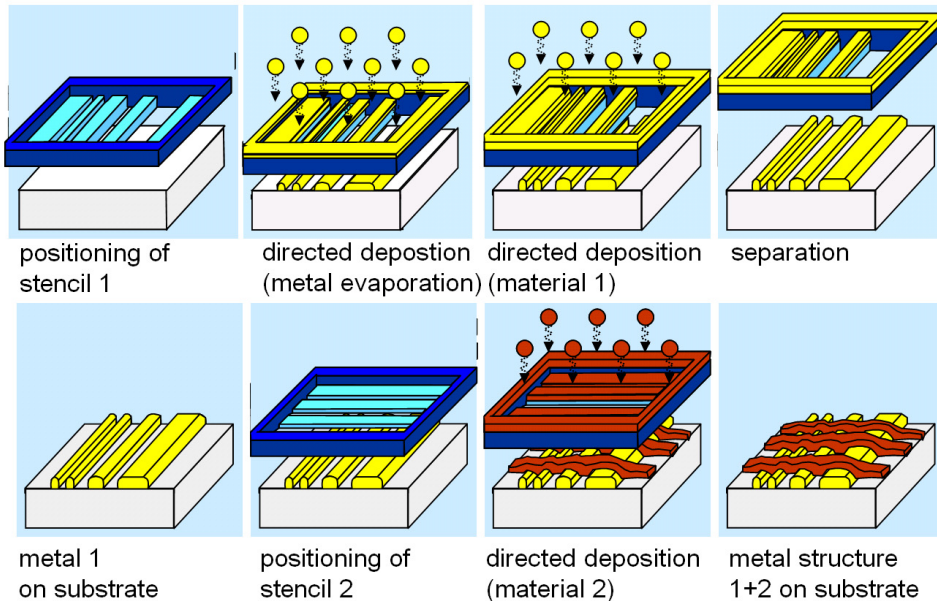


Figure 4.9: Process sequence for stencil lithography for two process steps (e.g. for metallization over non-flat surfaces).

Stencil Lithography : Process description

The stencil is placed in constant distance to the substrate. While evaporation takes place, the material builds up both at the substrate and the membrane.

Main application

- Mix- and match applications with optical lithography.
- Materials which are difficult to handle in dry and wet etching

Advantages

- Patterning over topography.
- Multiple layers
- Dynamic stenciling to fabricate wedges with defined thickness variation

Restrictions

- UHV process
- Topology of stamps (closed openings needed).
- Cleaning of stencil after evaporation needed.
- Distorsion and cloggings during evaporation have to be minimized.

References:

- [1] J. Brugger and G. Kim: *Nanofabrication by shadow deposition through nanostencils*: Chapter (7) in "Nanolithography and patterning techniques in microelectronics". Editor D.G. Bucknall, Woodhead Publishing, Cambridge, England, CRS-Press, hardback. ISBN: 1 85573 931 3, September 2005, 424 pp. (2005) 218-237.

5. Nanoimprint Lithography

5.1 Overview

The main focus of NaPANIL is on Thermal Nanoimprint Lithography (NIL or T-NIL, often also called Hot Embossing Lithography), i.e. the patterning of thin thermoplastic films on solid substrates. It is low-cost and easy to employ because it uses non-transparent stamps, and can be used with standard hot presses without any kind of alignment. However, because of the relatively high viscosity of the resists, a high pressure has to be used, and the final thickness of the resist is much dependent on structure sizes and densities (fill factor). Therefore NIL can be quite simple if a regular pattern of nano- or microstructures is imprinted, but can become more complex if structure sizes and density varies over the surface of a stamp. A good example is shown in Figure 5.1.

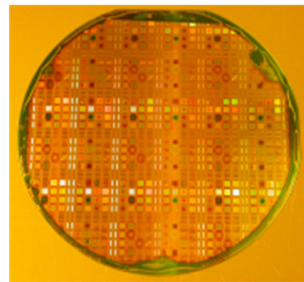
Large Area Simulation of Imprints

In thermal imprint, your resist can look like



regular micrometer sized holes
($5\mu\text{m}$ squares, $10\mu\text{m}$ pitch)
→ very homogeneous residual
layer thickness (70nm)

or ...

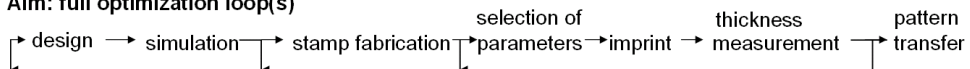


$2 \times 2 \text{mm}^2$ areas with strong local
variation of structure sizes
→ residual layer thickness
variation due to local bending

Figure 5.1: Photographs of typical resist patterns on a full wafer after imprint.

Both results can be further processed, but while in the first case the pattern transfer is easy due to the homogeneous thickness of the residual layer of the resist, the second case the process window has to fit into the tolerances given by the variation of residual layer thickness (shown by the different colors of the resist). The optimum case would be to optimize a process according to the following sequence:

Aim: full optimization loop(s)



This process chain includes **two optimization loops**: The first loop includes a **simulation** step after the design, which means that the imprint of areas of a few mm up to the entire wafer area should be simulated and critical spots for molding and pattern transfer identified and avoided by adapting the design. Then structures can be optimized before expensive stamp manufacturing begins. The second loop characterizes the **optimization of an imprint process** with a given stamp **by experiment** and variation of process parameters. The whole process, however, is only complete if the complete process sequence, i.e. the process including the pattern transfer, and consequently all processes needed for the final application are considered. Simulation tools for large areas are currently being developed, and in the following we present a software tool from Cognoscens which has been setup and tested during the NaPANIL project. It is an alternative to the solution developed during the NaPa project.

In the applications developed within NaPANIL, NIL is also understood as the patterning of thin thermoplastic polymer sheets or foils (with up to a few 100s of μm thickness). This means that functional layers are directly patterned (without pattern transfer into the substrate), and thickness variations are less important due to the fact that only the surface of a rather thick bulk of material backbone is patterned.

5.2 Modeling of the thermal nanoimprint process

5.2.1 Introduction – the Stefan’s equation

Simple Newton squeeze flow is used to describe the sinking of stamp protrusions into a thin film of viscous material can be described with. Figure 5.2 shows the interplay of different parameters for calculation of imprint times and Figure 5.3 the dominant role of large protrusions:

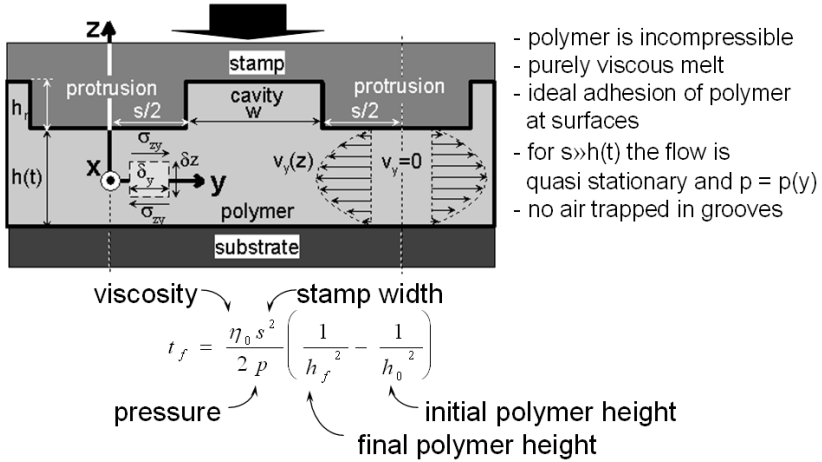


Figure 5.2: Schematics of a squeeze flow molding process according to Stefan’s equation for a single protrusion of size s , cavity width w and depth h_r . Note that arrays of identical protrusions will sink as fast as a single protrusion, as long as cavities are not completely filled.

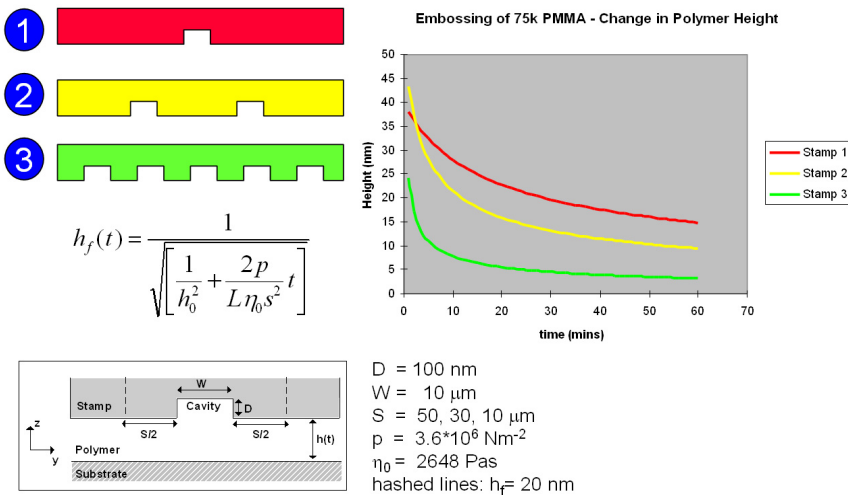


Figure 5.3: Variation of film height with time for three different densities of cavities (and hence the size of protrusions). Large protrusion dominate the sinking of the entire stamp.

References:

- [1] L.J. Heyderman, H. Schiff, C. David, J. Gobrecht, and T. Schweizer, Flow behaviour of thin polymer films used for hot embossing lithography, *Microelectron. Eng.* 54, 229-245 (2000)
- [2] H. Schiff and L.J. Heyderman, *Nanorheology - squeezed flow in hot embossing of thin films*, Chapter (4) in "Alternative lithography – unleashing the potential of nanotechnology". Vol. editor C. Sotomayor Torres, Hardbound, ISBN 0-306-47858-7, Nov. 2003, 425 pp., 46-76 (2003).

5.2.2 Nanoimprint simulation

As with analytical formulas, software based simulation tools calculate the time dependent sinking of stamp protrusions for entire stamp designs. They need a Computer Aided Design (CAD) representation of the stamp that represents a multitude of structures with different sizes and locations within a stamp area of interest. Then they are able to calculate the time dependent sinking of these protrusions into the resist with the aim to achieve a specific residual layer thickness and homogeneity. In case of the large arrays of identical protrusions from Figure 5.1, software based on Stefan's equation will result in a homogeneous sinking of the stamp until all cavities are filled and the stamp sinking is finished. For more complex designs, i.e. with strong local variation of structure sizes, some protrusions and thus areas will sink faster than others (due to their local maximum protrusion size s). However, the entire stamp (a wafer-like substrate) has only limited ability to bend over small distances in order to allow for different sinking speeds and equilibrate areas of different density after filling. Therefore, the stamp's ability to bend under pressure has to be taken into account, too. Simulation tools can identify "hot spots", i.e. critical protrusions, which are dominating the sinking or even might light to the failure of the imprint and subsequent pattern transfer process. In the ideal case, the tools include a feedback mechanism that finds the best process conditions for fast processing and homogeneous resist thickness or even proposes design modifications according to specific rules. The current software modules are still in a test phase and require a decent knowledge about the underlying processes. However, they enable to simulate different process conditions that often require the comparison of many imprints.

For typical wafers it is known that it can equilibrate a few 100 nm depth difference by bending over millimeters, without further interaction over large distances. This means that for simulation, it is often sufficient to restrict the simulated area to typical sizes of a few millimeters. In case of the design in Figure 5.1, local "frames" around structural sub-areas of $2 \times 2 \text{ mm}^2$ were used to compensate for specific density mismatch between neighboring sub-areas. Within the sub-area, local compensation structural density variations is often limited to the inclusion of auxiliary structures, because a total rearrangement of structures is often not possible without affecting the structure's function.

Aim of a nanoimprint process optimization

Simulation tools calculate the sinking of stamp protrusions for different designs. In the ideal case, they can propose the best process conditions or even design modifications according to

Requirements

- Stamp design (e.g. GDS II, DXF from stamp fabrication) with lateral and vertical dimension and translation into a parametric language which can be simulated
- Temperature dependent viscosity of thermoplastic materials in the pure viscous regime
- Information about initial resist thickness, stamp thickness and Young's modulus, equilibration process (compliance)
- Basic knowledge about micro- and nanorheology and equivalence of structures and parameters

Optimization of stamp designs

- Adding of auxiliary structures to achieve a homogeneous distribution of stamp protrusions
- Dislocation of large dominating protrusions to avoid accumulation of protrusion areas

Optimization of process parameters (temperature, pressure, time schedule)

- Enabling a fast imprint process
- Homogeneous sinking of protrusions

Challenges

- Measured material parameters are often only a rough approximation of reality in imprint
- Large and small structures a difficult to simulate (because of difference in grid size)
- Identification of singularities and suitable parameter window

References:

- [1] V. Sirotkin, A. Svintsov, H. Schiff, and S. Zaitsev, Coarse-grain method for modeling of stamp and substrate deformation in nanoimprint, *Microelectron. Eng.* 84, 868–871 (2007).
- [2] NIL simulation suite, Cognoscens, Lyon, France, URL: <http://www.cognoscens.com/>.

5.2.3 Optimization of structures by the NIL Simulation Suite

Within NaPANIL, Cognoscens has developed a new software tool, the NIL Simulation Suite (NSS). It allows for the optimization of structures starting with the stamp geometry (e.g. given in GDS II format). For a specific resist thickness, it calculates the constitutive response using the temperature dependent viscosity, by taking into account the ability of the stamp to bend.

NanoImprint Simulation Software – Modeling complex structures

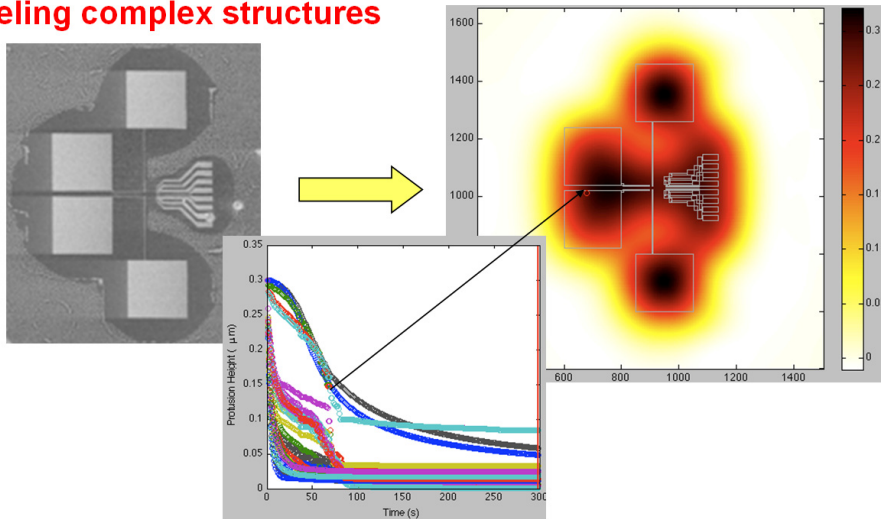


Figure 5.4: NIL Simulation Suite with example of a device consisting of large electrode pads and small wires, and the corresponding map of the residual layer thickness (left side: SEM micrograph of imprint, center: sinking of different protrusions, right side: simulation).

“Anomalities” in Simulation and Experiment

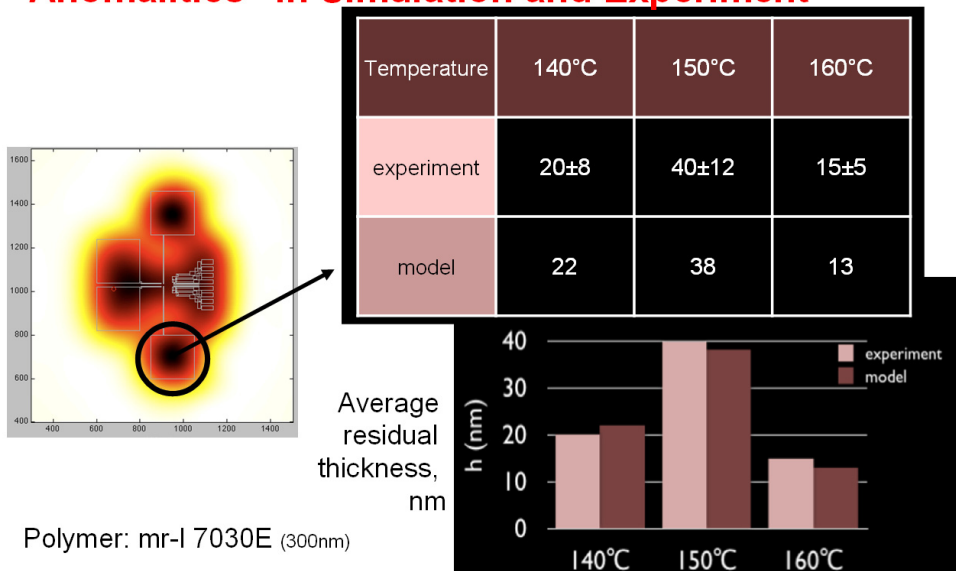


Figure 5.5: Example of residual layer optimization using the NIL Simulation Suite. Interestingly, for the given case an intermediate temperature imprint at 150°C is resulting in a higher residual layer thickness than with higher and lower temperatures.

5.3 Soft and hard elements in nanoimprint: stamps and tools

Any kind of surface relief can be replicated by imprint, however, depending on the resist viscosity different stamp hardnesses are needed. In thermal NIL (hot embossing) high pressure is needed to equilibrate unevenness or pattern densities during squeeze flow, for which hard stamps offer stiffness and structural precision. For UV-NIL, soft stamps enable a conformal contact to the substrate without high pressures. The resists, in contrast, are low-viscous liquids that enable to fill the surface cavities by capillary action. In addition to stamp hardness, different factors contribute to the overall ability of the system tool-stamp-resist to equilibrate wedges, defects, lateral differences in pattern densities and any kind of unevenness present.

5.3.1 Hard stamps

Hard stamps are typically made of silicon or glass wafer-like substrates. They have the same thermo-mechanical properties as the substrates used for imprint. Apart from the hard surface protrusions, which are considered non-deformable under typical imprint pressures, the hardness of the backbone has a significant meaning considering its ability to bend. For thermal NIL, it is of advantage to use silicon wafers rather than electroplated metal molds (avoiding thermal expansion mismatch between stamp and substrate). Apart from standard silicon micromachining techniques, a process for the coating of antisticking layers is needed.

Short description

Silicon as a stamp material for thermal nanoimprint is widely used.

Main application

- All kinds of thermal NIL processes where the substrate is silicon
- Moderate number of imprints due to limited mechanical strength (in contrast to SiC and Si₃N₄)

Advantages

- Standard material in semiconductor industry with high surface quality, availability, suitable for standard cleanroom processing such as RIE, KOH etching, anodic bonding in quartz and Pyrex.
- Possibility to coat antiadhesive layer with silane chemistry.
- Thermal expansion coefficient matched to substrate.

Disadvantages

- Non-transparent and not very resistant to damages due to notches.
- Cannot be easily clamped or fixed by screws (avoid strain due to thermal expansion mismatch)

Table 5.1. Comparison of different materials for hard stamps.

Material	Young's modulus (GPa)	Poisson's ratio	thermal expansion (10 ⁻⁶ K ⁻¹)	Knoop micro-hardness (kg mm ⁻²)	thermal conductivity (Wm ⁻¹ K ⁻¹)	specific heat J·kg ⁻¹ ·K ⁻¹
Hard stamp materials						
silicon	131	0.28	2.6	1150	170	705
fused silica (SiO ₂ , bulk)	73	0.17	0.6	500	1-6	700
quartz (SiO ₂ , fused)	70-75	0.17	0.6	>600 (8 GPa)	1.4	670
silicon nitride (Si ₃ N ₄)	170-290	0.27	3	1450	15	710
Diamond	1050	0.104	1.5	8000-8500	630	502
Nickel (Ni)	200	0.31	13.4	700-1000	90	444
Titane nitride (TiN)	600	0.25	9.4	2000	19	600

5.3.2 Soft and hybrid layered stamps

Soft stamps are often made from silicone or rubber. Particularly popular is Sylgard 184, a poly(dimethoxy siloxane) (PDMS), which is transparent in UV-light and can be used for UV-NIL. Replicas can be easily made of silicon or PMMA originals. Since PDMS is considered as too soft for sub-μm resolution, harder silicone (h-PDMS) is often used. For better handling, hybrid solutions have been

developed, e.g. by casting of PDMS on glass wafer-like substrates. Furthermore, hybrid polymer based molds (e.g. OrmoStamp[®]) combine ultra-high resolution capabilities (due to mechanical stability in sub-50 nm regime) and sufficient bulk flexibility.

Table 5.2. Comparison of different materials for polymeric working stamps

Material	Characteristic	η @ T and E	Comments
Thermocurable (thermally initiated crosslinking during heating)			
s-PDMS	precursor + initiator, fully cross-linked after curing	4.575 Pa·s 1.8 MPa	elastomeric, thermocurable silicone (Sylgard 184 from Dow Corning Inc., USA) used for stamp copying by casting, elongation at break 160, significant porosity (O ₂ absorbance, reduced life-time)
h-PDMS	four parts + solvent	tunable 8.2 MPa	improved mechanical stability for sub-1 μ m features, elongation at break 7, moderate porosity (less O ₂ absorbance, slight life-time improvement)
UV-curable precursor (UV-initiated crosslinking after spincoating or casting)			
OrmoStamp [®] *	UV-curable prepolymer, O ₂ insensitive	0.4 \pm 0.2 Pa·s 0.650 GPa	organic-inorganic hybrid polymer for stamp copies used in T-NIL and UV-NIL, sub-10 nm resolution, high mechanical stability for aspect ratio \geq 5, long stamp lifetime (cf. PDMS), release force optimized (fluorine-based modification), high material-network density (insignificant O ₂ absorbance)

* commercially available from NaPANIL partner *micro resist technology* GmbH, Berlin, Germany

5.4 The Replication technology toolbox

The nanoimprint process chain mainly consists of the three different process steps stamp fabrication, imprinting and pattern transfer (by RIE into a substrate etc.). This stems from the approach known from silicon micromachining and heading towards devices where the resist is only used as a transfer layer. A more general description of replication techniques involves different methods for pattern generation that are subsequently transferred into a molding tool, either a stamp or a mold insert. The final replication is then often creating the final product, which can be represented by a polymer element which is further coated or assembled (e.g. polarizer, microfluidics, ...). The replication toolbox therefore comprises a lot of different processes which can be combined according to the tasks, due to the fact that not every pattern generation, molding tool and molding process fulfils the requirements given by the application. An essential part, however, is the fabrication of a molding tool with appropriate surface topography, mechanical stability, stability and ability to integrate into an existing molding process.

Replication Technology Toolbox

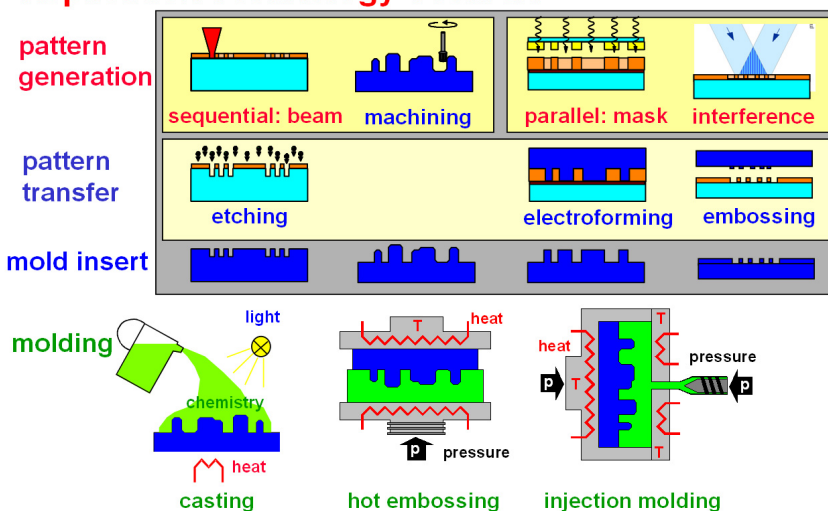


Figure 5.6: Process toolbox that summarizes a range of process variants from origination and tooling to molding.

5.4.1 Methods for stamp origination

Stamps are often made by serial or parallel methods. A typical serial method is a pattern generator based on a scanned focused probe such as laser or electron beam. For NIL, electron beam lithography (EBL) has become the standard for stamp fabrication, because not only many research laboratories own their in-house pattern generator, but also mask shops are available which provide standard solutions with high-speed machines. However, even then, serial processes are slow and costly. For large areas and high resolutions, EBL is still strongly limited in throughput. Therefore, for large volume fabrication, high-end mask-based DUV-photolithography is used. Particularly interesting for regular patterns (dot or line arrays), interference or Talbot-effect based projection lithography methods have become popular. Here, specialized suppliers provide gratings, however often for niche markets. For 3-D surface patterns, solutions are far from being standards. New approaches –two developed within NaPANIL – have proven to meet a market demand

5.4.2 Serial patterning methods – Electron Beam Lithography (EBL)

In Gaussian beam EBL tool an electron beam the pattern is formed by overlapping point exposures in a raster pattern. Each point exposure may “spill” to other points due to the so-called proximity effect (a backscattering of electrons due to interaction with substrate or resist atoms) and therefore a proximity correction has to be done dependent on the density and size of structures. Different **raster and vector scan modes** are used to reduce writing time. Specific issues are the high resolution at low currents (e.g. 1 nA), the address grid. Due to the limited scanning width of a few 100 μm the design is divided into writing fields. These writing fields are “stitched” together by moving the stage. The alignment accuracy of high-end machines is typically around 30 nm, which result in low stitching errors.

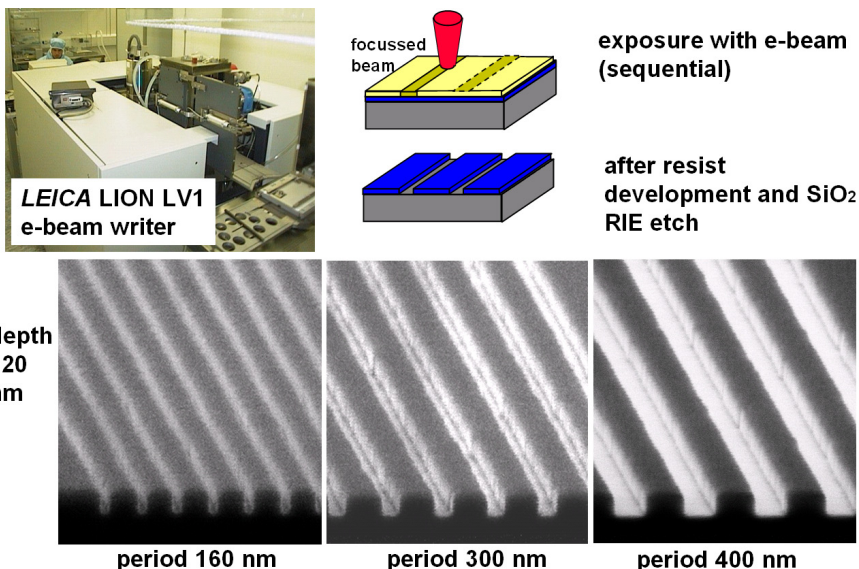


Figure 5.7: Exposure and pattern transfer for stamp fabrication by electron beam lithography and reactive ion etching.

Apart from binary structures, EBL has also 3-D patterning capabilities. Using dose modulation, the etching rate in wet developing solutions can be varied. Because high-energy electrons (e.g. 100 keV) penetrate thick resist layers, they deposit their energy homogeneously over the depth. This means that at a specific development time, areas exposed to different doses will etch with different depths. This method, called grayscale lithography, can achieve different steps in resists. It can be further advanced to continuous profiles if thermal reflow techniques are used. These techniques are quite new and make use of the fact that not only the development conditions, but also the thermo-mechanical behavior is modified using exposure. The underlying effect is that upon exposure, in a positive resist (typically PMMA with molecular weight of 120 kg/mol or 950 kg/mol), the molecular weight is reduced and thus both the etching rate enhanced and the glass transition temperature reduced. The latter en-

ables a selective reflow of exposed structures at specific temperatures while the unexposed areas are unaffected.

Electron beam lithography is a serial process, only one point is exposed at a time. The exposure time is therefore directly proportional to the area and can be calculated using the following equation:

$$time = \frac{dose \cdot area}{current}$$

in which the time t (in s) is calculated from the dose D required to expose the resist (in $\mu\text{C}/\text{cm}^2$), the current I (in C/s) of the beam and the area A (in cm^2). For typical values of $I = 1 \text{ nA}$ and $D = 300 \mu\text{C}/\text{cm}^2$, a time of $5000 \text{ min} = 40 \text{ h}$ can be calculated for an area of $A = 1 \text{ cm}^2$ (which would be fully covered by nanostructures with half the area exposed). For a moderate cost of $1'000 \text{ €/hour}$, this would result in a price of more than $40'000 \text{ €}$ for one exposure. Therefore, strategies have to be employed to reduce writing time and consequently cost:

- Enhance current: This is limited by the beam extraction and can often be only enhanced if larger apertures can be used. However, then the maximal resolution will be affected, too.
- Resists with higher sensitivity: This is the proper strategy for mask production; however, PMMA has gained significant importance in research laboratories because of its high resolution and known process characteristics that researchers barely switch to different solutions.
- If the density of structures is low or high (i.e. much more or less of half the area is covered), the tone of exposure can be switched in a way that only much less than 50% of the area has to be exposed. In any case, of the example above, this would mean that much less, than 40 h exposure time would be needed.
- Modification of design and writing strategies: Often only part of the structure needs highest resolution. A good strategy is therefore to manufacture the structure by mix and match, i.e. either by exposure with different apertures or by writing only areas of highest resolution using EBL and adding larger structures using photolithography. However, users lose flexibility (if they have to generate a separate mask) and risk errors due to overlay and interaction between the two processes.

In most cases, more than one of these factors has to be changed to achieve lower writing times, however, this can only be done if these parameters are known and open. A minimum knowledge about the machine and the processes employed is needed and will help to set-up optimum exposure strategies. In any case, EBL is expensive and should be carefully planned.

Grayscale lithography allows the generation of multilevel structures due to the fact that the development rate of a positive resist can be modified by local dose variation. The final resist height is defined by a dose / development rate relation at specific conditions in a wet developer solution.

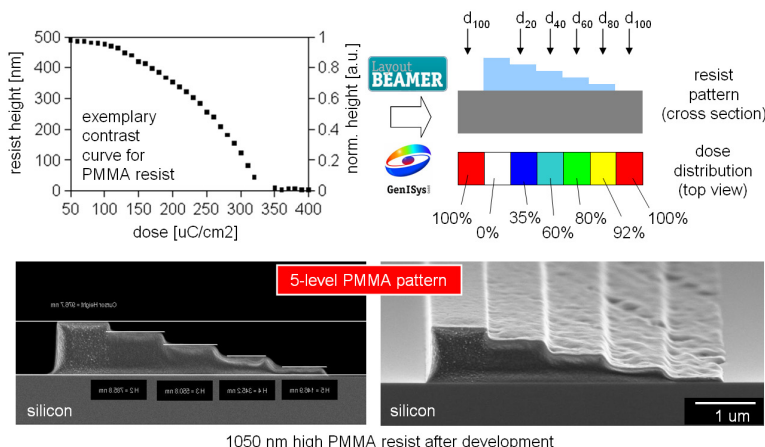


Figure 5.8: Grayscale electron beam lithography for generation of 3-D resist profiles using dose modulation at a fixed development time. Only at the highest dose (dose-to-clear) a full development is achieved.

What is Electron Lithography? – Short description

Electron beam lithography uses a focused high energy beam of electrons to exposure radiation sensitive resist. It is the standard method

Electron Beam Lithography in daily life? – Examples

Does not exactly exist, since structures are not ablated, but created by exposure AND development

- Exposure: Sandblasting through a nozzle (on cars or walls) – does not change chemistry
- Degrading sugar using a gas burner on to melt create a caramel coating on crème brûlée

When do you use Electron Beam Lithography ? – Main applications

- Masks for high-end photolithography, originals soft lithography, nanoimprint, nanostencil
- Fast prototyping and R&D applications with high resolution and flexibility/variation in patterns

Advantages

- CAD based process to write single lines or pattern entire surfaces
- Patterning of a vast range of materials, which can be evaporated.
- Patterning over topography.

Restrictions

- Expensive (> 500 k€) and high cost of ownership (> 500 to 5000 € / hour).
- Limited in throughput for large area high resolution (several hours for a few cm²)
- Design errors due to proximity effects and stitching errors
- Charging effects and limited resist sensitivity (e.g. PMMA: 200 μC/cm² at 100 keV).

How do you start Electron Beam Lithography ? – Main tools, materials, processes

- Design software such as L-Edit or AutoCAD, possibly with proximity correction software
- Basic cleanroom facilities with laminar flow and processes (silicon cleaning, plasma processes for ashing, residual layer etching) are of advantage.
- Dedicated electron beam pattern generator or modified scanning electron microscope
- Scanning electron microscope (high resolution) or scanning force microscope for quality control

Beginners' "kit" for Electron Beam Lithography

- Modify scanning electron microscope with beam scanning software (e.g. Elphy from Raith)
- Equip with a scanning stage for stitching.
- Basic spincoaters and wet chemistry for development

5.4.3 Parallel patterning methods – Interference lithography (IL)

Coherent beams of light can interfere in space, retrieving the phase information of the individual beams within the area of their spatial coherence. These techniques profit from the availability of high power lasers with long coherence lengths and do not need masks. Typically, one beam is split into two arms of same length, extended and superimposed in the plane where the resist-coated wafer is located. This enables to pattern entire wafer surfaces with one grating period. Apart from line grating, dot gratings can be fabricated using double exposure schemes, or even multiple beam superposition. Interference lithography is used if large areas have to be patterned with periods below 1 μm, for which other (serial EBL or parallel DUV-PL) methods are either not available or too expensive. However, today also highest resolutions are achieved using interference techniques, e.g. EUV-IL has achieved sub-10 nm resolution on areas of a few 10's of μm. These techniques require coherent beams in the EUV wavelength range, which is provided by state-of-the-art synchrotron facilities with undulator beam generation devices. Due to their unmatched resolution capabilities, they are therefore considered as new techniques for advanced research and testing of EUV-PL resists. In NaPANIL, IL with optical wavelengths are used to generate dot patterns for antireflective grating, but also to generate a fishnet structure with a double period in x-y direction, i.e. a period of 400 nm in one direction and of 10 μm in the other direction. This is possible using multiple beam exposure.

5.4.4 Parallel patterning methods – DUV Photolithography (DUV-PL)

Deep Ultraviolet photolithography with 193 nm wavelength is currently the workhorse for microchip fabrication, achieving 17 nm resolution for the fabrication of microprocessors (2014: 14 nm). Since long the transition to alternative patterning methods is expected, however, DUV has marked considerable success in developing optical enhancement techniques to push the resolution limits beyond typical diffraction limits. New developments are immersion techniques and double exposure strategies. For the next generation of microchips, Extreme UV photolithography using 13.6 nm wavelength is expected to be mature to meet the requirements given by modern chip manufacturing. Although DUV tools are normally reserved for high throughput manufacturing, in NaPANIL we were able to use state-of-the-art equipment for the fabrication of multilevel stamps. The processes for generation multiple layers of exposures had to be developed because they deviate from the typical patterning schemes for transistor manufacturing. In total, a 4-level stamp with resolutions down to 100 nm and a total depth of 200 nm was manufactured. Masks for DUV-processes cost between 20'000 € and 40'000 €. The process is described in more detail in the second part of the Library of Processes.

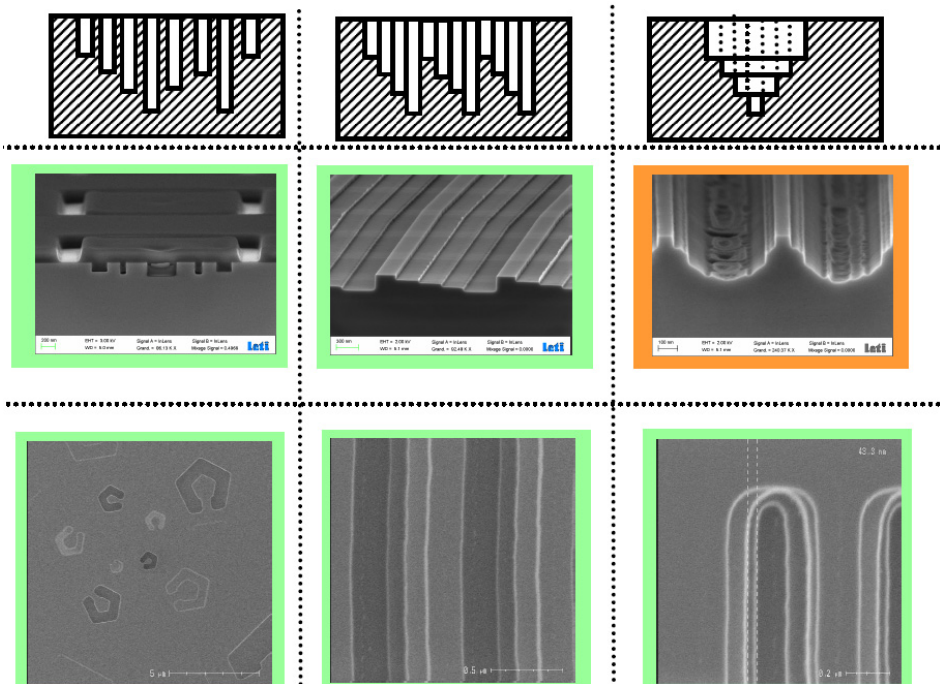


Figure 5.9: Multilevel stamp fabrication using DUV- projection lithography. Depending on the arrangement of the layers, different strategies for pattern transfer need to be applied.

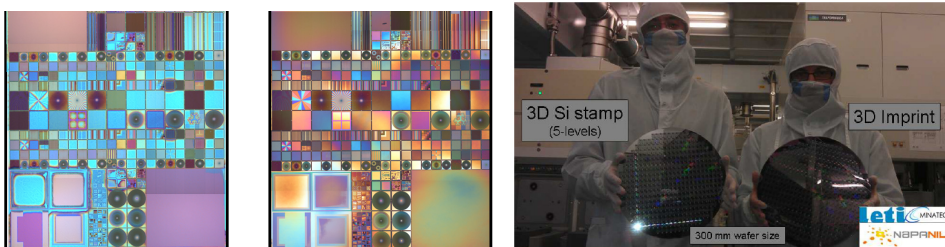


Figure 5.10: One area of the stepping field (24x18mm²). Using the step and repeat mode of DUV-projection, stamps were fabricated from 300 mm wafers and replicated by thermal NIL.

5.4.5 Selective shape transformation by thermal reflow

Thermal reflow is a postprocessing of resist structures that melt upon heating. Due to lateral restrictions, i.e. pinning at the boundaries of resist cylinders or lines, the box-type resist structure collapses and assumes a convex spherical or cylindrical shape. This is due to the tendency to minimize surface energy. Resist height and shape can therefore determine the final shape of the lens-like structures. Reflow lithography is often performed with photoresists for the generation of microlens arrays and thus enables the transformation of photolithographically generated resist patterns on full wafer size. Recently, these techniques have also been developed for resist structures made by electron beam lithography. As an alternative to reflow at high temperatures, i.e. in a regime where the resist becomes liquid with low viscosity, a new technique was developed which enables to reflow structures with linear sloped structures or even concave structures. This is possible because in EBL of typical positive resists like poly(methyl methacrylate) (PMMA), the molecular weight is reduced due to exposure. This can be used to generate thickness contrasts due to the dose-dependent etch rate in specific developer solutions but also because of the dose-dependent glass transition temperature. The process has large potential for generating a range of 3-D surface relief structures and will be presented in more detail in the second part of the Library of Processes.

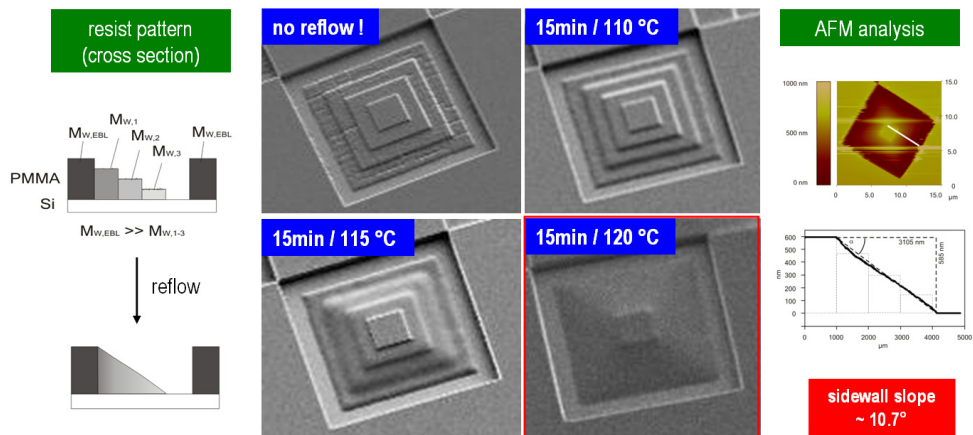


Figure 5.11: Thermal post-processing of 3-D PMMA patterns fabricated by grayscale electron beam lithography. Upon exposure, the molecular weight of the exposed areas and consequently the glass transition temperature is lowered, which allows a selective reflow of structures due to the thermal activated selective topography equilibration - the TASTE process [1,2].

References:

- [1] A. Schleunitz, V.A. Guzenko, M. Messerschmidt, H. Atasoy, R. Kirchner, and H. Schiff, *Novel 3D micro- and nanofabrication method using thermally activated selective topography equilibration (TASTE) of polymers*, Nano Convergence 1:7 (2014). doi:10.1186/s40580-014-0007-5
- [2] R. Kirchner, A. Schleunitz and H. Schiff, *Energy-based Thermal Reflow Simulation for 3D Polymer Shape Prediction using the Surface Evolver*, J. Micromech. Microeng. 24 (2014).

5.4.6 Working stamp fabrication

As it is usual with a mask in PL, replication techniques such as NIL make use of stamps to pattern multiple structures while the stamp is retrieved undamaged after each step and can be repeatedly used. The nature of lithography enables to use the same processes available to fabricate patterns also to generate new masks and stamps. Different processes such as electroplating, NIL + etching, casting, reverse imprint are used to fabricate structures, which can be used as tools for further processing by replication. This can be used to generate almost identical mask and stamp copies. Copies are used for a range of reasons:

- 1) Improper handling or extensive use may damage masks and stamps, which need to be replaced. Some processes therefore spare the original and use it only for the generation of

working masks or stamps. Then only copies are used for processing and backups are generated to plan for damage when damage occurs or yield drops due to damage of single structures.

- 2) Scale-up of processes may need multiple identical masks and stamps for parallel use.
- 3) Stamps need to be made in different materials, with different hardness, material composition, flexibility or optical properties. E.g. transparent stamps in quartz may be needed for UV-NIL while originals are easier to be made on opaque silicon substrates. The same strategy is needed for masks used for X-ray lithography, where thick gold absorber structures instead of thin chromium layers are needed. For roll-to-roll processes, bendable stamp with metal or polymer backbone may be needed and are better to be fabricated by copying from flat wafer-like stamp substrates than using the flexible backbone in electron beam writers or mask aligners. Also for non-fast devices bendable stamps are needed and can be used in processes e.g. by crowning and thermoforming to generated nanostructure reliefs on on lens-like structures and calottes.
- 4) Working stamps in materials such as Hybrid Polymers (e.g. ORMOCER[®]-based OrmoStamp[®] commercially available from NaPANIL partner *micro resist technology* GmbH) are low-cost alternative to electroplated stamps. They can be used for several 10's or 100's of replicas before degradation sets in. In some cases, disposable strategies ("lost mold" or one time stamp) are employed to avoid any cross-talk and proliferation of defects from one replication to the next (e.g. to encapsulate particles which are on the substrate).
- 5) Copies can be fabricated on special substrates, e.g. with a pre-machined mesa (i.e. an elevated area defining the stamp area which is separated from the stamps' holder), which may be needed for S&R processes.
- 6) Inverse tone of masks may be needed to facilitate processing, e.g. using NIL and reactive ion etching (RIE) the stamp copy automatically has the inverse polarity. Therefore for generation of polarities identical of the original (the second generation), the copying process has to be repeated with the first generation copy.
- 7) Stamp copies can exhibit modified structures, e.g. with different line width, sidewall inclination and reduced roughness for easier demolding. This can be done by overetching or modified reflow techniques, e.g. the so-called structure perfection by liquification (SPEL). Particularly interesting is aspect ratio enhancement. This enables to use originals with low aspect ratio and transform them into stamps with higher aspect ratio which are difficult to fabricate or more prone to defects and demolding errors.
- 8) Copies can also simply be reserved for process characterization and comparison with replicated structures. E.g. if replicas are made in brittle materials (e.g. sol-gel), they can be cleaved and used to examine cross-sections of structures while the original is preserved. Also different antiadhesive coating strategies can be tested and comparisons between stamps of the same generation can be made.
- 9) Multiple stamp copies can be used to recombine them to a large area stamp. Instead of aligning and assembling different stamps in a matrix, step & repeat imprint techniques have been developed to stitch stamp fields together on the same substrate or resist. The replicated large area structure can then be directly used for pattern transfer or to manufacture a large area stamp, e.g. for roll-to-roll embossing. Particularly interesting are step&repeat NIL processes where stamps are not just stitched together in a orthogonal manner, but with a defined pattern of rotated imprints.
- 10) Any kind of adding structures, e.g. frames, large area patterns such as antireflective gratings or macroscopic alignment structures (e.g. with holes or registration marks), auxiliary cavities for residual layer equilibration can be achieved by mix and match techniques. This can be done by double imprint (nano after micro) with different stamps, by additional scanning laser or electron beam lithography or by photolithography. Backside patterning of the stamp or generation of stamps with surface reliefs on both sides may also help to improve process conditions, increase yield, functionality or throughput.

Working stamp manufacturing has become a decisive step in manufacturing, since defectivity is one of the major topics in nanoimprint lithography. Surface enlargement is also needed since stamp originals are often too small to be used in industrial applications. This can range from a few square centimeters for optical sensors to smart phone and e-book readers and up to window sizes of a few square meters. In NaPANIL, sizes were restricted to research-like devices but were tested for applicability of larger areas.

Mask shops and dedicated industrial suppliers of origination and stamp copying services

In the past mask shops using advanced electron beam patterning services have been established for the fabrication of masks. This activity has also been extended to special serices for nin-standard processes such as thick resists or direct writing on silicon wafres. For the fabrication of stamps for NIL, similar activities have been established, however on a much less standardized level than masks. This is mainly due to the fact that stamps have a much larger variety of strutures, and depths and sidewall inclination and defects play a much more critical role than with mask absorber structures. Stamp fabrication also involves a minimum knowledge about the replication process used afterwards. As with simulation, the optimization loops involve design and processes. Currently, different stamp-shops are established, which provide solutions from generic or custom-made stamps.

5.5 Anti-sticking coating and antiadhesion surface treatment

Since silicon is not hydrophobic, we need a kind of ultrathin Teflon-like coating. The common material for that is Heptadecafluoro-1,1,2,2-tetrahydrooctyl)-trichlorosilane (F13-TFS), a silane with a reactive end group and a long hydrophobic tail group. The anti-adhesion treatment of the surface can be done in liquid or in gas phase. In the first case, difficulties are reported for stamps with structures of very high resolution and aspect ratio, due to the incomplete wetting of recessed surface areas. However, wet phase treatment is usually simpler and adequate for stamps with structures down to hundreds of nanometers.

Processes for coating

- Chemical Vapor Deposition (CVD) using evaporation of fluorinated silanes by heating or in vacuum, as described by ref. [1] and [2]
- Optool: wet coating of using Optool DXF a fluorinated silane in a fluorinated solvent, <http://www.daikin.com/chm/>, [3]
- CVD tools fro NanoNex Ultra-100 Integrated tool for mold cleaning and surface release treatment for Nanoimprint Lithography, <http://www.nanonex.com/>
- Molecular Vapor Deposition (MVD) from Applied MicroStructures, Inc., 1020 Rincon Circle, San Jose, California 95131-1325, <http://www.appliedmst.com/>

5.5.1 Treatment in liquid phase

The silane containing solution has to be prepared possibly in inert atmosphere, such as argon or nitrogen, in order to avoid water contamination. The solvent typically used is toluene, but other solvents, with lower water solubility such as heptane or dodecane have been used successfully to maintain the solution with a water content sufficiently low to avoid bulk polymerization. A typical process could be done under the following conditions:

- 1) Solution of perfluoroalkyltrichlorosilanes (for example (F13-TFS)) 0.1-1 mM in toluene or (heptane, octane, dodecane), prepared in inert atmosphere.
- 2) Immersion of the samples for 1 h at room temperature.
- 3) Rinsing in toluene.

5.5.2 Treatment in vapour phase

The most reliable surface treatment is obtained by chemical vapour deposition (CVD), by applying a moderate vacuum of some mbar in an atmosphere containing perfluoroalkyltrichlorosilanes molecules. One of the most prominent advantages of the vapour deposition method is that it is not affected by the wetting ability of a surface, so that it is suitable for stamps with extremely small nanostructures.

A possible surface treatment by chemical vapour deposition (CVD) is the following

- 1) Injection of perfluoroalkyltrichlorosilanes (for example F13-TFS) into a previously evacuated process chamber (with a 1-10mbar residual pressure of inert gas) at room temperature. The amount of molecules is in the range of 10 μL per liter of the chamber volume.
- 2) Optional: inject a small amount of water ($\sim 2 \mu\text{L}$ of the chamber volume).
- 3) Leave the samples under this atmosphere between 10 min and 1 hour (depending on setup).
- 4) Rinse with toluene

Fluorinated organosilane as molecular anti-adhesive layer

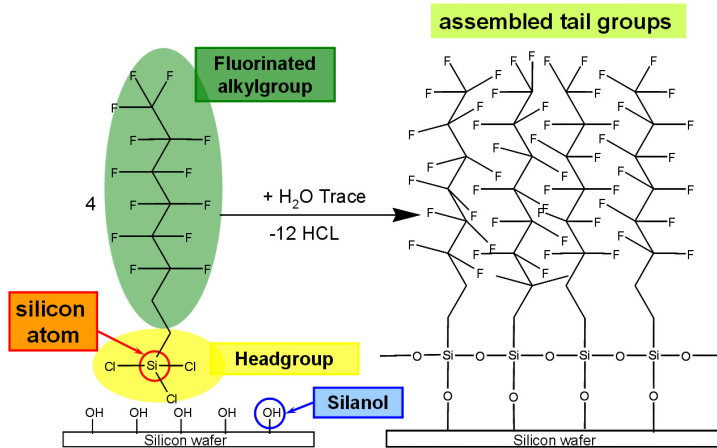


Figure 5.12: Silane binding on silicon dioxide.

Short description

Before wet or CVD coating, cleaning and activation is either done by so-called Pyranha etch, or by O_2 -plasma (RIE) or UV ozone cleaning. The qualities are different but oxygen plasma seems to be best to activate the surface for silane chemistry.

Main application

- Critical processes with high aspect ratio
- Isothermal processes are possible (no cooling needed before demolding)

Advantages

- The crosslinked resist can be demolded more easily, and the resist is more stable in subsequent processes.
- The resist can be used in a mix- and match process (exposure by optical lithography)

Disadvantages

- The molding and curing step have to be temporarily separated.
- Resist cannot be dissolved easily, e.g. if resist is sticking to the stamp.

References:

- [1] H. Schiff, S. Saxer, S. Park, C. Padeste, U. Pieleles and J. Gobrecht, *Controlled co-evaporation of silanes for nanoimprint stamps*, *Nanotechnology* **16** (2005) S171-S175.
- [2] M. Beck, M. Graczyk, I. Maximov, E.-L. Sarwe, T.G.I. Ling, M. Keil, and L. Montelius, *Improving stamps for 10 nm level wafer scale nanoimprint lithography*, *Microelectron. Eng.* **61-62** (2002) 441-448.
- [3] J. Tallal, M. Gordon, K. Berton, A.L. Charley, and D. Peyrade, *AFM characterization of anti-sticking layers used in nanoimprint*, *Microelectron. Eng.* **83** (2006) 851-854.

5.6 Resists, substrates and tools

5.6.1 Thermoplastic NIL-materials (thermal-NIL)

Resists for thermal NIL can be easily prepared by dissolving thermoplastic polymer, e.g. PMMA or PS (powder, pellets) in appropriate solvents. They provide reasonable flow characteristics and etching selectivity. In addition, a range of commercial NIL resists is available with enhanced rheological and process properties specifically developed for NIL. Particularly important are new developments of resists with inherent anti-sticking properties [1]. However, the addition of organic components for the reduction of release forces also reduces the T_g of a material, furthermore good adhesion to the substrate needs to be maintained. By adding silicon-containing components the etch selectivity during pattern transfer by dry etching processes can be enhanced [2].

Table 5.3. Thermoplastic or thermocurable materials used as resist layers for thermal and combined thermal and UV-NIL processes, with values for glass transition temperature T_g , recommended imprint temperature range T_{im} , viscosity η and Young's modulus E.

Resist (M_w)	T_g , T_{im}	η @ T and E	Comments
Thermoplastic (for varithermal molding)			
poly(methyl metacrylate) (PMMA)	T_g 100-120 °C, T_{im} 140-190 °C	$10^3 - 10^7$ Pas @ 170 °C; 380-540 MPa	the "classic" NIL resist, also suitable for grayscale electron beam lithography
poly(styrene) (PS)	T_g 100 °C T_{im} 120-180 °C	$10^4 - 10^7$ Pas @ 170 °C;	integrated optics, bio-applications
NEB22 (3k)	T_g 80 °C		negative EBL resist, high etch resistance in fluoro- and chloro-based plasmas
mr-I 7000R*	T_g 50 °C T_{im} 120-140 °C	$< 3 \cdot 10^4$ Pas @ 120 °C	low T_g NIL polymer with very good flow ability and high plasma etch resistance, effective release force reduction due to fluorinated additives, 12 nm resolution proved
mr-I 8000R*	T_g 105 °C T_{im} 150-180 °C	$< 10 \cdot 10^4$ Pas @ 175 °C	NIL polymer with very good flow ability, good thermal stability and high plasma etch resistance, effective release force reduction due to fluorinated additives
mr-I T85*	T_g 85 °C T_{im} 130-150 °C	$300 \cdot 10^4$ Pas @ 140 °C	thermoplastic NIL polymer for micro optical and bio applications with high chemical stability and excellent UV and optical transparency
SIPOL*	T_g 63 °C T_{im} 110-130 °C		thermoplastic NIL polymer with high Si content used for aspect ratio enhancement (AR >> 3) using a bilayer system with organic transfer layer UL1
Thermocurable (crosslinking during heating – for outstanding pattern stability during thermal loading)			
mr-I 9000M*	T_g 35 °C (before imprint, no T_g after imprint) T_{im} 90-100 °C		low T_g thermally curable NIL resist allowing almost isothermal imprint (demolding at 100°C) with high plasma etch resistance, particularly suited for demanding sub-100 nm patterns
Thermoplastic and UV-curable (crosslinking during photo-radiation - for combined NIL and UV-photolithography)			
mr-NIL 6000E*	T_g 1 °C (before imprint, no T_g after imprint) T_{im} 65-70 °C	$< 0.2 \cdot 10^4$ Pas @ 100 °C	low T_g NIL resist for combined thermal and UV-NIL (STU™ from Obducat), mix-and-match, multi-level patterning, reverse UV-NIL

* Commercially available from NaPANIL partner *micro resist technology* GmbH, Berlin, Germany

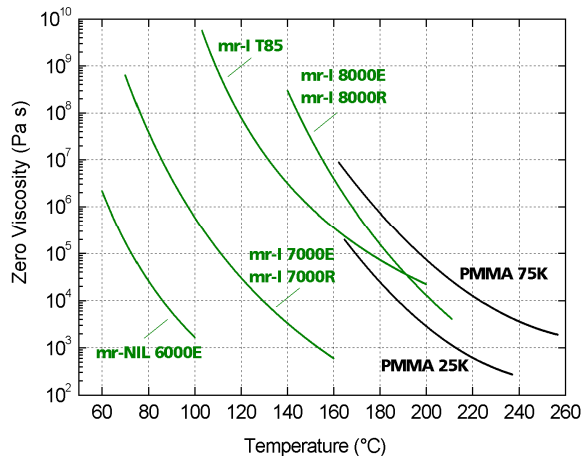


Figure 5.13: Zero shear viscosity of typical polymers for thermal NIL, e.g. the “classical” PMMA (poly methyl methacrylate) and commercial resists from *micro resist technology* GmbH: due to the strong dependence of the viscosity from temperature, small changes in imprint temperature can have a strong impact on resist flow and imprint times.

5.6.2 UV-curable NIL materials (UV-NIL)

UV-NIL is a combination of nanoimprint and photo-curing. The exposure is done in a flood exposure mode either through the transparent stamp or through substrate. Resists for UV-NIL consist of different components for photo-initiation and crosslinking. NIL resists affected by oxygen inhibition do not cure in ambient condition that means that only the resist below a hard stamp will crosslink when exposed to UV light, while the material at the stamp borders will not cure. For oxygen permeable stamps (such as PDMS or PFPE) NIL resists are necessary which cure in the presence of oxygen and which are not affected by any inhibition reaction caused by oxygen. In contrast, Oxygen inhibitant materials, might be used, if hard stamps are printed in a step&repeat mode onto areas adjacent to already imprinted areas which were already exposed (e.g. by straylight). Because they are not yet hardened, damage can be avoided (though uncured material might accumulate at the stamp edges over time, if no intermediate cleaning step is performed. Particularly important are new developments of resists with inherent anti-sticking properties. Fully crosslinked materials are often well suited as stamp copies, which can be used for thermal as well as UV-NIL. New developments are hybrid (organic-inorganic) polymers such as OrmoStamp® and resists with inherent anti-adhesive properties.

Table 5.3. Photo-curable resist materials for Photo-NIL (UV-NIL) and combined NIL and photolithography processes, preferably to be used with UV broad band or i-line exposure.

Resist	Characteristic	η (film)	Comments
mr-UVCur21*	100% organic, sensitive to O ₂ , low viscosity	30 mPas	1. Solvent containing version for broad film thickness range (40 nm up to 1 μ m) using spin-coating 2. Solvent-free version (mr-UVCur21SF) for dispensing
mr-XNIL26*	100% organic, sensitive to O ₂	140 mPas	1. formulation with high amount of fluorinated components for imprints with bare stamps without anti-sticking layer due to inherent release properties 2. solvent-free version (mr-XNIL26SF) for dispensing
AMONIL**	Si- and Zr-containing, not sensitive to O ₂	50 mPas	UV-NIL resist for soft (PDMS) stamps Not compatible to oxygen plasma
mr-NIL200*	100% organic, not sensitive to O ₂	>200 mPas	Processable using soft stamps (PDMS, PFPE)
mr-UVCur26SF XPC*	100% organic, sensitive to O ₂	16 mPas	Formulation for inkjet dispensing at room temperature

* from NaPANIL partner *micro resist technology* GmbH, Berlin, Germany

** from NaPANIL partner AMO GmbH, Aachen, Germany

5.6.3 Resists with inherent antiadhesive properties

Often it is sufficient to coat the stamp with antisticking layer (ASL). Ideally, this ASL lasts for the total lifetime of the stamp. However, it is known that ASL degrades (particularly with reactive imprint resists) after some tens or hundreds of imprints and has to be renewed. Here the main question is to detect the point when degradation sets in, often characterized by areas of ripped-off resist and determined by the number of imprints when defects cannot be tolerated any more. This is why inherent antiadhesive properties are considered as a solution for crucial processes, e.g. high aspect ratio structures or when stamps cannot be subjected to the ASL coating procedure without damage. For this, preferably fluorinated components are applied in the resist formulations, either as surfactant in low concentrations, mostly far below 1 wt%, or as major reactive component, like PFPE. Fluoro-based surfactants segregated during spincoating and imprint and accumulate at the resist surface to enable a lower release force at the separation boundary to the stamp. At the same time, adhesion towards the substrate has to be maintained to enable a good balance of demolding forces. Thus, for mr-I 7000R, a reduction of the release force of 40% was measured compared to the base material mr-I 7000E [1].

5.6.4 NIL materials for combined processes (photo- and e-beam lithography)

Combined processes are enabled, if materials can be both imprinted and selectively exposed simultaneously. For combined nanoimprint and photolithography, this is done by locally transparent stamps, for the so-called TASTE process, but thermal imprint of a resist whose molecular weight can be altered using electron beam lithography or other probes.

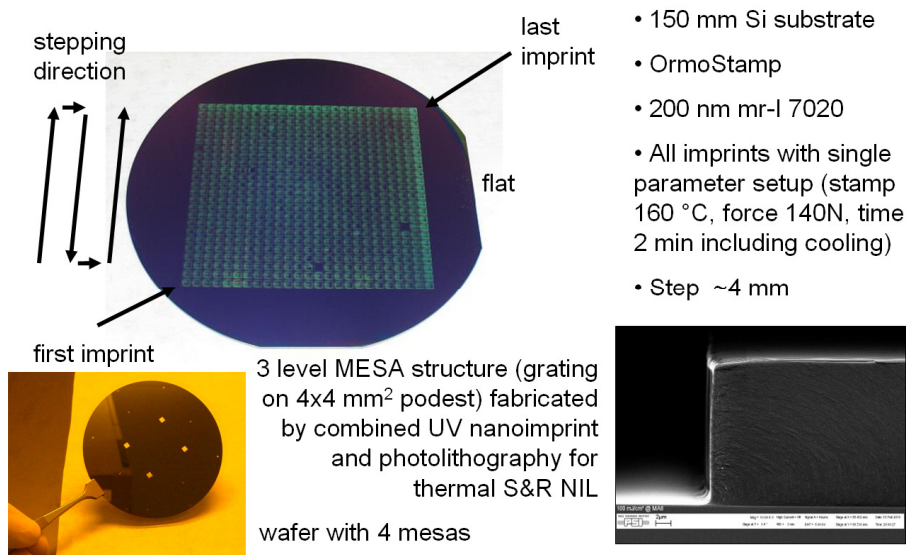


Figure 5.13: Large area S&R thermal NIL with OrmoStamp® copy: In order to create a 4x4 mm² mesa on a base of a 10x10 mm² large stamp (to decouple the active area from the heated base), the imprint into the OrmoStamp® layer was combined with a masked exposure of the 4x4 mm² wide mesa. Afterwards the non-crosslinked material was dissolved.

References:

- [1] H Atasoy, M Vogler, T Haatainen, A Schleunitz, D Jarzabek, H Schiff, F Reuther, G Gruetzner, Z Rymuza *Microel Eng* 88 2011 1902.
- [2] M Messerschmidt, A Schleunitz, C Spreu, T Werner, M Vogler, F Reuther, A Bertz, H Schiff, G Grützner *Microel Eng* 98 2012 107.
- [3] C. Schuster, M. Kubenz, F. Reuther, M. Fink, and G. Gruetzner, *Proc. SPIE* **6517** (2007), 65172B.
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- [6] T. Haatainen, T. Mäkelä, A. Schleunitz, G. Greci, and M. Tormen, *Microelectron. Eng.* **98**(8) (2012), 180 .

5.6.5 Sol-gel materials and hybrid polymers

The sol-gel process is a wet-chemical technique used for the fabrication of both glassy and ceramic materials. Sol-gels are therefore often used as coatings, if their optical, mechanical and chemical properties are superior to those of polymers (e.g. hard coatings on polymer substrates) or are needed to match those of the substrate (e.g. glass windows). For NIL, three kinds of sol-gel are used: spin-on glass resists such as HSQ, sol-gels for functional coatings and hybrid polymers such as the ORMOCER[®]s[#].

- 1) Protective coatings made from sol-gel materials are hard films on glass or polymer substrates. The aim is to imprint a pattern into a still viscous sol-gel precursor that will be transferred into a hard film with high fidelity by the following process route: Drying, thermal annealing, sintering (vitrification). The removal of the remaining liquid (solvent) phase is typically accompanied by a significant amount of shrinkage and densification. The thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages is that densification is often achieved at a much lower temperature than with other techniques. Due to their complex chemistry, the lifetime of its precursors is often restricted.
- 2) Hydrogen silsesquioxane (HSQ) by Dow Corning has been successfully used as high-resolution resist used for exposure with electrons or photons (EUV 13.6 nm) but can also be patterned by NIL. After cross-linking and developing, the HSQ material becomes a layer of SiO₂. This mechanically tough coating is stable in vacuum, at extremely high temperatures, and against the effects of radiation. Also here, the precursor lifetime is often restricted.
- 3) Inorganic-organic hybrid polymers such as the ORMOCER[®]s[#] are designed to be used without firing step, which means that the organic component is not removed (low shrinkage). Consequently, their mechanical, chemical and thermal properties are different from glassy materials. Furthermore, they exhibit optimized chemical stability and thus increased lifetime (at least 6 months). The application of hybrid polymers in NIL is twofold:

(a) Working stamps in materials derived from hybrid polymers, such as OrmoStamp[®]*, are low-cost alternative to silicon-based or electroplated stamps. It is a UV-curable material system with i-line characteristics. Its precursor can be spincoated or cast, depending on the thickness needed. The high UV-transparency in cured OrmoStamp[®]* is preserved after thermal treatment. Stamps can be coated using standard silane chemistry and used for several 10's or 100's of replicas before degradation sets in. OrmoStamp[®]* is designed to be slightly elastic for improved imprint properties. See Table 5.2 for comparison with PDMS.

(b) ORMOCER[®]s[#] are highly attractive as directly imprintable functional coating materials for optical (permanent) application. Commercialized types, like OrmoComp[®]* or OrmoClear[®]*, can be applied for the fabrication of micro-optical structures, diffractive optics, and waveguides. Furthermore, the inert surface chemistry makes OrmoComp[®] an ideal micro-fluidic chip fabrication material.

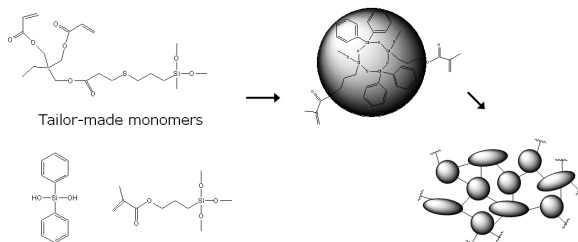


Figure 5.14: Sol-gel chemistry (simplified) - nanoscaled oligomers with inorganic backbone are completely crosslinked upon UV exposure.

References:

- [1] C. Peroz, V. Chauveau, E. Barthel, and E. Sondergard, *Advanced Materials*, 21(2009) 555-559.
- [2] H. Schiff et al., *J. Vac. Sci. Technol. B* 27(6), 2846-2849 (2009); doi: 10.1116/1.3250207.
- [3] M. Peuker et al., *Microelectron. Eng.* 61–62 (2002) 803–809.

[#] ORMOCER[®] is a registered trademark of the Fraunhofer-Gesellschaft zur Förderung der Angewandten Forschung in Deutschland e.V.

* OrmoStamp[®], OrmoClear[®], and OrmoComp[®] are registered trademarks of NaPANIL partner *micro resist technology* GmbH.

5.7 Machines and tools using molding processes

5.7.1 Full wafer flat stamper tools for nanoimprint lithography (NIL)

A press for hot embossing should be able to apply pressures over 10 bars and should have a temperature range between 60 and 200°C. The size of the stamp should be selected according to the pressure achievable.

Heating by electrical resistance heating is most suitable, and can also be integrated into a compact setup. Homogeneity is ensured by using large metal plates on top. However, this also enhances the thermal mass (slow heating and cooling). Cooling can be done by blowing nitrogen gas or air through holes in the holder. Cooling by air convection is extremely slow. Additional water cooling below an insulating sheet may be helpful to keep the heat away from the alignment and pressing unit. Because the wafers do not need to be attached to the stampers of the press, the only need is to use hard plates with flat surfaces. Be aware that the whole setup can bend during the high pressures involved, and if pressure is not equally distributed, even 5mm thick metal plates can bend. This means that silicon wafers can even cut into soft metals. Large wafers are therefore more likely to print homogeneously than small pieces of chips, as long as a compliance layer (e.g. a 1 mm thick layer of silicon – PDMS) is used for the homogenization of thickness variations (both due to tolerances of wafers and local pressure inhomogeneities during imprint).

Pressing mechanism

It is advisable that the pressure is not built-up in an instant, but softly during a few seconds. The PDMS will also ensure that there is a gentle pressure build-up. NIL presses are easier to build than presses for high aspect ratio microstructures, because an equal distribution of the pressure can be ensured by the compliance layer, and does not need a totally stiff setup where a precise lateral alignment and a precise vertical movement is needed, involving an attachment of the stamp (and substrate). The stack can be removed from the press after embossing, and the demolding is done manually outside the press, using a doctor's blade. Therefore, after the imprint process, the pressure can be released instantly.

Hot Embossing Equipment (in PSI)



embossing press from Specac

hydraulic press for nanolithography machine parameters:

- press : hydraulic (oil)
- lateral resolution : < 50 μm
- stamp : 15 x 15 mm², up to 100 mm wafers, substrate silicon spincoated PMMA (thermoplast)
- samples : up to 100 mm wafers
- temperature : up to 280 °C
- applied force : up to 40 kN
- conditions : ambient, laminar flow (clean room)
- heating : electrical
- cooling : water / air
- control : automatic

process area for sample and mold insert

Figure 5.15: A simple (oil) hydraulic imprint machine.

Pressure Equilibration – Cushion / Compliance Layer

A thick (1 mm) sheet of standard silicone, called PDMS (polydimethylsilane), is sufficient to equilibrate any kind of unevenness, e.g. caused by substrate undulations or even dust particles. The stamp can bend around these particles and leaves some “halo”, where the imprint is not complete. PDMS can be taken from any kind of workshop. When made hot, it tends to glue, which is an advantage to

keep the substrate or stamp fixed, but if not wished, a polyimide layer can be used as an intermediate layer for separation. The cushion layer can be placed at the backside of the stamp (or the substrate). Normal PDMS will expand when pressed (e.g. some cm over the borders of a 100 mm wafer). The initial size should be slightly bigger than the stamp.

Compliance Layer on Top – Induced Stamp Bending

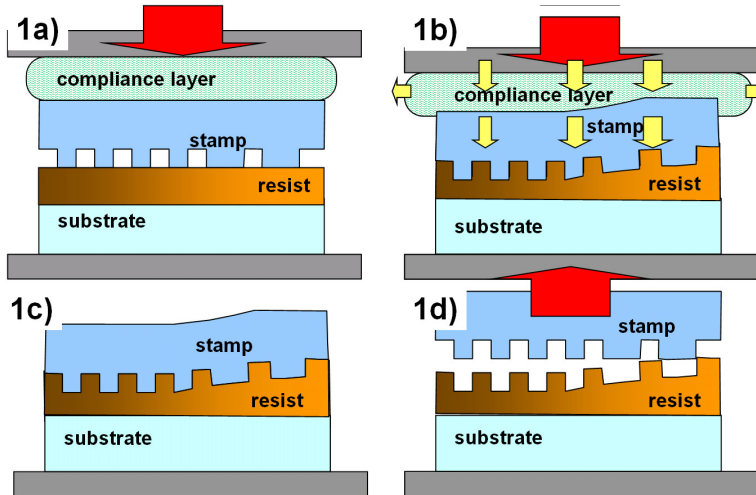
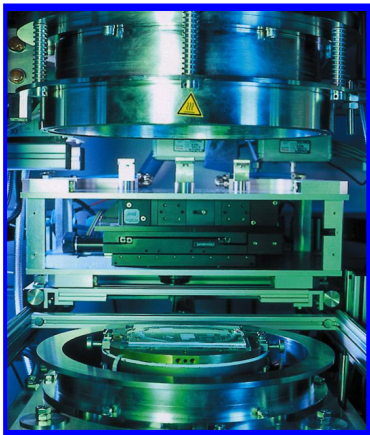


Figure 5.16: Principle of a cushion / compliance layer for pressure equilibration at the backside of the stamp. The bending of the stamp due to the variation of structure density in the stamp is exaggerated.

HEX03 Nanoimprint Machine from Jenoptik



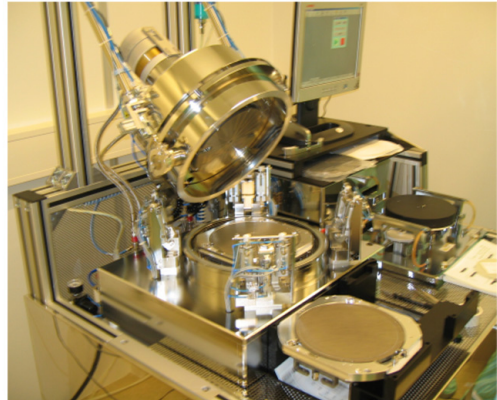
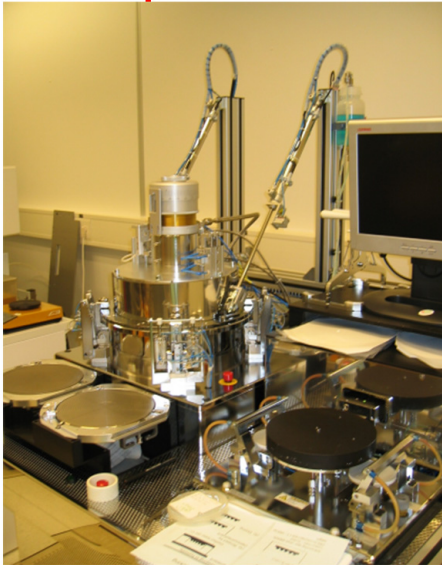
front side with opened embossing chamber and inserted microscope

Main Features

- molding of thermoplastic polymers with resolutions of below 10nm
- pressing force up to 200kN (operation force/position controlled)
- embossing temperature up to 320°C (heating electrical, cooling with oil)
- embossing under **vacuum**
- automatic mold release
- optical alignment with 3 μ m
- overlay accuracy for double sided / aligned embossing

Figure 5.17: Integrated optical microscope in a hot embossing machine (Jenoptik HEX03).

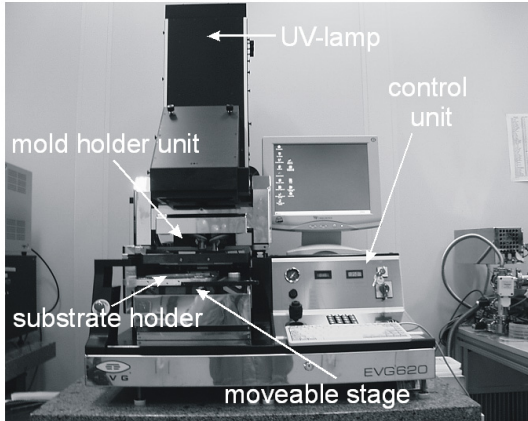
Nanoimprint Machines from EVG: 520 HE



- 8" imprint bonder in LETI / Gr noble
- imprint under vacuum
 - alignment separately in mask aligner
 - (+) good accessibility, usable for anodic bonding
 - (-) low pressure, speed (no water cooling)

Figure 5.18: Nanoimprint machine from EV Group based on an anodic bonder. Alignment is possible by using an appropriate mask aligner.

Nanoimprint Machines from EVG: 620



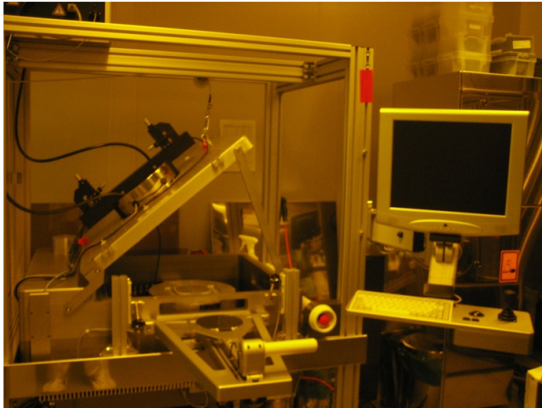
EVG-620

- Full wafer Soft-UV-NIL tool
- Semiautomatic tool
- Modified mask aligner
- 1000 W mercury lamp
- 6 inch exposure uniformity 4%
- 4 or 6 inch chuck system

- 4"-6" imprint tool at AMO / Aachen
- imprint with PDMS stamps using UV-NIL
 - alignment
- (+) combined with mask aligner
(-) low pressure, only with soft stamps

Figure 5.19: Nanoimprint machine from EV Group based on a mask aligner.

Nanoimprint Machines from EVG: 770



EVG-770:

- S&R-UV-NIL tool
- Quartz & soft stamps
- Semiautomatic tool
- 1000 W lamp
- 6 & 8 inch chuck system
- Alignment system

S&R UV imprint tool at AMO / Aachen

- imprint under vacuum
- alignment

(+) vacuum good for overprinting using inhibiting resists

(-) low pressure, access

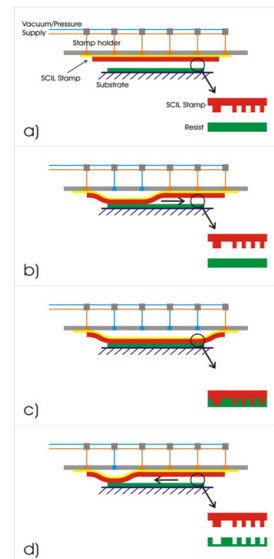
Figure 5.20: Nanoimprint machine from EV Group for S&R UV-NIL.

Nanoimprint Machines from SÜSS : MA8-SCIL



MA8-SCIL tool:

- Substrate Conformal Imprint Lithography (SCIL)
- Composite soft stamps
- Demonstrated with UV-curable resists and Sol-gel materials
- Semiautomatic tool
- 1000 W lamp
- 6 & 8 inch system
- Alignment system



6"-8" imprint tool at AMO / Aachen

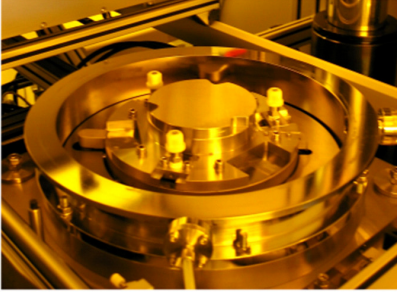
- UV imprint of large areas
- alignment

(+) molding and demolding

(-) layered stamp needed

Figure 5.21: Nanoimprint machine from SÜSS based on a mask aligner for hybrid soft masks.

JENOPTIK HEX03 Adapter Mount with SÜSS Alignment Fixture



An adaptor for the SÜSS alignment fixture for the bonder can be integrated in the HEX.

- pre-alignment of the stamp to the substrate is possible in the SÜSS mask aligner (MA6).
- fast embossing possible (constant T)

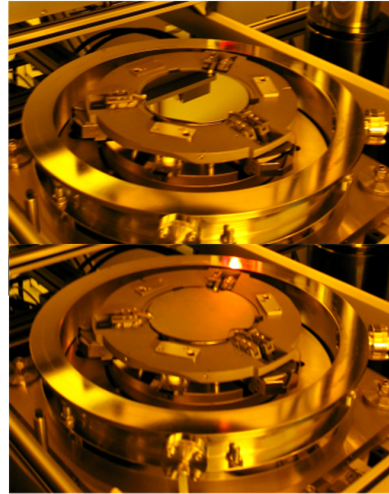


Figure 5.22: Jenoptik HEX03 nanoimprint machine with and integrated adapter for a Süss alignment fixture for an anodic bonder. Alignment is possible by using the appropriate mask aligner.

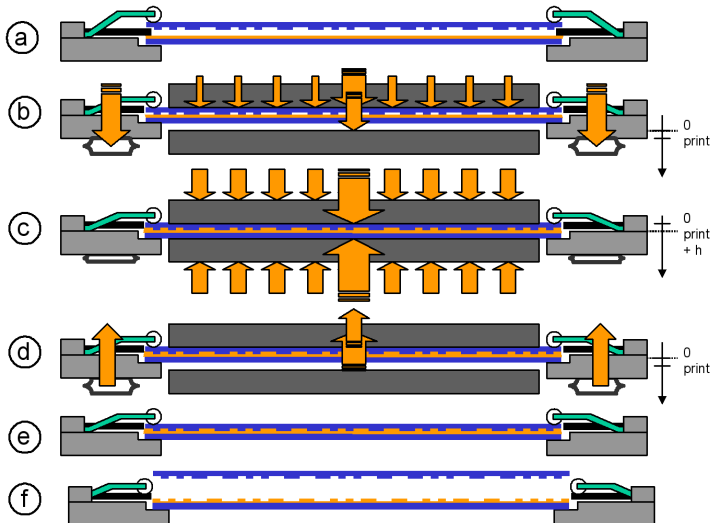
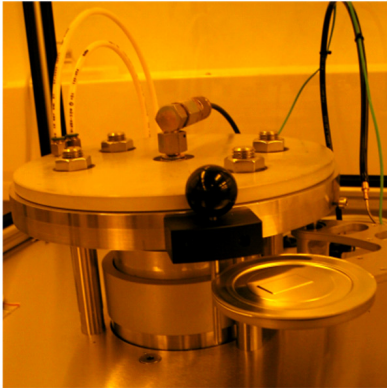
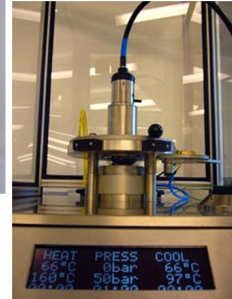
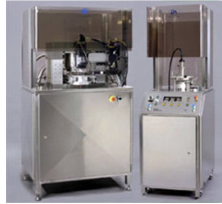


Figure 5.23: Schematic of a fast imprint with an alignment fixture: a) alignment and clamping of stamp (top) and substrate (bottom), b) contact of upper plate and down-movement, c) begin of molding upon contact to lower plate, d) pressure release and lift-up, e) cooling, f) manual demolding outside the press. For fast processing, the press plates are kept at constant (molding) temperature.

Nanoimprint Machines from OBDUCAT



- From 2.5" to 6" imprint
- imprint under vacuum, up to 250°C, 70 bar
- alignment possible
- (+) simple setup, fast embossing, versatile tool for NIL
- (-) membrane tends to glue (small stamp on large substrate); not well adapted for micro-embossing



Thermal imprint: soft press technology, uniformity of pressure by using a membrane with air pressure over the entire imprint area
UV-cured imprint: simultaneous application of thermal and UV imprint

Figure 5.24: Nanoimprint machine from Obducat using a pressurized membrane on one side instead of a hard stamper (call soft imprint – not to be confused with soft lithography). By using a transparent membrane, thermal imprint can be combined with UV-curing.

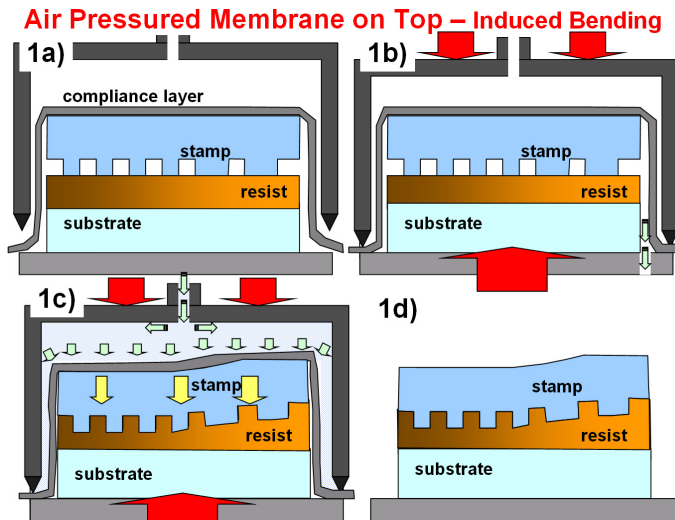
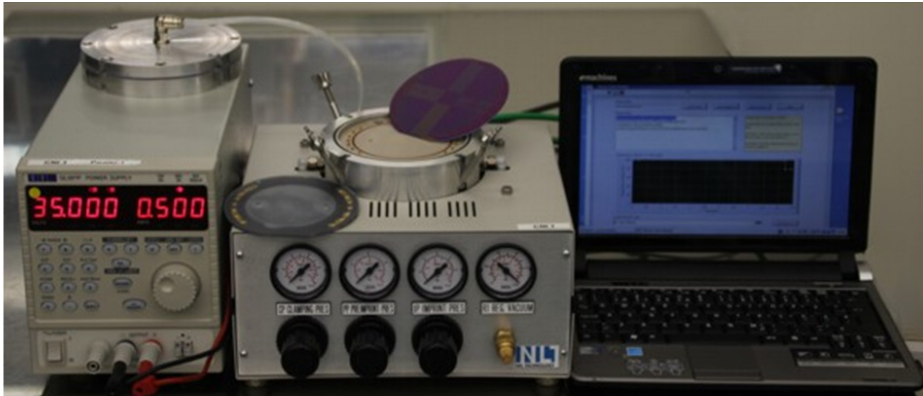


Figure 5.25: Principle of soft imprint approach by using a pressurized membrane (a compliance layer made from PDMS, a thin aluminium or plastic foil). By applying an air pressure on the sealed stack, a homogeneous pressure cushion is created at the backside of the stamp and maintained throughout the sinking of the protrusions.



Heating: Integrated stamp heating in conductive Si-wafer (highly p-doped implanted layer) and temperature control
Imprint temp: up to 200° C

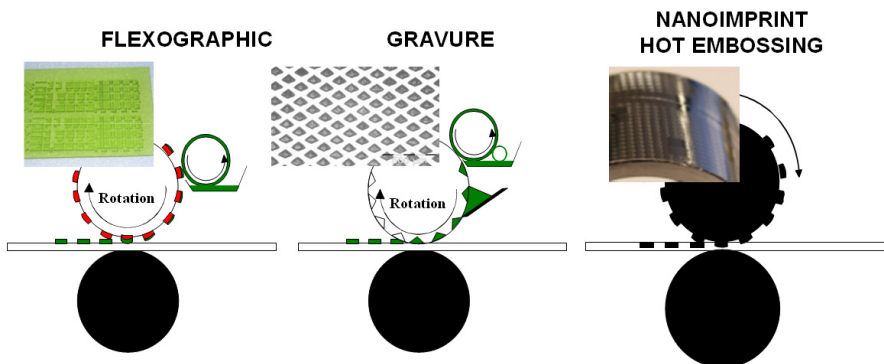
Stamps: Semi-flexible, segmented Si-wafers°. The mechanical membrane° can control imprint and de-molding conditions. Also use of PDMS and polymer foils possible (with heatable Si-dummy).

Pressure: Bellow (from above), up to 6 bar compressed-air system)

Figure 5.26: Compact NIL-2-GO nanoimprint machine from NILT using a pressurized membrane on one side instead of a hard stamper (call soft imprint – not to be confused with soft lithography). Additionally to this, segmented heatable silicon stamps can be used.

5.7.2 Roll-to-roll embossing tools (R2R)

Roll processing is a process in which a bent template is pressed against a thin foil that is continuously fed into the gap between two rolls. By controlling roll temperature, pressure, length of imprint (“nib”) and speed, physical conditions can be achieved similar to flat stamp nanoimprint. However, due to the simultaneous heating/cooling and pressing, dynamic equilibrium has to be maintained.



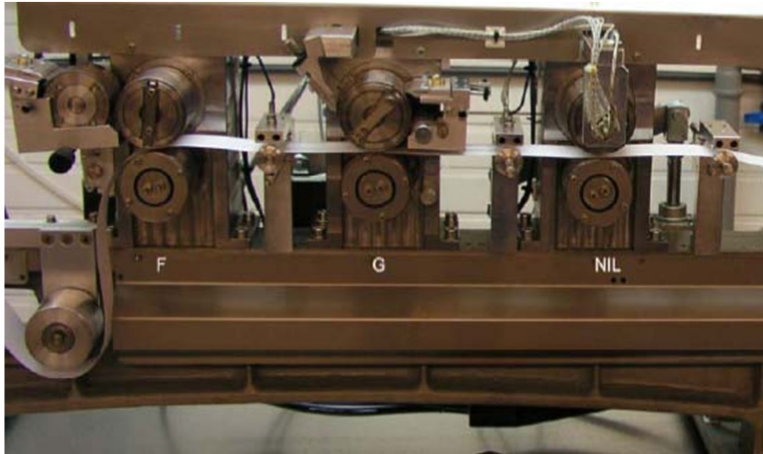
Newspapers, magazines, books, packages, etc...

- 50-100 um at minimum
- Speed up to ca. 500 m/minute
- *Flexo*: Water based inks, mineral oil etc..
- *Gravure*: Organic solvent (possible)

Holograms, decorative elements, etc..

- now (500 -1000 nm) 50 nm at minimum
- speed 0.1- 10 m/minute

Figure 5.27: Schematic of different roll-to-roll processes.



Starting Roll Flexoprint Gravure Nanoimprint Collecting Roll

Figure 5.28: Table-top roll embossing setup at VTT consisting of different roll-to-roll processes.

5.7.3 Micro injection molding tools (IM)

Polymer injection molding uses a closed cavity with temperature control and can be filled with a liquid polymer. After opening the cavity, a solidified part with the exact outlines of the total cavity is removed. Typically thermoplastic polymers are used which change their thermomechanical properties from solid to viscoelastic and viscous. There are different modes of operation: In the isothermal case, the hot melt is injected into a cooler cavity, leading to immediate freezing of the polymer upon contact with the mold surface. In the variothermal case (similar to hot embossing), the cavity is heated to a temperature at which cooling is slowed down and cooled after injection to a temperature where the demolding can take place. On the cost of longer process times, better replication fidelity is achieved. The structured insert can be glued, welded, soldered or clamped. The main advantage of clamping is that forces originating from different coefficients of thermal expansion between steel and silicon or nickel can be compensated due to more flexibility. Moreover, the wafer can be changed quickly for the production of small lots without destruction and used for analysis after the injection molding process. In order to avoid breakage of the wafer during processing, thin polyimide (PI) films counterbalance irregularities of the steel surface and movements of the wafer in relation to the steel insert.

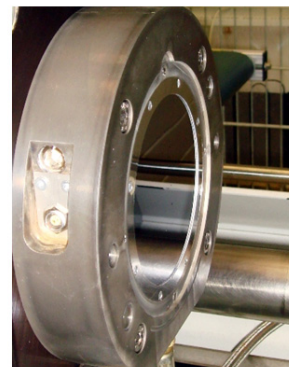
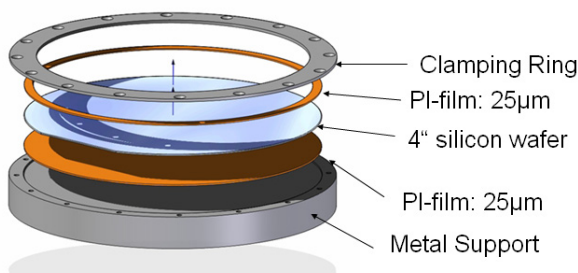


Figure 5.29: Left side: Clamping system for a 4" wafer used as insert for injection molding. Right side: Tool with ejection side of the injection mold with structured 4" silicon wafer.

5.8 Processes – Part 1 : Thermal Nanoimprint with simple pattern transfer

NIL was first reported as thermoplastic molding, and is therefore often referred to as hot embossing lithography (HEL). The unique advantage of a thermoplastic material is that the viscosity can be changed to a large extent by simply varying the temperature. The first stage of the NIL process is the molding of a thin thermoplastic film using a hard master. During a process cycle the resist material is made viscous by heating, and shaped by applying pressure. Here the thermoplastic film is compressed between the stamp and substrate and the viscous polymer is forced to flow into the cavities of the mold, conforming exactly to the surface relief of the stamp. For thermal NIL the pressure must be maintained during the sinking of the stamp. Due to stamp protrusion density and size variations this speed is different and the stamp tends to bend. For the equilibration of pressure compliance layer is needed is needed.

When the cavities of the stamps are filled, the polymer is cooled down, while the pressure is maintained. Thus the molten structure is frozen. After relieving the pressure, the stamp can be retrieved (demolded) without damage and reused for the next molding cycle. The demolding step is often done by peeling and only by using stamps and substrates attached to the press stampers, or by using small stamps of a few mm size, parallel demolding can be anticipated. In a second step, the thickness profile of the polymer film can now be used as a resist for pattern transfer. For this, the residual layer remaining in the thin areas of the resist has to be removed, which is done by homogeneously thinning down the resist in an (ideally) anisotropic etching process. In this way, process windows are opened to the substrate and the polymer can be used as a masking layer for further processing steps.

Thermal-NIL (Hot Embossing)

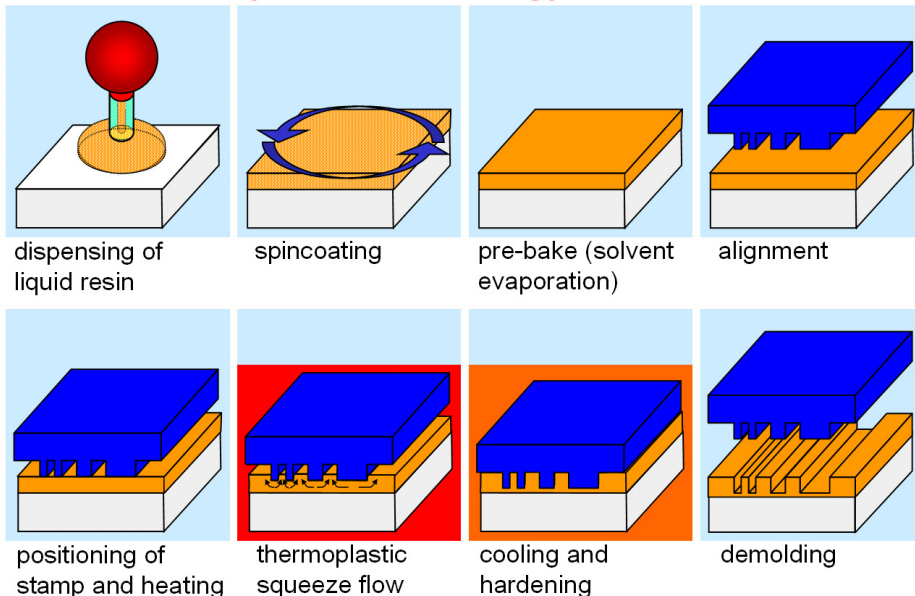


Figure 5.30: Process sequence for thermal nanoimprint (spincoating, imprint and demolding).

De-Molding – Forces – Vertical Sidewalls

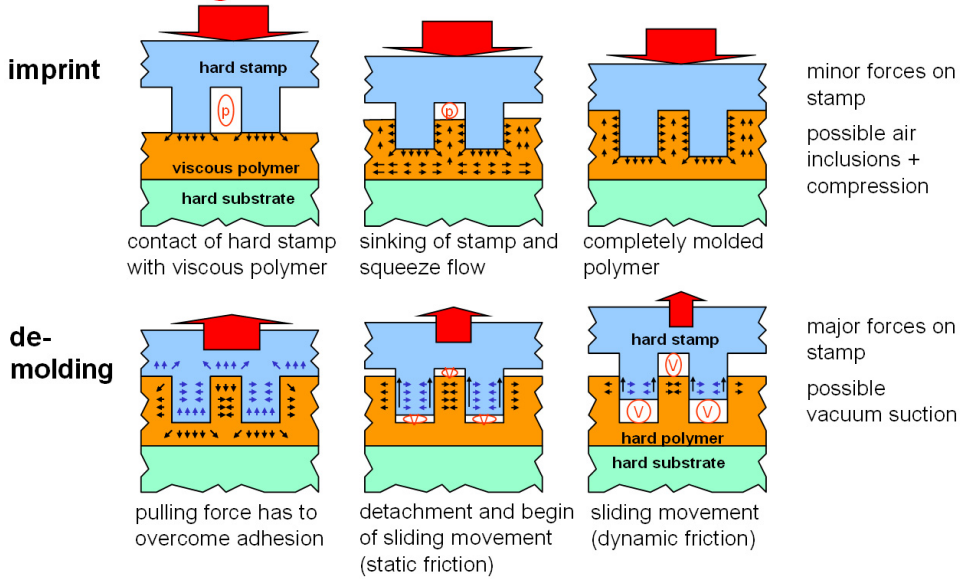


Figure 5.31: Forces present during the demolding of stamp structures.

Demolding – Bending and Peel off

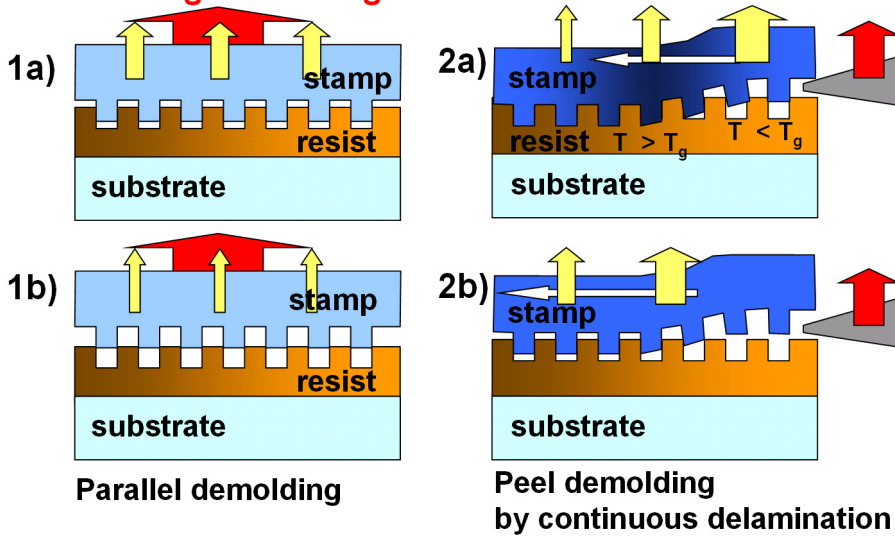


Figure 5.32: Principle for parallel and wedge induced demolding.

Residual Layer Etch (Substrate Window opening)

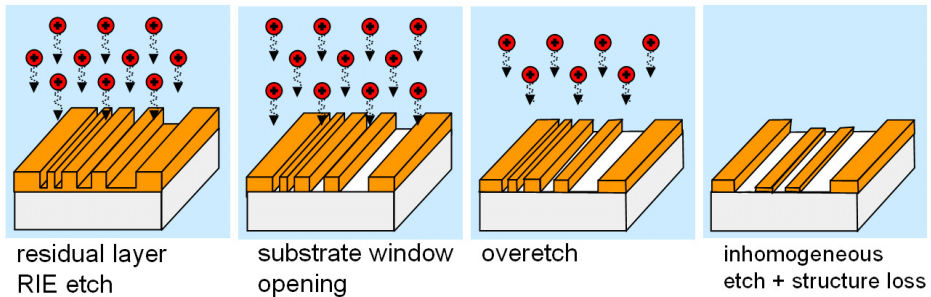


Figure 5.33: Process sequence for residual layer etching.

Short description

The residual layer is a result of the limited ability to mechanically squeeze material out of gap. In order to open windows to the substrate, the layer has to be removed, which is normally done by homogeneously thinning the resist by RIE.

Advantages

- By opening the substrate window, the substrate is chemically “activated”.

Disadvantages

- Possible dependence on structure size and depth results in inhomogeneous layer thickness.
- The exposure of the substrate to the RIE may result in damage, e.g. for biological coatings.
- Isotropic etching of structures may result in structure loss

Alternative solutions

- A hard mask below the resist may enhance the selectivity of the patterned structure with respect to the underlying substrate.
- Imprint at very high pressures was reported to result in a zero-residual layer
- A combination of imprint and exposure through a semitransparent stamp makes it possible to dissolve the residual layer in a developer after exposure of the elevated structures.

References:

- [1] M. Li, L. Chen, W. Zhang, and S.Y. Chou, *Pattern transfer fidelity of nanoimprint lithography on six-inch wafers*, *Nanotechnol.* **14** (2003) 33–36
- [2] H. Schiff, S. Park, and J. Gobrecht, *Nano-imprint - molding resists for lithography*, *J. Photopolym. Sci. Technol. (Japan)* **16** (3) (2003) 435–438.
- [3] H. Schiff, S. Park, C.-G. Choi, C.-S. Kee, S.-P. Han, K.-B. Yoon, and J. Gobrecht, *Fabrication process for polymer photonic crystals using nanoimprint lithography*, *Nanotechnol.* **16** (2005) S261–S265.

Window Opening + Substrate Etching

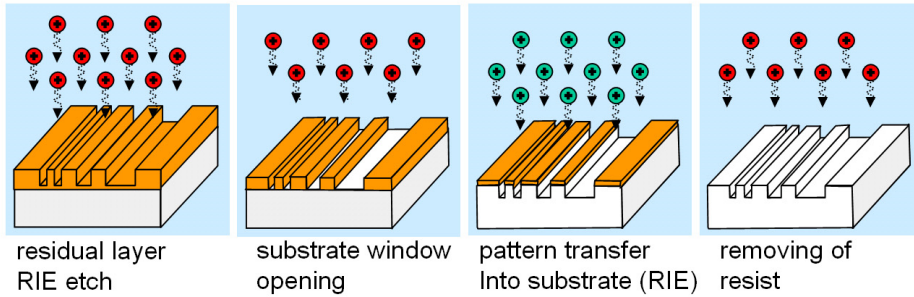


Figure 5.34: Process sequence for residual layer and substrate etching.

Short description

Etching of the substrate can be done as in normal resist processes. There is no major difference to optical or electron beam lithography

Advantages with respect to other pattern transfer processes

- Etching is the process of choice in industry because the pattern transfer is more precise than in additive processes.

Disadvantages

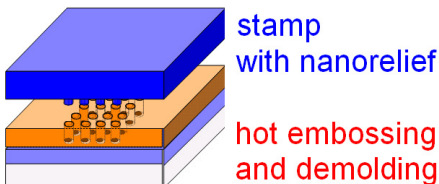
- Suitable etching gases have to be found for RIE with high selectivity.

References:

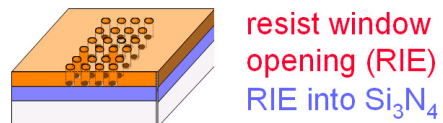
- [1] L.J. Heyderman, B. Ketterer, D. Bächle, F. Glaus, B. Haas, H. Schiff, K. Vogelsang, J. Gobrecht, L. Tiefenauer, O. Dubochet, P. Surbled, and T. Hessler, *High volume fabrication of customised nanopore membrane chips*, *Microelectronic Eng.* **67-68** (2003) 208-213.

Fabrication of Sieves

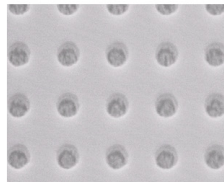
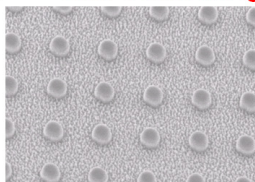
compression molding



pattern transfer



stamp



pores in Si_3N_4
period 1 μm

Figure 5.35: Example for etching as a pattern transfer process after NIL.

Lift-off

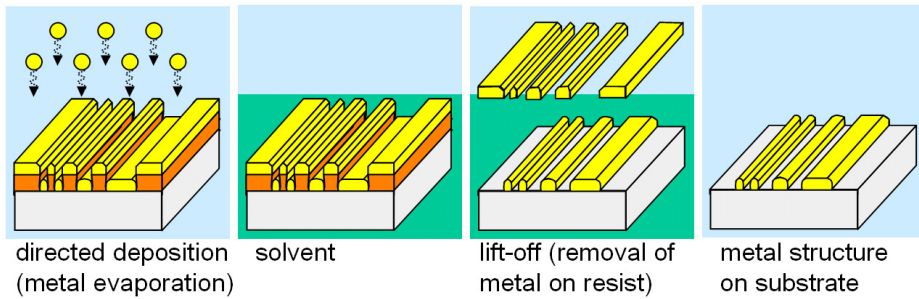


Figure 5.36: Example for lift-off as a pattern transfer process after NIL.

Short description

Lift-off is the adding of material by evaporation, and partial release of the material by dissolving the underlying resist. Lift-off works best if the resist has undercuts, which can be adjusted in optical or electron beam lithography, but not in NIL.

Advantages with respect to other pattern transfer processes

- Lift-off can be applied for a range of materials.

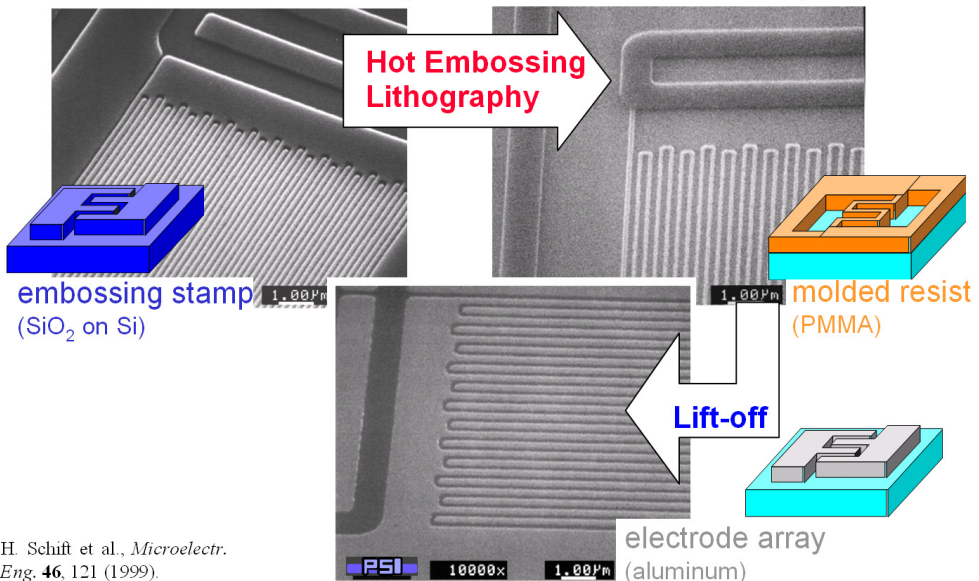
Disadvantages

- Directed evaporation avoiding sidewall coverage is crucial. Dependent on structure sizes.

References:

- [1] H. Schiff, R.W. Jaszewski, C. David, and J. Gobrecht, *Nanostructuring of polymers and fabrication of interdigitated electrodes by hot embossing lithography*, *Microelectron. Eng.* **46** (1999) 121-124.

Fabrication of Interdigitated Electrode Arrays



H. Schiff et al., *Microelectr. Eng.* **46**, 121 (1999).

Figure 5.37: Example for lift-off as a pattern transfer process after NIL.

Electroplating

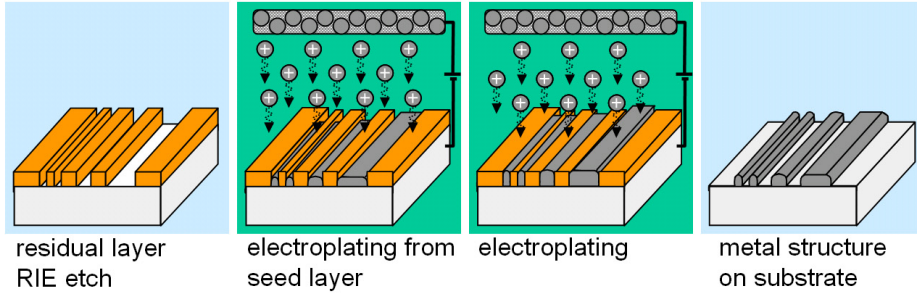


Figure 5.38: Example for electroplating as a pattern transfer process after NIL (with a conducting substrate).

Short description

Electroplating is a deposition by growing material from a solution. Lift-off works best if the resist has undercuts, which can be adjusted in optical or electron beam lithography, but not in NIL.

Advantages with respect to other pattern transfer processes

- Electroplating fills structures well from the bottom. Overplating is possible.

Disadvantages

- The range of materials is limited.
- A plating base (seed layer) has to be deposited before plating and often has to be removed selectively after plating.

References:

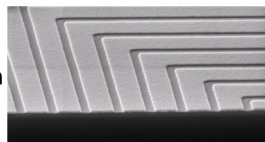
[1] L.J. Heyderman, H. Schiff, C. David, B. Ketterer, M. Auf der Maur, and J. Gobrecht, *Nanofabrication using hot embossing lithography and electroforming*, *Microelectron. Eng.* **57-58** (2001) 375-380.

Fabrication of Electrodes using Electroplating

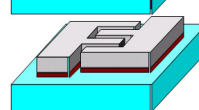
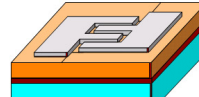
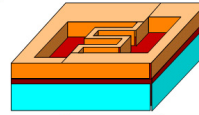
compression molding



metal lanes
(period 1 μm)
PMMA: 50 nm
Nickel: 45 nm



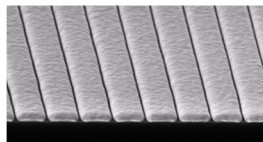
pattern transfer



seed layer window opening

electroforming

removing of resist and seed layer



500% overplated PMMA: 45 nm
Nickel: 270 nm

Figure 5.39: Example for electroplating as a pattern transfer process after NIL.

5.9 Processes – Part 2 : Process variants for resist patterning

NIL is a parallel patterning method in which a surface pattern of a stamp is replicated into a material coated on a hard substrate by mechanical contact and 3D material displacement, to be used in fields until now reserved to electron beam lithography (EBL) and photolithography (PL). This definition fits very well for thermal NIL and UV-NIL, and can be extended to resists which can be both molded by heat and pressure and cured. It can also include all variants processes of reversal imprint, as long as a pre-patterned film is transferred and bonded to another substrate. However, often the term nanoimprint is often used when a pattern with nano-dimensions is molded in a functional material, without any further pattern transfer (e.g. fluidic or optical application). Then the process is rather taking advantage of the toolbox of NIL than being a NIL process. The table 5.3 below gives an overview about the basic differences between thermal NIL and UV-NIL, but – as can be seen in the following and in Part II of this library – does not cover all possible variants of NIL processes.

Table 5.4. Comparison of thermal NIL (hot embossing) and UV-assisted NIL (UV-imprint), with typical parameters of current state-of-the-art processes.

type of NIL / properties	thermal NIL hot embossing	UV-assisted NIL UV-imprint
basic process sequence	1) spin-coat thermoplastic film 2) place stamp on film 3) heat until viscous 4) emboss at high pressure 5) cool until solid 6) demold stamp	1) dispense liquid resin 2) parallel alignment of stamp with defined gap 3) imprint at low pressure 4) expose with UV-light through stamp and crosslink 5) demold stamp
pressure p	20-100 bar	0-5 bar
temperature T_{mold}	100-200°C	20°C (ambient)
temperature T_{demold}	20-80°C	20°C (ambient)
Resist	solid, thermoplastic $T_g \approx 60-100^\circ\text{C}$	liquid, UV-curable
viscosity	10^3-10^7 Pa·s	$10^{-3}-10^{-1}$ Pa·s
stamp material	Si, SiO ₂ , OrmoStamp® opaque	glass, SiO ₂ , OrmoStamp® transparent
stamp area	full wafer, ≤ 300 mm diameter	25x25 cm ² , limited by control of gap
stamp contact	facilitated by bending	planarization layer
embossing time	from sec to minutes	< 1 min (per exposure)
Advantage	low-cost, large area equipment and stamps	room temperature, low pressure, alignment through stamp
Challenge	process time, thermal expansion due to thermal cycle	step and repeat needed for large areas
development needed	alignment, residual layer homogeneity	material variety and resist stripping
Hybrid approaches	thermoset resists: embossing and curing before demolding	thermoplastic resists: hot molding and UV-curing before demolding
Advantage (hyb. app.)	low temperature variation cycle: demolding at high temperature possible	solid resist: full wafer single imprint possible

Thermal-NIL + Thermal Curing (before Demolding)

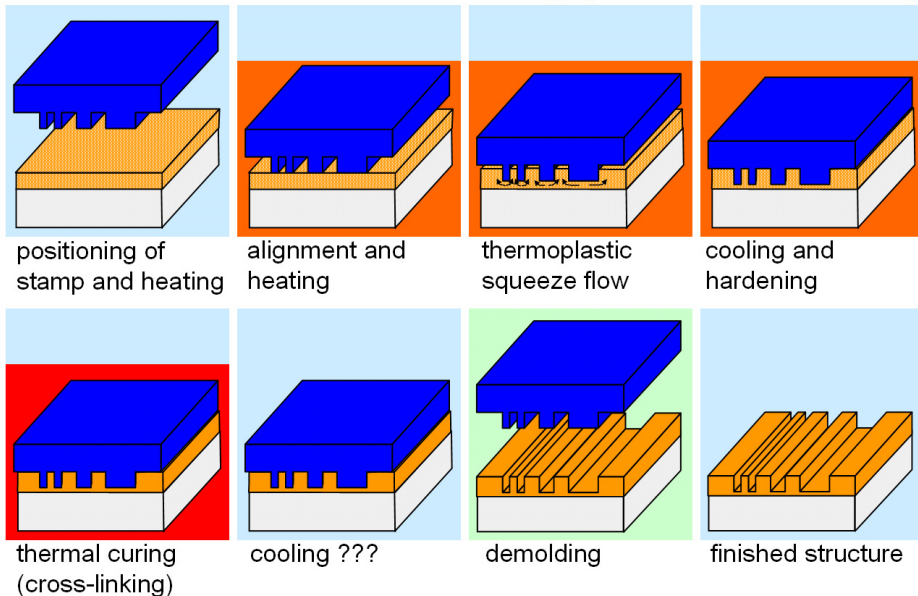


Figure 5.40: Process sequence for thermal NIL with a curable resist.

Short description

Thermal curing imprint uses a thermoset resist instead of a purely thermoplastic resist, which can be crosslinked after imprint. This is normally done before demolding, while the stamp is still within the molded resist. Maintaining the pressure during curing can compensate for shrinkage.

Main application

- Critical processes with high aspect ratio
- Isothermal processes are possible (no cooling needed before demolding)

Advantages

- The crosslinked resist can be demolded more easily, and the resist is more stable in subsequent processes.
- The resist can be used in a mix- and match process (exposure by optical lithography)

Disadvantages

- The molding and curing step have to be temporarily separated.
- resist cannot be dissolved easily, e.g. if resist is sticking to the stamp.

References:

- [1] H. Schulz, D. Lyebdyev, H.-C. Scheer, K. Pfeiffer, G. Bleidiessel, G. Grützner, and J. Ahopelto, *Master replication into thermosetting polymers for nanoimprinting*, J. Vac. Sci. Technol. B **18**(6) (2000) 3582-3585.
- [2] K. Pfeiffer, F. Reuther, M. Fink, G. Gruetzner, P. Carlberg, I. Maximov, L. Montelius, J. Seekamp, S. Zankovych, C.M. Sotomayor-Torres H. Schulz, and H.-C. Scheer, *A comparison of thermally and photochemically cross-linked polymers for nanoimprinting*, Microelectron. Eng. **67-68** (2003) 266-273.

Thermal NIL + UV-Curing (after Demolding)

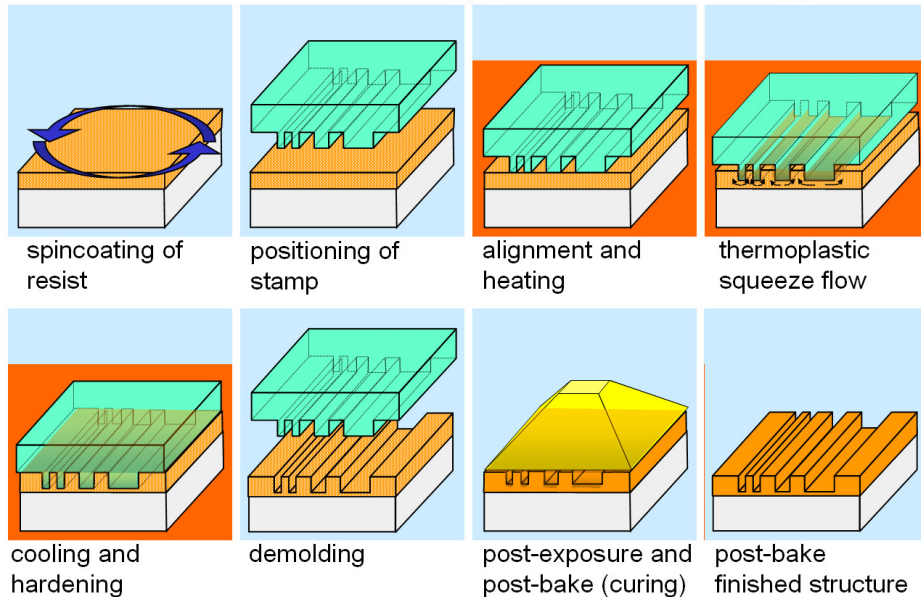


Figure 5.41: Process sequence for sequential thermal NIL into a low T_g thermoplastic material and subsequent curing.

Short description

Thermal imprint of a UV-curable material uses a thermoplastic resist instead of a liquid resin, which can be crosslinked after imprint and demolding. This can be done through exposure through the stamp (or substrate).

Main application

- Mix- and match applications.
- Isothermal processing

Advantages

- The resist can be prepared as a solid layer by spincoating before imprint. The crosslinked resist is more stable in subsequent processes.
- The resist can be used in a mix- and match process (exposure by optical lithography)

Disadvantages

- Transparent stamps or substrates needed.
- Material can be too soft for demolding before crosslinking (low T_g). Crosslinked resist cannot be dissolved easily, e.g. if resist is sticking to the stamp.

References:

- [1] F. Reuther, K. Pfeiffer, M. Fink, G. Gruetzner, H. Schulz, H.-C. Scheer, F. Gaboriau, and C. Cardinaud, *Mix and match of nanoimprint and UV lithography*, Proc. SPIE **4343** (2001) 802-809.
- [2] K. Pfeiffer, M. Fink, G. Gruetzner, G. Bleidiessel, H. Schulz, and H.-C. Scheer, *Multistep profiles by mix and match of nanoimprint and UV-lithography*, Microelectron. Eng. **57-58** (2001) 381-387.

UV-NIL + Residual Layer Etch + Substrate Etching

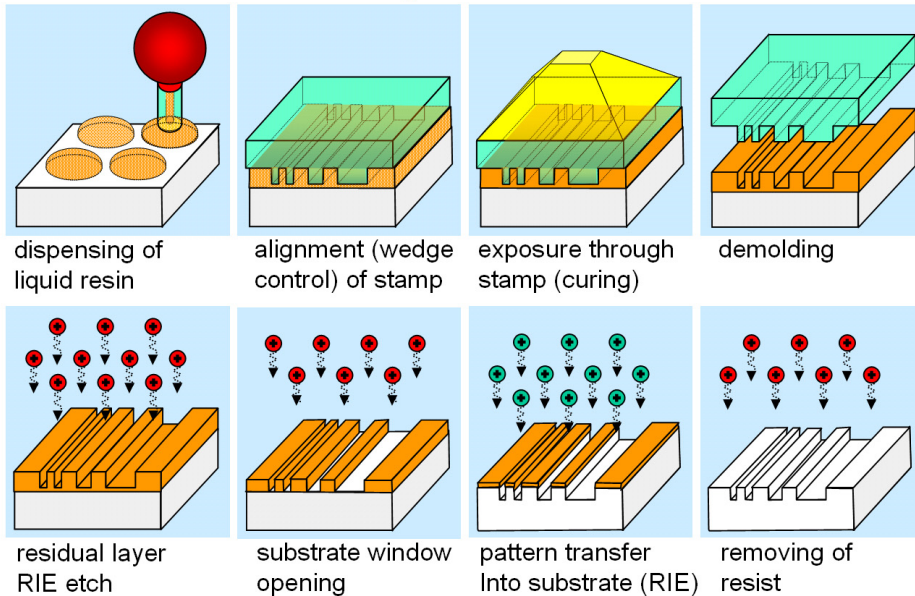


Figure 5.42: Process sequence for UV-NIL, residual layer etch and substrate etching.

Short description

With the integration of light sources into imprint machines, UV-NIL was developed for photocurable resists. The basic difference between UV-NIL and NIL is that a resin, which is liquid at room temperature, is shaped by a moderate pressure, which is then crosslinked and hardened.

Main application

- Step & Flash Imprint Lithography (SFIL) process.

Advantages

- Low viscosity resist makes molding fast.
- Alignment through mask possible
- Room temperature process.

Disadvantages

- Liquid resist has to be applied before imprint by dispensing. Transparent stamps needed (quartz).
- Equilibration (wedge control) before exposure, low pressure does not squeeze stamp around dust particles

References:

- [1] M.D. Stewart, S.C. Johnson, S.V. Sreenivasan, D.J. Resnick, and C.G. Willson, *Nanofabrication with step and flash imprint lithography*, J. Microlith. Microfab. Microsyst. 4(1) (2005) 011002.
- [2] D.J. Resnick, W.J. Dauksher, D. Mancini, K. J. Nordquist, T.C. Bailey, S. Johnson, N. Stacey, J.G. Ekerdt, and C.G. Willson, S. V. Sreenivasan, N. Schumaker, *Imprint lithography: lab curiosity or the real NGL?*, Proc. SPIE 5037 (2003) 12-23.
- [3] D.J. Resnick, S.V. Sreenivasan, and C.G. Willson, *Step & flash imprint lithography*, Materials Today 8 (2005) 34-42.

Thermal + UV-NIL (before Demolding)

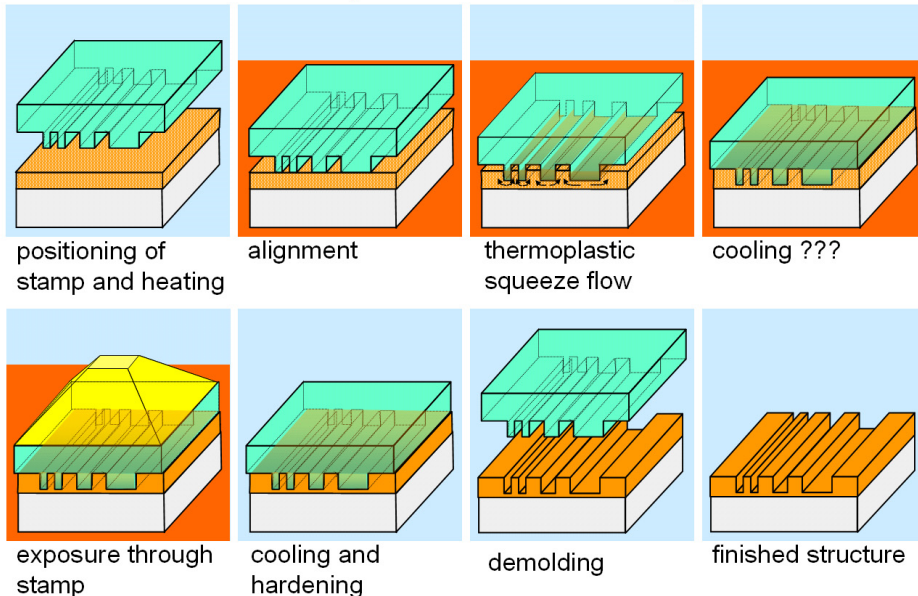


Figure 5.43: Process sequence for combined thermal and UV-NIL.

Short description

Thermal imprint of a UV-curable material uses a thermoplastic resist instead of a liquid resin, which can be crosslinked after imprint (but before demolding). This can be done through exposure through the stamp (or substrate).

Main application

- Mix- and match applications.
- Isothermal processing

Advantages

- The resist can be prepared as a solid layer by spincoating before imprint. The crosslinked resist is more stable during demolding and in subsequent processes.
- The resist can be used in a mix- and match process (exposure by optical lithography)

Disadvantages

- Transparent stamps or substrates needed.
- Crosslinked resist cannot be dissolved easily, e.g. if resist is sticking to the stamp.

References:

- [1] M. Beck and B. Heidari, *Nanoimprint lithography for high volume HDI manufacturing*, OnBoard Technology Sept. 2006, 52-55, URL: <http://www.Onboard-Technology.com/>, accessed July 11, 2007.

NIL + Photolithography (with locally transparent stamp)

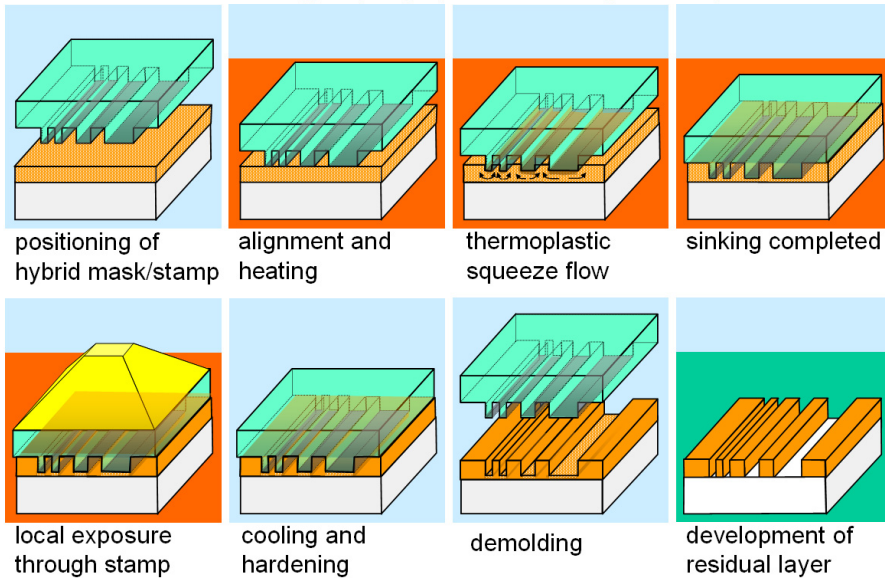


Figure 5.44: Process sequence for combined thermal and photolithography (CNP) with a semi-transparent stamp.

Short description

Thermal imprint of a UV-curable material through a semitransparent stamp uses a thermoplastic resist instead of a liquid resin, which is a negative photoresist resist can be crosslinked after imprint (but before demolding). This can be done through exposure through the stamp. If the elevated are nontransparent, then the thinned regions of the resist (residual layer) stay soluble and can be selectively removed in a developer.

Main application

- Processes where the reduction of process steps is of advantage.
- Isothermal processing

Advantages

- The resist can be prepared as a solid layer by spincoating before imprint. The crosslinked resist is more stable in subsequent processes.
- The resist can be used in a mix- and match process (exposure by optical lithography)

Disadvantages

- Semi-transparent stamps or substrates needed. Possible problems with diffraction.
- Works only for very thin residual layer thickness.

References:

- [1] X. Cheng and L.J. Guo, *A combined-nanoimprint-and-photolithography patterning technique*, *Microelectron. Eng.* **71** (2004) 277–282.
- [2] X. Cheng and L.J. Guo, *One-step lithography for various size patterns with a hybrid mask-mold*, *Microelectron. Eng.* **71** (2004) 288–293.
- [3] M.B. Christiansen, M.Schøler, and A. Kristensen, *Combined nano-imprint and photolithography (CNP) of integrated polymer optics*, *Proc. SPIE* **6462** (2007) 64620.
- [4] A. Schleunitz, C. Spreu, T. Haatainen, A. Klukowska, and H. Schiff, *Fabrication of mesas with micro- and nanopatterned surface relief used as working stamps for step & stamp imprint lithography*, *J. Vac. Sci. Technol. B* **28**(6) (2010) C6M37–40.

Reversal Imprint (Hot Embossing)

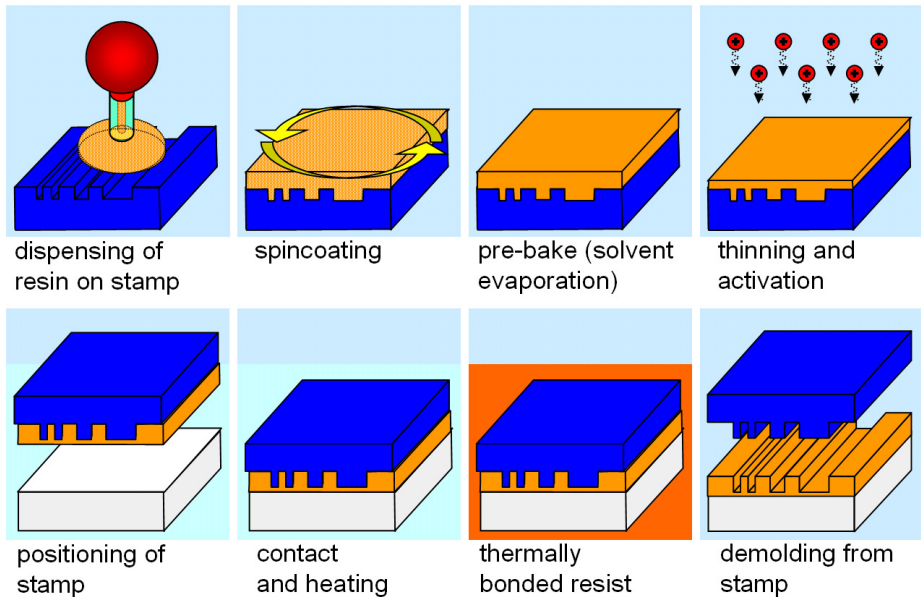


Figure 5.45: Process sequence for reversal imprint by thermal bonding of a resist layer from a stamp to a separate substrate.

Short description

Reversal imprint makes it possible to structure a resist before transfer to another substrate. The transfer is done via thermal bonding of the resist and demolding is done after bonding.

Main application

- Applications where a larger degrees of freedom is needed.
- 3D structures (embedded channels) possible

Advantages

- Patterning of substrates is possible which do not support solvents.
- Reduction of residual layer thickness possible

Disadvantages

- Spincoating on stamp with antiadhesive coating not easy.
- Possible dependence of transfer on local structure size and aspect ratio.

References:

- [1] T. Borzenko, M. Tormen, G. Schmidt, and L.W. Molenkamp, *Polymer bonding process for nanolithography*, Appl. Phys. Lett. **79**(14) (2001) 2246-2248.
- [2] X.D. Huang, L.-R. Bao, X. Cheng, L.J. Guo, S.W. Pang, and A.F. Yee, *Reversal imprinting by transferring polymer from mold to substrate*, J. Vac. Sci. Technol. B **20**(6), (2002) 2872-2876.
- [3] T. Yoshikawa, T. Konishi, M. Nakajima, H. Kikuta, H. Kawata, and Y. Hirai, *Fabrication of 1/4 wave plate by nanocasting lithography*, J. Vac. Sci. Technol. B **23**(6) (2005) 2939-2943.
- [4] K. Sogo, M. Nakajima, H. Kawata, and Y. Hirai, *Reproduction of fine structures by nanocasting lithography*, Microelectron. Eng. **84**(5-8) (2007) 909-911.

5.10 Processes – Part 3 : Hybrid processing

Combined NIL and UV-PL (CNP) – MESA Fabrication

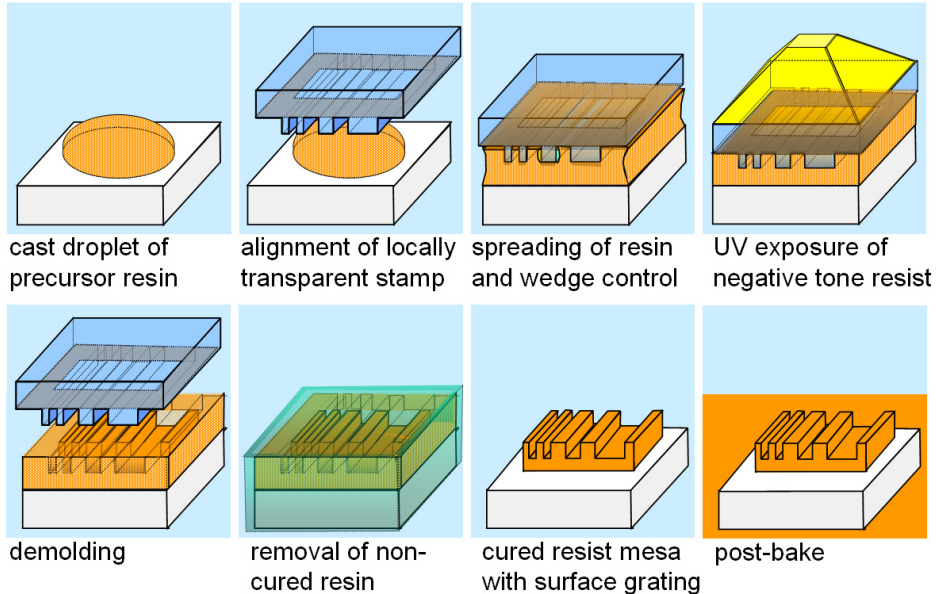


Figure 5.46: Process sequence for combined nanoimprint lithography and UV-photolithography (CNP) enables to combine surface patterning on mesas.

Short description

Surface structured mesas can be fabricated by restricting the UV-exposure to an area which defines its outline. Instead of thin absorbers on the stamp protrusions, here a larger stamp area is covered, either on all protrusions, or at an intermediate or back-side of the mask-mold. Hence, nanostructures can be placed on large microstructures.

Main application

- Waveguides (or lasers) with surface gratings for light filtering and feedback.
- Stamps with defined protrusion used in step & repeat nanoimprint

Advantages

- Two-level patterning, e.g. if the active surface has to be decoupled from the surface.
- Complex shapes can be generated independently (ring waveguides).

Disadvantages

- Not easily possible with thermoplastic resists (e.g. by pulsed NIL).
- Due to shrinkage, the surface of the mesa may not be optimally flat.

References:

- [1] K. Pfeiffer, M. Fink, G. Gruetzner, G. Bleidiessel, H. Schulz, and H. Scheer, *Multistep Profiles by Mix and Match of Nanoimprint and UV-Lithography*, *Microelectronic Engineering, Microelectron. Eng.* **57–58** (2001) 381-387.
- [2] X. Cheng and L.J. Guo, *A Combined-Nanoimprint-and-Photolithography Patterning Technique*, *Microelectron. Eng.* **71** (2004) 277-282.
- [3] M. B. Christiansen, F. Arango, M. Schøler, and A. Kristensen, *Integration of active and passive polymer optics*, *Opt. Express* **15** (2007) 3931-3939.
- [4] A. Schleunitz, C. Spreu, T. Haatainen, A. Klukowska, and H. Schiff, *Fabrication of mesas with micro- and nanopatterned surface relief used as working stamps for step & stamp imprint lithography*, *J. Vac. Sci. Technol. B* **28**(6) (2010) C6M37.

Electron Beam Lithography and Thermal-Reflow

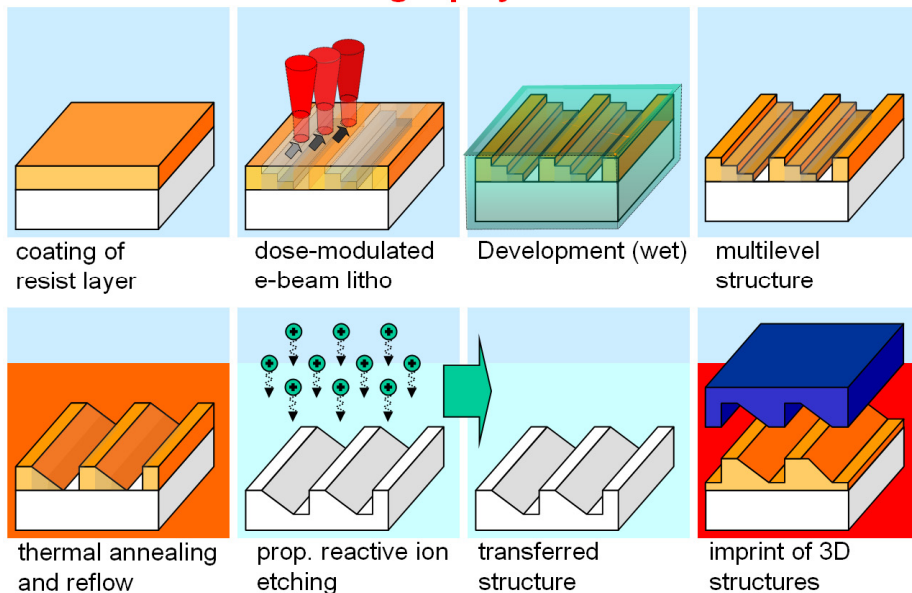


Figure 5.47: Process sequence for a TASTE (see below) process, here demonstrated for combination of dose-modulated (grayscale) electron beam lithography (here process variant with grayscale electron lithography for 3D patterning).

Short description

The TASTE process (Thermally Activated Selective Topography Equilibrium) is a 3D surface patterning process for a wide range of surface topographies. It is based on a molecular weight dependent reflow of resist structures. This molecular weight reduction can be performed by irradiation with electron-beams, X-rays, protons etc.

Main application

- Outcoupling prisms for backlight illumination, lenses with concave and convex shapes.
- Shallow slopes for microfluidics.

Advantages

- Locally selective reflow enables to generate multiple shapes in the same resist.
- Final shape is determined by geometrical factors enabling different structures in the same resist.

Disadvantages

- Currently limited to micrometer sizes (0.5-2 μm resist thickness) and up to 45°.
- Relies on exact dose control if multistep profiles are generated by grayscale electron beam

References:

- [1] A. Schleunitz and H. Schiff, *Fabrication of 3-D nanoimprint stamps with continuous reliefs using dose-modulated electron beam lithography and thermal reflow*, J. Micromech. Microeng. **20** (2010) 095002.
- [2] A. Schleunitz and H. Schiff, *Fabrication of 3-D patterns with vertical and sloped sidewalls by grayscale electron-beam lithography and thermal annealing*, Microelectron. Eng. **88**(8) (2011) 2736-2739.
- [3] A. Schleunitz, V.A. Guzenko, A. Schander, M. Vogler, and H. Schiff, *Selective profile transformation of electron-beam exposed multilevel resist structures based on a molecular weight dependent thermal reflow*, J. Vac. Sci. Technol. B **29**(6) (2011) 06F302.
- [4] A. Schleunitz and H. Schiff, *Combining nanoimprint lithography and a molecular weight selective thermal reflow for the generation of mixed 3-D structures*, J. Vac. Sci. Technol. B **29**(6) (2011) 06FC01.
- [5] A. Schleunitz, V.A. Guzenko, M. Messerschmidt, H. Atasoy, R. Kirchner, and H. Schiff, *Novel 3D micro- and nanofabrication method using thermally activated selective topography equilibration (TASTE) of polymers*, Nano Convergence **1:4** (2014),.

Combined NIL, E-Beam Litho and Thermal Reflow

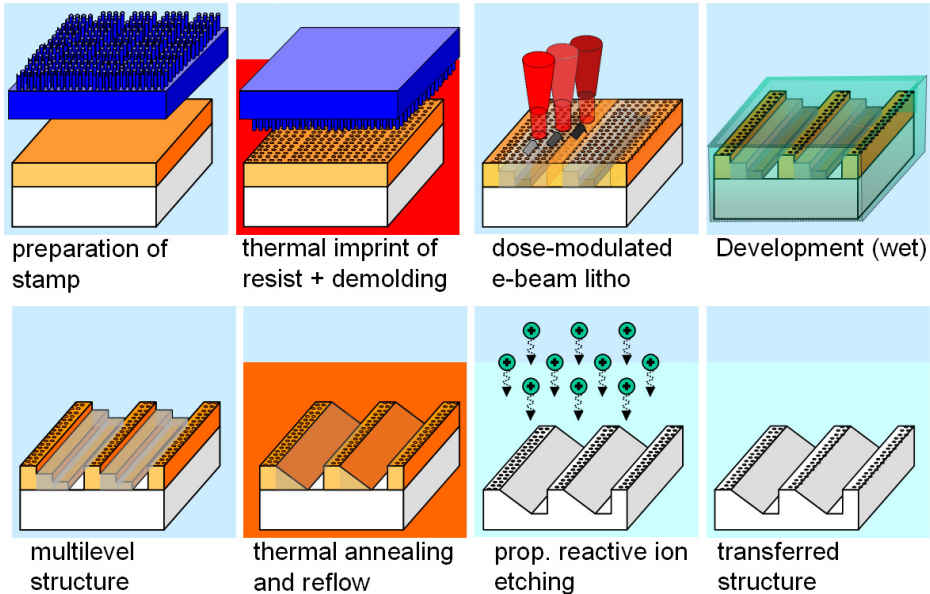


Figure 5.48: Process sequence for a hybrid TASTE process, by combining nanoimprint lithography, dose-modulated electron beam lithography, selective thermal reflow and proportional pattern transfer by reactive ion etching.

Short description

Since the TASTE process typically uses thermoplastic materials, it can be imprinted prior to exposure. By choosing a resist with a molecular weight suitable for NIL and e-beam lithography. Due to the difference in imprint (30° to 60°C over T_g) and reflow temperature (around the T_g of the original resist), the imprinted structures and nonexposed areas are not affected by reflow.

Main application

- Antireflection (moth-eye) structures on optical devices by adding of gratings to resist surface).
- Fluidic nanochannels on larger structures

Advantages

- Large areas can be patterned by imprint, while EBL is restricted to 3D only.
- By pattern transfer, a stamp with combined micro- and nanostructures can be fabricated.

Disadvantages

- Proportional pattern transfer restricted to small heights.
- Structures cannot be added to slopes.

References:

- [1] M. B. Christiansen, F. Arango, M. Schøler, and A. Kristensen, *Integration of active and passive polymer optics*, Opt. Express **15** (2007) 3931-3939.
- [2] A. Schleunitz, C. Spreu, T. Haatainen, A. Klukowska, and H. Schiff, *Fabrication of mesas with micro- and nanopatterned surface relief used as working stamps for step & stamp imprint lithography*, J. Vac. Sci. Technol. B **28**(6) (2010) C6M37.
- [3] A. Schleunitz and H. Schiff, *Combining nanoimprint lithography and a molecular weight selective thermal reflow for the generation of mixed 3-D structures*, J. Vac. Sci. Technol. B **29**(6) (2011) 06FC01.
- [4] A. Schleunitz, V.A. Guzenko, M. Messerschmidt, H. Atasoy, R. Kirchner, and H. Schiff, *Novel 3D micro- and nanofabrication method using thermally activated selective topography equilibration (TASTE) of polymers*, Nano Convergence **1:4** (2014),

5.11 Step and Repeat Nanoimprint Lithography

Step and Stamp Imprint Lithography (SSIL) is complementary to full wafer single imprint (FWSI), because it allows to pattern entire wafers by repeated imprint of a small stamp with a lateral movement after each imprint. New setups such as the NPS300 from SET S.A.S. (formerly SÜSS MicroTec) are equipped with heating stages, and can imprint thermoplastic resists, which makes the process comparable to thermoplastic molding of full wafer stamps. Small stamps allow to employ small forces, which results in pressures similar to full wafer single imprint. By using a low density of sub-micron sized protrusions on a stamp, an extremely small residual layer thickness can be achieved, due to the high local pressure of the protrusions and the ease of the polymer to flow laterally. Then standard RIE processes, with pure oxygen at low pressure, as common in many laboratories, can be used for the etching of the residual layer with good control of CDs. In this report this is demonstrated along with the pattern transfer using standard fluorine plasma chemistry.

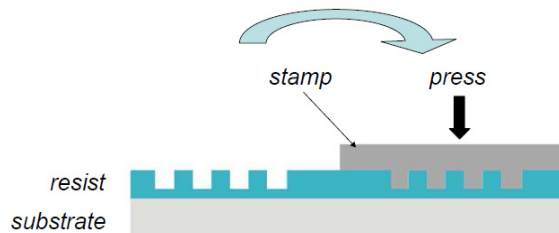


Figure 5.49: Process sequence for step and repeat imprint.

Process description: Step and Stamp Nanoimprint Lithography

Sequential imprint method, in which stamp heating and cooling are repeated in each pressure applying cycle.

Stamp and materials

Small stamp (size: few millimeters). Stamp is attached to SiC-support by glue or vacuum chuck. Antiadhesive coating recommended

Process parameters

- Imprinting at 50-70 °C stamp temperature (in viscous state) and substrate temperature 0-10 °C above T_g .
- Pressure is applied until stamp and substrate are cooled 10-20 °C below T_g .
- Stamp to substrate levelling (collimation) needed before imprints. Possibility to align stamp to substrate using automatic or manual alignment
- Imprint time: From few seconds to several minutes depending on stamp size, feature density and lateral dimensions (collimation and alignment increase cycle time by 10-20 s.)

Restrictions

Wafer backside must free of particles. Wafer bending leads to failure during collimation.

References:

- [1] T. Haatainen, J. Ahopelto, G. Grueztner, M. Fink, and K. Pfeiffer, *Step & stamp imprint lithography using a commercial flip chip bonder*, Proc. SPIE **3997** (2000) 874 – 880.
- [2] T. Haatainen and J. Ahopelto, *Pattern transfer using step&stamp imprint lithography*, Physica Scripta **67** (4) (2003) 357 – 360.
- [3] T. Haatainen, T. Mäkelä, A. Schleunitz, G. Greci, and M. Tormen, *Microelectron. Eng.* **98**(8) (2012), 180-183.

Step & Repeat Nanoimprint Lithography (S&R NIL)

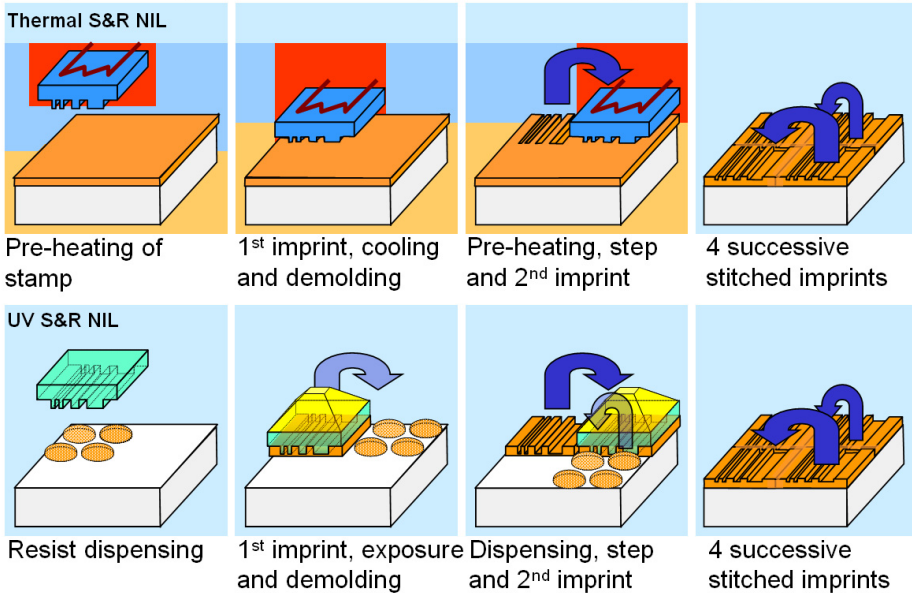


Figure 5.50: Step&Repeat imprint processes.

Short description

Reversal imprint makes it possible to structure a resist before transfer to another substrate. The transfer is done via thermal bonding of the resist and demolding is done after bonding.

Main application

- Applications where a larger degrees of freedom is needed.
- 3D structures (embedded channels) possible

Advantages

- Patterning of substrates is possible which do not support solvents.
- Reduction of residual layer thickness possible

Disadvantages

- Spincoating on stamp with antiadhesive coating not easy.
- Possible dependence of transfer on local structure size and aspect ratio.

Company: ThunderNIL by NaPANIL partner Dr. Massimo Tormen from IOM-CNR.

- Pulsed NIL and nanopatterning of thermoplastic polymer films within ~100 μ s.
- Design and manufacturing of ultrafast thermal machines

Contact information: Maurizio Tormen, e-mail : maurizio.tormen@thundernil.com

[1] M. Tormen, *Ultrafast Nano Imprint Lithography*, http://www.thundernil.com/bin/Ultrafast_Nano_Imprint_Lithography_web401.pdf.

Different machines are directly involved in developing S&R techniques. The machines are often custom made or derived from flip-chip bonders such as the EVG770 from EV Group at AMO and the NPS300 from S.E.T. S.A.S. (formerly SÜSS MicroTec) at VTT (Fig. 12). These are the NPS 300 in ICN, the EVG770 at LTM and the Imprio100 from Molecular Imprints (MII) at DTU. The specifications and main differences of the major two S&R NIL machines are presented in Table 1. The main difference is found in the imprint modes. The EVG770 is able to perform S&R UV-NIL. The NPS300 is able to perform both imprint methods by changing the imprinting head.

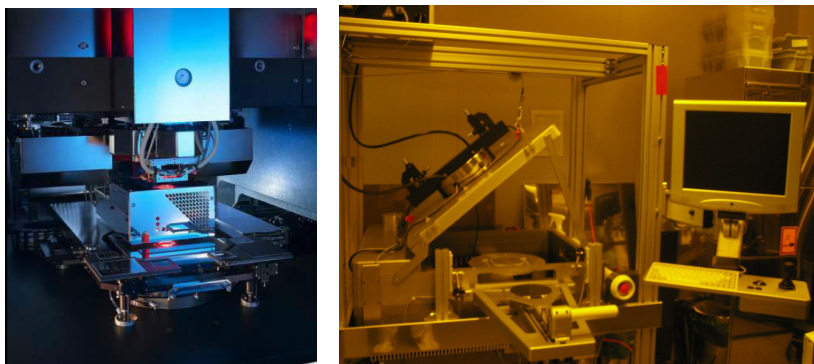


Figure 5.51: Left side: NPS300 from SET at VTT. Right side: EVG770 from EVG at AMO.

The NPS300, which was developed within the NaPa project, will be mostly used in the thermal S&R NIL mode. In NaPANIL, the integration of a rotation head and a high resolution alignment module will be decisive to improve the quality currently achieved with the ASE machine. This is needed for the exact placement of sawtooth structures for PDOE, as well as for surface enlargement with minimum stitching errors. The EVG770, with its UV-NIL module, will be used for NIL using soft imprint stamps, and is most suitable for large area imprint for the LDIR application. There are other – non-commercial S&R machines, which are not made for NIL, but are used as a standard tool for surface enlargement of metal stamps into thick polymer plates (which is often called “hot embossing” and the step&repeat mode “recombination”). This mode can be also be employed with the NPS300, but with a much better wedge compensation and control of alignment. The disadvantage in NIL is that only small stamps can be used since small surface undulations (wafer waviness can lead to an uneven imprint). The Toray recombination tool at modines is similar to S&R embossing with fast S&R thermal NIL. Recombination is a term used in hologram industry when – like in S&R NIL approaches, a small metal shim with a surface relief is stepwise printed on a polymer sheet, from which another shim is drawn by electroplating. Thus, the patterns of a small hologram are recombined to a large flexible shim appropriate for roll embossing. The characteristics of the machines are compared in Table 5.4.

Table 5.5. Comparison of two machine types for step and repeat NIL (S&R) using thermal NIL (hot embossing) and UV-assisted NIL, with typical parameters of current processes.

Nanoimprint Process	Thermal NIL	UV-NIL
NaPANIL partner	VTT (ICN)	AMO
Tool	NPS300	EVG 770
Manufacturer	SET S.A.	EV Group
Stamp holder	50x50mm ²	25x25mm ²
Typical stamp size	< 10x10mm ² (4x4 mm ²)	25x25mm ²
Substrate size	20-200 mm (round or square)	Circular 150 or 200 mm
Max. imprint force (N)	150 (4000 optional)	
Temperature range (°C)	Room temperature to 450 °C	Room temperature
Cycle time (s)	> 30 s	
Rotated imprint	±180° (with head rotation)	
Stitching distance (nm)	< 100 nm	N/A
Conditions		Low pressure environment

5.12 Roll-to-Roll Nanoimprint Lithography

Roll embossing is a continuous fabrication process, making use of a rotation movement to imprint a profile from a roll onto a flat surface, a continuous foil or a plate.

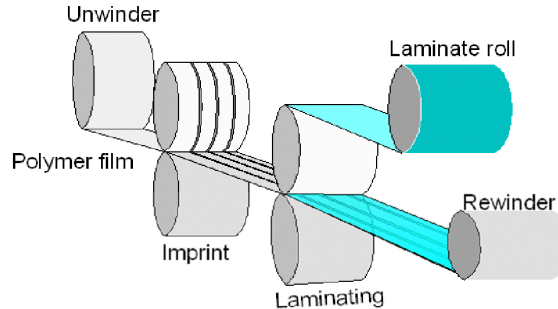


Figure 5.52: Schematic of roll-to-roll process using in-line imprint and lamination.

Process description : Step and Stamp Nanoimprint Lithography

Continuous imprint method, in which a stamp is fixed around a cylindrical roll and pressed against a counter roll. During rotation, a continuous foil carrier (the "web") is fed into the gap between the rolls and is embossed by the line-like pressure zone.

Stamp and materials

Bendable molds (electroplated or hybrid shims made from a flexible backbone and a coating with a surface relief). Depending on the process (thermal or UV-assisted) a thermoplastic foil (single or multilayer) or a UV-lacquer coated on a foil carrier is imprinted.

Process parameters

- In thermal R2R imprint, the foil is heated during the first contact with the hot rolls (at 50-70°C stamp temperature) to its viscous state and cooled after leaving the gap. Imprint time is determined by the contact zone (the "nip") which can be controlled via speed and softness of the rolls. Slow imprints might lead to uniform heating and deformation of entire foil.
- In UV-assisted R2R, the lacquer is cured online during (at the end) of the imprint process to enable hardening while the rolls are still in contact.

Restrictions

Process optimization needs to be made online, i.e. parameters can be changed while imprinting goes on. Heating, cooling and curing cycle is interlinked with imprint process.

References:

- [1] H. Schiff, *Roll embossing and roller imprint*, Chapter (5) in "*Science and new technology in nanoimprint*". Volume editor Y. Hirai. Frontier Publishing Co., Ltd., Japan, ISBN4-902410-09-5, June 2006, 281 pp., English 74-89, Japanese translation (extract) 90-93 (2006).
- [2] A. Laurberg Vig, T. Mäkelä, M. Majander, V. Lambertini, J. Ahopelto, and A. Kristensen, *Roll-to-roll fabricated lab-on-a-chip devices*, *J. Micromechanics and Microengineering* 21(3) 035006 (2011).

Company: PTMTEC OY by NaPANIL partner Tapio Mäkelä from VTT offers R2R NIL laboratory equipment, consumables and consulting (machine design, manufacturing etc.)

- Combination of traditional R2R coating/printing techniques and NIL (in small scale) with typical web width 10 cm or smaller
- Design and manufacturing of thermal R2R NIL and R2R UVNIL machines

Contact information: Dr. Tapio Mäkelä, e-mail: pmttec@gmail.com

5.13 Injection Molding

Injection molding is performed by three partners in NaPANIL, by CRFiat, University of Glasgow and FHNW (INKA institute, subcontractor of PSI, a joint institute of PSI and FHNW).

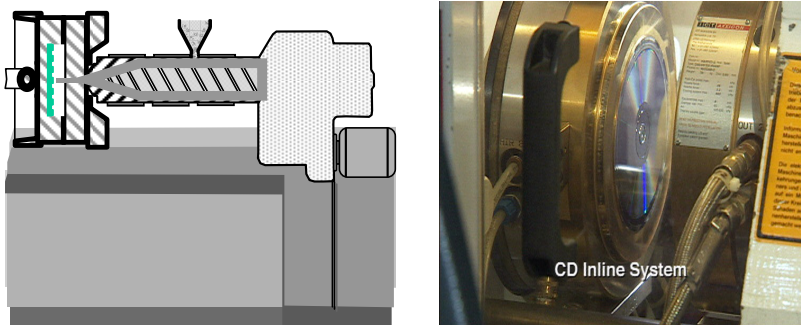


Figure 5.53: Schematic of an injection molding machine used for Compact Disk manufacturing.

Process description: Micro-Injection Molding (μIM)

A cavity with a mold insert is closed and viscous polymer is injected into the cavity. After opening the cavity, a solidified part with the exact outlines of the total cavity is removed.

Stamp and materials

Molds are normally quite expensive because they have to fit into the mechanical tool, therefore standardized, wafer-like tools are of advantage. Often electroplated metal molds are taken, but for test and rapid prototyping it is favorable to use silicon wafers or replicated stamps such as polymer foils or hybrid Ormostamp[®] on glass molds.

Process parameters

- Typically thermoplastic polymers are used which change their thermomechanical properties from solid to viscous. The mold is kept below or near to the T_g of the polymer material.
- In the isothermal case, the hot melt is injected into a cooler cavity, leading to immediate freezing of the polymer upon contact with the mold surface. In the variothermal case (similar to hot embossing), the cavity is heated to a temperature at which cooling is slowed down and co.

Restrictions

Stress during demolding is critical. Also molds need to support the high melt temperature.

References:

- [1] H. Schiff, C. David, M. Gabriel, J. Gobrecht, L.J. Heyderman, W. Kaiser, S. Köppel, and L. Scandella, *Nanoreplication in polymers using hot embossing and injection molding*, *Microelectron. Eng.* **53**, 171-174 (2000).
- [2] A. D'Amore, M. Gabriel, W. Haese, H. Schiff, and W. Kaiser, *Nanoreplikation - Informationsverdichtung*, *Kunststoffe 94 (2/2004)*, 54-58 (2004). English version: *Nano-replication - concentration of information*, *Kunststoffe plast europe 94 (2/2004)*, 4-7 (2004).
- [3] P.M. Kristiansen, H. Schiff, *Kleinste Strukturen in der Massenfertigung abformen*, *Plastics.now!* Oktober, 20-21 (2011).

Partner: FHNW (University of Applied Sciences Northwestern Switzerland) is offering tool design, manufacturing, new processes, services etc. on polymer processing.

- Fabrication of nanostructures by injection molding and polymer analysis

Contact information: Prof. Dr. Per Magnus Kristiansen, e-mail: magnus.kristiansen@fhnw.ch

5.14 Metrology

Metrology involves measurement of critical dimensions and assessment and validation of process quality and stability. In microchip fabrication with its hundreds of process steps, it also includes the assessment of yield and functioning of the device. The reason that genuine metrology often is not applied in research is that it is often based on statistics and needs several 10's of structures. This means that many identical processes have to be performed without mayor variations of setup and parameters, and processes have to be controlled during all the manufacturing cycle. For research and origination, where this is often not the case, therefore often preliminary results are achieved. Often process evaluation is performed of individual or representative structures according to their critical dimensions (CD). This assessment is often a rough estimation on the limitations of processes and needed for finetuning of process. Its aim is to analyse how process variations affect the dimensions of all structures. Particularly difficult is this if structural variety of 3-D structures has be examined. In the next section, we are presenting the different methods in more detail.

Types of metrology

Direct view (visualization): This is done using visualization of shapes and profiles by advanced microscopy (optical, scanning electron (SEM), scanning force microscopy (SFM/AFM), and white light interferometry (WLI) and 3-D white light scanning microscopy (WLSM). They are different in resolution, depth of focus, and their ability to detect vertical sidewalls. By using scale bars and comparison, quantitative evaluation of single structures can be done. Using scanning (by automated step&repeat), many structures can be examined. In case of profilometry and SFM/AFM, due to the convolution of the probe tip and the sample geometry, results have to be interpreted with care. In most cases the methods are non-destructive and non-invasive, however, often cross-sections of samples have to be taken for which samples have to be cleaved. Furthermore for SEM (and often for AFM), thin metal coatings are needed for providing a non-charged surface. A possibility to circumvent problems of sample destruction or non-accessability, copies from surfaces (e.g. by casting or electroplating) can be examined instead of the original. In case of replicated samples, the comparison is then done between a positive and negative.

Indirect measurement (inverse method): Often it is easier to take an "image" of a transformation of the original pattern and extract essential geometrical parameters from it by calculation. E.g., the optical diffraction pattern from a regular grating reveals its period, simply by analyzing the distances of diffraction orders after transmission with a coherent laser beam. Similarly, geometrical parameters of more complex gratings and deviations from their ideal shape can be characterized by its inverse image (signature), by calculating its Fourier transform. However, often it is important to know something about the structure in advance, to avoid ambiguity and misinterpretation. Instead of single structures, large ensembles, i.e. gratings with identical shapes of each individual line ridge are analyzed, to examine systematic errors such as incomplete filling, rounding or demolding defects. Therefore rather small deviations from ideal structure are detected, to allow for process optimization. The minimum size of the area to examine is often determined by the laser beam used in reflection or transmission and the measurement is the statistical result of the entire grating

References:

- [1] D. Fuard, C. Perret, V. Farys, C. Gourgon, and P. Schiavone, Measurement of residual thickness using scatterometry, *J. Vac. Sci. Technol. B* 23, 3069 (2005); <http://dx.doi.org/10.1116/1.2130345> (6 pp.).

5.14.1 Introduction to scatterometry

Scatterometry is an optical metrology technique based on the measurement of light polarization modification due to a reflection on a patterned sample: an initially linearly polarized light becomes elliptically polarized after the reflection. It cumulates two advantages:

- It is a non-destructive and non-invasive method. Consequently, the measured sample is still fully usable after the measurement.
- It can be used, in principle, both for *in-* and *ex-situ* measurement, which make it a perfect tool to a real time control.

Practically, the quantity measured by a scatterometer is the rate between these two reflection coefficients, which define the fundamental equation of scatterometry:

$$\rho = \frac{r_p}{r_s} = \tan(\Psi) \exp(j\Delta)$$

with $\Psi = \arctan\left(\frac{r_p}{r_s}\right)$ and $\Delta = \delta_p - \delta_s$, called scatterometric angles, linked to two intensities, I_s

$$\text{and } I_c: \begin{aligned} I_s &= \sin(2\Psi) \cdot \sin(\Delta) \\ I_c &= \sin(2\Psi) \cdot \cos(\Delta) \end{aligned}$$

Ψ and Δ depends on some parameters, such as the incident angle, the wavelength or the refractive index of the materials.

Stack profile of the studied sample cannot be directly determined from these observables. Numerical methods based on the comparison of a simulated response of standard shapes to experimental ones, i.e. an inverse method, are used to resolve the profile shapes.

Some numerical algorithms can solve the electromagnetic problem of scatterometric measurement and produce simulated responses of the problem. These responses are compared to the experimental ones and when a simulated signal matches the experimental one, we consider that the parameter set used in this simulation is a good approximation to the physical one. The real physical parameters of the stack are then considered to be known.

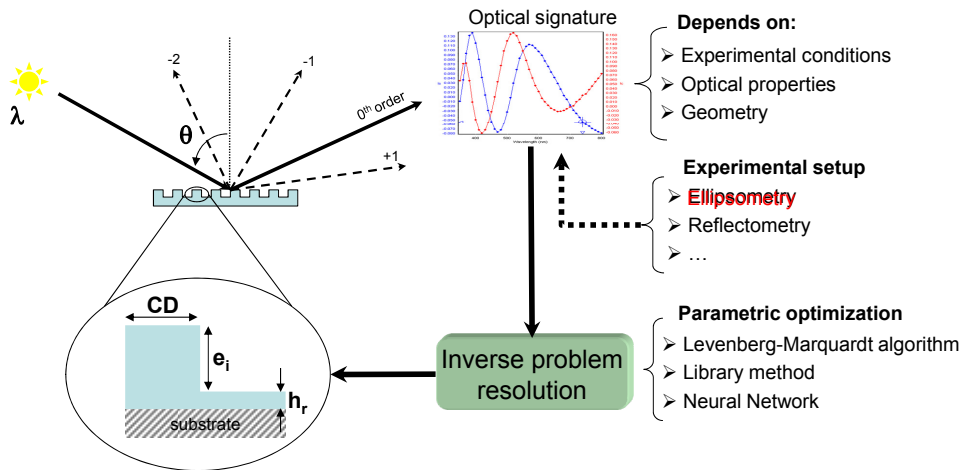


Figure 5.54: Schematic of scatterometry: From the diffraction pattern the shape of the original pattern can be determined by advanced mathematics.

Scatterometry exhibits high accuracy and high speed for lines on silicon wafers. It can be used to measure line width, imprinted depth and residual thickness, with some limitations: the grating period has to be smaller than 2 μm , and the patterns have to be uniform. In these cases, it is also possible to introduce other parameters such as top rounding or slope of the pattern sidewalls.

Circular imprinted pillars have been characterized by scatterometry. Patterns need a specific complex model to take into account the circular section. Scatterometry can be used to measure such structures, but computing time is main limitation. The accuracy of measurement is also more dependent on pattern uniformity, as compared to the case of lines.

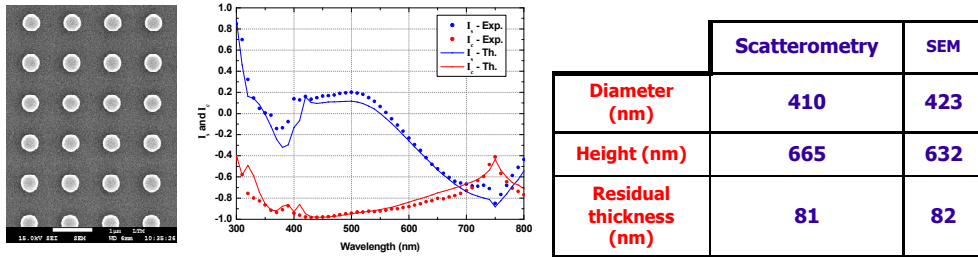


Figure 5.55: Scatterometry measurements of geometrical parameters of 2D profiles (circular imprinted pillars), compared to values extracted from SEM micrographs.

5.14.2 Measurements of lines and 3-D structures: Example

Multilevel lines can be measured with high accuracy if they exhibit high uniformity and regular profiles. These resist lines were characterized by scatterometry and results are in good agreement with SEM analysis.

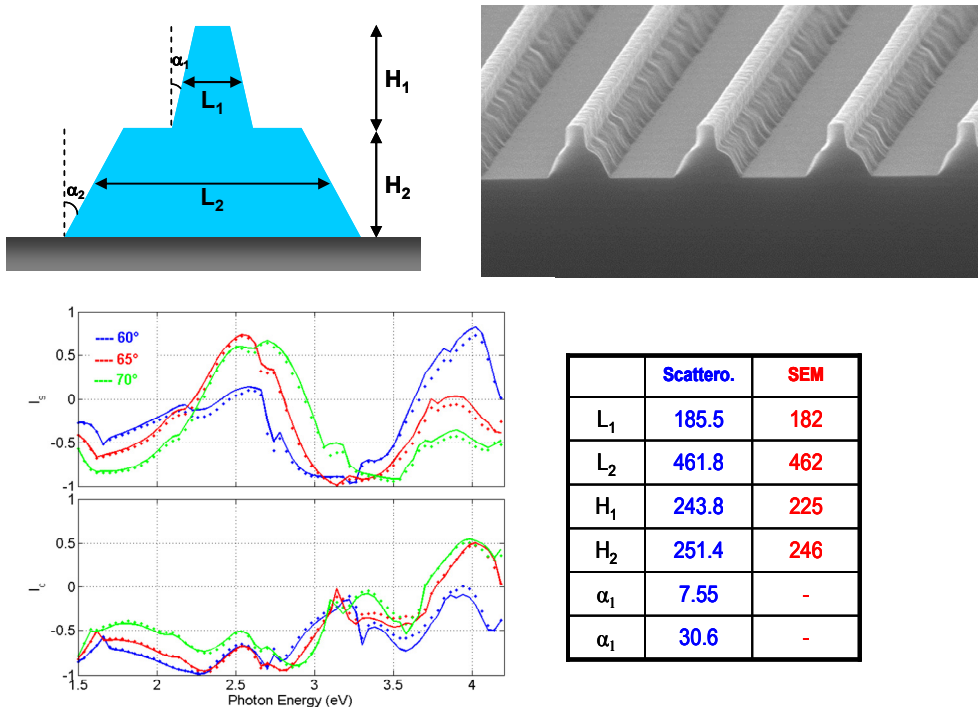


Figure 5.56: Scatterometry measurements geometrical parameters of 3D profiles (two-level structures with ridges on pedestals with sloped sidewalls), compared to values extracted from SEM micrographs.

5.15 References

An introduction into nanoimprint for engineers and scientists:

- [1] H. Schiff and A. Kristensen, *Nanoimprint lithography - patterning resists using molding*. Chapter (Part A/9) in "*Handbook of nanotechnology*", Volume editor B. Bhushan, third edition, revised and extended, 2010, Springer Verlag Berlin Heidelberg, Germany. ISBN: 978-3-642-02524-2, XLVIII, 1964 p. 1577 illus. in color, with DVD, Hardcover, 271-312 (2010).
- [2] C. Sotomayor Torres: *Alternative Lithography – Unleashing the Potential of Nanotechnology*, book series on Nanostructure Science and Technology, book series on Nanostructure Science and Technology in Kluwer Academic/Plenum Publishers, Springer, editor D.J. Lockwood. Hardcover, ISBN 0-306-47858-7, November 2003, 425 pp. (2003).
- [3] NaPa Library of Processes, ed. H. Schiff, published by the NaPANIL-consortium represented by J. Ahopelto, first edition (2008), ISBN 978-3-00-024396-7.
- [4] S. Landis, *Nano-lithography*, ed. S. Landis, John Wiley & Sons, London, UK: ISTE, Hoboken, NJ: Wiley, 2010, ISBN 1848212119.

A good overview about the state of the art in nanoimprint and critical issues:

- [1] L.J. Guo, *Recent progress in nanoimprint technology and its applications*, J. Phys. D: Appl. Phys. **37**(11) (2004) R123-R141.
- [2] L.J. Guo, *Nanoimprint lithography: methods and material requirements*, Adv. Mater. **19** (2007) 495–513.
- [3] H. Schiff, *Nanoimprint lithography: An old story in modern times? A review*, J. Vac. Sci. Technol. B **26**(2) 458-480 (2008).

Review article with emphasis on nanorheology and material deformation:

- [1] G.L.W. Cross, *The production of nanostructures by mechanical forming*, J. Phys. D: Appl. Phys. **39**(20) (2006) R363–R386.
- [2] H.-C. Scheer, Y. Hirai, M. Nishihata, N. Bogdanski, *Polymer elasticity effects during thermal nanoimprint, Polymer elasticity effects during thermal nanoimprint*. Part I: *Experimental evidence and simulation*. Part II: *Analysis with respect to imprint*. Mikro- und Nanostrukturierung. Bd. 2 # Pb., 96 S., 21 Abb. (2011) ISBN 9783899597745

A large list of references is given in the following book:



Figure 5.57: Nanoimprint Lithography in the Springer Handbook on Nanotechnology.

PART II : APPENDIX - PROCESS LIBRARY

Content

This appendix contains the process library with recipes both from NaPa and NaPANIL. At the bottom of the first page of each contribution a numbering can be found which enables to refer to the processes stemming from the first and second edition of the NaPa(NIL) library of processes.

1. Tools and Machines

Contributions to this section of the library are from

VTT Information Technology/Finland
Dr. Tapio Mäkelä / Dr. Tomi Haatainen /
Prof. Dr. Jouni Ahopelto

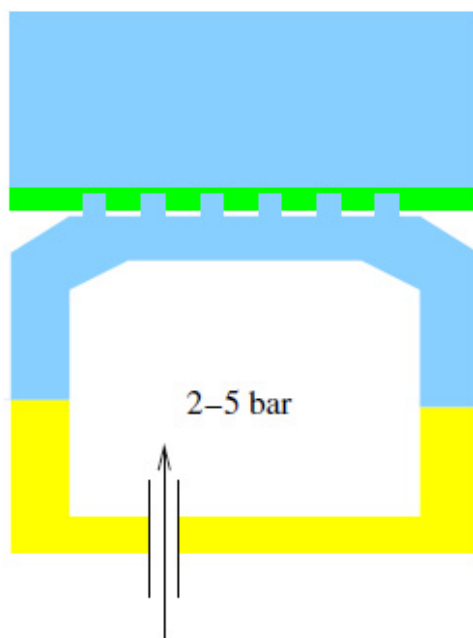
PSI/LMN - Villigen/Switzerland
Dr. Helmut Schiff / Dr. Arne Schleunitz /
Christian Spreu

PTMTEC OY / Finland
Dr. Tapio Mäkelä

FHNW/INKA - Windisch/Switzerland
Prof. Dr. Magnus Kristiansen

MIC/DTU - Lyngby/Denmark
Prof. Dr. Anders Kristensen

NILT - Denmark
Theodor Nielsen



1.1 Compact NIL-2-GO tool from NILT

Standard thermal nanoimprint process with Compact NIL-2-GO nanoimprint tool from NIL Technology (NILT)

Process: thermal nanoimprint lithography



Figure:
The frontside of the CNI Tool.

Process:
Electron beam lithography on positive or negative resists and plasma etching

Application:
NIL stamps for optical, photonic, electronic or micro/nano-fluidics.

Keywords: thermal nanoimprint, electron beam lithography, plasma etching, surface coating

Project leader: NIL Technology ApS
Address: 2800 Kongens Lyngby, Denmark
Web-Address: <http://www.nilt.com>

Process: Thermal Nanoimprint
Responsible: Theodor Nielsen
E-mail: tkn@nilt.com

Partner: Danish Technical University
Address: 2800 Kongens Lyngby, Denmark
Web-Address: <http://www.nanotech.dtu.dk>

Process: Thermal Nanoimprint
Responsible: Anders Kristensen
E-mail: anders.kristensen@nanotech.dtu.dk

Tool description: The NIL-2-GO tool is a table top imprint machine which works both with flexible stamps and process is described for fabrication of stamp and surface functionalization for reducing adhesion forces towards polymers after the imprinting step. The tool is used with CNI Stamps that come in different configurations (flexible) to match exact requirements

Purpose: The NIL-2-GO tool offers a NIL solution with unique temperature control and low imprinting pressure.

Major challenges: Flatness, compliance.

Application and state-of-the-art: Standard process

References:

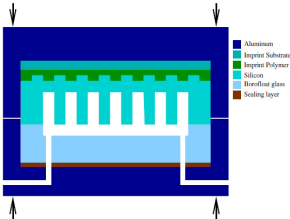
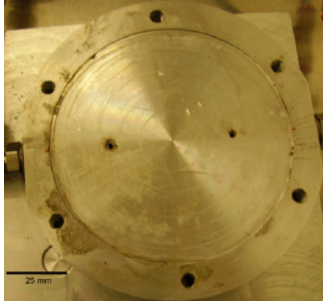

- [1] R.H. Pedersen, O. Hansen, A. Kristensen, A compact system for large-area thermal nanoimprint lithography using smart stamp, *J. Micromechanics and Microengineering*, Volume 18, Issue 5, pp. 055018 (2008).
- [2] T. Nielsen, A. Kristensen, and O. Hansen, "A flexible nanoimprint stamp", Patent WO2006026993, 2006-03-16.
- [3] K. Smistrup, T. Hedegaard, Brian Bilenberg, J. Nørregaard, S. Abadei, O. Hansen, A. Kristensen, and T. K. Nielsen, *Flexible stamp with in-situ temperature control*, 9th Int. Conf. Nanoimprint and Nanoprint Technology, NNT2010, Copenhagen, Denmark, October 13-15 (2010)
- [4] K. Smistrup, A. Mironov, B. Bilenberg, T. K. Nielsen, and A. Kristensen, *Polymer stamp imprinting in a desktop NIL tool using flexible stamps*, 9th Int. Conf. Nanoimprint and Nanoprint Technology, NNT2010, Copenhagen, Denmark, October 13-15 (2010)

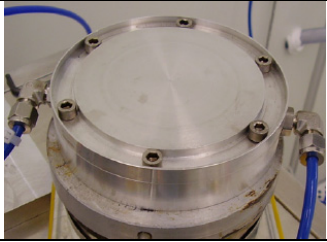

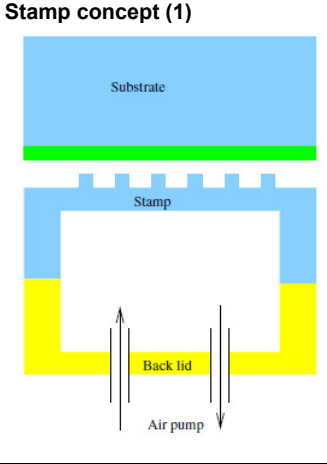
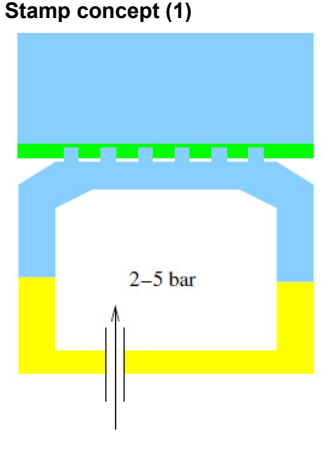
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Web: www.nilt.com

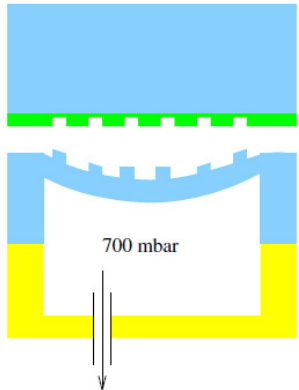
LoP2012_NIL001_CNI-Tool

Compact NIL-2-GO Nanoimprint tool

Process: thermal nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Wafer preparation	Silicon wafer format	
1.1	wafer selection and preparation	standard Si substrate Si substrate, 4", <100>, thickness d=400-600 μm one side polished	
1.2	System principle with flexible stamp 	pretreatment External system principle. A top and bottom chuck containing wafer-sized depressions are manufactured in aluminum. A screw arrangement can fix the two together. The bottom chuck contains air access holes and external fittings. To seal the transition to the stamp a thin layer of soft material is used. Drawing is not to scale.	
	End of Process 1		
2.0	Process 2: Resist coating	for electron lithography	
2.1	Proof-of concept on a hotplate 	System The imprint process in the compact-system. The total size of the system (excluding hotplate and pressure connections) is 128 mm diameter and 3 cm thickness. (a) The bottom chuck (PTFE sealing layer not shown)	
2.2	Proof-of concept on a hotplate 	Stamp/substrate mounting The stamp is mounted on the bottom chuck and a substrate is placed on top.	
2.3	Proof-of concept on a hotplate	Imprint Imprint in progress. The entire system is placed on a hotplate. Typical parameter values employed for imprints. $T_{\text{imprint}} \approx 190 \text{ }^{\circ}\text{C}^{\text{a}}$ $T_{\text{separation}} \approx 23 \text{ }^{\circ}\text{C}^{\text{a}}$	

		<p> t_{heating} 20 min t_{cooling} 20 min t_{imprint} 5 min p_{imprint} 3.5 bar $p_{\text{separation}}$ 700 mbar ^a Exact temperature not monitored </p>	
<p>2.4</p>	<p>Proof-of concept on a hotplate</p> 	<p>De-mounting Imprint is complete. Due to the integrated demolding capability, the substrate is easily removed by hand.</p>	
<p>End of Process 2</p>		<p>Process 3: Lithography</p>	<p>Electron beam lithography</p>
<p>3.2</p>	<p>Stamp concept (1)</p> 	<p>Setup before imprint By bonding a back lid containing access holes to a flexible stamp an intra-stamp cavity is formed.</p>	<p><i>For different resists datasheets are available with the range of exposure and development parameters.</i></p>
<p>3.3</p>	<p>Stamp concept (1)</p> 	<p>Imprint Pumping gas into the cavity supplies the pressure required for imprint. Due to frontside flexibility, the required pressure is low.</p>	

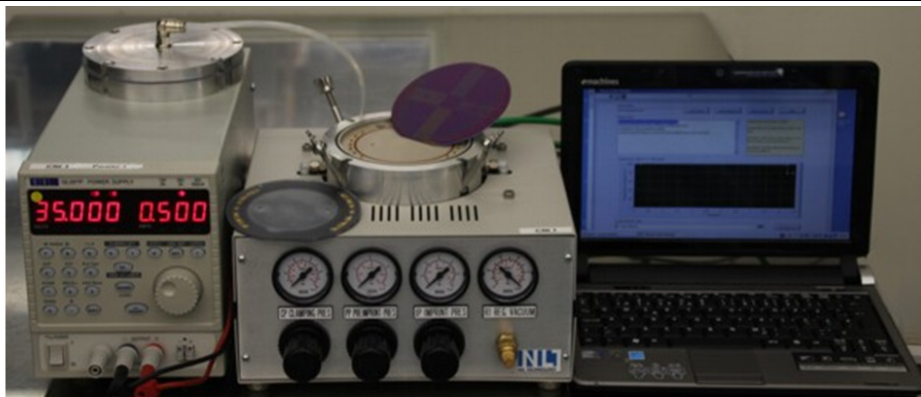
<p>3.3</p>	<p>Stamp concept (3)</p> 	<p>Demolding By applying a moderate vacuum to the cavity, the imprint features are pulled out of the imprint polymer, accomplishing integrated demolding. Note that the ambient pressure is atmospheric at all times.</p>	
	<p>End of Process 3</p>		
	<p>End of Total Process</p>		

General remarks:

We present a simple apparatus for thermal nanoimprint lithography. In this work, the stamp is designed to significantly reduce the requirements for pressure application on the external imprint system. By MEMS-based processing, an air cavity inside the stamp is created, and the required pressure for successful imprint is reduced. Additionally, the stamp is capable of performing controlled demolding after imprint. Due to the complexity of the stamp, a compact and cost-effective imprint apparatus can be constructed. The design and fabrication of the advanced stamp as well as the simple imprint equipment is presented. Test imprints of micrometer- and nanometer-scale structures are performed and characterized with respect to uniformity across a large area (35 mm radius). State-of-the-art uniformity for mu m-scale features is demonstrated.

About NIL Technology ApS

NIL Technology ApS (NILT) specializes in nanopatterning and nanoimprint lithography. NILT has experience in meeting complex demands for research and new product development activities, and assists customers in all stages from pattern design to imprinted pattern. NILT is located in Kongens Lyngby, Denmark.



Heating: Integrated stamp heating in conductive Si-wafer (highly p-doped implanted layer) and temperature control
Imprint temp: up to 200° C

Stamps: Semi-flexible, segmented Si-wafers^o. The mechanical membrane^o can control imprint and de-molding conditions. Also use of PDMS and polymer foils possible (with heatable Si-dummy).

Pressure: Bellow (from above), up to 6 bar compressed-air system)

Figure 1: NILT's compact NIL-2-GO nanoimprint tool

Thermal nanoimprint with NIL-2-GO tool: Process description

In a sealed 100mm wafer chamber, a flexible stamp with surface relief at the bottom is pressed against a resist-coated substrate by air pressure, while a pressurized bellow from the top is applying a counter force. The bottom wafer (stamp or dummy) is heated internally via a conducting layer. Alternatively, the pressure can be applied through a pressurized bellow force alone. Then rigid stamps can be used.

Stamp and materials (flexible, segmented stamp with internal heating)

- Stack of flexible stamp on bottom and resist coated substrate on top + through PTFE foils
- Alternatives: Foil stamps on top of a heatable dummy wafer, rigid or PDMS stamp on top
- Automated demolding possible by using house vacuum

Process parameters

- Imprint up to 200°C, sufficient for PMMA imprint (heating about 5 min from 20°C to 180°C)
- Pressure up to 6 bar, quite low for the 100mm substrates used as a standard (up 100 bar)
- Cooling by air fan (about 5 min from 180°C to 80°C)

Restrictions – and how to deal with them

- Pressure regime may be modified (contact pressure during heating instead of full pressure)
- No evacuation before imprint, automated demolding only with segmented flexible stamp

1.2 Step&repeat thermal NIL process with NPS300

Step&repeat thermal NIL for master enlargement with NPS300

Process: thermal nanoimprint lithography



Figure:
NPS300 NIL machine fabricated by SET installed at VTT.

Process: Thermal Step&stamp imprint lithography (SSIL) to pattern thermoplastic polymer using Nano imprinting Stepper.

Application:
Optical grating for light directing elements

Keywords: Thermal nanoimprint, Step&repeat, surface enlargement

Partner: VTT Technical Research Centre of Finland, VTT
Address: Helsinki, FI
Web-Address: <http://www.vtt.fi>

Process: Step & Repeat thermal NIL
Responsible: Tomi Haatainen
E-mail: tomi.haatainen@vtt.fi

Partner: S.E.T. SAS (Smart Equipment Technology)
Address: 74490 Saint Jeoire, France
Web-Address: <http://www.set-sas.fr>

Process: NPS300 Step&stamp Tool
Responsible: Gilbert Lecarpentier
E-mail: glecarpentier@set-sas.fr

Process description: A step&repeat thermal imprint process for fabrication of periodical structures using a NPS300 NIL machine fabricated by SET using sequential imprinting to pattern large areas. the parameters are valid for small stamps (< 5x5 mm²) and submicron scale features.

Purpose: The aim of this process is transfer periodical structures of stamp into thermoplastic polymer with low stitching errors which can be used as an etch mask, lift-off or a mold for fabrication of metal templates by electroplating.

Major challenges: Uniformity of residual layer on the large substrates due to waviness and wedging of the stamp in the single imprints.

Application and state-of-the-art: Anti-reflection gratings and light directing elements

References:

- [1] T. Haatainen, J. Ahopelto, G. Grueztner, M. Fink, K. Pfeiffer, Step & stamp imprint lithography using a commercial flip chip bonder, Emerging Lithographic Technologies IV, Proceedings of SPIE, Vol. **3997**. SPIE-The International Society for Optical Engineering (2000), 874 – 880.
- [2] T. Haatainen; J. Ahopelto, Pattern Transfer using Step&Stamp Imprint Lithography, Physica Scripta. Vol. **67** (2003) No: 4, 357 – 360.
- [3] T. Haatainen, P. Majander, T. Riekkinen, J. Ahopelto, Nickel stamp fabrication using step & stamp imprint lithography. Microelectron. Eng. **83** (2006), pp. 948-950. Microelectron. Eng. **83**, (2006) 948–950.
- [4] T. Haatainen, Stamp fabrication by step and stamp nanoimprinting, PhD thesis VTT report 758 (2011), available online <http://www.vtt.fi/inf/pdf/publications/2011/P758.pdf>.
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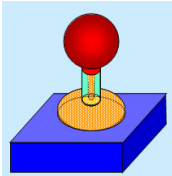
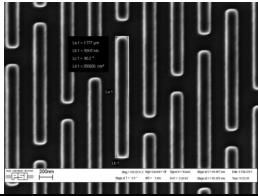
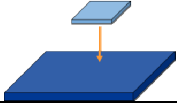

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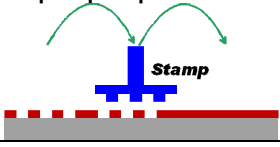
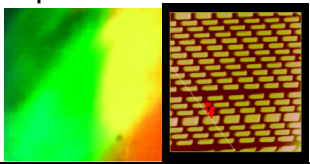
Dr. Tomi Haatainen
VTT Technical Research Centre of Finland
Tietotie 3
P.O.Box 1000
FI-02044 VTT, Finland

LoP2012_NIL002_SR-NIL Tool

Step&repeat thermal NIL for master enlargement with NPS300

Process: Thermal nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Primary silicon master	EBL and dry etching	
1.1	Substrate preparation	Silicon wafer 4" <100>	
1.2	Resist coating 	Spin-coating EBL resist. Prebake	
1.3	Pattern definition	Electron beam lithography	
1.4	Pattern transfer into Si 	Dry etching	<i>Height and profile control</i>
	End of Process 1		
2.0	Process 2: Stamp preparation		
2.1	Stamp preparation	Dicing the stamp into a small chip with size of 5x5 mm ²	<i>Particle contamination</i>
2.2	Glueing the stamp into large silicon chip 	Increase the vacuum contact area to the arm.	
2.3	Anti-adhesion coating	Dip-coating by Optool DSX Prevents stamp to polymer sticking	
2.4	Post bake	1 hour @ 60 °C	
	End of Process 2		
3.0	Process 3: Pattern enlargement	S&R NIL	
3.1		Step & Repeat hot embossing Thermal and UV-NIL capability. Alignment accuracy: 100nm Overlay Accuracy: 250 nm Template / Stamp size 50 ~ 65 mm (Option up to 100 mm). Substrate ≤ Sq.200mm (substrate 300mm).	

3.2	substrate preparation	silicon – substrate Si substrate, 6", <100>, thickness d=600-700 μm .	
3.3	Coating the substrate	2 μm thick layer of thermoplastic polymer mr-I T85 1.0 μm	<i>Alternative resist as used in Figure 1 below: mr-I 7000R (high resolution)</i>
3.4	Prebake	5 min @140 °C	
3.5	Step&repeat process 	Process parameters: Stamp temperature 140 °C, substrate temperature 60 °C. Force 140 N. Imprint time 15 s. + 60 s. cooling before demolding	<i>Stamp-to-substrate parallelism. Feature profile due to thermal flow near adjacent imprints. Stitching accuracy.</i>
3.6	Inspection 	Optical and atomic force microscopy to characterize the results of the step & repeat hot embossing process.	
3.7	Next steps	PDMS copy using polymer mold	
End of Process 3			
End of Total Process			

General remarks:

Since 2010 SET is focusing on flip-chip bonding and therefore does not offer the NPS300 for S&R NIL any more. For NaPANIL, a rotation arm was developed which enables rotated imprint.

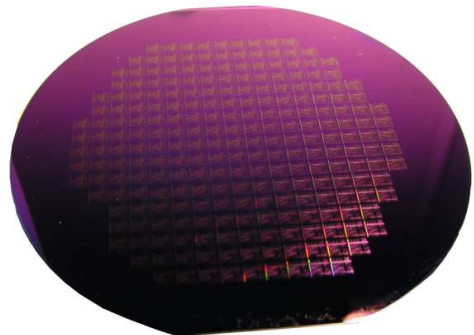
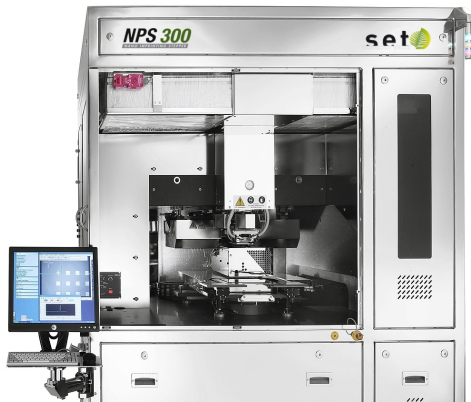
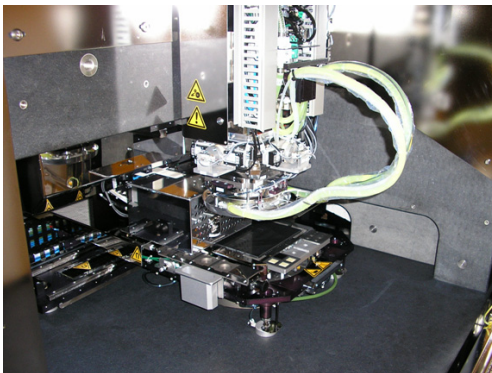


Figure 1: SET's NPS Step and Stamp machine for thermal and UV NIL used for these experiments (until 2007 SET was part of SÜSS Microtec), installed at VTT (left side), and example (right side) of a 237 consecutive thermal imprints into a 300 nm thick mr-I 7000R film (by *micro resist technology GmbH*) on a 100mm Silicon wafer. Stamp size 4x4mm², micrometer features with sizes of down to 2 μm and height of ~ 200nm. Stamp Temperature: 140 °C, substrate temperature 70 °C, cycle time ~ 3 minutes (without collimation and arm movements).

Nanoimprint Machine from SET: NPS 300

KEY FEATURES

- Aligned Hot & Cold Embossing
- Step & Repeat mode
- Sub-20 nm embossing capability
- Sub micron (250 nm) stamp-to-wafer alignment
- Rotation head: $\pm 90^\circ$
- Template / Stamp size up to 100 mm
- Substrate up to diameter 200mm (300mm option)
- Pre-leveling accuracy 20 μ radian
- Self leveling by flexure stage during application of the imprinting force
- Typical dry cycle time < 1 minute
- Includes alignment and contact, process not included
- Automatic stamp pick-up from fix tray



Imprinting Arm

Imprinting force: 5 ~ 4,000 N

Z stage resolution: 50 nm

Alignment XY θ Stage

XY: 400 x 400 mm, resolution 10 nm (step 100nm)

θ : $\pm 5^\circ$, resolution 0.4 μ radian

Top & Bottom Viewing Microscope

FoV: 870 x 690 μ m (20X) – Pixel ~ 0.67 μ m

Autocollimator for Pre-leveling

Sensitivity: 20 μ radian

1.3 Roll-to-roll UV-NIL tool from PTMTEC

Continuous roll-to-roll UV-NIL process and novel laboratory tool for various application

Process: UV-nanoimprint



Figure:

Continuous Roll to Roll UV nanoimprinting (R2RUVNIL) process. Novel R2R equipment consist polymer coating unit and UV-nanoimprinting unit.

Process:

Custom made Roll to Roll UV nanoimprint device use reverse gravure coating method to form UV-film on plastic web. After IR curing, patterns from the mold will be transfer to UV-polymer using UV NIL unit.

Application:

Roll to roll UV NIL in high volume applications. Continuous processing.

Keywords: UV nanoimprint, Roll to Roll, R2R, surface coating

Project leader: PTMTEC

Address: Jousimiehentie 4 | 00740 Helsinki, Finland

Web-Address: [http:// www.ptmtec.com](http://www.ptmtec.com)

Process: R2R UV-NIL

Responsible: Tapio Mäkelä

E-mail: tapio.makela@ptmtec.com

Partner: VTT Technical Research Centre of Finland, VTT

Address: Helsinki, FI

Web-Address: <http://www.vtt.fi>

Process: Step & Repeat thermal NIL

Responsible: Tapio Mäkelä

E-mail: tapio.makela@vtt.fi

Process description: Continuous nanopatterning of large areas, based on roll to roll UV nanoimprint (R2R UV-NIL) lithography technique.

Purpose: The aim of this process is to developed to provide a compact continuous nanoimprinting tool based on laboratory scale roll to roll tool using UV-patterning.

Major challenges: Combination of R2R coating and R2R UV-NIL process is challenging and a small-scale printing tool for scientific purposes was not designed before.

Application and state-of-the-art: Currently large-scale equipment for UVNIL processes is available in the market but no scientific tools with low consumption of UV-resist and polymer films.

References:

- [1] T. Mäkelä, T. Haatainen, J. Ahopelto and Y. Kawaguchi; Roll to Roll UV nanoimprinting using ulexible polymer stamp, 34th international conference on micro & nano engineering (MNE2008), proceedings, p 83, p-nano-115
- [2] T. Mäkelä, T. Haatainen, J. Ahopelto and Y. Kawaguchi, The 8th International Conference on Nanoimprint and Nanoprint Technology (NNT2009), CD proceedings
- [3] T. Haatainen, P. Majander, T. Riekkinen, J. Ahopelto, Nickel stamp fabrication using step & stamp imprint lithography. Microelectron. Eng. 83 (2006), pp. 948-950. Microelectron. Eng. **83**, (2006) 948–950.


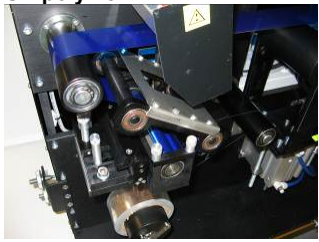
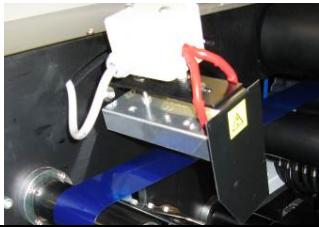
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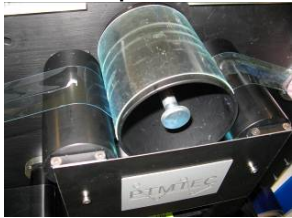
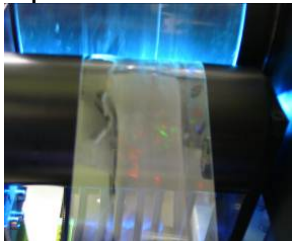

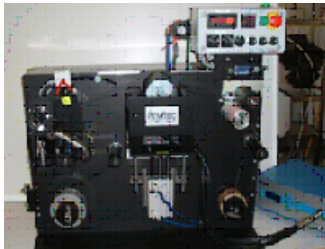
Dr. Tapio Mäkelä
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00740 Helsinki
Finland

LoP2012_NIL003_UV-R2R-Tool

Continuous roll-to-roll UV-NIL process

Process: UV-nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Substrate, Ink and Mold	50 - 100 mm wide polymer roll, UV-ink and flexible mold.	
1.1	Substrate selection	Flexible ca. 100 micrometre thick PET film with good adhesion properties	
1.2	Ink modification	Viscosity should be in the range of 1000 cP. No pre-treatment needed if wetting and adhesion good	<i>good adhesion to polymer film sometimes difficult</i>
1.3	Flexible mold 	Flexible polymer mold is bent around to the printing roll while rotated. Mold is attached using two-sided tape. Both Ni and polymer mold are possible.	
	End of Process 1		
2.0	Process 2: Polymer coating	for UV lithography	
2.1	Reverse gravure coating of UV-polymer 	resist UV curable imprint resist such as mr-UVcur06 from mrt. Groove depth in reverse gravure rod is 100 micron. Rod speed 60 rpm when web speed 0.4 m/min. Wet thickness ca. 1 micrometre.	<i>Web speed versus rod speed must optimize.</i>
2.2	Thermal (IR) curing 	curing of mr-UVcur06 speed: 0.4 m/min power: 75 W time: 8 s. Dry thickness after curing is ca. 300 nm.	<i>Polymer can also be semi cured, but then adhesion to the mold is problem.</i>
	End of Process 2		
3.0	Process 3: Lithography	R2RUV lithography	
3.1	Design and file generation	Functional structures Aspect ratio is typically 1:1 or 2:1.	<i>Higher aspect ratios might distort features.</i>
3.2	Unwinder	Polymer substrate roll is in unwinder	

			
3.3	UV-nanoimprint 	UV-mold printed against polymer using slight force (1000 N/10 cm)	
3.4	Exposure 	exposure with fiber mr-UVcur06 exposed using UV-source 20W/cm	
3.5	Rewinding 	Printed structure to roll R2RUV printed featured were rolled using rewinder	web tension has to be kept constant
3.6	Process control 	optical microscopy/camera inline meteorology can be inserted into tool	
	End of Process 3		
	End of Total Process		

General remarks: Tool can be easily modified and custom made

1.4 Variothermal Injection Molding tool from FHNW

Versatile variothermal injection (IM) molding tool

Process: Thermal injection molding

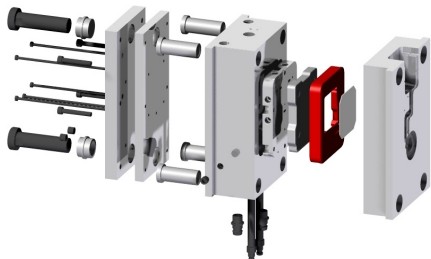


Figure:
Blow-up schematics of a variothermal injection molding tool

Process:
Variothermal injection molding requires sophisticated heating and cooling for rapid temperature cycling

Application:
High aspect ratio microstructures for microfluidics, DOEs, photonics, security features.

Keywords: thermal nanoimprint, variothermal processing, injection molding

Project leader: Institute of Polymer Nanotechnology
Address: 5210 Windisch, Switzerland
Web-Address: <http://www.fhnw.ch/inka>

Process: Thermal Injection Molding
Responsible: Per Magnus Kristiansen
E-mail: magnus.kristiansen@fhnw.ch

Partner: Paul Scherrer Institut (PSI)
Address: 5232 Villigen PSI, Switzerland
Web-Address: <http://www.psi.ch>

Process: Thermal Nanoimprint
Responsible: Helmut Schiff
E-mail: helmut.schiff@psi.ch

Tool description: The variothermal injection tool is used for molding of high aspect ratio structures. Due to a sophisticated heating and cooling system, short cycle times can be achieved. The tool is able to host metal and silicon as well as polymeric molds with functional structure areas of up to 50x50mm².

Purpose: Variothermal injection molding enables to inject the hot melt into a mold kept above the glass transition temperature. Thereby, immediate freezing of the melt upon contact with the mold surface can be avoided and high aspect nanostructures successfully molded.

Major challenges: High cycle time (heating and cooling overhead) reduces ability to use it in high volume fabrication.

Application and state-of-the-art: Increasing use in industry but not a standard process

References:

- [1] H. Schiff, C. David, M. Gabriel, J. Gobrecht, L.J. Heyderman, W. Kaiser, S. Köppel, and L. Scandella, *Nanoreplication in polymers using hot embossing and injection molding*, *Microelectron. Eng.* **53**, 171-174 (2000).
- [2] A. D'Amore, D. Simoneta, M. Gabriel, W. Kaiser, and H. Schiff, *Spritzgießen im Nanobereich - Kalibrierstrukturen für RSM*, *Kunststoffe* **90** (6/2000), 52-55 (2000). English version: *Nano injection moulding - calibration structures for scanning probe microscope*, *Kunststoffe plast europe* **90** (6/2000).
- [3] P.M. Kristiansen, C. Rytka, M.J. Cheung, H. Schiff, A. Schleunitz, C. Spreu, and H.H. Solak, Eulitha AG, *Kleinste Strukturen in der Massenfertigung abformen*, *Plastics/Swiss Engineering STZ*, Okt. (2011) 20-21.
- [4] P. Urwyler, J. Köser, H. Schiff, J. Gobrecht, and B. Müller, *Nano-mechanical transduction of polymer micro-cantilevers to detect bio-molecular interactions*, submitted to *Biointerfaces* **6**, SpringerOpen (2011).

Contact information:

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LoP2012_NIL004_variothermIM-Tool

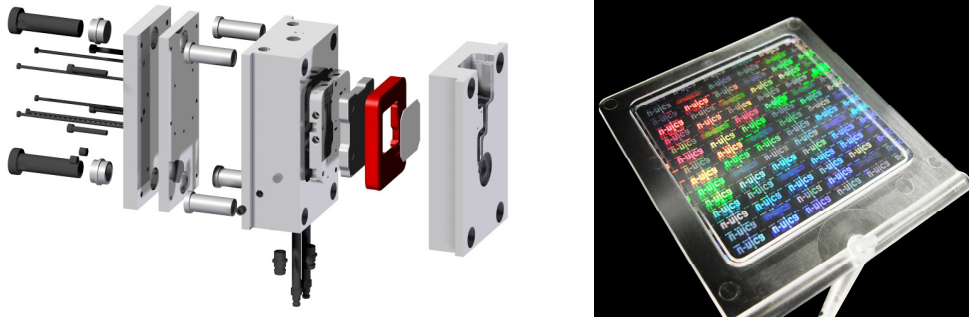


Figure 1: Versatile tooling for rapid variotherm injection molding (left) and sample of security feature replication (right).

A versatile injection molding tool with rapid variotherm temperature control was realized by the Institute of Polymer Nanotechnology (INKA) to distinctly study the replication area of large-area (max. $50 \times 50 \text{ mm}^2$) arrays of functional micro- and nanostructures. Rapid variotherm temperature control was realized by a thermally de-coupled mounting stage with fluidic channels optimized for heat transfer. A two-chamber water heating/cooling system (HB Therm) is used. For in-situ process monitoring, the variothermal molding tool is equipped with multiple pressure and temperature sensors which enable exact determination of process and rheological parameters in-situ during the injection molding process. Data acquisition is accomplished by a dedicated software tool developed by Priamus System Technologies GmbH.

Functional master structures of various kinds can be incorporated into the tooling. Examples used to date include galvanic nickel masters (thin & thick), laser-machined steel inserts, polymeric stamps (mainly high temperature polymers), OrmoStamp[®] (see page 28 & 40) on steel. For direct replication of silicon masters, a dedicated mold insert made of Invar is also available.

Thermal injection molding with variothermal injection molding tool: Process description

Variothermal molding is the ideal case for controlled processing. Injection of a hot melt into a cavity with temperatures above glass transition assures that flow into narrow cavities (and consequently high aspect ratio structures) is not inhibited by freezing at cold boundaries. However, due to the high heat capacity of metal tools cooling with oil rather slow. Instead of a few seconds, cycling will therefore require minutes. New tool concepts dealing with decoupled mounting stages and use of 2-chamber water system enable to store heat and remove heat quickly from mold cavities at cycle times below 1 minute.

Advantages of variothermal injection molding

- Mold temperature above glass transition temperature
- Lower stress and homogeneity due to slowed-down relaxation
- Higher optical quality (bi-refringence)

Process parameters (T_g for PMMA 100 °C, Tritan copolyester 110 °C, PC 140 °C)

- Melt up to 280 °C, sufficient for Tritan molding (heating about 2 min from 80 °C to 280 °C)
- Mold temperature during injection: 120 to 160 °C (heating about 20sec from 50 °C to 130 °C)
- Mold temperature during demolding 50 to 100 °C (about 20sec from 130 °C to 50 °C)

Restrictions – and how to deal with them

- Homogeneous cooling, addressable by mold design
- Switching between cold and hot state: electrical heating, cooling with thermalized oil

2. Stamps and Structure Origination

Contributions to this section of the library are from

VTT Information Technology/Finland

Dr. Tapio Mäkelä / Dr. Tomi Haatainen /
Prof. Dr. Jouni Ahopelto

ICN, Barcelona, Spain

Dr. Vincent Reboud / Dr. Nikolaos Kehagias /
Prof. Dr. Clivia Sotomayor-Torres

AMO GmbH, Aachen, Germany

Dr. Ulrich Plachetka

CRF Fiat - Orbassano/Italy

Dr. Vito Lambertini

CEA-LETI MINATEC- Grenoble/France

Dr. Stéfan Landis

LTM-CNRS - Grenoble/France

Dr. Cécile Gourgon

DTU - Lyngby/Denmark

Prof. Dr. Anders Kristensen

PSI/LMN - Villigen/Switzerland

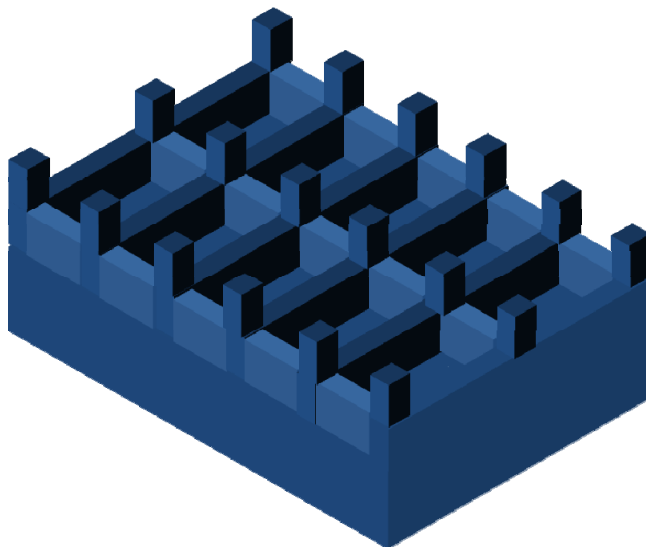
Dr. Helmut Schiff / Dr. Arne Schleunitz /
Christian Spreu

IOM CNR - Trieste/Italy

Dr. Massimo Tormen

University of Glasgow - Glasgow/ United Kingdom

Dr. Nikolaj Gadegaard / Dr. Mathis Riehle /
Dr. Kris Seunarine /
Prof. Dr. Christopher Wilkinson



2.1 Stamps for Nanoimprint Lithography

Standard fabrication process for stamps and antiadhesive surface coating for Nanoimprint lithography

Process: nanoimprint lithography

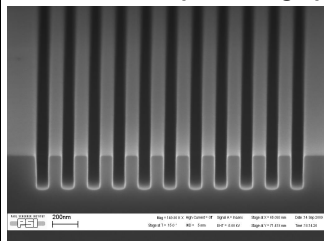


Figure:
SEM micrograph of a Grating with 100 nm period etched in Si using dry etching process (ICP) and PMMA resist as an etch mask.

Process:
Electron beam lithography on positive or negative resists and plasma etching

Application:
NIL stamps for optical, photonic, electronic or micro/nano-fluidics.

Keywords: thermal nanoimprint (T-NIL), electron beam lithography (EBL), plasma etching, coating

Project leader: TASC Laboratory
Address: 34012 Basovizza-Trieste, Italy
Web-Address: [http:// www.tasc-infm.it](http://www.tasc-infm.it)

Process: Thermal Nanoimprint
Responsible: Massimo Tormen
E-mail: tormen@tasc.infm.it

Partner: Paul Scherrer Institut (PSI)
Address: 5232 Villigen PSI, Switzerland
Web-Address: <http://www.psi.ch>

Process: Thermal Nanoimprint
Responsible: Helmut Schiff
E-mail: helmut.schiff@psi.ch

Process description: A general purpose process is described for fabrication of stamp and surface functionalization for reducing adhesion forces towards polymers after the imprinting step.

Purpose: The aim of this process is to produce large arrays of microstructures (e.g. lenses) with a high control of geometrical parameters of the elements.

Major challenges: Accurate pattern definition by Electron Beam Lithography, control of sidewall profile and roughness in the reactive ion etching process, durability of surface treatment process.

Application and state-of-the-art: Standard process

References (mainly on antiadhesive coatings):

- [1] H. Schiff, S. Saxer, S. Park, C. Padeste, U. Pieves, J. Gobrecht: *Controlled co-evaporation of silanes for nanoimprint stamps*, *Nanotechnology* **16** (2005) S171-175.
- [2] M. Beck, M. Graczyk, I. Maximov, E.-L. Sarwe, T.G.I Ling, M. Keil, L. Montelius, *Improving stamps for 10 nm level wafer scale nanoimprint lithography*, *Microelectron. Eng.* **61-62**, 441, (2002).
- [3] M. Keil, M. Beck, G. Frennesson, E. Theander, E. Bolmsjö, L. Montelius, and B. Heidari: *Process development and characterization of antisticking layers on nickel-based stamps designed for nanoimprint lithography*, *J. Vac. Sci. Technol. B* **22**(6) (2002) 3283-3287
- [4] S. Park, H. Schiff, C. Padeste, B. Schnyder, R. Kötz, J. Gobrecht: *Anti-adhesive layers on nickel stamps for nanoimprint lithography*, *Microelectron. Eng.* **73-74** (2004) 196-201
- [5] H. Schiff, S. Park, C.-G. Choi, C.-S. Kee, S.-P. Han, K.-B. Yoon, J. Gobrecht, *Fabrication process for polymer photonic crystals using nanoimprint lithography*, *Nanotechnol.* **16** (2005) S261–S265.

Contact information:

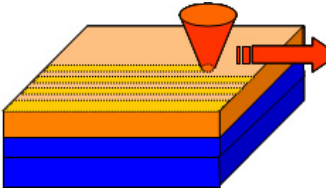
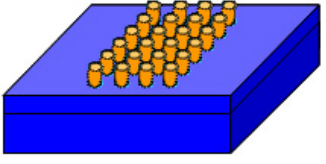
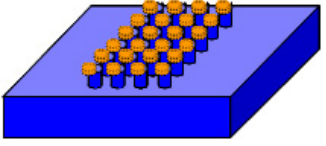
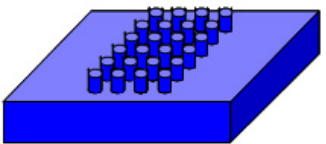
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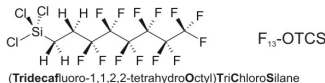
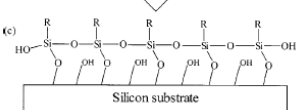
LoP2007_NIL001_Stamps for NIL

Stamps for Nanoimprint Lithography

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Wafer preparation	Silicon wafer format	
1.1	wafer selection and preparation	standard Si substrate Si substrate, 4", <100>, thickness d=400-600 μm one side polished	
1.2	substrate preparation	pretreatment no pre-treatment needed (if wafer is clean an hydrophilic)	
	End of Process 1		
2.0	Process 2: Resist coating	for electron lithography	
2.1	dispensing of resist	resist no priming, PMMA 4 % in ethyllactate (safer solvent) (EL) (600k), process lab (clean room)	<i>Ethyllactate or anisole are safer solvents (in contrast to chlorobenzene (CB)) and results in similar thickness. Only for very high concentrations of PMMA (e.g. 9%) CB is a better solvent.</i>
2.2	coating resist (homogeneous layer)	spincoating of PMMA speed: 3000rpm, acceleration: 3000rpm/sec, time: 45 s -> ~200 nm thickness	<i>PMMA is known for its high resolution as a positive resist, but has a limited sensitivity for electron exposure and etch resistance. An alternative positive resist with better etch resistance is ZEP520A. For stamps with low density of protruding structures, a solution is to use negative resists, such as NEB22, HSQ, SU8.</i>
2.3	post bake	solvent evaporation bake 1 min @ 170°C (hot plate)	<i>Alternative: convection oven at 180°C, for 30 min</i>
	End of Process 2		
3.0	Process 3: Lithography	Electron beam lithography	

3.1	Design and file generation	Functional structures if the stamp consists of large arrays of pillars, then either: crossed gratings can be exposed in a positive resist and transferred to the substrate by RIE single dots can be exposed in a negative resist and transferred by RIE crossed gratings can be exposed in a positive resist, a metal dot pattern created by lift-off and this hard mask transferred to the substrate by RIE	<i>The exposure strategy often depends on the preference for positive or negative resists and the pattern transfer process to be used. Often it is also dependent on the ability to reduce exposure time. For different resists datasheets are available with the range of exposure and development parameters.</i>
3.2	Pattern definition 	serial exposure with focused beam PMMA expose exposed to a 30 kV electron beam dose: 200 $\mu\text{C}/\text{cm}^2$	<i>For different resists datasheets are available with the range of exposure and development parameters.</i>
3.3	Resist development 	wet development in MIBK:IPA(1:3) ...60 sec and rinsed in IPA: 30 sec	
End of Process 3			
4.0	Process 4: Pattern transfer		
4.1	Substrate patterning 	Dry etching of silicon A typical process uses combination of gases (e.g. C_4F_8 45sccm / O_2 3 sccm / SF_6 30sccm). The etching parameters are usually strongly dependent on the tool. In an ICP system RF Power 450 W (ICP RF source), 30 W (Platen RF source), 5.5 mTorr) using PMMA as an etch mask.	<i>Reactive Ion Etching (RIE) or Inductively Coupled Plasma (ICP) tools are highly anisotropic etching processes and can generate deep structures with vertical sidewalls or sidewalls with defined (positive) slope. Control of critical dimensions is needed, undercuts and roughness have to be avoided, because this results in enhanced demolding forces and damage of structures in NIL</i>
4.2	Resist removal (stripping) 	RIE resist ashing A low bias oxygen plasma for few seconds allows to remove the resist without damage of the patterned silicon surface. For positive resist an alterna-	

		<p>tive solution is to dissolve the resist in a convenient solvent.</p>	
4.3	process control	<p>optical and electron microscopy <i>non-destructively</i></p>	<p><i>destructive (cleaving, metal coating) in SEM profilometry</i></p>
	End of Process 4		
5.0	Process 5: Anti-adhesive coating	<p>surface treatment by chemical vapor deposition</p>	
5.1	Preparation of stamp surface	<p>cleaning and activation Typically, RIE treatment with O₂ plasma removes organic contaminants and activates the surface (generation of free reactive silanol bonds for silane binding) for about 60 min. Alternatively, UV-ozone treatment can be used.</p>	<p><i>Alternatively to dry treatment of the surface, the cleaning and activation of the surface can be done in a fresh solution of H₂O₂:H₂SO₄ (1:4). Attention: danger of explosion! Dip the silicon stamp for 5-10 min.</i></p>
5.2	<p>Solution preparation</p>  <p>(Tridecafluoro-1,1,2,2-tetrahydroOctyl)TriChloroSilane</p>	<p>Diluted silane Prepare a solution 1-10 mM of perfluorotrichlorosilane molecules in toluene. The preparation of the solution and the surface treatment need to be performed in an atmosphere with low content of humidity. A convenient solution is to operate in glovebox.</p>	<p><i>Alternatively, chemical vapor deposition methods have been developed which allow generating the silane monolayer from the gas phase. The coating should be done within about 1 hour after surface activation</i></p>
5.3	<p>Coating</p>  <p>Silicon substrate</p>	<p>Dip of the stamp The stamp is inserted in the silane solution for 1-2 hours, where the silane reacts with the silanol groups of the surface, but also with neighboring molecules (crosslinking).</p>	<p><i>In order to avoid the formation of a bulky deposit of molecules instead of a monolayer, washing of the stamp in acetone has to be performed in dry atmosphere.</i></p>
5.4	Process control	<p>Optical microscope, AFM The quality of the antisticking layer can be done by contact angle (CA) measurement, for perfluorotrichlorosilane a CA 115° can be reached</p>	<p><i>Profile control not any more with SEM (exposure and damage of anti-adhesive layer); a high CA can also be a result of roughness due to deposits; these deposits are removed after a few imprints</i></p>
	End of Process 5		
	End of Total Process		

General remarks:

This is only one of many processes to fabricate stamps in a silicon substrate by e-beam lithography. Every cleanroom provides processes using different resists for electron beam or other lithographies. Apart from PMMA directly coated on Si, hard (metal, e.g. Cr) masks are beneficial for etch ratio enhancement. They can be applied at the bottom of the resist and etched, or evaporated onto the patterned resist and locally removed by lift-off. Furthermore negative resists are commonly used.

In case of substrate etching, care has to be taken that undercuts and high sidewall roughness are avoided. Sloped sidewalls are beneficial but no prerequisite for moderate aspect ratio structures. A further issue is that residual polymer or other contaminants deposited during the etching on the structure sidewalls should be fully removed before applying the antiadhesive coating. In most cases this can be effectively done in wet (oxidizing) etching or ashing in oxygen plasma, which is also the step to activate surface (creating silanol groups) for silane binding.

2.2 Laser Interference Lithography (LIL)

Master fabrication process for highly periodic gratings

Process: Laser Interference Lithography double patterning for gratings using Moiré effects

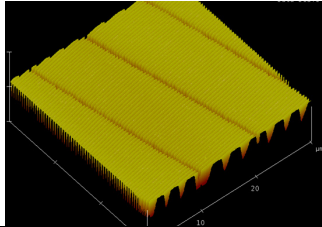


Figure:
AFM micrograph of a double grating with two distinct periods of 500nm and 10µm.

Process:
Patterning of a photoresist using laser interference lithography with Moiré-effect

Application:
Fabrication of NIL stamps for ladder-like transparent electrode.

Keywords: LIL, master fabrication , periodic structures

Partner: AMO GmbH

Address: 52074 Aachen, Germany

Web-Address: [http:// www.amo.de](http://www.amo.de)

Process: LIL

Responsible: M. Möller

E-mail: moeller@amo.de

Process description: Laser Interference Lithography is a holographic method used to expose highly periodic pattern into a sensitive resist. Here, instead of exposing just a single grating period the LIL system was converted to expose a second grating using a Moiré-effect. This way two distinct periods can be exposed (one 500 nm, the other 10 µm)

Purpose: In the current project, the system is used to fabricate imprint stamps for semitransparent metal electrodes.

Major challenges: Fine tuning of spectral noise and Moiré-effect.

Application and state-of-the-art: Fine tuning of optics, imprint and coating on massive topography

References:

[1] http://www.amo.de/fileadmin/user_upload/imgForReferences/ImgForDownload/AMO_IL.pdf

Contact information:

M. Moeller

Otto-Blumenthal-Strasse 25

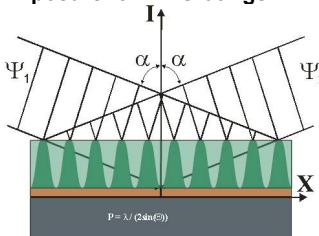
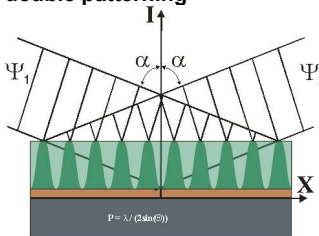
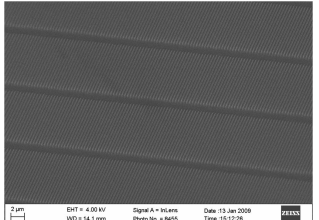
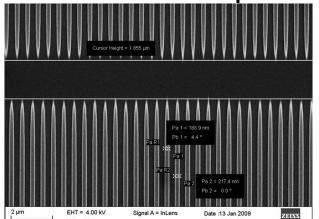
52074 Aachen

Germany

LoP2012_NIL005_LIL-Stamps

Laser Interference Lithography

Process: LTIL

	Process	Technical Parameters	Remarks
	Substrate preparation	how it should work	critical issues
1.1	Preparation of BARC layer	Spin coating of BARC (DUV5214) 45sec.@1800rpm -hardbake on hotplate 60sec@200°C	<i>BARC= bottom antireflection coating</i>
1.2	Preparation of DUV resist	Spin coating of standard DUV pos. resist for 248nm 30sec.@3000rpm -bake 60sec.@130°C	
1.3	Exposure for 1D-Gratings 	1st exposure -exposure dosis 40mJ/cm ² -alpha=15.24° -> 500nm period	$p1 = \lambda / (2\sin(\alpha))$
1.4	Second exposure for Moiré double patterning 	2nd exposure under rotated substrate angle beta=2.86° -> 10µm period	$p2 = p1 / (2\sin(\beta))$
1.5	Development of double patterned grating	development of resist in MF26@30sec.	
1.6	Process result 	After LIL process and standard etching into Silicon a double grating with two distinct periods of 500nm and 10µm is visible	
1.7	Process result close-up 	Close-up of etched LIL double grating in Silicon with two distinct periods of 500nm and 10µm	
	End of process		

General remarks:

The LIL-system uses a Nd:YAG laser with a wavelength of 1064nm as main exposure source. The laser source is doubled in frequency two times resulting in a 266 nm wavelength in order to pattern gratings with periods smaller than 200nm. The laser beam is split into two parts controlled separately in amplitude via attenuators. Two beams are then reflected onto the substrate via mirrors. The spatial filters act as a low-pass for optical speckle induced by every optical component in the light path. Roughness of these components would otherwise induce high frequency noise in the intensity pattern. The phase shift on the substrate is detected by sensor, which feeds the Pockels-cell in a feedback loop in order to expose a standing wave pattern on the substrates surface.

2.3 Saw-tooth stamps for optical applications

Blazed grating master stamps in Nickel for optical applications

Process chain: e-beam lithography, soft and deep X-ray lithography , electroplating

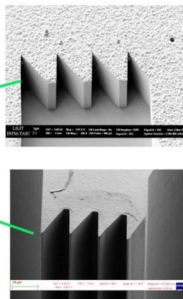
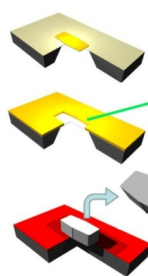


Figure:
Scheme of fabrication of a nickel master tool with a few-period saw-tooth grating. The released nickel shim is used for hot emboss the structure defined on its edge.

Main technologies required:

Electron beam lithography, Soft and Deep X-ray lithography, electroplating and assembly (modified LIGA)

Ancillary processes used: optical lithography, wet etching, sputtering.

Application:

Stamp for Step and stamp NIL for large area optical sheets for backlighting of flat panel displays.

Keywords: deep X-ray lithography, electron beam lithography, LIGA, electroplating, blazed gratings, sawtooth gratings, high aspect ratio structures, nickel master stamps, edge embossing

Project leader: TASC Laboratory
Address: 34012 Basovizza-Trieste, Italy
Web-Address: <http://www.tasc-infm.it>

Process: XR-lithography, electroplat.
Responsible: Massimo Tormen
E-mail: tormen@tasc.infm.it

Partner: University of Glasgow (UG)
Address: Glasgow, UK
Web-Address: <http://www.gla.ac.uk>

Process: EBL
Responsible: Nikolaj Gadegaard
E-mail: n.gadegaard@gla.ac.uk

Partner: Modines Oy
Address: Helsinki, FI
Web-Address: <http://www.modines.com>

Process: Design, application
Responsible: Kari Rinko
E-mail: kari.rinko@modines.com

Partner: VTT Technical Research Centre of Finland, VTT
Address: Helsinki, FI
Web-Address: <http://www.vtt.fi>

Process: Step & Repeat thermal NIL
Responsible: Tomi Haatainen
E-mail: tomi.haatainen@vtt.fi

Process description: Resist structures are fabricated via DXRL, resulting in 2 ½ dimensional patterns. After electroplating 100 µm high Ni parts are separated from the substrate and flipped in a way that the edge can be hot embossed into a plastic sheet. Thus, small patches (50x100 µm²) are created with sawtooth structures. Finally, the structure is assembled and glued onto a 10x10 mm² holder.

Purpose: The aim of this process is to use the metal structures as stamps for step&repeat.

Major challenges: Sub- µm precise pattern transfer of sawtooth structure during DXRL in more than 100 µm high resist. Furthermore assembly and surface treatment process.

Application and state-of-the-art: Partially standard process, but not yet tested for sawtooth.

References: G. Greci, A.Pozzato, Paper in preparation

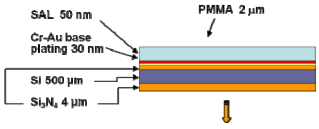
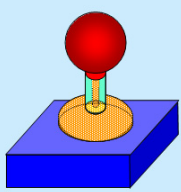
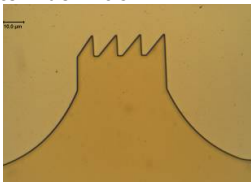
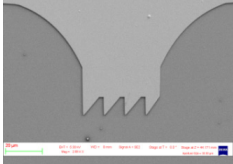
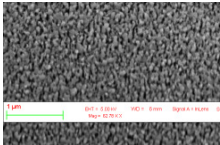
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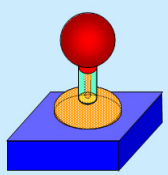
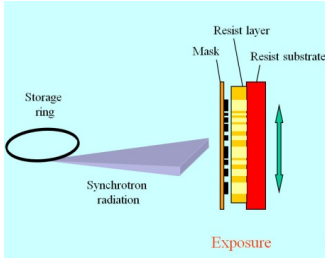
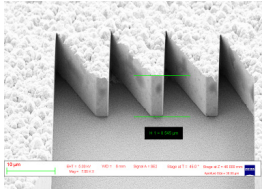
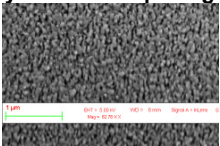
Dr. Massimo Tormen
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LoP2012_NIL006_Sawtooth-Stamps

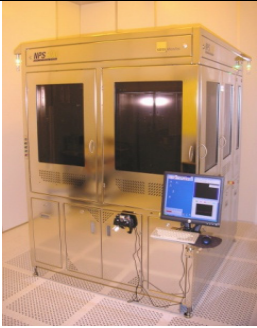
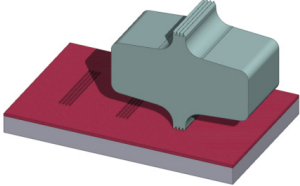
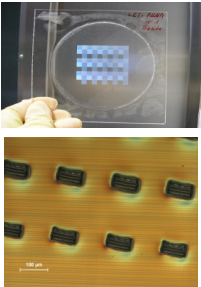
Saw-tooth stamps

Process chain: e-beam lithography, soft and deep X-ray lithography , electroplating

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Primary X-ray Mask fabrication (for soft X-rays)	EBL and electroplating	
1.1	substrate preparation 	silicon – mask blank Si substrate, 4", <100>, thickness d=400-600 μm two side polished with 4 μm Si3N4 deposited by PECVD and coated with Cr/Au (10/20 nm), and primed with 50 nm of SAL 607.	
1.2	resist coating 	spin-coating resist no priming. PMMA 4 % in ethyllactate (safer solvent) (EL) (600k) thickness d=2 μm	
1.3	pattern definition 	electron beam lithography Exposure of the pattern with 100 kV acceleration energy. Development in MIBK:IPA 1:1.	<i>No proximity correction required</i>
1.4	metal (absorber) deposition 	gold electroplating Electroplating of Au up to 0.8-1 μm.	
	End of Process 1		
2.0	Process 2: Daughter X-ray Mask fabrication (for soft X-rays)		
2.1	substrate preparation	silicon – mask blank Si substrate, 4", <100>, thickness d=400-600 μm two side polished with 4 μm Si3N4 deposited by PECVD.	
2.2	coating with nanorough Titania layer as electroplating seed 	Nano-rough TiOx layer was obtained by sputtering a 200 nm Ti film followed by oxidative corrosion in a solution of hydrogen peroxide and sodium hydroxide (21 mL of H2O2 (30%), 21 g NaOH in 1 L of de-ionized water at 60°C for 10 sec.	<i>Adhesion issues solved by introducing nanorough titania</i>

2.3	resist coating 	spin-coating resist no priming. PMMA 4 % in ethyllactate (safer solvent) (EL) (600k) thickness d=10 μm	
2.4	post bake	solvent evaporation bake 1 min @ 170°C (hot plate)	
2.5	soft X-ray lithography 	X-ray exposure with a photon spectrum in the 1-4 keV range of energy and photon flux peak at 2 keV at a dose of 12 J/cm ² using the mask of step 1.4. Development for 5 min at 23 °C in GG solution (60 vol% 2-(2-butoxy-ethoxy) ethanol, 20% tetra-hydro-1, 4-oxazine, 5 vol% 2-amino-ethanol-1 and 15 vol% water).	
2.6	Electroplating of the X-ray Absorber 	gold electroplating Electroplating of gold up to a thickness of 0.8-1 μm	
End of Process 2			
3.0	Process 3: Deep X-ray Lithography	DXRL	
3.1	substrate preparation	silicon – substrate Si substrate, 4", <100>, thickness d=400-600 μm .	
3.2	Coating with nanorough Titania layer as electroplating seed 	Nano-rough TiOx layer was obtained by sputtering a 2 μm Ti film followed by oxidative corrosion as in step 2.2.	<i>Adhesion issues solved by introducing nanorough titania</i>
3.3	resist coating	Coating with a PMMA precursor, obtained by mixing MMA powder (Röhm, Plexidon M727) and liquid MMA (Fluka 64200 base components) in a weight ratio of 85:15 and by adding for any 100 g of the previous mixture, 0.15 g Benzoyl peroxide (BPO, Fluka 33581), 0.1 g of	

		<p>methacryloxypropyltri-methoxy silane (MEMO), and 0.1 g of Dimethylaniline (DMA, Fluka 39430); The resulting PMMA precursor casted on the conductive nano-rough titania films to produce uniform PMMA layers of 200 μm thickness</p>	
<p>3.5</p>	<p>Deep X-ray Lithography</p>	<p>DXRL performed with “hard” spectrum (critical energy and peak of maximal intensity were 3.2 keV and 8 keV, respectively) using a DEX02 Jenoptik Scanner. The exposure dose was adjusted so that 3.5 kJ/cm³ were absorbed by PMMA at the bottom of the deposited layer. A 104 μm thick graphite filter was interposed in the optical path as a cut-off for the low energy end of the beam spectrum, resulting in a higher dose uniformity as a function of the depth in the PMMA layer.</p>	
<p>3.6</p>	<p>Development</p>	<p>Development was performed in the GG solution (60 vol% 2-(2-butoxy-ethoxy) ethanol, 20% tetra-hydro-1, 4-oxazine, 5 vol% 2-amino-ethanol-1 and 15 vol% water) for 80-90 min at 23 °C.</p>	
<p>3.7</p>	<p>Electroplating of Nickel</p>	<p>the formed template was introduced in a standard Watts bath (Ni-sulphate solution) and electroplating was obtained with DC current density of 10 mA/cm² at 56 °C, resulting in a mean growing rate of 4 nm/s. Ni shims with final thicknesses of 30, 80, 100 and 200 microns were fabricated.</p>	
<p>3.8</p>	<p>Release</p>	<p>The shims were finally released from the substrate by fully etching the silicon substrate and the titanium oxide in a 5 M KOH solution at 75 °C overnight.</p>	
<p>End of Process 3</p>			

4.0	<p>Process 4: Pattern enlargement</p>		
4.1	 <p>IMPRINTING TOOL: NPS300</p>	<p>Step & Repeat hot embossing:</p> <p>Thermal and UV-NIL capability. Alignment accuracy: 100nm Overlay Accuracy: 250 nm Template / Stamp size 50 ~ 65 mm (Option up to 100 mm). Substrate ≤ Sq.200mm (∅ 300mm).</p>	
4.2		<p>Clamping the nickel shim for step & repeat hot embossing.</p>	<p><i>Replication into thermo-plastic NIL materials (see page 34) or bulk polymer</i></p>
4.3		<p>Inspection:</p> <p>Optical and electronic microscopy to characterize the results of the step & repeat hot embossing process.</p>	
<p>End of Process 4</p>			
<p>End of Total Process</p>			

2.4 Three-dimensional surface topographies

Pattern origination for NIL stamp fabrication by Thermally Activated Selective Topography Equilibration (TASTE process)

Process: electron-beam lithography, thermal NIL and thermal reflow

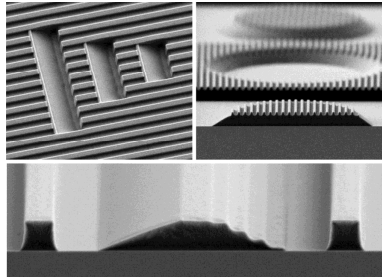


Figure:
Compilation of SEM micrographs illustrating the TASTE capabilities to manufacture sophisticated 3D surface structure with stepped, sloped and vertical sidewalls in close vicinity (here: 1 μm thick PMMA resist on silicon substrate).

Application:
True 3D structures with both smooth surfaces and sharp features as are decisive aspects for enhanced functionality in optics (e.g. back-lighting device) and life science (e.g. micro-nano-fluidics).

Keywords: electron-beam lithography, mix and match, 3D micro-nano-fabrication, thermal reflow

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Address: 5232 Villigen PSI, Switzerland
Web-Address: <http://www.psi.ch>

Process: EBL, reflow, pattern transfer
Responsible: Helmut Schiff
E-mail: helmut.schiff@psi.ch

Partner: micro resist technology GmbH
Address: Koepenicker Str. 325, 12555 Berlin, Germany
Web-Address: <http://www.microresist.de>

Process: polymer materials
Responsible: Marko Vogler
E-mail: m.vogler@microresist.de

Process description: Origination of true 3D surface structures and pattern transfer to mold material

Purpose: This hybrid mix and match fabrication process targets to overcome technical limitation of standard lithography methods by means of generating vertical, stepped and slopes pattern in close vicinity on the same (resist) substrate, thus providing enhanced 3D NIL stamps

Major challenges: Most critical aspect is the precise generation of stepped topographies (using EBL or 3D NIL) prior to reflow, since its geometry mainly predetermines the final (i.e. after reflow) contour.

Application and state-of-the-art: The beneficial flexibility of EBL processing is used to define the preliminary topography and thus accessible for stamp manufacture. Upscaling to application oriented large area patterns (i.e. cm^2) can be accomplished by step & repeat replication approaches.

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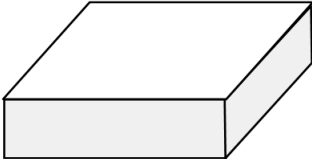
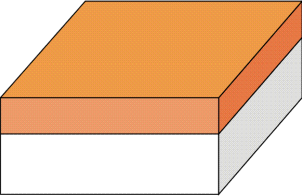
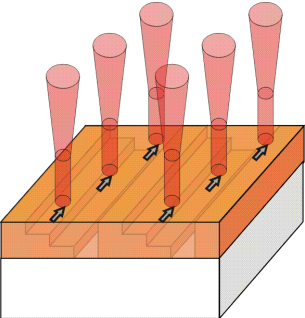
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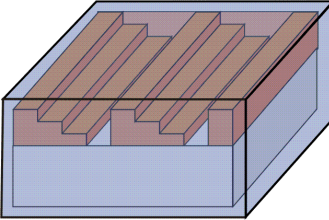
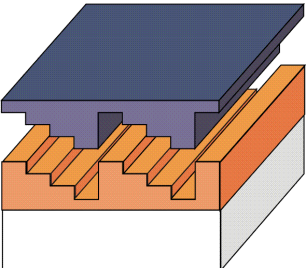
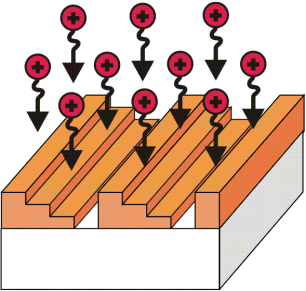
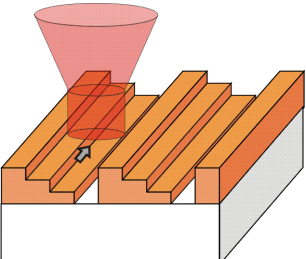
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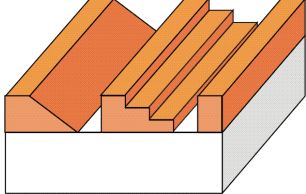
LoP2012_NIL007_3D-Stamps for NIL

Three-dimensional surface topographies

Process: electron-beam lithography, thermal NIL and reflow

	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	Process 1: substrate preparation	PMMA coated silicon wafer	
1.1	Substrate preparation 	Pretreatment Dehydration Surface activation (if needed) Oxygen plasma surface activation	
1.2	Dispensing, spin-coating and pre-baking of PMMA resist 	Polymethyl (methacrylate) with a molecular weight of 950, 600 or 120 kg/mol, e.g. diluted in anisole Standard spin-coating (few μm thick resists are achieved by multilayer deposition) Pre-bake at 175 °C on hot plate (or oven)	<i>The lower the molecular weight of the PMMA is chosen, the more easily is the thermoplastic film pre-patterned with a shallow surface relief using NIL prior to gray-scale EBL (e.g. to integrate moth eye type anti-reflective coating). According to references [1,2], PMMA 120 kg/mol was found to be most suitable.</i>
	End of Process 1		
2.0	Process 2: topography origination	Generation of stepped PMMA contours	
2.1a	Topography origination by grayscale EBL ... 	Dose modulated electron-beam exposure with commercial lithography system, e.g. VISTEC or JEOL: Acceleration voltage: 100 keV Beam step size: 5 nm Beam current: 1 nA Dose range: 50 ... 500 $\mu\text{C}/\text{cm}^2$ Dose-modulation is performed according to the contrast curve (i.e. etch depth vs. exposure dose)	<i>Dose modulation not only according to desired dose-depth variations, but also have to take the areal proximity effect into account.</i>

<p>2.2a</p>	<p>... and wet etching</p> 	<p>Development of PMMA exposed to different doses leads to variations in the etching rates, thus stepped contours</p> <p>Developer: Methyl isobutyl ketone (MIBK) Rinse: IPA and DI water</p>	<p><i>It is recommended to temperature control the developer bath to optimize the reproducibility.</i></p>
<p>2.1b</p>	<p>Topography origination by 3D thermal NIL ...</p> 	<p>Alternative way to generate stepped topographies is to replicate stepped stamps into PMMA by thermal NIL.</p> <p>Stamp: silicon or nickel PMMA molecular weight: ≤ 120 kg/mol Standard imprint parameter using Jenoptik HEX 03 press: 180 °C / 5 MPa / 15 min</p>	<p><i>Generation of stepped PMMA topographies by 3D NIL is more reliable compared to grayscale EBL. However, achievable pattern diversity is limited to structures available on the stamp.</i></p>
<p>2.2b</p>	<p>... and residual layer etching</p> 	<p>Residual layer etching is a crucial step when the topography is generated by NIL in order to enable pinning point on the substrate inevitable for the formation of linear slopes. For concave and convex pattern, this step is less important.</p> <p>Exemplary etch recipe: Power: 20 W Pressure: 20 mtorr Oxygen: 20 sccm</p> <p>Resulting etch rate: 30 nm/sec</p>	<p><i>Oxygen plasma might harm the stepped contours and thus lead to an unwanted pattern deviation.</i></p>
<p>End of Process 2</p>			
<p>3.0</p>	<p>Process 3: flood exposure</p>	<p>Adjusting thermo-mechanical properties</p>	
<p>3.1</p>	<p>Precisely aligned high dose exposure to stepped contours</p> 	<p>Flood (EBL) exposure with commercial lithography system, e.g. VISTEC or JEOL:</p> <p>Acceleration voltage: 100 keV Beam step size: 25 nm Beam current: 10 ... 100 nA Dose range: > 250 $\mu\text{C}/\text{cm}^2$</p>	<p><i>Electron beam exposure reduces the glass transition temperature T_g of locally exposed PMMA resist, in particular if dose is higher than 250 $\mu\text{C}/\text{cm}^2$. Here, the resulting molecular weight is below a T_g-critical value of 10 kg/mol.</i></p>

	End of Process 3		
4.0	Process 4: topography equilibration	Controlled transformation of steps into slopes	
4.1	Selective contour transformation 	Thermal treatment (e.g. on hot plate) allows to selectively transform stepped contours into continuous slopes. Heating temperature: e.g. 110 °C for 120 min. Instant cooling by removing sample from hotplate.	<i>Heating temperature according to modulation of thermal properties by previous flood exposure: For PMMA with reduced T_g below 90 °C (i.e. exposed to 400 $\mu\text{C}/\text{cm}^2$), a reflow at 110 °C ideal since the original T_g of 120k PMMA is at 120 °C.</i>
	End of Process 4		
	End of Total Process		

General remarks:

TASTE process here is exemplified with the thermoplastic resist mr-I PMMA120k*, which is exposed to high energy electron using conventional EBL systems. However, the modular concept of the TASTE process offers a high degree of freedom concerning the employed polymer material as well as subsequently applied sub-process variants. This means, besides choosing alternative polymer films like polystyrene etc., the local adjustment of the thermo-mechanical properties can be accomplished by exposure not only to high energy electrons, but X-rays, (deep) UV radiation, ions or protons. The thermal annealing might be performed on a conventional hotplate, but also convection oven or local exposure to laser light might be feasible.

Furthermore, the assigned dose modulation during grayscale exposure is not only applied according to the desired dose-depth variations, but also have to compensate the areal proximity effect. Here, suitable software tools are commercially available (i.e. 3D-PEC modul in E-Beam Lithography Software by GenISys GmbH).

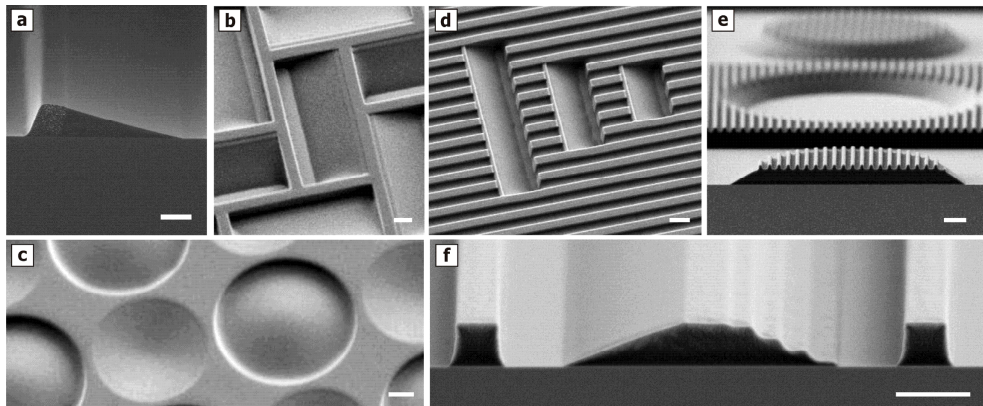


Figure 1: Compilation of exemplary 3D contours in a thin mr-I PMMA120k* film made by novel TASTE process. The SEM micrographs (angled views and cross sections) depict refined PMMA topographies after exposure of pre-patterned resist to high energy electrons and thermal annealing using hot-plate. Achievable contours comprise binary, stepped, sloped, convex and concave structures (a-c), as well as hybrid structures with specific pattern combinations (d-f). (scale bar: 1 μm)

[*] experimental sample provided by *micro resist technology* GmbH

2.5 Proportional RIE of 3-D resist structures

Standard fabrication process of 3-D stamps with proportional reactive ion etching

Process: Proportional reactive ion etching of 3D resist structures

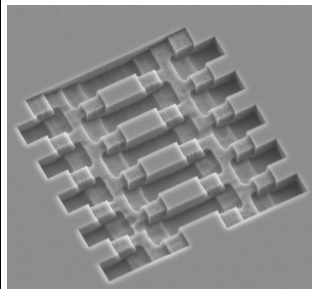


Figure:
SEM micrograph of a 3D structure fabricated with grayscale E-Beam lithography in PMMA and etched into silicon substrate.

Process:
Proportional pattern transfer with RIE of 3D resist structures
Application:
3D NIL stamps with stepped and continuous slopes intended for optical, photonic, electronic or micro-/nanofluidic devices.

Keywords: grayscale electron beam lithography, reactive ion etching, proportional etching

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Process: Proportional RIE

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Partner: TASC Laboratory

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Web-Address: [http:// www.tasc-infm.it](http://www.tasc-infm.it)

Process: Proportional RIE

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Process description: Pattern transfer of 3D resist structures (i.e. stepped contours and/or continuously inclined slopes) via proportional reactive ion etching (RIE) into the silicon substrate.

Major challenges: Most critical point in the fabrication process is to maintain a constant selectivity (e.g. 1) independent from the *silicon loading* during the dry etch process.

Application and state-of-the-art: Fabrication of rigid 3D structures in mold material which can be directly used for pattern replication or serves as robust template in casting procedures.

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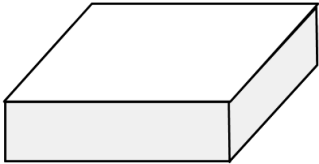
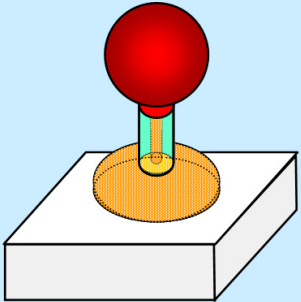
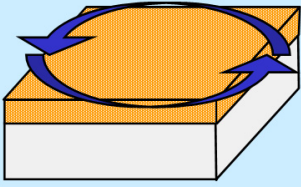
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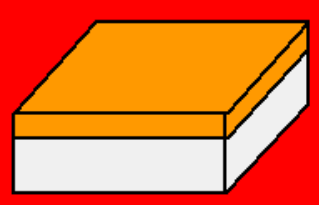
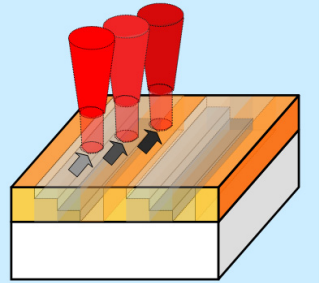
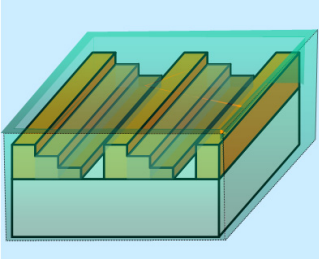
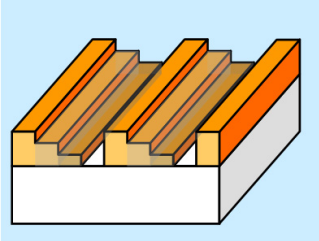
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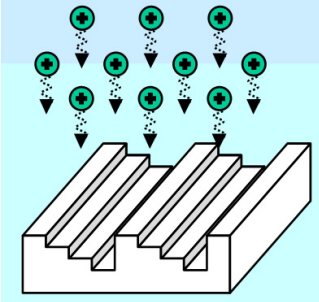
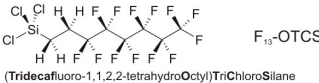
LoP2012_NIL008_3D RIE-Stamps

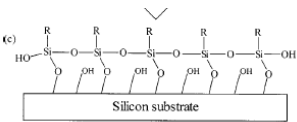
3-D stamps with proportional reactive ion etching

Process: Proportional reactive ion etching of 3D resist structures

	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	Process 1: Wafer preparation	Silicon Wafer format	
1.1	Wafer selection and preparation	Standard Si substrate Si substrate, 4", <100>, thickness d=400-600 μm one side polished	
1.2	Substrate preparation 	Pretreatment no pretreatment needed (if wafer is clean and hydrophilic)	
End of Process 1			
2.0	Process 2: Resist coating	For electron beam lithography	
2.1	Dispensing of the resist 	Resist mr-I PMMA120k*	* experimental PMMA sample provided by micro resist technology GmbH
2.2	Coating resist 	Spincoating of mr-I PMMA speed: 3000rpm, acceleration: 3000rpm/sec, time: 30 s thickness: 1 μm	homogeneous layer

2.3	Pre bake 	solvent evaporation bake 2 min @ 140°C (hot plate)	<i>Alternative: convection oven at 180°C, for 30 min</i>
End of Process 2			
3.0	Process 3: Lithography		
3.1		E-Beam lithography Dose modulated electron-beam exposure with commercial lithography system, e.g. VISTEC or JEOL: Acceleration voltage: 100 keV Beam step size: 5 nm Beam current: 1 nA Dose range: 50 ... 500 $\mu\text{C}/\text{cm}^2$ Dose-modulation is performed according to the contrast curve (i.e. etch depth vs. exposure dose)	
3.2		Development of PMMA exposed to different doses leads to variations in the etching rates, thus stepped contours Developer: Methyl isobutyl ketone (MIBK)	<i>It is recommended to temperature control the developer bath to optimize the reproducibility.</i>
3.3		Rinse: Thorough rinsing in IPA and DI water removes diluted PMMA.	<i>Residues left on the resist surface might lead to contamination during dry etching process, i.e. nucleation of polymer components during plasma step.</i>
End of Process 3			

4.0	Process 4: Pattern transfer	Reactive ion etching	
4.1		<p>A typical dry etch process for a depth from a few nanometers up to several micrometers uses a mixture of different gases e.g. (C₄F₈ 50 sccm and SF₆ 20 sccm, to stabilize the process noble gases like Ar could be added)</p> <p>The etch rate depends from the silicon load (means the exposed silicon) during the etch process and can change during the process.</p> <p>The etching parameters strongly dependent from the tool. "Oxford Plasmalab System 100 ICP 180 " ICP Power: 400 W RF Power: 40 W Pressure: 15 mTorr Temperature: 0° C</p>	<p><i>The use of a RIE system with a ICP head is beneficial for the etch result. The ICP head helps to generate a high density plasma at a low pressure. Also the RF power can kept quit low, so sputtering and damaging from the PMMA could be avoided.</i></p> <p><i>Wafer temperature can kept constant with He backside cooling. Heating of the substrate can lead to unwanted results e.g. isotropic profile due to spontaneous etching.</i></p>
4.2	End of Process 4		
5.0	Process 5: Anti-adhesive coating	surface treatment by chemical vapor deposition	
5.1	Preparation of stamp surface	<p>cleaning and activation Typically, RIE treatment with O₂ plasma removes organic contaminants and activates the surface (generation of free reactive silanol bonds for silane binding)</p>	<p><i>Alternatively to dry treatment of the surface, the cleaning and activation of the surface can be done in a fresh solution of H₂O₂:H₂SO₄ (1:2) at 90° C.</i></p> <p>Attention: <i>Strong exothermic reaction, bath temperature will reach 150° C. Wear safety glasses, gloves and clothes! Danger of explosion, if stamp surface contain solvent residues! Dip the silicon stamp for 5-10 min The etch bath will grow a thin SiO₂ layer on top of your substrate.</i></p>
5.2	<p>Solution preparation</p>  <p>(Tridecafluoro-1,1,2,2-tetrahydroOctyl)TriChloroSilane</p>	<p>Prepare a solution 1-10 mM of perfluorotrichlorosilane molecules in toluene. The preparation of the solution and the surface treatment is to be performed in an atmosphere with low content of humidity. A convenient solution is to operate in glovebox.</p>	<p><i>Alternatively, chemical vapor deposition methods have been developed which allow to generate the silane monolayer from the gas phase. The coating should be done within about 1 hour after surface activation</i></p>

5.3	Dip of the stamp 	The stamp is inserted in the silane solution for 1-2 hours, where the silane reacts with the silanol groups of the surface, but also with neighboring molecules (crosslinking).	<i>In order to avoid the formation of a bulky deposit of molecules instead of a monolayer, washing of the stamp in acetone has to be performed in dry atmosphere.</i>
5.4	Process control:	Optical microscope, AFM The quality of the antisticking layer can be done by contact angle (CA) measurement, for perfluorotrichlorosilane a CA 115° can be reached	<i>Profile control not any more with SEM (exposure and damage of anti-adhesive layer); a high CA can also be a result of roughness due to deposits; these deposits are removed after a few imprints</i>
End of Process 5			
End of Total Process			

General remarks:

The addition of oxygen to the gas mixture will increase the F atom density dramatically and therefore the silicon etch rate. The total amount of oxygen should be higher than 5% to shift the selectivity closer to one.

Repeatability of the processes depends strongly from the cleanness of the RIE tool; especially the use of C₄F₈ makes a chamber clean step necessary.

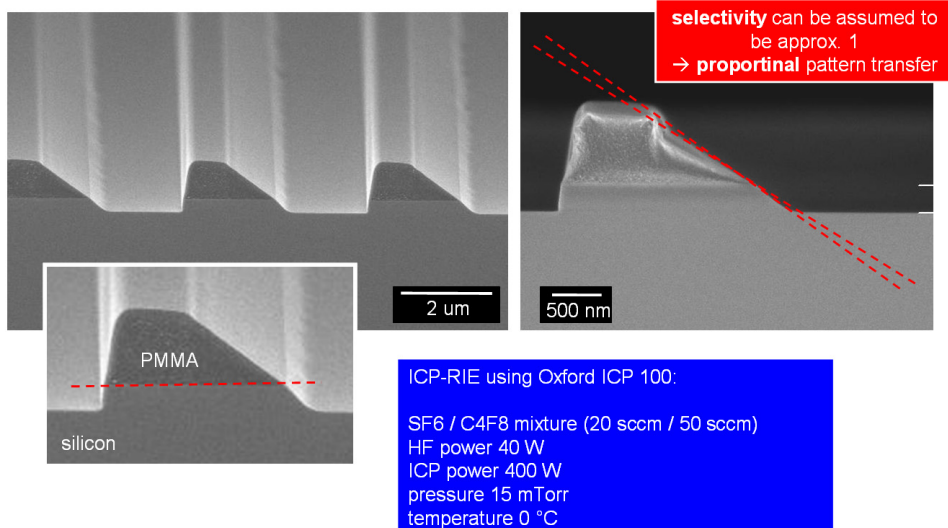


Figure 1: Demonstration of an almost proportional transfer of slopes in PMMA into the underlying silicon substrate using a RIE process. In the micrographs intermediate structures can be seen after stopping the etch procedure during RIE

2.6 Multilevel stamps

Fabrication process flow for 3-D 300 mm wafer scale Si stamp

Process: Deep ultra violet photo lithography

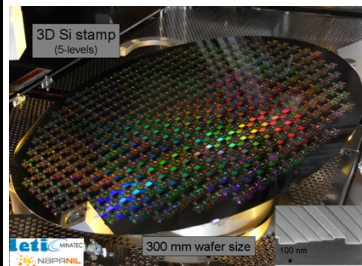


Figure:
SEM micrograph of a Grating with 100 nm period etched in Si using dry etching process (ICP) and PMMA resist as an etch mask.

Process:
Deep Ultra Violet (193 nm) photo lithography on positive tone resist and plasma etching.

Application:
3D NIL stamps for optical, photonic, electronic or micro/nano-fluidics.

Keywords: multilevel, wafer scale, thermal NIL, DUV optical lithography, plasma etching, coating

Project leader: CEA-LETI-Minatec
Address: 17 rue des martyrs 38054 Cedex 9
Web-Address: <http://www-leti.cea.fr/>

Process: DUV 193 nm-Lithography
Responsible: Stefan Landis
E-mail: slandis@cea.fr

Partner: Paul Scherrer Institut (PSI)
Address: 5232 Villigen PSI, Switzerland
Web-Address: <http://www.psi.ch>

Process: Thermal Nanoimprint
Responsible: Helmut Schift
E-mail: helmut.schift@psi.ch

Partner: TASC Laboratory
Address: S.S.14km 163,5; 34012 Basovizza (Trieste, Italy)
Web-Address: www.tasc-infm.it

Process: Isotropic wet etching / NIL
Responsible: Massimo Tormen
E-mail: tormen@tasc.infm.it

Process description: Fabrication of large area gratings based on nanoimprint lithography, high aspect ratio etching and electroplating.

Purpose: The aim of this process is to produce wafer scale 3D Si stamps with a wide range of feature size (above 70 nm), shape and density with aspect ratio larger than 2 in a industrial process scheme.

Major challenges: Not all-single process parameters are challenging but their combination to make a 3D Si stamp was not yet demonstrated.

Application and state-of-the-art: Any kind of feature size (above 70 nm), shape, and density are achievable. Up to 5 levels in Si stamp can be manufactured.

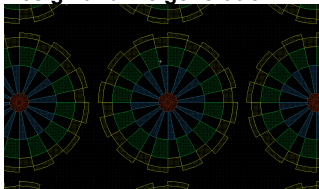
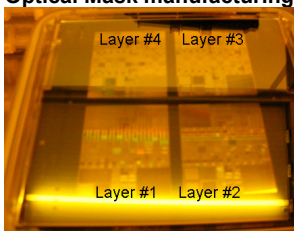
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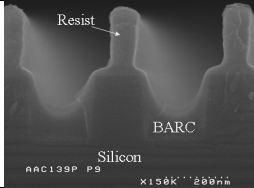
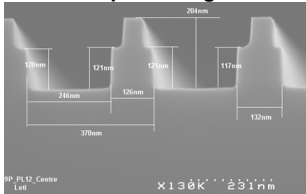
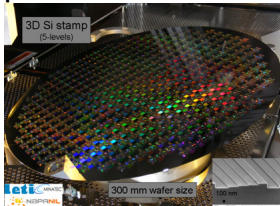
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LoP2012_NIL009_Multilevel DUV-Stamps

Multilevel stamps

Process: DUV 193 nm photolithography

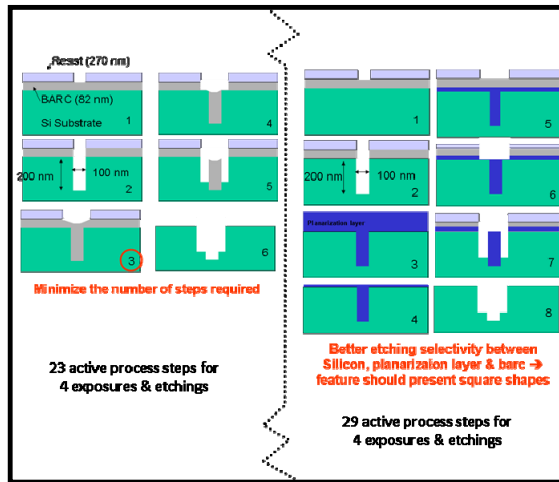
	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Wafer preparation	Silicon wafer format	
1.1	wafer selection and preparation	standard Si substrate, 12", <100>, thickness d=700-800 μ m two side polished	
1.2	substrate preparation	no pretreatment needed (if wafer is clean an hydrophilic)	
	End of Process 1		
2.0	Process 2: Resist coating	for DUV 193 nm optical lithography	
2.1	dispensing of resist after spin coating a (BARC) bottom anti reflective coating (requested for optical lithography)	Commercial DUV193 nm resist and BARC, no priming, positive tone resist for optical lithography, process lab (clean room)	<i>These commercial resists use safe solvents.</i>
2.2	coating resist (homogeneous layer)	Spin coating, see resist supplier specifications to target the optimized thickness with respect to the optical exposure conditions (thickness in the range of 200 nm to 300 nm)	<i>Automatic coating track or procedure is requested to obtain a thin uniform film over 12" wafer.</i>
2.3	post bake	solvent evaporation, see resist supplier specifications	
	End of Process 2		
3.0	Process 3: Lithography	DUV 193 nm photolithography	
3.1	Design and file generation 	Functional structures Draw patterns with Cadence, Layout Editor softwares (for example). Create a GDS file with one layer for one level that will be manufactured in you 3D stamp. Add some alignment marks compatible with the alignment strategy of you optical stepper or scanner.	<i>The exposure strategy often depends on the preference for positive or negative resists and the pattern transfer process to be used.</i>
3.2	Optical Mask manufacturing 	Transfer complete GDS file to a maskshop to manufacture your exposure mask.	<i>According to the final resolution and the final shape you are targeting, OPC (optical proximity correction) or PSM (Phase Shift Mask) may be needed. Several layers can be designe on the same mask. However, the expsd surface will be smaller.</i>
3.3	Mask alignment, resist exposure and development	wet development of the exposed resist, see resist supplier specifications	

			
	End of Process 3		
4.0	Process 4: Pattern transfer	dry etching of silicon	
4.1	Substrate patterning 	Dry etching of silicon A typical process uses combination of gases (e.g. $C_4F_8/O_2/Cl_2/HBr/SF_6$). The etching parameters are usually strongly dependent on the tool and the resist chemistry.	<i>Reactive Ion Etching (RIE) or Inductively Coupled Plasma (ICP) tools are highly anisotropic etching processes and can generate deep structures with vertical sidewalls or sidewalls with defined (positive) slope.</i>
4.2	Resist removal (stripping)	RIE or ICP resist ashing A low bias oxygen plasma for few seconds allows to remove the resist without damage of the patterned silicon surface. Then a final clean in wet chemistry may be used to remove fluoropolymer created during plasma treatments.	
4.3	process control 	optical and electron microscopy <i>non-destructively</i>	<i>destructive (cleaving, metal coating) in SEM profilometry</i>
	End of Process 4		
5.0	Process 5: Anti-adhesive coating	surface treatment by chemical vapor deposition	
5.1	Preparation of stamp surface	cleaning and activation Typically, RIE treatment with O_2 plasma removes organic contaminants and activates the surface (generation of free reactive silanol bonds for silane binding).	
5.2	Solution preparation	Prepare a solution 1/1000 of optool DSX in perfluorohexane solvent.	
5.3	Dip of the stamp	The stamp is inserted in the silane solution for 1 minute.	
5.4	Activate the ASL layer	Put the stamp in a hot (typically 70°) vapor contact environment for 1 hour.	
5.5	Rinse the stamp	Dip of stamp in perfluorohexane solvent for 5 minutes to remove the excess amount of anti sticking mole-	

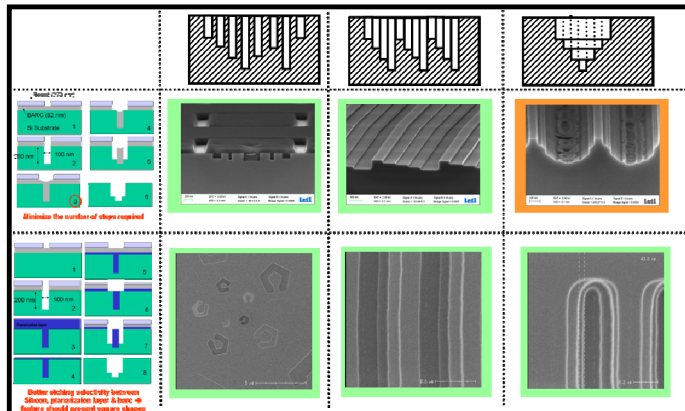
		cule (not grafted to the surface).	
5.6	Process control	optical and electron beam microscopy <i>non-destructively</i>	
	End of Process 5		
	End of Total Process		

General remarks:

To manufacture a multilevel stamp the processes from step 2 to 4 have to be repeated. Two processes flow may be used depending on the number of levels and control of the final exact shape. These two approaches are described below. In the second process flow, a planarization layer is used between each optical lithography exposure, in order to achieve better process window and protect already etched patterns from next steps.



Depending of the design of the 3D patterns, separated, close patterns or etching of patterns over already existing structures the two process flows described above will not give identical results for all structures. Process flow with planarization layer will give better result however this process is 26% more expensive.



2.7 Transparent auxiliary molds in OrmoStamp

Standard fabrication process for OrmoStamp working stamps

Process: UV-nanoimprint lithography

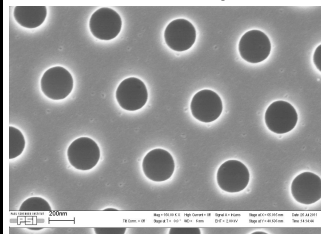


Figure:
SEM micrograph of a hexagonal hole pattern with a diameter of 200 nm replicated in OrmoStamp.

Transparent stamp copies and auxiliary stamps for bot, UV- and T-NIL

Application:
Transparent NIL stamps for UV-NIL

Keywords: UV-Nanoimprint, Auxiliary stamps, Transparent stamps

Project leader: Paul Scherrer Institut (PSI)

Address: 5232 Villigen PSI, Switzerland

Web-Address: <http://www.psi.ch>

Process: UV-Nanoimprint

Responsible: Helmut Schiff

E-mail: helmut.schiff@psi.ch

Partner: micro resist technology GmbH

Address: Koepenicker Str. 325, 12555 Berlin, Germany

Web-Address: <http://www.microresist.de>

Process: Polymer for nanofabrication

Responsible: Marko Vogler

E-mail: m.vogler@microresist.de

Process description: Fabrication of large area gratings based on UV nanoimprint lithography

Purpose: The aim of this process is to produce stamp copies and auxiliary stamps with an inorganic-organic hybrid polymer.

Major challenges: The defectless fabrication of auxiliary stamps with of OrmoStamp by avoiding air bubbles to be induced during dispensing or to be trapped in the stamp original due to unfavorable cavity geometry (e.g. closed ring patterns in Fresnel lenses).

Application and state-of-the-art: OrmoStamp seems only be limited by the stamp structure size. Copies with a structure size of down to 25 nm were successfully realized (see reference [2]).

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- [2] H. Schiff, C. Spreu, M. Saidani, M. Bednarzik, J. Gobrecht, A. Klukowska, F. Reuther, G. Gruetzner, H. H. Solak: *Transparent hybrid polymer stamp copies with sub-50-nm resolution for thermal and UV-nanoimprintlithography*, *J. Vac. Sci. Technol. B* **27** (2009) 2846
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- [4] D. Morihara, Y. Nagaoka, H. Hiroshima, Y. Hirai: *Numerical study on bubble trapping in UV-nanoimprint lithography*, *J. Vac. Sci. Technol. B* **27** (2009) 2866
- [5] A. Schleunitz, C. Spreu, T. Haatainen, A. Klukowska, and H. Schiff, *Fabrication of mesas with micro- and nanopatterned surface relief used as working stamps for step & stamp imprint lithography*, *J. Vac. Sci. Technol. B*, Vol. 28, No. 6, C6M37, 2010
- [6] A. Schleunitz, M. Vogler, I. Fernandez-Cuesta, H. Schiff and G. Gruetzner, *J. Photopolym. Sci. Technol.* **26** (2013), pp. 119-124.

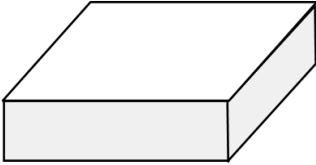
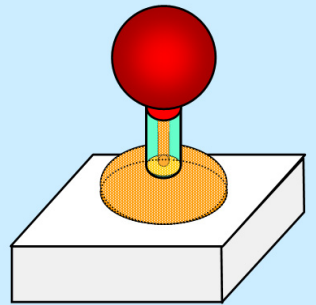
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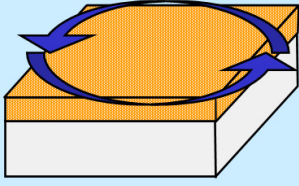
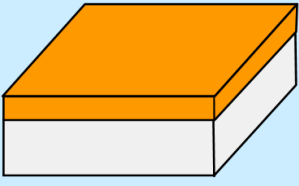
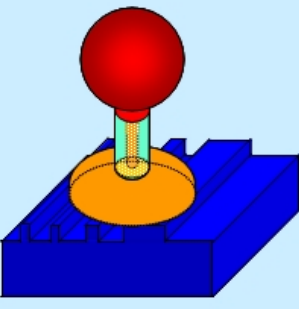
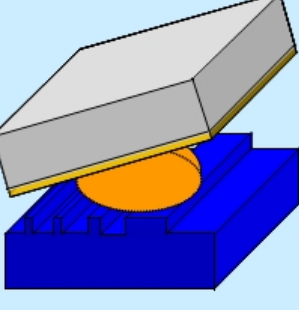
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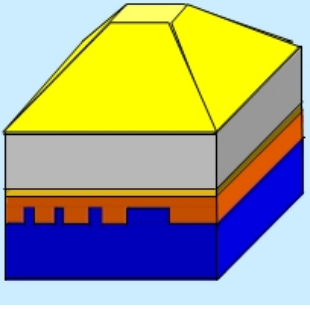
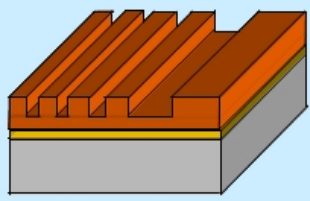
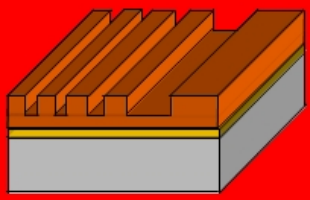
LoP2012_NIL010_OrmoStamp auxiliary stamps

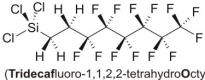
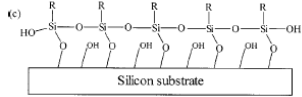
Standard fabrication process for OrmoStamp working stamps

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	Process 1: Wafer preparation	Borofloat® Wafer	
1.1	Wafer selection and preparation	Borofloat® substrate Glass substrate, 4", thickness d = 700 µm	
1.2	Substrate preparation 	Pretreatment <ul style="list-style-type: none"> • Acetone rinse to remove organic residues • Isopropanol to rinse away acetone • Nitrogen blow drying • DI-water rinse to remove solvent residues (this is very important for the following etch step) Piranha etch bath <ul style="list-style-type: none"> • H₂O₂:H₂SO₄ (1:2) at 90° C for 10 min. Attention: exothermal reaction bath heating up to 150° C. Danger of explosion, if stamp surface contain solvent residues! • DI-water rinse • Dehydration on a hot-plate 10 min. @ 200° C Surface activation <ul style="list-style-type: none"> • Oxygen plasma surface activation 	<i>Wear safety glasses, gloves and clothes!</i> <i>The etch bath will grow a thin SiO₂ layer on top of your substrate</i>
	End of Process 1		
2.0	Process 2: Primer coating	To improve the adhesion	
2.1	Dispensing of the primer 	Primer OrmoPrime08	<i>The hybrid polymers adhesion to substrates like glass, fused silica, or Si surface can be increased by substrate pre-treatment using OrmoPrime.</i>

2.2	Coating resist (homogeneous layer) 	Spincoating of OrmoPrime08 speed: 4000rpm, acceleration: 3000rpm/sec, time: 45 s	<i>Residue free removal of OrmoPrime08 films from a substrate is preferable achieved applying wet chemical etching using piranha solution or plasma etching with fluorine-coating plasma gases (e.g.: O₂/CHF₃). Residues would be left on the substrate after the treatment with pure oxygen plasma, since OrmoPrime08 contains silicon.</i>
2.3	Pre bake 	solvent evaporation bake 5 min @ 150°C (using hot plate)	<i>The prebake step removes possible air inclusions and improves the uniformity of the Ormocer layer after the coating process. The prebake is necessary when hybrid polymer diluted by a solvent is processed. Please note: Hybrid polymer does not harden during the prebake step and is still viscous thereafter! Alternative: convection oven at 180°C, for 30 min</i>
End of Process 2			
3.0 Process 3: Lithography			
3.1	Dispensing of OrmoStamp 	Dispense some droplets OrmoStamp with a pipette on the stamp surface, not on the BOROFLOAT! Try to continuously dispense the material to avoid air bubbles. The necessary amount to cover the whole surface will differ depending of the stamp size and cavity structures.	<i>Alternatively, it is also possible to spin-coat the OrmoStamp onto substrate or stamp. For details, we refer to the data sheet by micro resist technology GmbH.</i>
3.2	Stamp/Substrate alignment 	<ul style="list-style-type: none"> Carefully place the BOROFLOAT substrate with the primer upside down over the stamp origin with the OrmoStamp droplet on top. Bring the OrmoStamp droplet into contact with the glass substrate. Then, slowly lower the substrate. Slowly lower the substrate, while the OrmoStamp spreads in the closing gap. 	<i>If procedure properly followed, OrmoStamp will completely fill the gap between stamp and substrate due to capillary forces. OrmoStamp film thickness was observed to be in the range of 30 to 50 µm, when now additional pressure is applied during modling.</i>

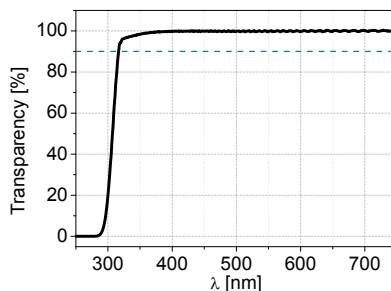
3.3	UV exposure 	Jenoptik HEX03 UV-Module Intensity: 2.8 mW/cm ² Wavelength: 365 nm Dose: 1000 mJ/cm ²	<i>Alternative any UV source with a wavelength of 356 nm can be used e.g. UV oven or maskaligner.</i>
3.4	Demolding 	Separation of the stamp from the substrate with a razorblade or scalpel.	<i>OrmoStamp provides inherent antiadhesive properties for improved demolding process without damage of pattern origination and replica.</i>
3.5	Hardbake 	Hotplate at 130° C for a minimum time of 10 minutes	<i>The sequence of steps 3.4 and 3.5 can also be switched: The stamp/ OrmoStamp/ substrate sandwich can also hardbaked before the separation of the stamp from the substrate. This might be necessary, when partial exposure of OrmoStamp is performed (as in reference [5])</i>
End of Process 3			
4.0	Process 4: Anti-adhesive coating	surface treatment by chemical vapor deposition	
4.1	Preparation of stamp surface	cleaning and activation Typically, RIE treatment with O ₂ plasma removes organic contaminants and activates the surface (generation of free reactive silanol bonds for silane binding) Oxford Plasmalab RIE80+ Power: 20 W Time: 20 sec. Oxygen: 20 sccm	Attention!!! <i>Use a very short and gentle oxygen process otherwise porous silicondioxid will be formed.</i>

<p>4.2</p>	<p>Solution preparation</p>  <p style="text-align: right;">F₁₃-OTCS</p> <p style="text-align: center;">(Tridecafluoro-1,1,2,2-tetrahydroOctyl)TriChloroSilane</p>	<p>Prepare a solution 1-10 mM of perfluorotrichlorosilane molecules in toluene. The preparation of the solution and the surface treatment is to be performed in an atmosphere with low content of humidity. A convenient solution is to operate in glovebox.</p>	<p><i>Alternatively, chemical vapor deposition methods have been developed which allow to generate the silane monolayer from the gas phase. The coating should be done within about 1 hour after surface activation</i></p>
<p>4.3</p>	<p>Dip of the stamp</p> 	<p>The stamp is inserted in the silane solution for 1-2 hours, where the silane reacts with the silanol groups of the surface, but also with neighboring molecules (crosslinking).</p>	<p><i>In order to avoid the formation of a bulky deposit of molecules instead of a monolayer, washing of the stamp in acetone has to be performed in dry atmosphere.</i></p>
<p>4.4</p>	<p>Process control:</p>	<p>Optical microscope, AFM The quality of the antisticking layer can be done by contact angle (CA) measurement, for perfluorotrichlorosilane a CA 115° can be reached</p>	<p><i>Profile control not any more with SEM (exposure and damage of anti-adhesive layer); a high CA can also be a result of roughness due to deposits; these deposits are removed after a few imprints</i></p>
<p>End of Process 4</p>			
<p>End of Total Process</p>			

General remarks:

The unique features of OrmoStamp are its high transparency for UV and visible light (see illustration), the mechanical and thermal stability, the excellent pattern transfer capabilities down to sub-50 nm features and the possibility to use standard lithography processing equipment.

OrmoStamp copies can be used for thermal and/or UV-NIL processes up to a temperature of 160° C for long time imprints or 300° C for a short time period, since the fully UV-cured hybrid polymer is three-dimensionally cross-linked, so that no glass transition occurs. Hybrid polymers are duromeric.



Technical remarks:

Avoid excess of OrmoStamp to the edges by dispensing only the necessary amount to cover the substrate surface with a thin film. Fixing the stack in step 3.3 (e.g. by small PDMS pieces placed at the sides) avoids drift movement of the substrate with respect to the mold during the phase of material spreading.

OrmoStamp is a material for permanent applications; hence for removal of the material from the substrate extreme conditions are necessary. A PGMEA solution at increased temperature ($\approx 60^\circ \text{C}$) assisted by ultrasonication for several hours or hot piranha etch will usually (especially on glass) result in peeling off of OrmoStamp. Alternatively $\text{O}_2 / \text{CHF}_3$ plasma can be used. Do NOT use pure oxygen plasma! Porous SiO_2 will be formed.

Further information can be found in the LoP: 5.3.2 Soft and hybrid layered stamps (Page 25) and 5.6.5 Sol-gel materials and hybrid polymers (Page 37), or at the webpage: <http://www.microresist.com>.

2.8 Two-level stamps for Nanoimprint Lithography

Iterative fabrication process for self-aligned nanopillars on silicon mesh for NIL applications

Structure description: Nanopillars fabricated on a silicon mesh

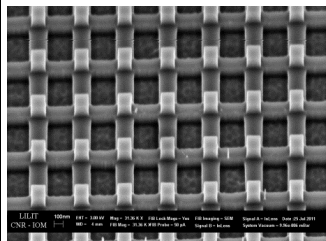


Figure:
SEM image of a nanopillars array self-aligned on a silicon mesh with a period of 500 nm.

Process:
Double NIL and plasma etching processes on silicon substrate.

Application:
NIL stamps for biological studies, optical, photonic, electronic or micro/nano-fluidics.

Keywords: thermal nanoimprint, nanopillars array, RIE plasma etching.

Project leader: TASC Laboratory
Address: 34149 Basovizza-Trieste, Italy
Web-Address: <http://www.tasc-infm.it>

Process: Thermal NIL
Responsible: Massimo Tormen
E-mail: tormen@tasc.infm.it

Process description: Nanopillars array on a silicon mesh is obtained with double NIL and pattern transfer by plasma etching. A grating of lines (AMO GmbH) is used as stamp for a first thermal imprinting on a mr-I 7000E resist layer (*micro resist technology* GmbH); pattern transfer into silicon substrate is then obtained by plasma etching in an ICP reactor. After resist mask stripping in oxygen plasma the silicon lines structures are spin-coated with the same resist. A second thermal NIL process is performed orientating the lines structures orthogonally with respect to the stamp's lines.

Finally, the second pattern transfer by dry etching produces a nanopillars array self-aligned on a silicon mesh.

Purpose: The aim of this process is to produce 3D self-aligned structures by superimposing of nanopillars arrays to mesh-like structures. The shape of nanopillars can be tailored ranging from rectangular to squared base. The multilevel process can be tailored to produce other multilevel structures.

Major challenges: The steps of plasma etching have to be finely calibrated in order to obtain a mesh with lines of well controlled lateral dimension in both directions. The coverage of the first transferred structures during the second resist spin coating must be sufficient to allow the second imprinting process.

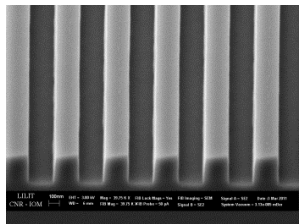
Application and state-of-the-art: Partially standard processes; however the intersection of NIL is not represented in literature yet.

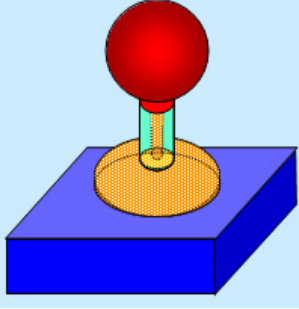
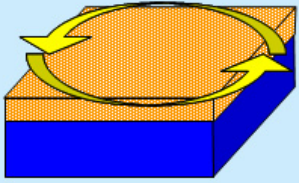
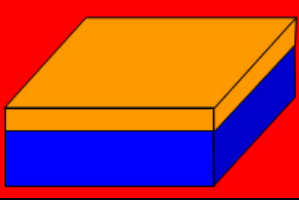
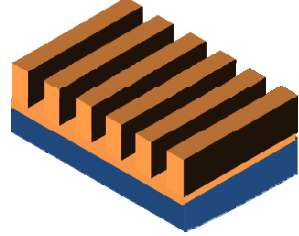
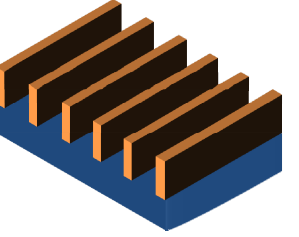
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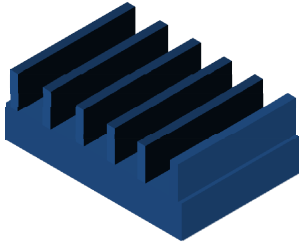
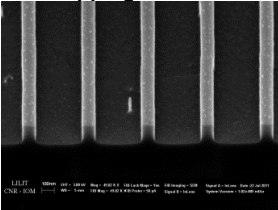
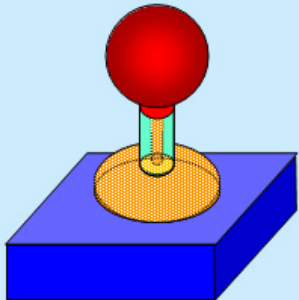
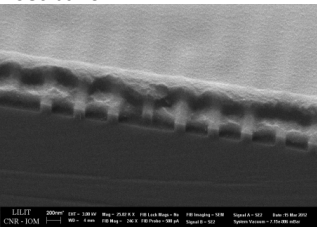
LoP2012_NIL011_Two-level Stamps

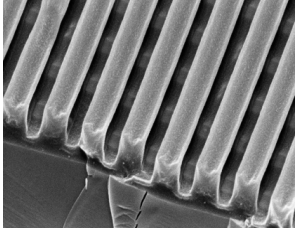
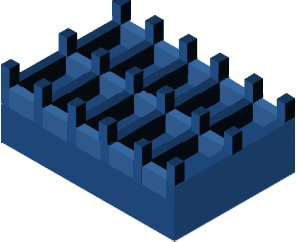
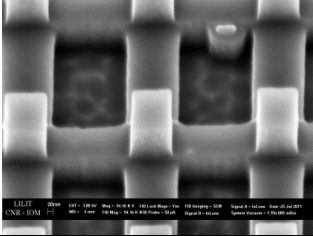
Iterative fabrication process for self-aligned nanopillars on silicon mesh for NIL applications

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Preparation of stamp	for nanoimprint lithography	
1.1	Stamp 	characteristics silicon substrate, 2x2cm ² , <100>, thickness d=400-600 μm, one side polished. The front side is patterned by interference lithography and plasma etching (AMO GmbH). Pattern: array of lines with period 500 nm, duty cycle 50% and height 260 nm.	
1.2	Preparation of stamp surface	activation and ASL deposition Typical cleaning and surface activation by oxygen plasma in RIE and deposition of an antisticking monolayer of octadecyltrichlorosilane by chemical vapor deposition from the gas phase.	
	End of Process 1		
2.0	Process 2: Wafer preparation	Silicon wafer format	
2.1	wafer selection and preparation	standard Si substrate Si substrate, 4", <100>, thickness d=400-600 μm, one side polished	
2.2	substrate preparation	pretreatment no pretreatment needed (if wafer is clean and hydrophilic)	
	End of Process 2		
3.0	Process 3: Resist coating	for nanoimprint lithography	
3.1	dispensing of resist	resist no priming resist mr-I 7010E process lab (clean room)	<i>mr-I 7000E is a high resolution thermoplastic polymer resist ("E" series was replied by "R", i.e. mr-I 7000R, see Page 34/35)</i>

			
<p>3.2</p>	<p>first coating resist (homogeneous layer)</p> 	<p>spincoating of mr-I 7010E speed: 1000rpm, acceleration: 1000rpm/sec, time: 30 s -> ~140 nm thickness</p>	
<p>3.3</p>	<p>post bake</p> 	<p>solvent evaporation bake 2 min @ 140°C (hot plate)</p>	
<p>End of Process 3</p>			
<p>4.0 Process 4: Lithography</p>			
<p>4.1</p>	<p>pattern definition</p> 	<p>Nanoimprint lithography imprinting of resist The resist is imprinted by a hot press applying to the assembly stamp-sample a pressure of 5 MPa, at a temperature of 140°C for 6 minutes. The stamp is released at 50°C.</p>	
<p>4.2</p>	<p>structures definition</p> 	<p>shrinking of resist structures The residual layer after NIL is removed in an ICP reactor by oxygen plasma; this step is also used to obtain a controlled lateral shrinking of the lines.</p>	<p><i>The etching parameters are usually strongly dependent on the equipment, thus <u>dimensional shrinkage</u> can be minimized under optimal etching conditions.</i></p>

4.3	<p>pattern transfer</p> 	<p>silicon etching The pattern is transferred into the silicon substrate by plasma etching in a ICP reactor. A fluorine based plasma allows the anisotropic silicon etching. A typical recipe is composed by SF₆ 30 sccm/ C₄F₈ 60 sccm/ Ar 10 sccm, pressure of 8 mTorr, RF power 400 W (ICP RF source), 20 W (Platen RF source).</p>	<p><i>The etching parameters are usually strong dependent on the tool.</i></p>
4.4	<p>resist stripping</p>  <p>End of Process 4</p>	<p>ICP resist ashing Resist is removed by a isotropic oxygen plasma with low bias in the ICP tool.</p>	
5.0	<p>Process 5: Resist coating</p>	<p>for nanoimprint lithography</p>	
5.1	<p>Dispensing of resist</p> 	<p>resist no priming resist mr-I 7020E process lab (clean room)</p>	<p><i>see step 3.1</i></p>
5.2	<p>Second coating resist</p>	<p>spincoating of mr-I 7020E speed: 2000rpm, acceleration: 1000rpm/sec, time: 30 s -> ~210 nm thickness on flat substrates</p>	
5.3	<p>Post bake</p>  <p>End of Process 5</p>	<p>solvent evaporation and partial planarization of resist layer bake 5 min @ 140°C (hot plate)</p>	<p><i>The actual thickness of the resist depends on the dimensions of underneath structures.</i></p>
6.0	<p>Process 6: Lithography</p>	<p>Nanoimprint lithography</p>	

<p>6.1</p>		<p>imprinting of resist The resist is imprinted by a thermal NIL, applying a pressure of 10 MPa to the assembly stamp-sample at a temperature of 90°C for 6 minutes. The stamp is released at 50°C.</p>	<p><i>In the space between the first series of lines etched in the substrate, the residual resist layer is less thick than the height of the lines themselves.</i></p>
<p>6.2</p>		<p>shrinking of resist structures The resist lines are shrunk in the oxygen plasma process, which also removed completely the residual layers.</p>	<p><i>After the oxygen plasma, silicon is exposed both on top of the first silicon lines and in the space between them.</i></p>
<p>6.3</p>		<p>silicon etching The pattern is transferred into the silicon substrate by the fluorine based plasma etching. This process is performed using the same recipe and time of the first pattern transfer.</p>	
<p>6.4</p>	<p>Resist stripping</p> 	<p>ICP resist ashing Resist is removed by an isotropic oxygen plasma with low bias in the ICP tool.</p>	
<p>End of Process 6</p>			
<p>End of Total Process</p>			

2.9 Microhollows for optical applications

Half hemi-cylindrical lenses for day lighting applications

Process: Wet etching

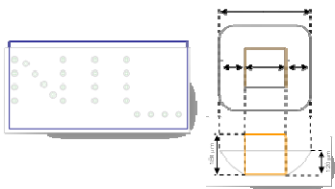


Figure:
CAD layout of the hollow lenses reproducing the "NIL" acronym, used as demonstrator for the process.

Process:
Isotropic wet etching of glass with patterned chromium mask.

Application:
Spherical or cylindrical microlens arrays with full control on radii of curvature and diameter, used as pseudo-parabolic mirrors for LEDs in eHUD displays.

Keywords: Electron beam lithography, wet isotropic etching

Project leader: TASC Laboratory
Address: 34012 Basovizza-Trieste, Italy
Web-Address: [http:// www.tasc-infm.it](http://www.tasc-infm.it)

Process: NIL, evaporation, dry etching
Responsible: Massimo Tormen
E-mail: tormen@tasc.infm.it

Partner: C.R.F. Societa' Consortile per Azioni, CRF
Address: Torino, Italy
Web-Address: <http://www.crf.it>

Process: EBL
Responsible: Vito Lambertini
E-mail: vitoguido.lambertini@crf.it

Process description: Fabrication of a quartz template with micro-lenses with a planar circular base.

Purpose: The aim of this process is to produce a patterned array of hollows with planar base in order to accommodate a LED; the spherical surface of the lens acts as a mirror to direct the light emitted by the LED.

Major challenges: Accurate pattern definition in a chromium layer on glass with high etching resistance to concentrated hydrofluoric acid; fabrication large area lenses.

Application and state-of-the-art: Research process, light concentrators for CCD's elements or photovoltaic cells

References:


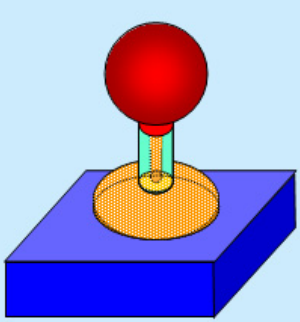
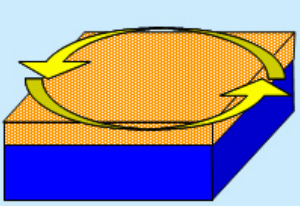
- [1] Massimo Tormen, Alessandro Carpentiero, Enrico Ferrari, Dan Cojoc and Enzo Di Fabrizio, *Novel fabrication method for three-dimensional nanostructuring: an application to micro-optics*, Nanotechnology 18, 385301 (2007).
- [2] Massimo Tormen, Alessandro Carpentiero, Lisa Vaccari, Matteo Altissimo, Enrico Ferrari, Dan Cojoc, Enzo Di Fabrizio, *Fabrication of three-dimensional stamps for embossing techniques by lithographically controlled isotropic wet etching*, Journal of Vacuum Science and Technology B 23, 2920 (2005).



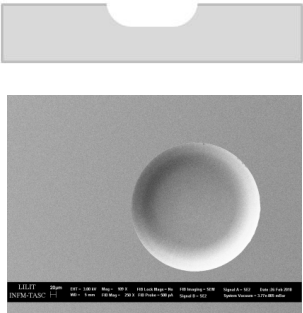
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LoP2012_NIL012_Microhollow-Stamps

Half hemi-cylindrical lenses for day lighting applications

Process: Isotropically wet etched micro-hollows in quartz plate			
	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Preparation of Substrate	10x10 cm wide quartz plate	
1.1	Substrate preparation	Sputter coating quartz glass with 100 nm chromium film.	<i>Quality of the deposited chromium film, that should be exempt from pin-holes</i>
	End of Process 1		
2.0	Process 2: Layout preparation		
2.1	Layout	Functional structures CAD design of the pattern, consisting of pixels of 280 µm, representing the informations for the head-up display on a plate 10x10 cm wide	
2.2	substrate preparation 	pretreatment no pretreatment of the surface is needed (if the substrate is clean)	
	End of Process 2		
3.0	Process 3: Resist coating	for nanoimprint lithography	
3.1	dispensing of resist 	resist no priming Allresist PMMA 671.05 process lab (clean room)	
3.2	First coating resist 	spincoating of PMMA (homogeneous layer) speed: 3000 rpm, acceleration: 1000rpm/sec, time: 30 s pre bake 10 min at 180° C -> ~500 nm thickness	
	End of Process 3		
4.0	Process 4: Mask preparation	EBL lithography	
4.1	Pattern definition	Lithography Standard EBL at 30 kV electron beam 200 µC/cm ² dose and developing in MIBK:IPA 1:1	

4.2	Chromium etching 	Open holes or trenches in the chromium layer by etching in aqueous solution of ammonium cerium (IV) nitrate (0.6 M) and acetic acid (1 M) for 1 min. The resist is stripped in solvents (e.g. acetone)	<i>Loss of resolution due to wet etching of Chromium. The alternative is to use dry etching techniques</i>
	End of Process 4		
5.0	Process 5: Metal mask annealing	Thermal treatment in oven	
5.1	Thermal annealing	The plate with patterned Cr layer is placed in an oven and maintained at 500° C for 3-6 h. Ramps are applied both in heating and cooling steps.	<i>The thermal annealing increases the resistance of the Cr layer to the prolonged (>1h) dipping in concentrated HF solutions. Without annealing step the maximum etching time is ~10 min.</i>
	End of Process 5		
6.0	Process 6: Isotropic wet etching	Wet chemical etching in HF solution	
6.1	Wet etching of quartz/fused silica 	Isotropic etching of quartz is performed in aqueous HF (48 wt.%) at room temperature, with an etching rate of ~1µm/min. The etching time is adjusted to the required etching depth (=radius of curvature), 80 µm.	<i>Etching of holes through pin-holes in chromium leads to the formation of spherical cavities in undesired locations of the substrate.</i>
	End of process 6		
7.0	Process 7: Mask stripping	Cr wet etching	
7.1	Thermal evaporation 	Stripping the chromium film by etching in aqueous solution of ammonium cerium (IV) nitrate (0.6 M) and acetic acid (1 M) for 1 min.	
	End of Process 7		
	End of Total Process		

3. Processes

Contributions to this section of the library are from

VTT Information - Technology/Finland

Dr. Tapio Mäkelä / Tomi Haatainen /
Päivi Majander / Prof. Dr. Jouni Ahopelto

ICN - Barcelona/Spain

Dr. Vincent Reboud / Dr. Nikolaos Kehagias /
Prof. Dr. Clivia Sotomayor-Torres

AMO GmbH - Aachen/Germany

Dr. Ulrich Plachetka

CRF Fiat - Orbassano/Italy

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Konrad Vogelsang

INFM TASC - Trieste/Italy

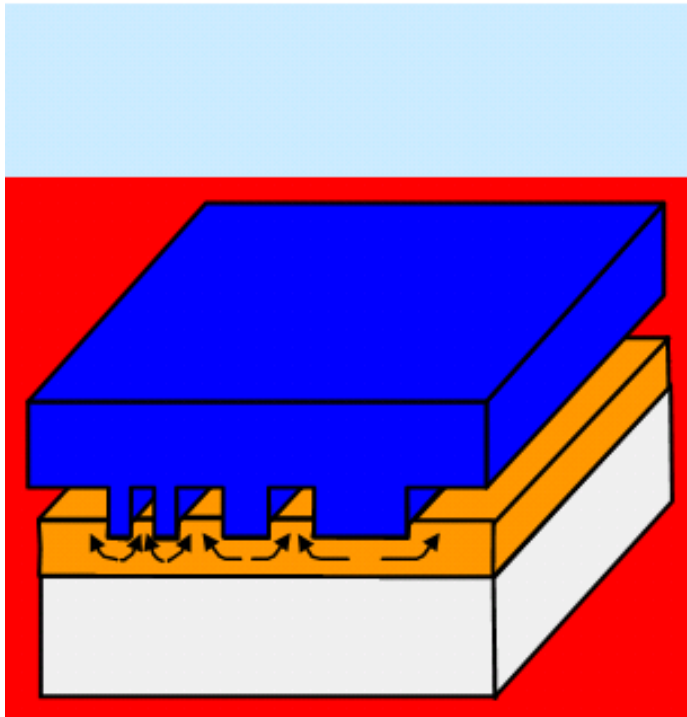
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Dr. Kris Seunarine / Johnny Stormonth-Darling /
Prof. Dr. Christopher Wilkinson /

micro resist technology – Berlin/Germany

Dr. Arne Schleunitz / Dr. Manuel Thesen /
Dr. Marko Vogler



3.1 Thermal NIL Process (thermoplastic resist)

Thermal NIL using thermoplastic polymers

Process: Standard mr-I 8000R (mr-I 7000R)

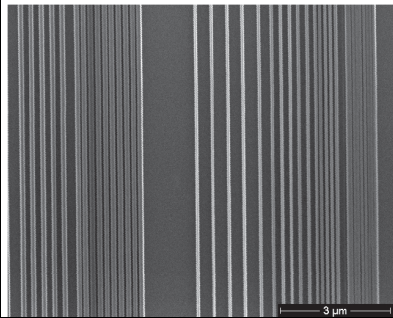


Figure:
Replicated line pattern, i.e. 75 nm and 100 nm lines imprinted in mr-I 8030R, varying pitch.

Application:
Etch mask for pattern transfer processes via RIE or ICP, wet etching, single and multilayer systems, high resolution (sub-20 nm).

Keywords: thermal nanoimprint, thermoplastic resist, release properties

Partner: *micro resist technology* GmbH

Address: Koepenicker Str. 325, 12555 Berlin, Germany

Web-Address: <http://www.microresist.com>

Process: polymer materials

Responsible: Marko Vogler

E-mail: m.vogler@microresist.de

Process description: Thermoplastic polymers with strongly improved release properties.

Purpose: The mr-I 8000R is a thermoplastic polymer system designed for nanoimprint lithography. Upon heating above the glass transition temperature (T_g), the viscosity of the resist is sufficiently reduced enabling the filling of the stamp cavities when pressure is applied during imprint step (the resist's T_g is 105 °C). The resist has excellent release properties and exhibits high plasma etch resistance. mr-I 8000R polymers are provided as ready-to-use solutions for various film thicknesses.

Major challenges: Minimized cycle times during imprint require comparatively low T_g of the resist. However, reduced T_g might be insufficient for plasma etching at elevated process temperatures to to pattern collapse and reflow behavior.

Application and state-of-the-art: Fabrication of nanopatterns for high brightness LEDs, photonic crystals, patterned media, nano-optical devices, subwavelength optical elements, microfluidics, and bio applications.

References:

- [1] H Atasoy, M Vogler, T Haatainen, A Schleunitz, D Jarzabek, H Schiff, F Reuther, G Gruetzner, Z Rymuza
Microel Eng 88 2011 1902.

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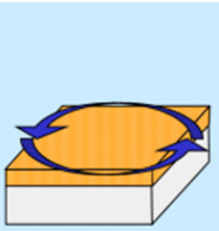
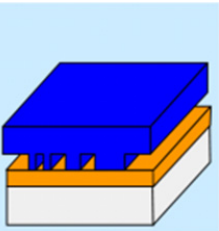
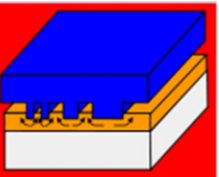
e-mail: m.vogler@microresist.de

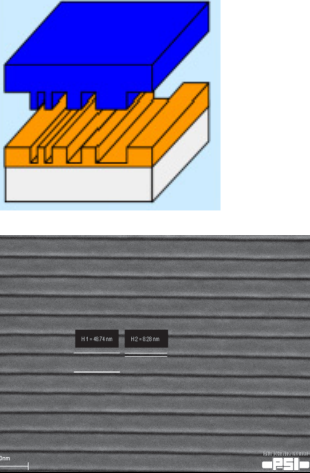
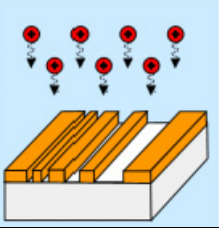
URL: <http://www.microresist.com>

LoP2014_SP01_Thermal-NIL_Thermoplastic

Thermal NIL using thermoplastic polymers

Process: Standard mr-I 8000R (mr-I 7000R)

	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	Process 1: substrate preparation		Best patterning results are obtained at 20 – 25 °C and a rel. humidity of 40 – 46 %.
1.1	Substrate preparation	Dehydration: baked at 200 °C for 30 min and cooled to room temperature immediately before coating). Surface activation (if needed): oxygen plasma surface activation	Substrates have to be free of impurities and moisture (dewetting of the polymer layer may be induced by surface impurities).
1.2	Dispensing, spin-coating and pre-baking of mr-I 8000R 	Standard spin-coating should be performed with 3000 rpm for 30 sec (acceleration 1000 rpm/s). Pre-bake at 100 °C on hot plate (or oven) for one minute.	Film thickness can be varied by using different standard resist formulation, i.e. mr-I 8010R (100 nm), mr-I 8020R (200 nm) and mr-I 8030R (300 nm) Further adaptations are accomplished by using appropriate resist spin-curves. The pre-bake step is necessary to evaporate residual solvent.
End of Process 1			
2.0	Process 2: Thermal Imprint	Pattern replication	
2.1a	Alignment of Stamp 	Stamp (e.g. made of Silicon, quartz, Nickel or OrmoStamp®) is positioned on and aligned to the coated substrate. Stack is heated to 150 – 180 °C to lower resist's viscosity (see Part 1 – 5.6).	mr-I 8000R can be imprinted in any tool suitable for doing thermal NIL, in tools combining thermal imprinting and UV exposure. Commercial nano-imprinters as provided e.g. by EV Group (Austria), Obducat (Sweden), and Suss MicroTec (Germany) may be used.
2.2a	Pattern replication 	Typically the polymers are heated to 150 – 180 °C (i.e. 50 – 80 K above $T_g \sim 105$ °C) and the stamp with nanometer-scale patterns is pressed into the films with a pressure of e.g. 2 – 4 MPa to transfer the pattern. Time at maximum temperature 60 – 240 sec (pattern dependent).	Main factors determining the imprint conditions are the rheological behaviour of the resist, the mould layout (feature size, density of the patterns etc.), the degree of cavity filling, the residual layer thickness to be attained and the imprinting tool. In case mr-I 8000R is used (elevated $T_g \sim 105$ °C), the imprint temperature is 150 – 180 °C.
End of Process 2			

3.0	Process 3: Demolding	Stamp release	
3.1	Separation of stamp and resist 	After having cooled to a temperature not higher than the T_g of the polymer, the stamp is released. Release temperature 85 – 105 °C. Examples shows replication of 12 nm wide lines pattern.	<i>For optimized demolding step, please see comments below.</i> <i>In case mr-I 7000R is used (lower $T_g \sim 50$ °C), the release temperature is 35 - 50 °C.</i>
End of Process 3			
4.0	Process 4: Residual Layer Removal	Opening Resist Windows	
4.1	Remove of Residual Layer 	Residual layer remaining in the recessed areas of the polymer film after the imprint is removed by oxygen reactive ion etching (RIE) in order to open the window to the substrate.	<i>After the whole process residue-free removal of mr-I 7000R is preferably achieved using common organic solvents such as acetone or 1-methoxy-2-propyl acetate (PGMEA). The polymer may also be removed by applying oxygen plasma.</i>
End of Process 4			
End of Total Process			

General remarks:

mr-I 8000R is a thermoplastic polymer system designed for nanoimprint lithography, which has excellent release properties and exhibits high plasma etch resistance. It has a glass transition temperature (T_g) of 105 °C. mr-I 8000R characteristics can be summarized as follows:

- Tailor-made for thermal nanoimprint lithography due to excellent properties
 - Short cycle times due to fast polymer flow
 - Low imprint pressure
 - Sub-20 nm resolution
 - Low residual layer thickness
 - Low release forces (easy demoulding, efficient release force reduction)
- Longer life-time of anti-sticking layers on the mould
- High uniformity of the residual layer thickness
- High plasma etch resistance comparable to novolak-based photoresists

For industrial use and fast processes it is recommended to treat the mould with a release agent like F13-OTCS or other fluorinated silanes before use. F13-OTCS (trichloro-(1H,1H,2H,2H-perfluorooctyl)-silane, CAS number [78560-45-9]) is commercially available from many suppliers of laboratory chemicals. The anti-sticking character of the mr-I 8000R polymer system prolongs the lifetime of the release coating on the mould. Using moulds without any anti-sticking layer may work in certain cases, but this has not been fully investigated so far. A process with such a mould would require very diligent substrate pretreatment.

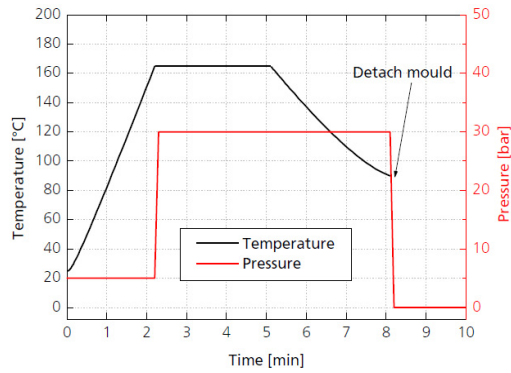


Figure 1: Example of a process cycle with mr-I 8030R. Imprint temperature 165°C, time at max. temperature 3 min and demoulding at 90 °C (air cooling).

3.2 Thermal NIL Process (thermoset resist)

Thermal NIL using thermosetting polymers

Process: Standard mr-I 9000M

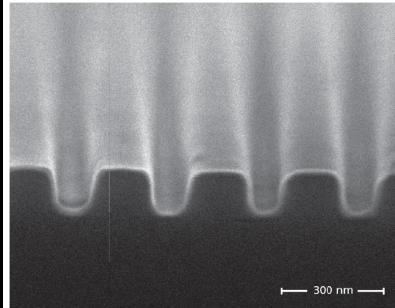


Figure:
Replicated line pattern, i.e. 100 nm trenches, 300 nm pitch, on silicon substrate.

Application:
Etch mask for pattern transfer processes, dry and wet etching, single and multi-layer systems.

Keywords: thermal nanoimprint, thermoset resist, isothermal processing

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Process: polymer materials

Responsible: Marko Vogler

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Process description: Advanced thermoset for pattern transfer

Purpose: The mr-I 9000M is a thermosetting polymer system (thermally curing) designed for thermal nanoimprint lithography. Upon heating, the viscosity of the resist is reduced which enables the filling of the stamp cavities when pressure is applied during imprint step. The initial glass transition temperature (T_g) is around 35 °C. Due to the thermosetting behavior, a thermally induced curing sets in while the resist is heated. Thus, processed mr-I9000M polymer exhibits a drastically increased T_g (depending on the imprint conditions) allowing the demolding even at elevated temperature (i.e. reduced thermal cycling). Furthermore, the cured polymer has high thermal and mechanical stability after the imprint process. This particularly enables imprinting and etching of dense nanostructure designs in the sub-100 nm range. Besides being applied as etch mask for pattern transfer mr-I 9000M can also be used for permanent applications.

Major challenges: As the mr-I 9000M polymer forms three-dimensional polymer networks during thermal curing, drastic conditions for wet-chemical removal are necessary. However, a residue-free removal of processed mr-I 9000M is achievable by applying oxygen plasma. Since mr-I 9000M does not contain any inorganic components like silicon, there are no residuals left on the substrate after plasma treatment with pure oxygen.

Application and state-of-the-art: Fabrication of nanopatterns e.g. for nanooptical devices, photonic crystals, high-brightness LEDs (by means of dry or wet etching of substrates).

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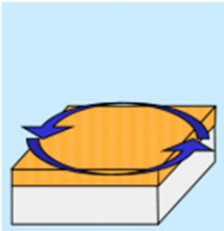
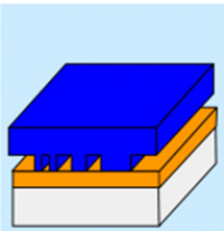
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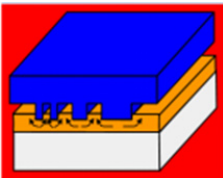
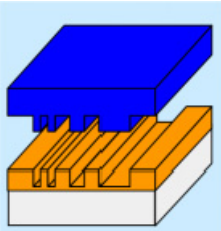
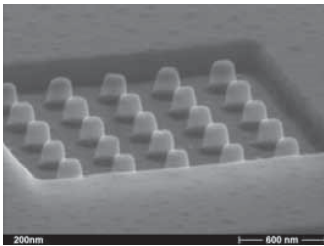
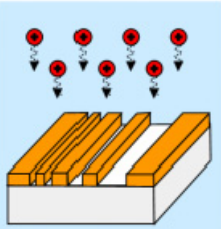
URL: <http://www.microresist.com>

LoP2014_SP02_Thermal-NIL-Thermoset

Thermal NIL Process using Thermosetting Polymers

Process: Standard mr-I 9000M

	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	Process 1: substrate preparation		<i>Best patterning results are obtained at 20 – 25 °C and a rel. humidity of 40 – 46 %.</i>
1.1	Substrate preparation	Dehydration: baked at 200 °C for 30 min and cooled to room temperature immediately before coating. Surface activation (if needed): oxygen plasma surface activation	<i>Substrates have to be free of impurities and moisture</i>
1.2	Dispensing, spin-coating and pre-baking of mr-I 9000M 	Standard spin-coating should be performed with 3000 rpm for 30 sec Pre-bake at 100 °C on hot plate (or oven) for 2 min.	<i>Film thickness can be varied by using different standard resist formulation, i.e. mr-I 9010M (100 nm), mr-I 9020M (200 nm), mr-I 9030M (300 nm), mr-I 9050M (500 nm) and mr-I 9100M (1 µm). Further adaptations are accomplished by using appropriate resist spin curves. The pre-bake step is necessary to evaporate residual solvent.</i>
	End of Process 1		
2.0	Process 2: Thermal Imprint	Pattern replication	
2.1a	Alignment of stamp 	Stamp (e.g. made of Silicon, quartz, Nickel, polymer mold or OrmoStamp®) is positioned on and aligned to the coated substrate. Stack is heated to 90–120 °C to lower resist's viscosity.	<i>The mr-I 9000M series can be imprinted in any tool suitable for doing thermal nanoimprint lithography. Commercial nanoimprinters as provided e.g. by EV Group (Austria) or Obducat (Sweden) may be used.</i>

<p>2.2a</p>	<p>Pattern replication</p> 	<p>Substrate coated with mr-I 9000M ($T_g = 35\text{ }^\circ\text{C}$; before curing) is heated to $120\text{ }^\circ\text{C}$ in the imprint machine and the stamp is pressed into the resist film with a pressure of $\sim 10 - 40\text{ bar}$ to transfer the pattern, flow time is $1 - 5\text{ min}$ (pattern depended).</p> <p>Optional: two-step imprint process for improved pattern stability (see descriptions below).</p>	<p><i>Main factors determining the imprint conditions are the rheological behaviour of the polymer, the mould layout (feature size, density of the patterns etc.), the residual layer thickness to be attained and the imprinting tool. Typically nanoimprint polymers are heated to $50 - 80\text{ K}$ above T_g.</i></p>
<p>End of Process 2</p>			
<p>3.0</p>	<p>Process 3: Demolding</p>	<p>Stamp release</p>	
<p>3.1</p>	<p>Separation of stamp and resist</p>  	<p>Isothermal imprint processes are possible, since the T_g of the thermosetting mr-I 9000M polymer is increased during the imprint and can reach values higher than the imprint temperature itself.</p> <p>Recommendations for suitable imprint conditions:</p> <ul style="list-style-type: none"> - For micron size patterns an imprint temperature of $90\text{ }^\circ\text{C}$ may be sufficient. - Nanometre size patterns require at least $100\text{ }^\circ\text{C}$ imprint temperature. ($T_{im} = T_r = 90 - 140\text{ }^\circ\text{C}$). <p>Examples shows replication of 200 nm pillars.</p>	<p><i>Alternatively, to isothermal process, the stack can also be cooled down prior to demolding, e.g. $60\text{ }^\circ\text{C}$. (less risk of re-flow, but increased processing time).</i></p>
<p>End of Process 3</p>			
<p>4.0</p>	<p>Process 4: Residual Layer Removal</p>	<p>Opening Resist Windows</p>	
<p>4.1</p>	<p>Remove of Residual Layer</p> 	<p>The residual layer remaining in the recessed areas of the polymer film after the imprint is removed by oxygen reactive ion etching (RIE) in order to open the window to the substrate</p>	<p><i>Since mr-I 9000M does not contain any inorganic components like silicon, there are no residuals left on the substrate after plasma treatment with pure oxygen. As the mr-I 9000M polymer forms three-dimensional polymer networks during thermal curing, drastic conditions for wet-chemical removal are necessary. The solvent PGMEA or NMP-based solvents in an ultrasonic bath at higher temperature ($40 - 60\text{ }^\circ\text{C}$) for several hours will</i></p>

			<i>usually result in a peel off. Hot piranha etch is also suitable.</i>
	End of Process 4		
	End of Total Process		

General remarks:

mr-I 9000M is a thermosetting polymer system (thermally curing) designed for thermal nanoimprint lithography. The mr-I 9000M series is provided as ready-to-use solutions for various film thickness ranges. The cured polymer has high thermal and mechanical stability after the imprint process. This particularly enables imprinting and etching of dense nanostructure designs in the sub 100 nm range. Besides being applied as etch mask for pattern transfer mr-I 9000M can also be used for permanent applications. The unique features can be summarized as follows:

- Thermosetting polymer for outstanding pattern stability and for demanding imprint designs
- No reflow in subsequent process steps with thermal load
- Mold release at imprint temperature possible (no cooling step), i.e. nearly isothermal imprint process:
 - Imprint temperature 120 °C
 - Mould release at 100 °C
- Very low residual layer thickness down to 5 nm
- Excellent pattern transfer fidelity
- High plasma etch resistance comparable to Novolak-based resists
- Attainable smallest feature size at least 50 nm (depending on mould resolution)
- Ready-to-use solutions
- Safe solvents

Hard stamps: For defect-free imprints and low release forces with hard moulds it is highly recommended to treat the stamp before use with a release agent. The most common release agent for silicon or silicon dioxide is F13-TCS (trichloro-(1H,1H,2H,2H-perfluorooctyl)-silane, CAS number [78560-45-9]), commercially available from many suppliers of specialty chemicals.

Polymer stamps: As polymeric working stamps various materials can be applied. One common commercially available product is OrmoStamp® which is fully compatible with the mr-I 9000M series. Other options are PFPE-based polymer systems.

Alternative two-step process: With the two-step process one can achieve higher thermal stability of the imprinted patterns (up to 260 °C), e.g. important in permanent applications. In case of demanding pattern designs, e.g. very dense nanometre-scale structures like voids with hole diameters < 100 nm, a two-step imprint increases pattern stability and avoids the risk of pattern reflow upon minor thermal load. In the optional second nanoimprint step the imprint temperature is raised to 140 °C. The pressure can be lowered e.g. to 10–15 bar. Increasing imprint times at 140 °C lead to increasing thermal stability of the patterns imprinted in the mr-I 9000M polymer (up to 260 °C). The stamp can be released at 140 °C (no need for a cooling phase). In this process option the duration of the first imprint step should not exceed 10 min. Otherwise the typically attainable thermal stability of the nanostructures after imprinting cannot be guaranteed.

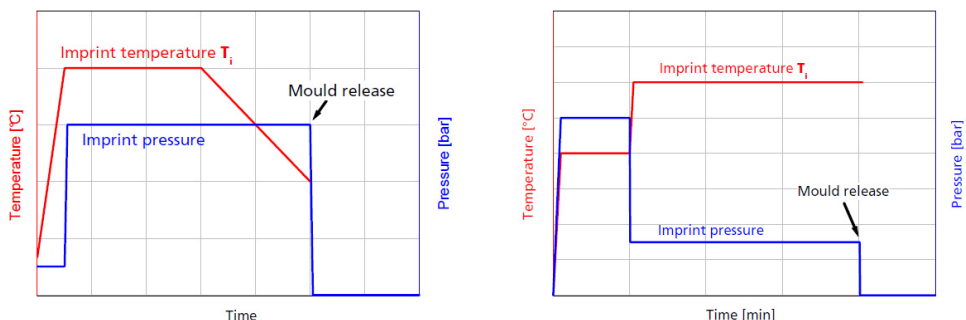


Figure 1: Principle schemes of the imprint process for mr-I 9000M: one-step (left) and two-step (right).

3.3 UV-NIL Process

UV-NIL using UV-curable polymers

Process: Standard mr-UVCur21

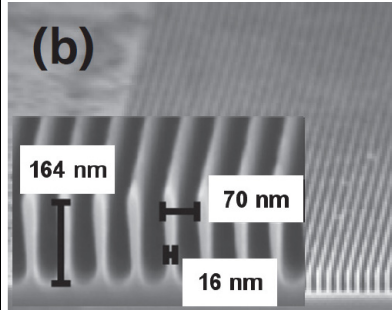


Figure:
Dry etched Si grating after line pattern replication and pattern transfer using mr-UVCur21 resist: 16 nm linewidth, 164 nm height, AR > 5.

Application:
Etch mask for pattern transfer processes, dry and wet etching.

Keywords: UV NIL, UV-curable polymer, liquid film

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Process description: UV-based NIL process

Purpose: The mr-UVCur21 is a liquid UV-curable polymer system with low viscosity and high curing rate designed for UV-based nanoimprint lithography. The liquid resist fills the stamp cavities predominantly by capillary forces, thus only low pressure is applied. The replication of stamp pattern is subsequently enabled by UV-curing the resist prior to demolding. Since the resist is UV-cured at room temperature, process times are minimized (i.e. no need to thermally cycle the imprint system). Furthermore, a dense three-dimensional polymer network is formed during UV-curing. Thus, the resist exhibits high stability towards thermal load (no reflow during etching) as well as greatly withstands the exposure to a variety of dry- and wet-etching chemicals.

Major challenges: Since the deposited resist film remains liquid on the substrate, the risk of particle contamination is increased. This means general processing environment has to be controlled at additional effort and sufficient pre-cautions are required when storing pre-coated substrates. Furthermore, only transparent stamp materials are applicable during replication step.

Application and state-of-the-art: Fabrication of nanopatterns e.g. for nanooptical devices, photonic crystals, high-brightness LEDs (by means of dry or wet etching of substrates).

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[1] C Peroz, S Dhuey, M Cornet, M Vogler, D Olynick, S Cabrini Nanotechnol 23 2012 015305

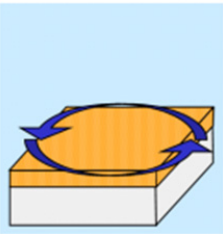
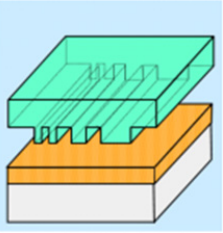
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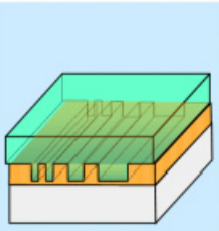
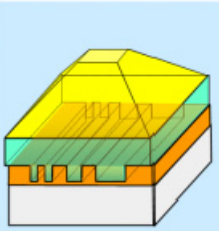
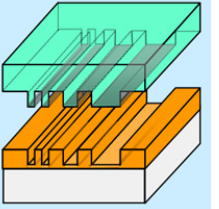
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LoP2014_SP03_UV-NIL

UV-NIL using UV-curable Polymers

Process: Standard mr-UVCur21

	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	Process 1: substrate preparation		<i>Best patterning results are obtained at 20 – 25 °C and a rel. humidity of 40 – 46 %.</i>
1.1	Substrate preparation	Dehydration: baked at 200 °C for 30 min and cooled to room temperature immediately before coating. Surface activation (if needed): oxygen plasma surface activation. For improving the polymer film adhesion to Si or SiO ₂ substrates it is advisable to apply an adhesion promoter. Using mr-APS1 () is recommended. HMDS (hexamethyl-disilazane) is not suitable.	<i>Substrates have to be free of impurities and moisture.</i>
1.2	Dispensing, spin-coating and soft-baking of mr-UVCur21 	Standard spin-coating should be performed with 3000 rpm for 60 sec (). Soft-back at 80 °C for 60 s on hot plate (or oven). The soft-bake step is necessary to evaporate residual solvent.	<i>Film thickness can be varied by using different standard resist formulation, i.e. mr-UVCur21-100nm, mr-UVCur21-200nm, and mr-UVCur21-300nm. Further adaptations are accomplished by using appropriate resist spin-curves. A spin time of 60 s is recommended, since lower film thicknesses and a higher film quality can be achieved compared to 30 s.</i>
	End of Process 1		
2.0	Process 2: Thermal Imprint	Pattern replication	
2.1a	Alignment of transparent stamp 	Transparent stamp (e.g. made of Quartz, polymer (i.e. IPS – intermediate polymer stamp) or OrmoStamp) is positioned on and aligned to the coated substrate.	<i>mr-UVCur21 can be imprinted in any tool suitable for doing thermal nanoimprint lithography, in tools combining thermal imprinting and UV exposure. Commercial nanoimprinters as provided e.g. by Obducat (Sweden), EVG (Austria) and Suss MicroTec (Germany) may be used.</i>

<p>2.2a</p>	<p>Pattern replication</p> 	<p>Substrate coated with mr-UVCur21 is imprinted at room temperature. The UV-transparent stamp is pressed into the resist film with a low imprint pressure of > 100 mbar to transfer the pattern. Imprint in vacuum or under atmospheric pressure. UV exposure: broad band or i-line, curing time few seconds.</p>	<p><i>The imprint pressure and time necessary to get complete filling of the mould cavities depends on the pattern density and pattern width. Since mr-UVCur21 has a very low viscosity, the time necessary to build up the imprint pressure is sufficient to completely fill the patterns. Main factors determining the imprint conditions are the viscosity of the polymer system, the mould layout (feature size, density of the patterns etc.), the residual layer thickness to be attained and the imprinting tool.</i></p>
<p>End of Process 2</p>			
<p>3.0</p>	<p>Process 3: Crosslinking Resist</p>	<p>Pattern curing</p>	
<p>3.1</p>	<p>UV-exposure through transparent stamp while imprinting</p> 	<p>Exposure dose ~700 mJ/cm² using broadband UV light (320 – 420 nm), intensity measured at λ = 365 nm</p> <p>Options: UV broadband, Monochromatic (365-395 nm), LED up to 395 nm</p> <p>curing in vacuum</p>	<p><i>Applying higher doses or broader UV wavelength ranges do not affect the imprint quality or the properties of the cured polymer. Exposure applying a smaller UV range of e.g. 350 - 400 nm or applying the 365 nm line works as well, but will require higher doses. The degree of shrinkage of mr-UVCur21 during the UV exposure is approximately 3 – 4 % (linear shrinkage). Reproducible exposure conditions will lead to reproducible shrinkage values.</i></p>
<p>End of Process 3</p>			
<p>4.0</p>	<p>Process 4: Demolding</p>	<p>Stamp release</p>	
<p>4.1</p>	<p>Separation of stamp and resist</p> 	<p>Release at room temperature</p>	

		Examples shows replication of mould patterns with demanding filling factors, i.e. 100x100 μm^2 squares.	
	End of Process 4		
5.0	Process 5: Residual Layer Removal	Opening Resist Windows	
5.1	Remove of Residual Layer 	The residual layer remaining in the recessed areas of the imprint is removed by oxygen reactive ion etching (RIE) in order to open the window to the substrate	<i>After the whole process residue-free removal of mr-UVCur21 is preferably achieved applying oxygen plasma. Since mr-UVCur21 does not contain any inorganic components like silicon, no residues are left on the substrate after plasma treatment with pure oxygen.</i>
	End of Process 5		
	End of Total Process		

General remarks:

mr-UVCur21 is a liquid UV-curable polymer system with low viscosity and high curing rate designed for UV-based nanoimprint lithography. It is provided as a ready-to-use solution. Optimum imprint results on Si or SiO₂ substrates are achieved by applying adhesion promoter mr-APS1 before coating mr-UVCur21. If required, the resist is also available in a solvent-free version, i.e. mr-UVCur21SF. It is also provided as a ready-to-use liquid and can be spin-coated or dispensed on the substrate.

The main resist characteristics can be summarized as follows:

- Vacuum-stable resist films (>10 mbar)
- Short imprint cycle times:
 - Fast filling of mold cavities due to low viscosity
 - Low UV doses, fast polymerization rates
- Pattern resolution down to 10 nm (mr-UVCur21)
- Compatibility to different UV exposure systems (Hg, LED)
- High uniformity of the residual layer thickness
- Excellent plasma etch resistance

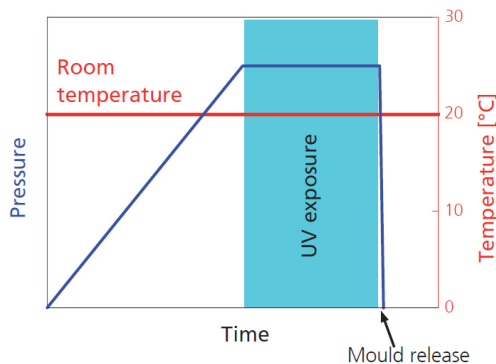


Figure 1: Example for a typical process cycle of mr-UVCur21 demonstrating the isothermal process with UV exposure step finalizing the imprint step.

3.4 Combined Thermal and UV-NIL Process

Combined T- and UV-NIL using photochemically curing resist

Process: Standard mr-NIL 6000E

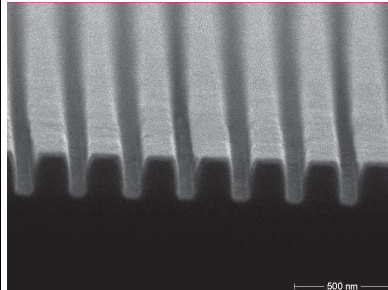


Figure:
Replicated line pattern, i.e. 100 nm trenches, 300 nm pitch, on silicon substrate

Application:
Etch mask for pattern transfer processes, dry and wet etching, single and multi-layer systems.

Keywords: combined nanoimprint and photolithography, STU

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Process: polymer materials

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Process description: High performance resist with decreased imprint temperature

Purpose: mr-NIL 6000E is a photochemically curing resist for combined thermal and UV-based nanoimprint lithography (i.e. bringing together the technical benefits of both processes). Upon heating above the glass transition temperature (T_g), the viscosity of the initially solid resist is sufficiently reduced enabling the filling of the stamp cavities when pressure is applied during imprint step (the resist's T_g prior to curing is 40 °C). Once cavity filling is completed, the resist is UV flood exposed in order to initiate the curing of the polymer. Thus, the process allows the imprinting, UV-curing, post exposure bake and mould release at constant temperature. mr-NIL 6000E is well suited for pattern transfer processes as well as for permanent structures e.g. in microfluidics and microoptics. The resist can be patterned under isothermal conditions applying lower imprint temperatures compared to other nanoimprint materials.

Major challenges: Curing of the mr-NIL 6000E upon UV exposure increased the T_g (enabling an isothermal process). The T_g increase is caused by a three-dimensional cross-linking of the polymer network which. Thus, the elevated T_g is permanent.

Application and state-of-the-art: Fabrication of nanopatterns e.g. for nanooptical devices, photonic crystals, high-brightness LEDs (by means of dry or wet etching of substrates).

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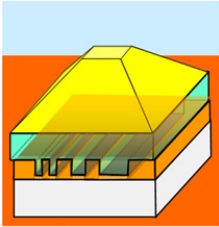
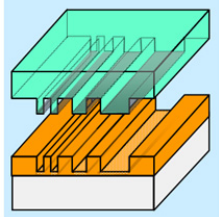
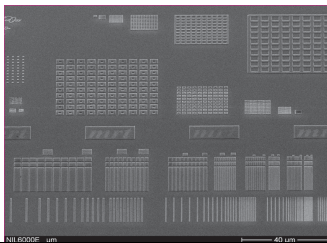
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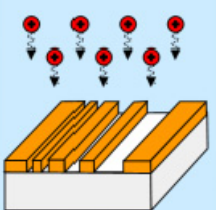
LoP2014_SP04_Combined-Thermal-and-UV-NIL

Combined T- and UV-NIL using photochemically curing resist

Process: Standard mr-NIL 6000E

	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	Process 1: substrate preparation		<i>Best patterning results are obtained at 20 – 25 °C and a rel. humidity of 40 – 46 %.</i>
1.1	Substrate preparation	Dehydration: baked at 200 °C for 30 min and cooled to room temperature immediately before coating. Surface activation (if needed): oxygen plasma surface activation	<i>Substrates have to be free of impurities and moisture</i>
1.2	Dispensing, spin-coating and pre-baking of mr-NIL 6000E	Standard spin-coating should be performed with 3000 rpm for 30 sec Pre-bake at 90 °C on hot plate (or oven) for one minute.	<i>Film thickness can be varied by using different standard resist formulation, i.e. mr-NIL 6000.1E (100 nm), mr-NIL 6000.2E (200 nm) and mr-NIL 6000.3E (300 nm). Further adaptations are accomplished by using appropriate resist spin-curves. The pre-bake step is necessary to evaporate residual solvent.</i>
	End of Process 1		
2.0	Process 2: Thermal Imprint	Pattern replication	
2.1a	Alignment of transparent stamp	Transparent stamp (e.g. made of quartz, polymer (i.e. IPS – intermediate polymer stamp) or OrmoStamp [®]) is positioned on and aligned to the coated substrate. Stack is heated to 65 – 70 °C to lower resist's viscosity.	<i>mr-NIL 6000E can be imprinted in any tool suitable for doing thermal nanoimprint lithography, in tools combining thermal imprinting and UV exposure. Commercial nanoimprinters as provided e.g. by Obducat (Sweden), EVG (Austria) and Suss MicroTec (Germany) may be used.</i>
2.2a	Pattern replication	Substrate coated with mr-NIL 6000E is heated to 65 – 70 °C in the imprint machine and the UV-transparent stamp is pressed into the resist film with a pressure of ~30 bar to transfer the pattern, flow time is 20 – 100 sec (pattern depended).	<i>Main factors determining the imprint conditions are the rheological behaviour of the resist, the mould layout (feature size, density of the patterns etc.), the degree of cavity filling, the residual layer thickness to be attained and the imprinting tool.</i>

	End of Process 2		
3.0	Process 3: Crosslinking Resist	Pattern curing	
3.1	<p>UV-exposure through transparent stamp while imprinting</p> 	<p>Exposure dose [mJ/cm^2] ~ 350</p> <p>Options: UV broadband, i-line (365 nm), Monochromatic (365-395nm)</p>	<p><i>After the time required to allow the resist flowing and conforming to the mould (flow time depending on the mould layout) the resist is UV flood exposed (under pressure at the imprint temperature in the imprinter). The dose to be applied depends on the imprint temperature and the desired thermal pattern stability: Lower imprint temperatures require a somewhat higher exposure dose. Also if a very high thermal pattern stability is necessary for the subsequent processing a higher exposure dose is recommended. Alternatively, an even higher imprint temperature of up to 100 °C can be applied if a very high thermal pattern stability is decisive.</i></p>
	End of Process 3		
4.0	Process 4: Demolding	Stamp release	
4.1	<p>Separation of stamp and resist</p>  	<p>Release temperature 65-70 °C (= imprint temperature)</p>	<p><i>Additional annealing after the exposure – which would correspond to the post exposure bake (PEB) in radiation based lithography – is not necessary. The stamp is released at the imprint temperature. This isothermal process is possible, since T_g of the resist has increased to roughly the imprint temperature due to the curing reaction initiated by the exposure.</i></p>
	End of Process 4		
5.0	Process 5: Residual Layer Removal	Opening Resist Windows	
5.1	Remove of Residual Layer	<p>The residual layer remaining in the recessed areas of the polymer film after the imprint is removed by oxygen reactive ion etching (RIE) in order</p>	<p><i>After the whole process residue-free removal of mr-NIL 6000E is achieved applying oxygen plasma. Also the</i></p>

		to open the window to the substrate	ready-to-use removers <i>mr-Rem 600</i> (based on <i>N-methylpyrrolidon (NMP)</i>) or <i>mr-Rem 500</i> (NMP-free) at temperatures of 40 – 60 °C assisted by ultrasonics are suitable.
	End of Process 5		
	End of Total Process		

General remarks:

The mr-NIL 6000E is a photochemically curing resist for thermal nanoimprint lithography. It forms a solid resist film after spin coating. mr-NIL 6000E is well suited for pattern transfer processes as well as for permanent structures e.g. in microfluidics and microoptics. The resist can be patterned under isothermal conditions applying lower imprint temperatures compared to other nanoimprint materials. The main resist characteristics can be summarized as follows:

- Solid resist film after spin coating
- Short imprint cycle times due to isothermal NIL process (no cooling step)
- Excellent film quality on various substrate materials e.g. Si, SiO₂, Al, Al₂O₃
- Designed for combined thermal and UV nanoimprint lithography
- T_g ~ 1 °C before curing
- Imprinting, UV curing during imprinting, and mould release at the same temperature
- Low imprint temperature (65 – 70 °C), low thermal load
- High uniformity of the residual layer thickness
- Very low residual layer thickness < 10 nm
- Excellent pattern transfer fidelity
- High plasma etch resistance comparable to conventional novolak-based photoresists
- Ready-to-use solutions
- Safe solvents

It is highly recommended to treat the mould with a release agent like F13-OTCS or other fluorinated silanes before use. F13-OTCS (trichloro-(1*H*,1*H*,2*H*,2*H*-perfluorooctyl)-silane, CAS number [78560-45-9]) is commercially available from many suppliers of laboratory chemicals.

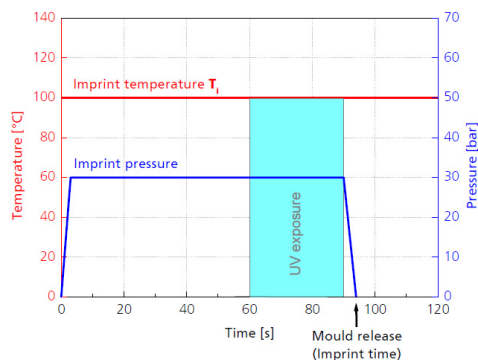


Figure 1: Example for a typical process cycle of mr-NIL 6000E demonstrating the isothermal process with UV exposure step finalizing the imprint step.

3.5 Nanoimprint Lithography of 3D structures

Thermal nanoimprint lithography of 3D structures and contact angle based filling of cavities with sloped sidewalls

Process: nanoimprint lithography

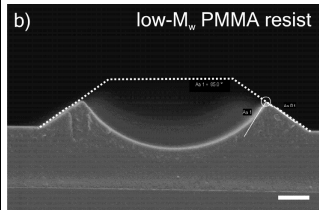


Figure:
SEM micrograph of pre-fill state in a symmetric cavity with sloped sidewalls (scale bar 500 nm). Due to surface energy of mold and material (PMMA 9k), a contact angle of around 98° is forming.

Process:
Nanoimprint of 3D structures with pre-filling states

Application:
Analysis of contact angle dependent cavity filling in thermal NIL processes.

Keywords: thermal nanoimprint, 3D stamps, cavity filling, surface coating, contact angle

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Process: Thermal Nanoimprint
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Process description: During thermal imprint, microcavities are both filled by capillary action and squeeze flow. Already in the contact phase of the mold with the resist (i.e. in a low pressure regime at elevated temperature) pre-fill states form due to the surface energy of the mold and resist material, leading to voids with defined contact angles, before squeeze flow is able to fill the cavity from the side.

Purpose: Pre-fill states can lead to uneven residual layer thickness after thermal imprint resulting in specific defects during RIE pattern transfer. Due to the constant contact angle at the cavity sidewall, the meniscus is more pronounced in cavities with sloped sidewalls.

Major challenges: Predict contact angles and specific evolution in 3D cavities.

Application and state-of-the-art: 3D filling is still a research topic with high relevance to applications in optics.

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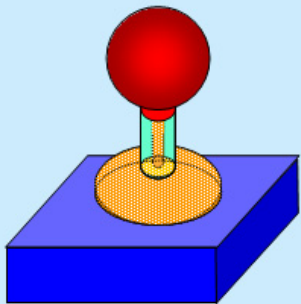
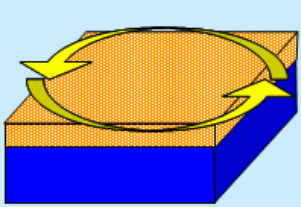
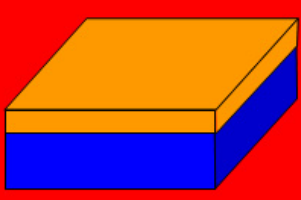
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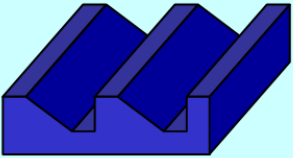
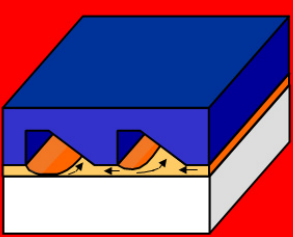
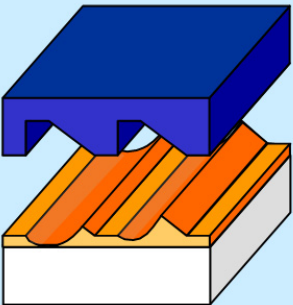
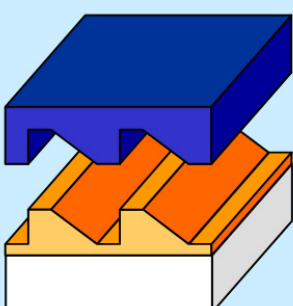
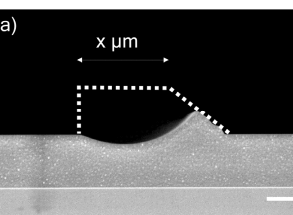
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LoP2012_NIL013_3D NIL molding process

Thermal nanoimprint lithography of 3D structures and contact angle based filling of cavities with sloped sidewalls

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Wafer preparation	Silicon wafer format	
1.1	wafer selection and preparation	standard Si substrate Si substrate, 4", <100>, thickness d=400-600 μm one side polished	<i>Alternatively, 0.7 mm thick Borofloat glass has proven to be a good substrate (if transparency is needed)</i>
1.2	substrate preparation	pretreatment no pretreatment needed (if wafer is clean and hydrophilic)	
	End of Process 1		
2.0	Process 2: Resist coating	for nanoimprint lithography	
2.1	dispensing of resist 	resist no priming PMMA 25 kg/mol in ethyl-lactate (safer solvent)	<i>Ethyl-lactate is a safer solvent (in contrast to chlorobenzene (CB)) and results in similar thickness. Only for very high concentrations of PMMA (e.g. 9%) CB is a better solvent.</i> <i>Alternative materials: commercially available resists from micro resist technology GmbH, e.g. mr-I 8000E (see Page 34)</i>
2.2	coating resist (homogeneous layer) 	spincoating of thermoplastic resist PMMA -> ~990 nm thickness	<i>PMMA and mr-I 8000E are NIL resists with relatively high glass transition temperature</i> <i>T_g of ...</i> <i>PMMA (low Mw): 120 °C</i> <i>mr-I 8000E: 115 °C</i>
2.3	post bake 	solvent evaporation bake 1 min @ 170°C (hot plate)	<i>Alternative: convection oven at 180°C, for 30 min</i>
	End of Process 2		
3.0	Process 3: Thermal imprint	dry etching of silicon	
3.1	Stamp with 3D surface topography	Stamp preparation A 3D stamp with microcavities with sloped (30°) and	<i>Asymmetric structure</i>

		<p>vertical sidewalls was prepared using grayscale electron beam lithography and the TASTE process. With a fixed height of 1 μm and a varying footprint of 3 – 5 μm</p>	<p><i>TASTE (thermally assisted selective topography equilibration) – see Page 100.</i></p>
<p>3.2</p>	<p>Resist removal (stripping)</p> 	<p>Thermal imprint A typical imprint process consists of a contact phase in which polymer is able to assume a surface of minimum energy due to the wetting of the sidewalls</p>	
<p>3.3a</p>	<p>process control</p> 	<p>Incomplete molding Stamp and resist show partially identical (opposite polarity) profiles but large areas where the surface profile of the resist is determined by a meniscus Capillary action completed and squeeze flow not yet completed</p>	<p><i>Asymmetric structures are more prone to pinning at vertical sidewalls, while sloped enable a smooth filling without pinning</i> <i>Pinning at vertical sidewall and contact angle formation at sloped sidewall, meniscus forming with depth below initial resist level</i></p>
<p>3.3b</p>	<p>process control</p> 	<p>Complete molding Stamp and resist show identical (opposite polarity) profiles</p>	<p><i>Complete molding is achieved if squeeze flow of is enabled and enough material is flowing to fill the entire cavity</i></p>
<p>3.4</p>	<p>process control</p> 	<p>electron microscopy asymmetric structures resist: PMMA destructive (cleaving, metal coating) in SEM The three micrographs show different pre-fill states for different cavity lengths, all of them in equilibrium (volume conservation) While different meniscus depths are generated, the</p>	<p><i>non-destructive process control would be possible using profilometry</i></p>

		<p>contact angle of about 90° is maintained over the entire slope.</p> <p>Contact angle PMMA 34kg/mol: 90° mr-I 8000E: 85°</p>	
<p>End of Process 3</p>			
<p>End of Total Process</p>			

General remarks:

Filling is dependent on surface energy of the ASL coated mold and the resist, along with pinning and the tendency of the polymer to assume surfaces of minimum energy.

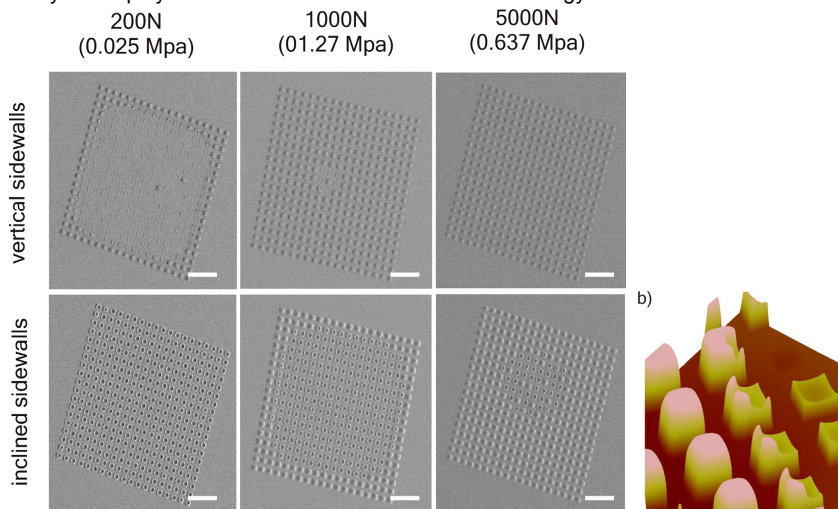


Figure 1: During imprint of extended arrays of microcavities (which are not too extended for the stamp to bend), transport of material for the filling of cavities is done by squeeze flow from the borders of the array. Due to the lack of material flow in the center, pre-fill states are generated in which capillary action dominates.

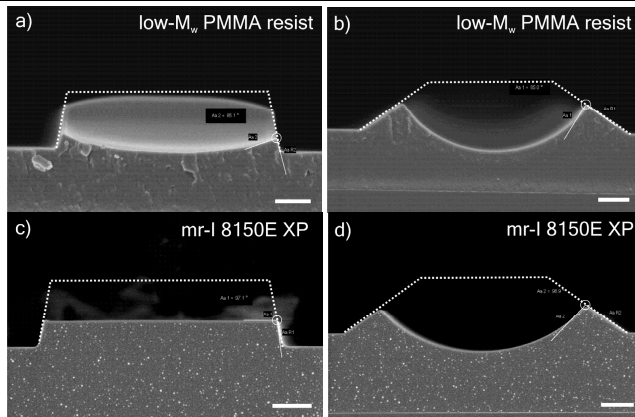


Figure 2: In case of (almost) vertical sidewalls, the filling is abrupt, i.e. the structures are filled by spontaneous wetting of sidewall surfaces (particularly at corners) and “jumps” up to the cavity top. In case of inclined sidewalls, a contact angle forms and results in the generation of a resist surface with the form of a meniscus, being the result of volume conservation and formation of a surface of minimum energy. These states are also forming in absence of pressure. They are stable, as long as squeeze flow does not interfere with the formation of an equilibrium. Different resists types result in different contact angles, which in case of PMMA 9k is about 98° and in case of mr-I 8000E (here: experimental sample mr-I 8150E XP provided by *micro resist technology GmbH*) is about 85° .

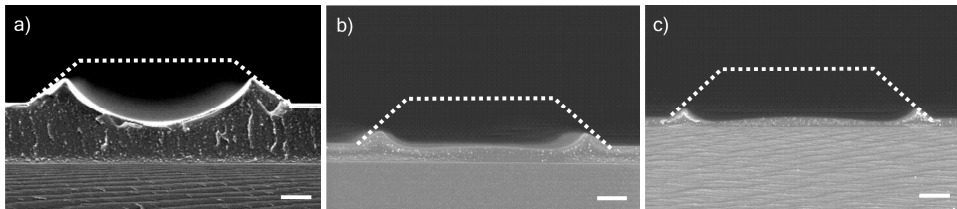


Figure 3: A lens- or cylinder-like depression below the cavity can only form for thick resist layers (PMMA), assuming the optimum contact angle. For thin resists, the same contact angle forms at the sidewalls, but instead of depletion down to the substrate, flow towards the borders is inhibited and the substrate stays wetted. (scale bar: 500 nm)

3.6 Suspended polymer membranes

Fabrication of suspended polymer membranes on LOR resist

Process: nanoimprint lithography

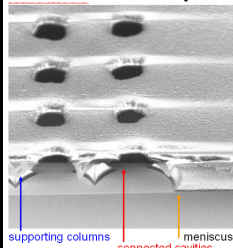


Figure:

SEM micrograph of a pore array in 1 μm thick polystyrene supported by 2 μm high pillars with 3 μm hole diameter and 5 μm period (cleaved sample)

Process:

Thermal nanoimprint of a thermoplastic polymer on top of a sacrificial polymer. Pattern transfer using RIE and underetch.

Application:

Microfluidic devices (alternative to sieves based on pillar array)

Keywords: thermal nanoimprint, double resist, sacrificial layer, perforated membrane

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Process: Thermal Nanoimprint

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Process description: A process for polymeric sieve structures is presented. It is based on a two-layer resist (LOR) with a sacrificial layer below a thermoplastic resist. Because the two polymer layers have different sensitivities to solvents, the LOR can be selectively dissolved through the pores.

Purpose: The aim of this process is not the fabrication of a specific device, but to demonstrate a process sequence which the specific requirements on NIL processing.

Major challenges: While the thermoplastic molding step is standard therefore standard resists such as PMMA, PS or COC, as well as the commercially available resist (by *micro resist technology* GmbH) can be interchanged, the LOR dissolution is dependent on structure sizes, resist thickness and process conditions.

Application and state-of-the-art: Research process, used for DNA separation

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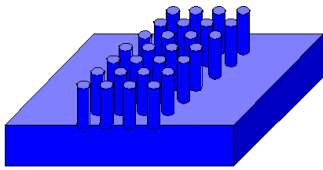
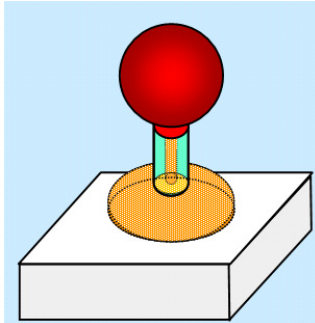
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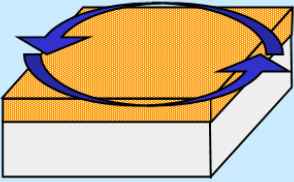
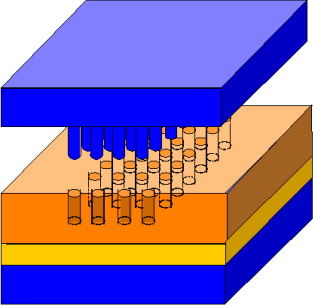
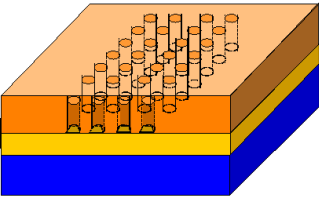
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LoP2007_NIL002_suspended polymer membranes

Suspended polymer membranes

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	Process 1: Wafer preparation		
1.1	wafer selection and preparation	standard Si substrate Si substrate, 4", <100>, thickness d=465 μm one side polished	
1.2	substrate preparation	no pretreatment	
	End of Process 1		
2.0	Process 2: Stamp preparation		
2.1	layout 	Functional structures the stamp consist of large arrays of pillars (about 1mm ² area) with a 10 mm pitch between arrays, all over the wafer. Arrays consist of orthogonal patterns with pillar diameters from 1.5 to 6 μm and periods of 5 to 15 μm (800 nm deep). The (p : a) combinations were (5:1.5), (5:3), (10:2), (10:4), (15:4) and (15:6) μm.	<i>microstructures are very good for the set-up of the process, because the process control can be done using optical microscopy</i>
2.2	antiadhesive coating	silane CVD evaporation standard process	<i>silane coating from gas phase is beneficial for sidewall coating</i>
	End of Process 2		
3.0	Process 3: Lithography		
3.1	coating of layer 1 (sacrificial layer) 	double-spincoating of LOR no priming LOR 10B from MicroChem Corp. 3000rpm, 60 s -> ~1000nm bake 3 min @ 190°C (hot plate) 3000rpm, 60 s -> ~1000nm bake 3 min @ 190°C (hot plate) total thickness: 2000 nm	<i>long prebake of 3 min at 190°C on a hot plate was chosen in order to achieve a high T_g and a low etching rate almost independent from further heat treatment</i>
3.2	coating of layer 2 (functional NIL layer)	spincoating of PS no priming of LOR Polystyrene 125kg/kmol, Polyscience GmbH, dissolved in dissolved in tolu-	<i>PS was chosen because of its excellent optical and physiological properties.</i> <i>Resist with inherent anti-</i>

		<p>ene 3000rpm, 60 s -> ~1000nm bake 1 min @ 170°C (hot plate)</p>	<p><i>adhesive properties (by micro resist technology) have the potential to further improve the subsequent thermal NIL and demolding step with less defects.</i></p>
<p>3.3</p>	<p>Nanoimprint Lithography</p> 	<p>Jenoptik HEX03 (PSI) no vacuum stack preassembled before heating and pressing (order from top to bottom): PI (polyimide) 50µm, PDMS (standard) 1mm, PI 50µm stamp (loose or clamped) substrate with resist, PI 50µm tempera- ture.(heat).....180°C pressure.....20 bar heating time (80-180°C).. cooling time (180-80°C).. hold time (180°C).....30min overall time.....40 min tempera- ture.(release)....70°C residual polymer thickness in grooves 150 nm</p>	<p><i>the PI (polyimide) reduces the adhesion of the PDMS to the silicon) the loosely assembled stack is first fixed with contact force(for better heat transfer), then heated to T_{process}, then equilibrated, and pressure applied cooling while pressure is kept constant The thickness of the resist h_{top} (1000nm) was chosen in order to have a sufficient lateral flow of material with the 800 nm high structures. Similar values and process parameter were used for PS, PMMA and COC</i></p>
<p>3.4</p>		<p>demolding pressure release at about 70°C demolding manually by applying a razor blade between stamp and substrate and inducing a wedge</p>	<p><i>demolding of dense array of pillars more difficult reduction of thermal expansion by molding at low / demolding at high temperatures</i></p>
<p>3.5</p>	<p>process control</p>	<p>optical microscopy <i>non-destructively</i></p>	<p><i>destructive (cleaving, metal coating) in SEM profilometry</i></p>
	<p>End of Process 3</p>		
<p>4.0</p>	<p>Process 4: Pattern Transfer</p>		
<p>4.1</p>	<p>Residual Layer (Breakthrough) Etching</p> 	<p>RIE Oxford Plasmalab 100: thinning of resist PMMA etch with no cooling O₂.....20 sccm gas pressure 20 mtorr power 20 W temperature 300 K etching rates PS 30 nm/min, LOR 10B 48 nm/min</p>	<p><i>residual layer can either be measured by profilometry (near the relevant structures) PS etching rate in oxygen plasma is significantly lower relative to LOR, which means that once the windows are opened, the etching continues at a higher speed in the LOR</i></p>
<p>4.2</p>	<p>process control</p>	<p>Profilometer /Microscope</p>	
<p>4.3</p>	<p>Sacrificial layer etching</p>	<p>LOR wet etching</p>	<p><i>The developer penetrates</i></p>

		<p>Microposit MF319 (from MicroChem Corp.) dilution of MF319/water of 3:2 (60%) underetching rates of LOR range from 2.5 nm/sec for smaller to 5 nm/sec for larger periods For the (10:2) μm combination a time t_{min} of about 13 min for half the distance etch was observed. Stopping the process was possible by extensive rinsing in de-ionized water. After drying in nitrogen, the water is completely removed from the cavities.</p>	<p><i>the pores and dissolves the LOR isotropically.</i></p> <p><i>In order to reduce the process time, the dilution was changed to 5:1 (85%). In this case the underetching rates were enhanced and range from 22 nm/sec to 36 nm/sec.</i></p> <p><i>Although for combinations of smaller periods and pore diameters the underetching rate slows down, no limitation for the application of this technique for smaller diameters of below $1\mu\text{m}$ could be seen.</i></p>
<p>4.4</p>	<p>process control</p> <p>b) connected cavities with supporting columns</p>	<p>optical microscope 100 x</p> <p>Connected cavities with supporting columns (PS $1\mu\text{m}$ / LOR $1\mu\text{m}$, view size $30 \times 30\mu\text{m}^2$). The area between the pores and the sidewalls of the undercuts (bright) defines the membrane, and contrasts well the border and columns (dark) in diamond shape</p>	<p><i>online, without breaking substrate pores and undercuts with $<0.4\mu\text{m}$ can be resolved, not suitable for nanopores ($< 200\text{nm}$)</i></p>
<p>4.5</p>	<p>process control</p> <p>supporting columns connected cavities meniscus</p>	<p>SEM</p> <p>Micrograph of a pore array in $1\mu\text{m}$ thick polystyrene supported by $2\mu\text{m}$ high pillars with $3\mu\text{m}$ hole diameter and $5\mu\text{m}$ period (cleaved sample)</p>	
<p>End of Process 4</p>			
<p>End of Total Process</p>			

General remarks: Further information on alternative resists (including those with inherent antiadhesive properties) are described in 5.6 Resists, substrates and tools.

3.7 Polymer multilayers by reverse UV-NIL

Fabrication of multiplayered woodpiles by reverse UV-NIL

Process: nanoimprint lithography

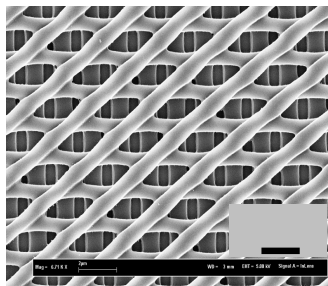


Figure:
SEM images of a three-layer woodpile-like structure fabricated by the reverse contact imprinting technique.

Process:

A lift-off resist and a UV cross-linkable polymer are spin-coated successively onto a patterned UV mask-mold. These thin polymer films are then transferred from the mold to the substrate by contact at a suitable temperature and pressure. The whole assembly is then exposed to UV light. After separation of the mold and the substrate, the unexposed polymer areas are dissolved in a developer solution leaving behind the negative features of the original stamp.

Application:

Microfluidic devices, Photonic crystals

Keywords: reverse nanoimprint lithography, three-dimensional nanofabrication

Project leader: Tyndall National Institute
Address: Lee Maltings, Prospect Row, Cork, Ireland
Web-Address: <http://www.tyndall.ie>

Process: Thermal nanoimprint
Responsible: C.M. Sotomayor Torres
E-mail:

Process description: A lift-off resist and a UV cross-linkable polymer are spin-coated successively onto a patterned UV mask-mold. These thin polymer films are then transferred from the mold to the substrate by contact at a suitable temperature and pressure. The whole assembly is then exposed to UV light. After separation of the mold and the substrate, the unexposed polymer areas are dissolved in a developer solution leaving behind the negative features of the original stamp.

Purpose: This process delivers a resist pattern transfer without a residual layer thereby rendering unnecessary the etching steps typically needed in the imprint lithography techniques for three-dimensional patterning. Three-dimensional woodpile-like structures were successfully fabricated with this new technique.

Major challenges: At a too high temperature and pressure, the polymer layer will flow in the underlying structure. The UV exposure dose must be controlled to avoid the formation of a residual layer. The UV light diffracted by the metallic protrusion of the stamp may be back-scattered from the imprinted substrate. The control of the exposure dose can be done by selecting the light intensity and the exposure time.

References:

- [1] N. Kehagias, V. Reboud, G. Chansin, M. Zelsmann, C. Jeppesen, F. Reuther, C. Schuster, M. Kubenz, G. Gruetzner, C. M. Sotomayor Torres, Sub-micron three-dimensional structures fabricated by reverse contact UV nanoimprint lithography, *J. Vacuum Science and Technology B*, 24, 6, 3002-3005, 2006.
- [2] N. Kehagias, V. Reboud, G. Chansin, M. Zelsmann, C. Jeppesen, C. Schuster, M. Kubenz, F. Reuther, G. Gruetzner, C. M. Sotomayor Torres, *Reverse contact UV nanoimprint lithography for three-dimensional fabrication*, *Nanotechnology*, 18, 17, 175303, 2007.

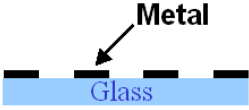
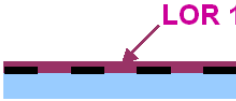
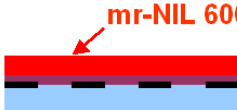
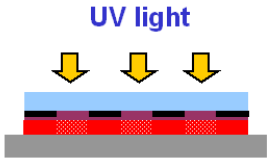
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LoP2007_NIL003_RUVNIL woodpile

Polymer multilayers by reverse UV-NIL

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	Process 1: Wafer preparation		
1.1	wafer selection and preparation	Standard Si substrate Si substrate, <100>, thickness $d=500\ \mu\text{m}$ one side polished Standard glass or Pyrex substrate	
1.2	substrate preparation	no pre-treatment for the first layer	
	End of Process 1		
2.0	Process 2: Stamp preparation	Standard glass or Pyrex substrate with metal protrusion	
2.1	layout 	Functional structures the stamp consist of gratings (about $5\ \text{mm}^2$ area) with a pitch variation from $200\ \text{nm}$ to $10\ \mu\text{m}$ between lines, all over the wafer.	
2.2	Spin coat sacrificial polymer layer 	A thin film of lift-off resist (LOR 1A from MicroChem Corp.) is spin coated at $1000\ \text{rpm}$ for $1\ \text{min}$ on the stamp and baked at $150\ ^\circ\text{C}$ for $5\ \text{min}$. This sacrificial polymer layer is used as an adherence promoter, a planarization layer and to protect the stamp from contamination by the photocuring resist.	<i>No antiadhesive coating needed</i>
2.3	Spin coat UV crosslinkable polymer 	A film of a UV crosslinkable polymer (mr-NIL 6000 from micro resist technology GmbH) is spin coated at $3000\ \text{rpm}$ on the LOR layer and soft-baked at $120\ ^\circ\text{C}$ for $5\ \text{min}$ to evaporate the residual solvent	<i>mr-NIL 6000E is a low T_g NIL resist for combined thermal and UV-based NIL (see Page 34).</i>
	End of Process 2		
3.0	Process 3: Lithography		
3.1	Reverse imprint  Heat, pressure, UV light exposure apply	The polymer bilayer is reverse imprinted onto a Si substrate. Stamp and substrate are then heated to a temperature above the T_g of mr-NIL 6000 and exposed to UV radiation. Optimized imprint parameters on a non-flat substrate	<i>The UV exposure dose must be controlled to avoid the formation of a residual layer. The UV light diffracted by the metallic protrusion of the stamp may be back-scattered from the imprinted substrate. The control of the exposure dose can be done by</i>

	<p>Schematic of RUVNIL process showing the time at which point of UV light exposure occurs and the time of post exposure baking.</p>	<p>are: temperature of 90 °C, UV exposure time of 3 s, pressure of 40 bars and PEB time of 30 s. Nanoimprint has been performed with a 2.5" Obducat embosser.</p>	<p>selecting the light intensity and the exposure time. In our experiments the dose was controlled by the time duration of UV light exposure. As shown in Figure, the UV light must be applied just before the pressure is applied in order to avoid a polymer flow in the underlying first imprinted layers. The trade-off of the imprint process has been performed.</p>
<p>43.2</p>	<p>Separation and development.</p>	<p>Demolding Demolding in a developer bath. Unexposed polymer areas as well as the LOR layer are removed with acetone and/or remover 1165 (Shipley) leaving behind the negative features of the original stamp. No residual layer in final structure.</p>	<p>The oxygen plasma-etching step, usually necessary in standard NIL is avoided.</p>
<p>End of Process 3</p>			
<p>4.0 Process 4: Pattern Transfer</p>			
<p>4.1</p>	<p>First layer transfer mr-NIL 6000</p>	<p>Test of the technique on a flat Si substrate. The imprint temperature was carried at 90 °C with 40 bars of pressure applied for 30sec. UV light exposure was applied for 3 sec prior applying the pressure.</p>	<p>Due to the difference of surface energies between the stamp surface and the Si substrate, the polymers are successfully transferred onto the Si substrate.</p>
<p>4.3</p>	<p>Second layer transfer mr-NIL</p>	<p>Imprint parameters on a non-flat substrate are: temperature of 90 °C, UV exposure time of 3 s, pressure of 40 bars and PEB time of 30 s.</p>	<p>Surface patterned about 4 mm²</p>
<p>4.4</p>	<p>Third layer transfer mr-NIL 6000</p>	<p>Imprint parameters on a non-flat substrate are: temperature of 90 °C, UV exposure time of 3 s, pressure of 40 bars and PEB time of 30 s.</p>	<p>Surface patterned less of 0.5 mm²</p>

4.5	Process control	Optical microscopy <i>non-destructively</i> SEM <i>destructive (cleaving, metal coating)</i>	
	End of Process 4		
	End of Total Process		

Other references:

- [3] N. Kehagias, G. Chansin, V. Reboud, M. Zelsmann, C. Schuster, M. Kubenz, F. Reuther, G. Gruetzner, C. M. Sotomayor Torres, Embedded nano channels fabricated by non-selective reverse contact UV nanoimprint lithography technique, *Microelectron. Eng.* 84(5–8), 921–924 (2007)

3.8 Combined Nanoimprint and Photolithography

Fabrication of optical SU-8 integrated optics by Combined Nanoimprint and Photolithography (CNP)

Process: Combined Nanoimprint and Photolithography (CNP)

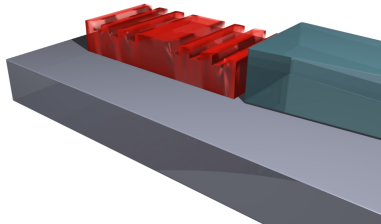


Figure:

Schematic illustration of a polymer DFB laser made of Rhodamine 6G laser dye doped SU-8, integrated with an undoped SU-8 waveguide

Process:

Combined nanoimprint and photolithography using a hybrid stamp/UV mask

Application:

Definition of arbitrary structures containing nm to mm sized features, and made from an imprintable and UV definable material

Keywords: combined nanoimprint and photolithography, CNP, polymer optics, integrated optics

Project leader: DTU - Department of Micro- and Nanotechnology

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Web-Address: www.nanotech.dtu.dk

Process: CNP

Responsible: Anders Kristensen

E-mail: anders.kristensen@nanotech.dtu.dk

Process description: A process is described for waferscale definition of nm to mm sized optical structures by combining nanoimprint lithography with UV lithography. A hybrid stamp/UVmask is used and additional structures are added in a standard UV lithographic process. Both active (lasers) and passive (waveguides) optics are defined.

Purpose: Definition of rhodamine 6G laser dye doped SU-8 first order DFB lasers integrated with optical waveguides

Major challenges: Stamp/mask fabrication. The fact that the stamp is made of quartz complicated E-beam lithography somewhat, but once the stamp is done, the process is quite straight forward.

Application and state-of-the-art: Research process, used for definition of polymer lasers and integrated waveguides.

References:

- [1] M. B. Christiansen, M. Schøler, and A. Kristensen, "Integration of active and passive polymer optics", *Optics Express* 15(7) pp. 3931-3939 (2007)

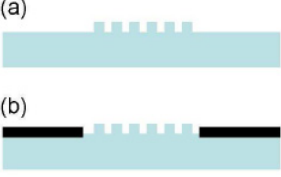

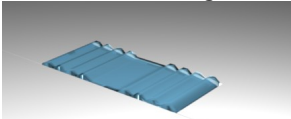
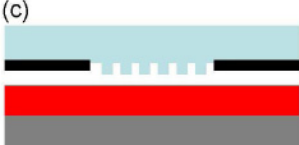

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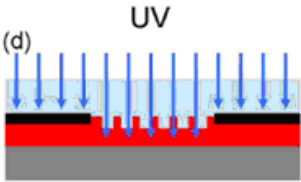

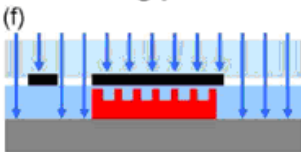


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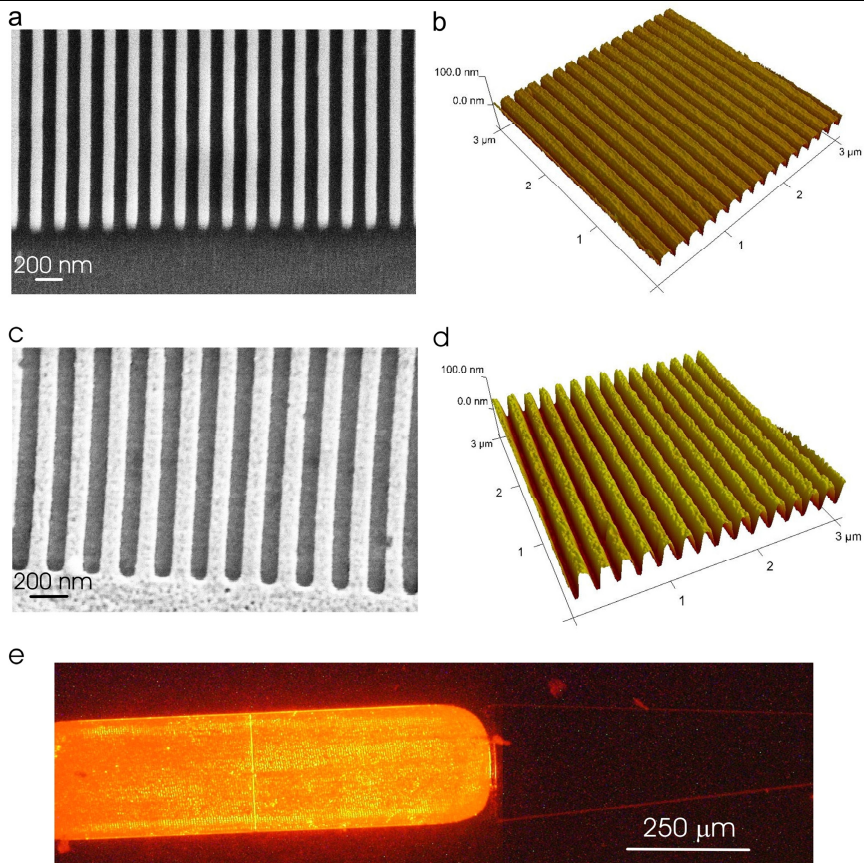
LoP2007_NIL004_CNP Combined NIL and PL process

Combined Nanoimprint and Photolithography

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Wafer preparation		
1.1	wafer selection and preparation	Si substrate, 10 cm,	
1.2	substrate preparation	oxidation thermal oxide, approximately 3 μm	
	End of Process 1		
2.0	Process 1: Stamp preparation		
2.1	layout 	Functional structures the stamp is made of fused silica, with an integrated Cr shadow mask. In the mask windows, which are 1 mm by 250 microns, 100 nm tall glass lines with a width of approx. 100 nm and a period of approx. 200 nm are protruding.	
2.2	antiadhesive coating  <i>Stamp layout</i>	FDTS coating Standard recipe in MVD 100 molecular vapour deposition tool from Applied Microstructures Inc.	<i>Rather slow deposition is chosen to allow good sidewall coverage</i>
	End of Process 2		
3.0	Process 3: Combined nanoimprint and UV lithography (CNP)		
3.1	coating of layer 1	spincoating of Rh6G doped SU-8 no priming SU-8 2002 from MicroChem Corp. thinned to 20% with 3.2 μmol Rh6G dye per g solid. Spun at 7000 RPM, 3000 RPM/s, 60s. Pre-baked @ 90°C for 1 min	
3.2	thermal imprint 	EVG 520HE imprinter stack preassembled before heating and pressing (order from top to bottom): Al foil graphite (standard) 0.5 mm, stamp substrate with resist, graphite Al foil temperature.(heat).....100°C pressure.....(10 kN)	

		<p>hold time (100°C).....10 min overall time.....45 min tempera- ture.(release)....40°C residual polymer thickness in grooves 150 nm on pur- pose. We just want a sur- face corrugation</p>	
3.3	<p>UV exposure</p> 	<p>SÜSS mask aligner 9 mW/mm² 30 s x 11 with 15 s breaks PEB: 90°C, 2 min</p>	
3.4	<p>Demolding</p>	<p>Separation using scalpel</p>	
3.5	<p>Development</p> 	<p>PGMEA 30s IPA rinse N2 or spin dry</p>	
3.6	<p>process control</p>	<p>SEM and AFM</p>	
End of Process 3			
4.0	<p>Process 4: Waveguide defini- tion</p>		
4.1	<p>Spin coat</p>	<p>spincoating of undoped SU-8 no priming SU-8 2005 from Micro- Chem Corp. Ramp to 500 RPM at 100 RPM/s. Ramp to 3000 RPM at 300 RPM/s, spin for 30 s Pre-baked @ 90°C for 1 min</p>	
4.2	<p>UV exposure</p> 	<p>Cr Mask used. Aligned to laser layer SÜSS mask aligner 9 mJ/mm² Hard contact 20 s PEB: 90°C, 2 min</p>	
4.3	<p>development</p> 	<p>PGMEA 3 min IPA rinse N2 or spin dry</p>	
4.4	<p>process control</p>	<p>Optical microscope, AFM and SEM, see figure below:</p>	



End of Process 4

End of Total Process

3.9 Fast isothermal imprint

Fast isothermal imprint for full wafers

Process: nanoimprint lithography

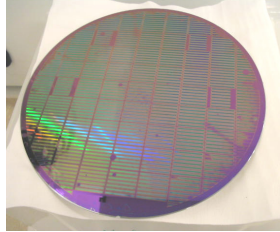


Figure:

Photograph of a 200 mm wafer imprinted using a 2 min process

Process:

A 200 mm wafer is imprinted uniformly in a 2 minutes process with features sizes down to 250 nm or 50 nm.

Application:

Large scale imprint applications

Keywords: thermal nanoimprint, throughput

Project leader: LTM

Address: 17 R. Martyrs, 38 054 Grenoble, France

Web-Address: <http://www.ltm-cnrs.fr/>

Process: Fast isothermal imprint

Responsible: Cécile Gourgon

E-mail: cecile.gourgon@cea.fr

Partner: CEA-LETI

Address: 17 R. Martyrs, F- 38 054 Grenoble

Web-Address: <http://www.cea.fr>

Process: Fast isothermal imprint

Responsible: Stefan Landis

E-mail: Stefan.landis@cea.fr

Process description: The fast imprint process is based on a constant temperature of the equipment. The spin-coated wafer is introduced directly on the heated chuck, and its temperature uniformity is obtained very fast thanks to the equipment design. The resist is fluid enough to induce a very fast imprint as soon as the pressure is applied on the mold, and the demolding is performed outside of the machine. The mold/wafer stack is removed from the heated chuck at high temperature. The adhesion forces between the mold and the imprinted patterns guarantee a stability of the features when the pressure is stopped, until the external cooling. The demonstration is made in this library with 250 nm dense lines. It has also been proved that the same result can be obtained with 50 nm features, but the patterns are not covering the complete surface since a mold fully covered with such high resolution structures is still a challenge.

Purpose: The aim of this process is the increase of the NIL throughput on large surfaces. It was demonstrated that a process can be performed in 2 minutes. This value could be decreased by a upgrade of the equipment with a faster chamber pumping and a automatic loading.

Major challenges: The polymer film has to be heated as fast as possible with a good uniformity. This is a limitation for the fast imprint of very thick polymers. The mold cavities have to be filled very quickly and this is more difficult to achieve for very deep structures. But this fast process is really optimized for the production of nanostructures on large surfaces.

References:

- [1] C. Gourgon, N. Chaix, S. Landis, M. Zelsmann, J. Boussey, and C. Perret, *The impact of the cycle time on the pattern filling and uniformity in thermal Nanoimprint lithography*, Nanoimprint and Nanoprint Technology Conference, San Francisco, December 2006
- [2] C. Gourgon, N. Chaix, H. Schiff, M. Tormen, S. Landis, C.M. Sotomayor-Torres, A. Kristensen, R.H. Pedersen, M.B. Christiansen, I. Fernandez-Cuesta, D. Mendels, L. Montelius, and T. Haatainen, *Benchmarking of 50 nm features in thermal Nanoimprint*, J. Vac. Sci. Technol. B 25(6)(2007) 2373-2378

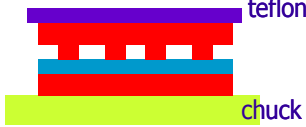
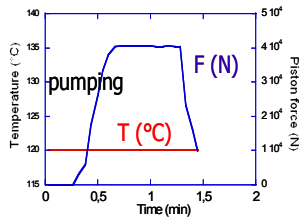
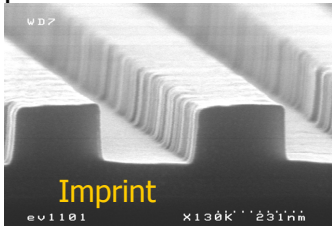
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LoP2007_NIL010_Fast isothermal imprint

Fast isothermal imprint

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: chamber and wafers preparation		
1.1	Pre-heating of the equipment	EVG® 520HE Heating up to T_{imprint} 5 min waiting time to stabilize the temperature	
1.2	Mold/wafer assembly 	200 mm Si wafers Thin film of resist spin-coated on the Si substrate Mold coated with a standard anti-sticking layer Teflon sheet to improve the printing uniformity	<i>The resist thickness has to be in the range of few 10 nm to few 100 nm. A micrometer thick film could result in a limited temperature uniformity</i>
	End of Process 1		
2.0	Process 2: imprint process		
2.1	Pumping and temperature uniformization	Pressure down to 100 mbars in 30 seconds	<i>Limited by the pumping speed</i>
2.1	imprint 	Applied force: 40 kN During 1 minute In the case of NEB22 resist and mr-I7000 polymers, the viscosity is low enough to induce to fast filling at a moderate temperature of 120°C	<i>The filling is uniform after less than 1 minute only if the mold depth is limited to ~200 nm and if the pattern size is in the few 100 nm range. mr-I 7000E is a low T_g polymer with very good flow ability (i.e. large area compatible).</i>
2.3	decrease of the force and chamber venting	T = T imprint	
	End of Process 2		
3.0	Process 3: demolding		
3.1	Unloading of the stack	The mold/wafer stack is put on a plate cold with water to fasten the cooling Waiting time: 2 minutes	
3.2	Demolding	Manual demolding with a razor blade	
3.3	process control 	SEM 250 nm dense lines covering the 200 mm wafer	
	End of Process 3		
	End of Total Process		

3.10 Pattern transfer optimization

Pattern transfer optimization for full wafer NIL

Process: development of anisotropic transfer processes

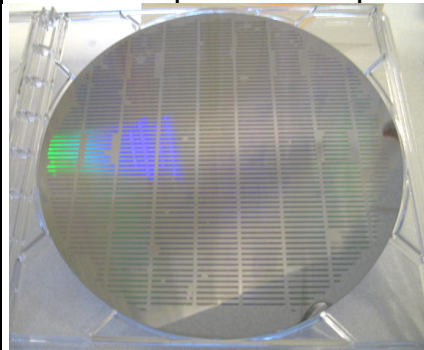


Figure:

Photograph of a 200 mm wafer imprinted and etched using an anisotropic process

Process:

Plasma etching processes are optimized to anisotropic pattern transfer, allowing the transfer of various densities of structures

Application:

Si devices with various patterns size and densities

Keywords: plasma etching, critical dimension, residual layer

Project leader: LTM

Address: 17 R. Martyrs, 38 054 Grenoble, France

Web-Address: <http://www.ltm-cnrs.fr/>

Process: anisotropic pattern transfer

Responsible: Cécile Gourgon

E-mail: cecile.gourgon@cea.fr

Process description: Large surfaces require a high imprint uniformity, which is easier to achieve with residual layers in the 50-100 nm range. A anisotropic plasma etching process is developed to remove this residual polymer film. The anisotropy allows a high quality transfer into patterns with various densities, with a good fidelity of the pattern size. This process uses a $O_2/Cl_2/Ar$ plasma chemistry in a ICP reactor.

Purpose: The aim of this process is the development of etching processes which allow a high quality transfer in patterns with different densities or sizes, and therefore with different residual layer thickness.

Major challenges: A challenge of this process is the reduction of the resist budget which limits the Si depth that can be achieved finally. Indeed a high difference of the residual thickness implies longer etching processes. The fidelity of all the patterns is guaranteed by the anisotropy, but the polymer is still vertically etched in the features whose residual layer is opened first. The resist mask for the following Si etching is therefore reduced.

References:

- [1] N. Chaix, C. Gourgon, C. Perret, S. Landis, T. Leveder, NIL processes on 200 mm Si wafer for optical applications : residual thickness etching anisotropy, J. Vac. Sci. Technol. B 25 (6) (2007) 2346-2351
- [2] N. Chaix, S. Landis, C. Gourgon, S. Merino, V.G. Lambertini, G. Durand, C. Perret, Nanoimprinting lithography on 200 mm wafers for optical applications, Microelectronic Engineering 84 (2007) 880-884


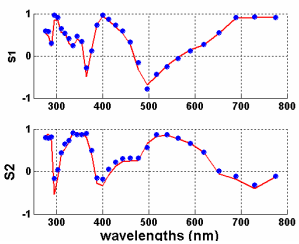
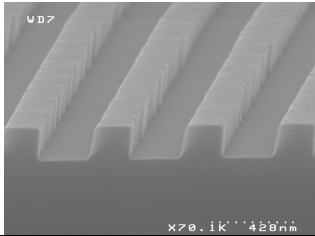
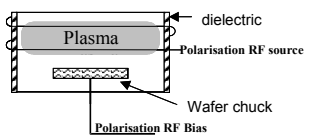
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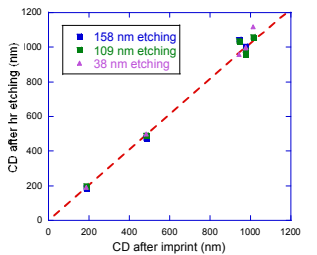
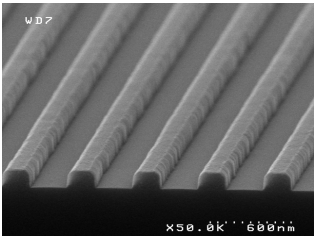
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LoP2007_NIL011_Pattern Transfer Optimization

Pattern transfer optimization

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: imprint		
1.1	Wafers preparation 	200 mm Si wafers Thin film of resist spin-coated on the Si substrate Mold coated with a standard anti-sticking layer Teflon sheet to improve the printing uniformity	
1.2	Imprint process	EVG®520HE 40 kN, 120°C, 5 minutes	
	End of Process 1		
2.0	Process 2: residual thickness (hr) measurement		
2.1	Ellipsometry for scatterometry	Spectroscopic ellipsometer 300 – 800 nm Spot size 40 μm Mapping on the 8" surface	
2.2	Fit of the ellipsometry spectra 	Calculation time determined by the pattern geometries: few seconds for 200 nm dense lines, but few hours for 3D structures	<i>A high accuracy measurement of $n(\lambda)$ and $k(\lambda)$ has to be performed before.</i> <i>Limitation : homogeneous pattern gratings with standard geometries</i>
2.3	SEM characterization 	Top-down SEM for pattern quality and homogeneity control, or cross-section SEM Line width: 209 nm	<i>test wafer needed if cross-section measurement</i>
	End of Process 2		
3.0	Process 3: hr etching		
3.1	Loading of the imprinted wafer	Platform 5200 from applied Materials, DPS ICP reactor	
3.2	Etching process 	O₂/Cl₂/Ar plasma O ₂ : 30 sccm, Cl ₂ : 40sccm, Ar:30sccm Pressure 10 mTorr Source power: 500 W Bias power: 60 W for NEB22 resist	<i>The anisotropy is mostly dependent on the bias power. Some resists, which are less resistant, require lower bias, and this limits the anisotropy control.</i>

<p>3.3</p>	<p>process control</p>  	<p>SEM and scatterometry to measure the pattern size after the hr etching and compare it to the imprinted one</p> <p>Line width: 202 nm</p>	
	<p>End of Process 3</p>		
	<p>End of Total Process</p>		

3.11 Liquid Transfer Imprint Lithography (LTIL)

Imprint process for rough and nonflat surfaces with an improved filling behaviour

Process: resist coating and UV-imprint

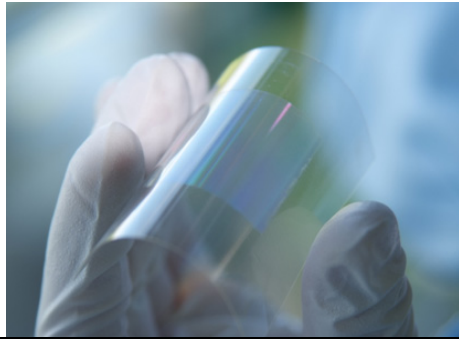


Figure:
Plastic foils with resist grating.

Application:
Imprint over massive topography especially on all kinds of substrates (like plastic foil) where resist cannot be spin coated or dispensed upon.

Keywords: UV-NIL, surface coating, conformal imprinting on topography

Partner: AMO GmbH

Address: 52074 Aachen, Germany

Web-Address: [http:// www.amo.de](http://www.amo.de)

Process: LTIL

Responsible: J.W. Kim

E-mail: kim@amo.de

Process description: This process is used to imprint over massive topography especially on all kinds of substrates (like plastic foil) where resist cannot be spin coated or dispensed upon. The stamp is coated using an inking wafer that can be coated using standard processes as spin coating or dispensing. During a contact step with a soft stamp (PDMS/PFPE, etc.) resist fills up the pattern on the stamp. Then the stamp is peeled off from the inking substrate thereby splitting the liquid resist layer in half. The coated stamp can then be set down on the target substrate that may have massive roughness (like mc-Si-wafers) or structures (like lens arrays or blazed gratings) on its surface. The soft imprint stamp conformal envelopes the structures and sets down the patterned resist layer that is cured by UV-light after conformal contact between substrate and stamp is achieved.

Purpose: Imprint process for very rough and uneven surfaces, especially where spin-coating or dispensing are not suited. The process also improves pattern filling and residual resist uniformity.

Major challenges: The stamp material must be adapted in modulus to conformal contact different topographies.

Application and state-of-the-art: Fine tuning of optics, imprint and coating on massive topography.

References:

- [1] N. Koo, J.W. Kim, M. Otto, C. Moormann, and H. Kurz , Liquid transfer imprint lithography: A new route to residual layer thickness control, J. Vac. Sci. Technol. B **29** (2011) 06FC12 (4 pages), <http://dx.doi.org/10.1116/1.3660792>




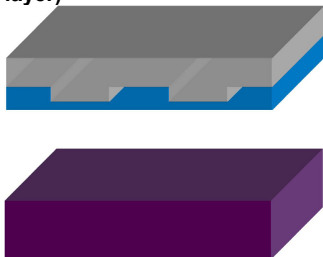
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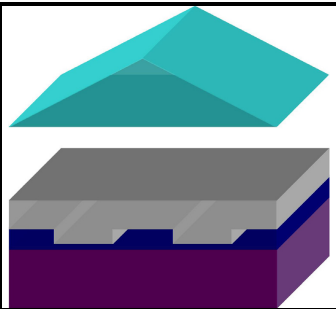
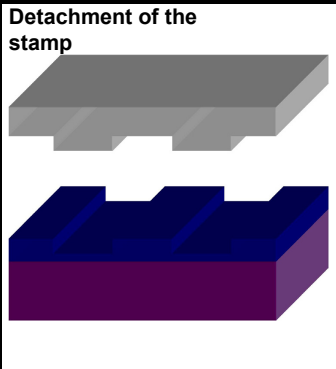
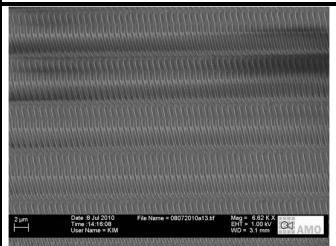
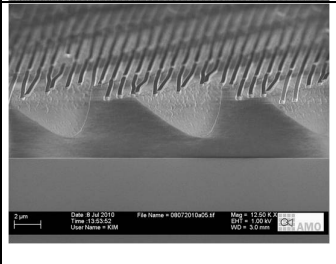
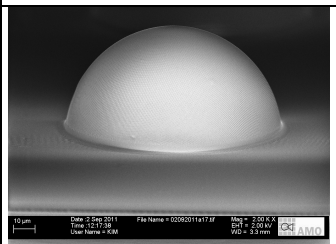
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52074 Aachen
Germany

LoP2012_NIL014_LTIL-process.

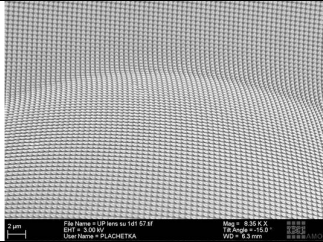
Liquid Transfer Imprint Lithography (LTIL)

Process: resist coating and UV-imprint

	Process	Technical Parameters	Remarks
	LTIL-process	how it should work	critical issues
1.1	Preparation of inking substrate 	-standard Si substrate -spin coating of UV-sensitive resist (AMONIL) onto substrate	
1.2	Conformal contact with soft stamp for resist transfer 	-Polymeric soft stamp (PDMS/PFPE, etc.) is pressed into liquid resist -conformal contact on flat inking substrate is achieved -structures are completely filled	
1.3	Splitting of resist layer 	-soft stamp is peeled off from the surface -liquid resist layer is split in half -filling stays the same	
1.4	Resist Transfer (homogeneous layer) 	-stamp with liquid resist layer is moved to target substrate (may have massive topography)	
1.5	Imprinting on target substrate and UV-exposure	-inked stamp is set down on target substrate -conformal contact is forced (pressure depends on topography) -resist is cured via UV-exposure	

			
<p>1.6</p>	<p>Detachment of the stamp</p> 	<ul style="list-style-type: none"> -polymeric stamp is removed from the cured resist layer -residual layer thickness is thinner and more uniform than with normal Soft UV-NIL [1] -Structure fidelity is improved 	
End of Process			
<p>2.0</p>	Process results		
<p>2.1</p>		<p>Top down view on μ-sized blazed grating with imprinted nanograting on top</p>	
<p>2.2</p>		<p>Cross section of μ-sized blazed grating with imprinted nanograting on top</p>	
<p>2.3</p>		<p>Lens with 100μm diameter and imprinted nanopillars on top</p>	

2.4



Close-up of nanopillars on surface of 100µm diameter lens

General remarks:

The process is used to imprint onto substrates that cannot be used for spin coating or dispensing due to substrate mechanical instability (thin plastic foils) or nonflat surfaces with massive topography (like lens arrays, blazed gratings, mc-Si-wafers, etc.).

3.12 Nanoimprinting of hydrogels

UV and Thermal imprinting of hydrogels

Process: Thermal and UV-nanoimprint lithography

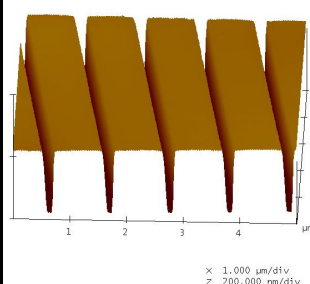


Figure:
AFM image of 250nm
PEGDMA nanoimprinted by
UV-NIL

Process:
UV and Thermal Nanoimprint

Application:
Biosensing, reconfigurable sur-
faces, lenses.

Keywords: thermal and UV nanoimprint, hydrogel

Project leader: TECNALIA

Address: Pº Mikeletegi 2, 20009 San Sebastian, Spain

Web-Address: www.tecnalia.com

Process: UV-NIL

Responsible: Isabel Obieta

E-mail: isabel.obieta@tecnalia.com

Partner: Catalan Institute of Nanotechnology

Address: 08193 Bellaterra (Barcelona), Spain

Web-Address: <http://www.icn.cat>

Process: Step and Repeat NIL

Responsible: Achille Francone

E-mail: achille.francone@icn.cat

Process description: Fabrication of 3D nanopatterns on hydrogels

Purpose: The aim of this process is to obtain 3D nanopatterns in different hydrogels

Major challenges: The material does not easily fill in the cavities

Application and state-of-the-art: Currently patterns below 50nm have been demonstrated and 3D nanostructures have been obtained

References (mainly on antiadhesive coatings):

- [1] A. Z. Khokhar, A. Gaston, I. Obieta et al., Compact LED based nanoimprinter for UV-NIL, Microelectron. Eng. 88(11) (2011) 3347-3352, DOI: 10.1016/j.mee.2011.06.023
- [2] A. Gaston, A.Z. Khokhar, L. Bilbao et al., Nanopatterned UV curable hydrogels for biomedical applications, Microelectron. Eng. 87(5-8) (2010) 1057-1061, DOI: 10.1016/j.mee.2009.11.089



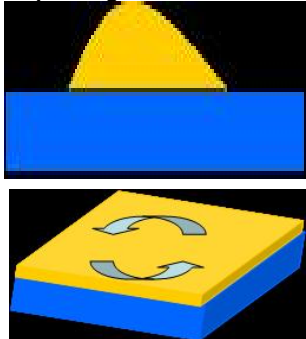
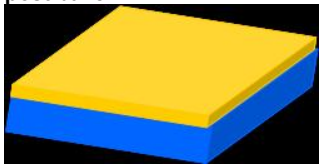

Contact information

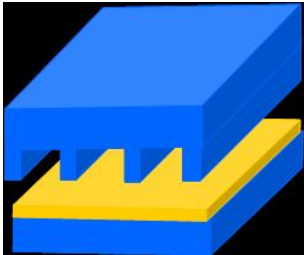
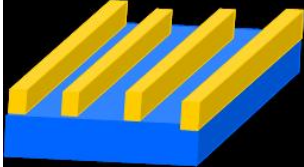
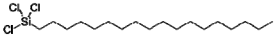
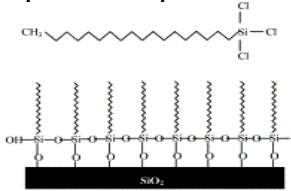
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20009 San Sebastian, SPAIN

LoP2012_NIL015_Hydrogel imprint-process

Nanoimprinting of hydrogels

Process: UV and thermal nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Wafer preparation	Silicon wafer format	
1.1	wafer selection and preparation	standard SiO ₂ substrate	
1.2	substrate preparation 	pretreatment TPM (3-trichlorosilyl propyl methacrylate) coating	<i>In samples without TPM treatment, hydrogel layer peels off the substrate when it swells</i>
	End of Process 1		
2.0	Process 2: Resist coating	for UV - NIL	
2.1	Hydrogel concentration 	Hydrogel dilution in order to get thin homogeneous layers Depending on the hydrogel formulation.	<i>Less concentration than P30 (30%w) does not get uniform layers.</i>
2.2	dispensing of resist 	DROP DISPENSING or SPINNER	
2.3	post bake 	solvent evaporation Not necessary	
	End of Process 2		
3.0	Process 3: Lithography	UV-NIL	
3.1	Stamp 	Stamp characteristics It works with soft and hard stamps	

<p>3.2</p>	<p>Pattern definition</p> 	<p>NIL protocol Pressure applied: depend on the stamp geometry.</p> <ul style="list-style-type: none"> • For 2D structures <1bar • For 3D structures >3bars <p>Time of exposure:600seg (wavelength 365nm -- 13mJ/cm²)</p>	
<p>3.3</p>	<p>Resist development</p> 	<p>Residual layer etch. The residual layer is etched by RIE, using a combination of gases:Ar (1sccm) – O₂(5sccm) 100W and 40mtorr</p>	
<p>End of Process 3</p>			
<p>4.0</p>	<p>Process 4: Anti-adhesive coating</p>	<p>surface treatment</p>	
<p>4.1</p>	<p>Preparation of stamp surface</p>	<p>Surface activation Not necessary</p>	
<p>4.2</p>	<p>Solution preparation</p> 	<p>OTS solution Prepare a solution 100:1 of octadecyltrichlorosilane molecules in hexane. The preparation of the solution and the surface treatment have to be performed in an atmosphere with low content of humidity.</p>	<p><i>Other SAMs work worse than OTS.</i></p>
<p>4.3</p>	<p>Dip of the stamp</p> 	<p>The stamp is dipped into the silane solution for 5-8minutes. Afther that, rinse the stamp with hexane and then DI water.</p>	
<p>End of Process:4</p>			
<p>End of Total Process</p>			

4. Applications and Processes for Upscaling

Contributions to this section of the library are from

VTT Information Technology - Finland

Dr. Tapio Mäkelä / Dr. Tomi Haatainen /
Päivi Majander / Prof. Dr. Jouni Ahopelto

ICN - Barcelona/Spain

Dr. Vincent Reboud / Dr. Nikolaos Kehagias /
Dr. Timothy Kehoe / Achille Francone /
Prof. Dr. Clivia Sotomayor-Torres

AMO GmbH - Aachen/Germany

Dr. Ulrich Plachetka

LTM-CNRS - Grenoble/France

Dr. Cécile Gourgon

DTU - Lyngby/Denmark

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Dr. Morten Bo Mikkelsen

**CNRS/Saint-Gobain, Unité Mixte
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Dr. Elin Søndergård / Dr. Jeremie Teisseire

CRF Fiat - Orbassano/Italy

Dr. Vito Lambertini

PSI/LMN - Villigen/Switzerland

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Christian Spreu / Konrad Vogelsang

IOM-CNR - Trieste/Italy

Dr. Massimo Tormen / Dr. Gianluca Greci

**University of Glasgow - Glasgow/United
Kingdom**

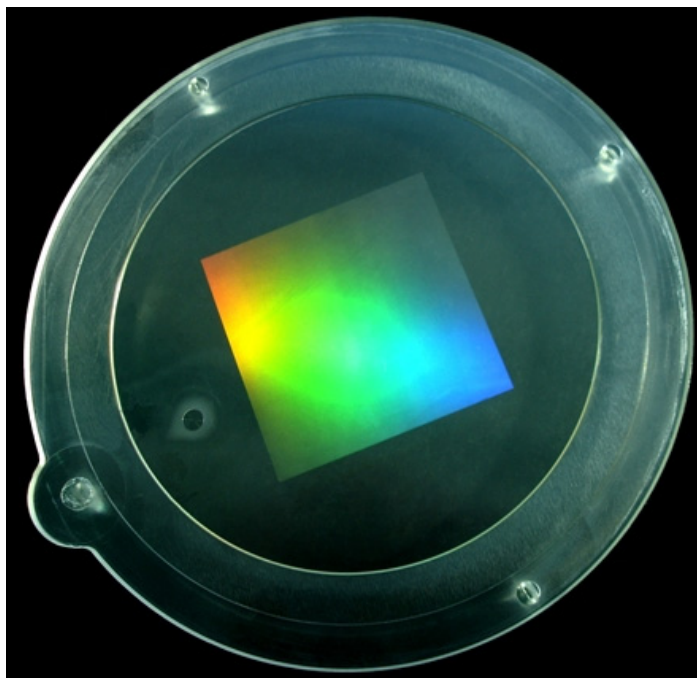
Dr. Nikolaj Gadegaard / Dr. Mathis Riehle /
Dr. Kris Seunarine /
Prof. Dr. Christopher Wilkinson

Modilis Oy - Helsinki/Finland

Kari Rinko / Tero Tuohioja

Tecnalia – Donostia-San Sebastian/Spain

Dr. Isabel Obieta



4.1 Double side patterned OLED

Fabrication of OLED device with double side patterned substrate

Process: nanoimprint lithography

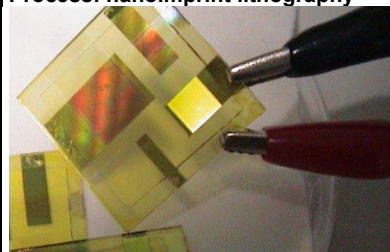


Figure:

Organic light emitting device with both side nanopatterned surfaces with squared shape (resolution 1 μm and height 300 nm).

Process:

OLED device fabrication on double side UV nanoimprinted substrate.

Application:

Lighting systems and displays.

Keywords: OLED, UV nanoimprint

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Web-Address: www.crf.it

Process: OLED fabrication
Responsible: Vito Lambertini
E-mail: vitoguido.lambertini@crf.it

Process description: A process is described to fabricate a light emitting devices based on organic materials deposited by spin coating onto a double side nanopatterned substrate. The process described for the double side patterning is UV nanoimprinting.

Purpose: The aim of this process is demonstrate the increasing of efficiency more than 50% introducing low cost nanostructured surfaces enhancing the light extraction.

Major challenges: Anti-sticking treatments and deposition of ITO on plastic materials.

Application and state-of-the-art: the structuring of OLED device has been proposed in several work mainly based on microstructuring. Only in the last 2 years the introduction of sub-wavelength patterns has been proposed.

References:

- [1] Improvement of the external extraction efficiency of OLED by using a pyramid array, Stanley Electric Co., Ltd. (Japan)
- [2] Nanohole OLEDs embedded in the 2D periodic SiO₂ nanohole array. Yoon-Chang Kim R&DCenter, Samsung SDI Co. Ltd., Young Rag Do Dep. of Chemistry, Kookmin Un., Seoul, 2005 Optical Society of America.

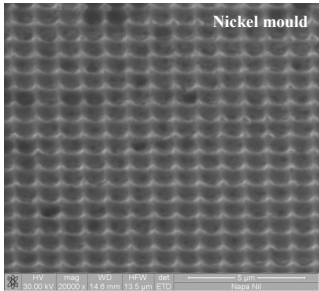
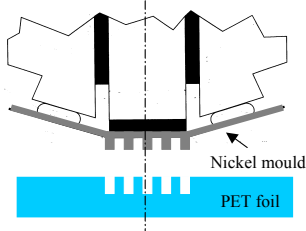
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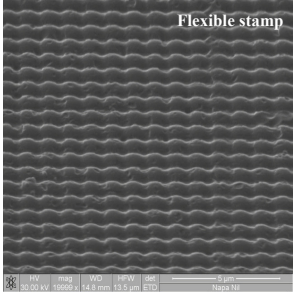
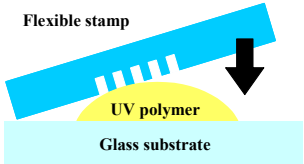
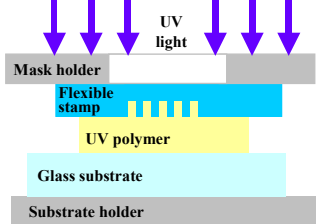
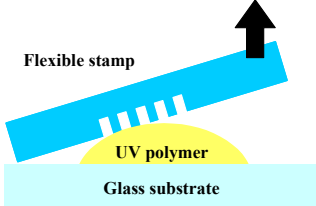
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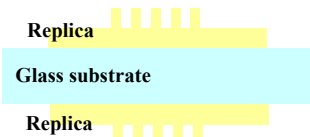
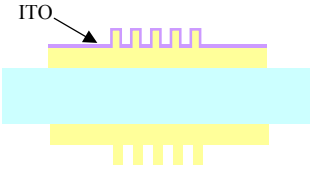
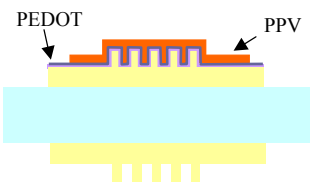
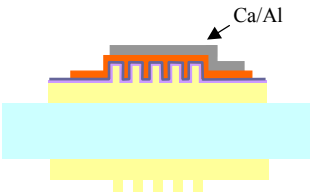
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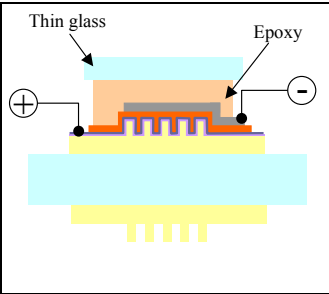
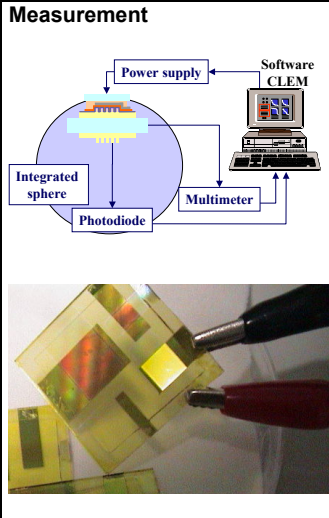
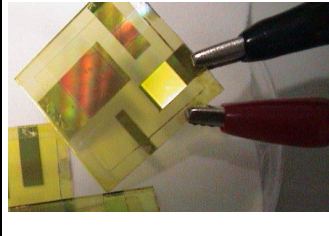
Double side patterned OLED

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Substrate preparation		
1.1	wafer selection and preparation	transparent substrate Glass substrate 35x45 mm Thickness 1 mm	
1.2	substrate preparation	Cleaning washing in Micro90 solution diluted (2%); ultrasonic baths cycles (5 min) in water and ethanol	
1.3	adhesive coating	treatment spin coating of MICROPOSIT or AP300 followed by 80°C for 2 min.	
	End of Process 1		
2.0	Process 2: Flexible stamp preparation		
2.1	Layout	Functional structures the stamp consist of: nickel mould squared pattern height 300 nm period 1 µm wafer selection 100 µm sheet PET	
			
2.2	stamp preparation	Hot embossing JRP recombiner machine: Nickel shim thickness 50 µm; Shim dimensions 30x40 mm; Heating time 0.5 s Cooling time 10 s DC current 80 A Pressure 1.4 tons	
			

<p>2.3</p>	<p>Process control</p> 	<p>SEM</p>	
<p>2.4</p>	<p>antiadhesive coating</p>	<p>silane saturation chamber 1 min</p>	
<p>End of Process 2</p>			
<p>3.0</p>	<p>Process 3: Double UV imprinting</p>		
<p>3.1</p>	<p>UV resin casting</p> 	<p>UV polymers: UV acrylates (bisphenol-A-diglycidyl-ether-diacrylates BGEDA, bi-functional acrylates EBECRYL 210, 270, 600); organic modified alkoxy silanes (OrmoClad).</p>	<p><i>No bubbles formation during flexible stamp positioning.</i></p> <p><i>OrmoClad is a commercially available hybrid polymer for optical waveguide fabrication (see Page 37 and www.microresist.com)</i></p>
<p>3.2</p>	<p>UV curing</p> 	<p>EVG620 mask aligner stack pre-assembled before UV exposition outside the machine. Exposition time 10 s.</p>	
<p>3.3</p>	<p>Demolding</p> 	<p>Manual demolding HEX03 (PSI) demolding manually by peeling the flexible stamps.</p>	

3.4	 <p>Replica Glass substrate Replica</p>	Repeat processes form 2.1 to 2.3 to get the second side patterned.	The process can be done in a single UV exposition using a stack composed by 2 flexible stamps.
End of Process 3			
4.0 Process 4: OLED fabrication			
4.1	Anode deposition  <p>ITO</p>	DC/RF sputtering system Target: Indium-tine oxide 10-90 (Lesker) 2 inches Vacuum 5×10^{-3} mbarr Current 300 mA	<i>Rotating sample holder to increase homogeneity; Alternating on/off of plasma to avoid overheating of the polymer layer.</i>
4.1	Process control	Profilometer Thickness 250 nm UV/Vis spectra Transmittance 75% Multimeter Resistance 100 W/	
4.2	Active layers deposition  <p>PEDOT PPV</p>	Spin coating SÜSS RC8 spin coater Double layer: PEDOT/PSS suspension (Bayer) no vacuum 2500 rpm 5000 rpm/s 20-40 nm PPVs (yellow/orange from Merck) no vacuum 2000-2500 rpm 5000 rpm/s 75-90 nm	
4.3	Cathode deposition  <p>Ca/Al</p>	Thermal vacuum evaporation AUTO306 coater Double layer: Ca Vacuum 9×10^{-6} mbarr 20-40 nm Al (capping layer) Vacuum 9×10^{-6} mbarr 20-40 nm	
3.4	Packaging	Epoxy resin casting The liquid epoxy resin (UV or thermal) is placed directly onto the cathode and a thin glass (microscope glass) is used to close the device. The curing is made:	<i>The contact of the device with oxygen degrades the device quickly; the oxygen exposition time has to be reduced as much as possible. The ideal</i>

		<p>Thermal Tamb 2 hours UV (spot light) : 60 mW/cm² 10 s</p>	<p><i>condition is to use a glove box.</i></p>
<p>4.5</p>	<p>Measurement</p>  	<p>Electro-optical analysis I/V curves Efficiency curves (Lm/W) Software CLEM (CRF): power supply HP3432A multimeter HP34401 photodiode/integrated sphere IL1700</p> <p>Characterization devices: four square shapes with different area (4, 16, 36,100 mm²)</p>	
	<p>End of Process 4</p>		
	<p>End of Total Process</p>		

General remarks:

The architectures of devices with double side nanoimprinted glass substrates showed an increasing of external efficiency in OLED technology is in the range of 65-70%.

4.2 Optical grating by step&stamp NIL

Fabrication of periodical optical structures by step&stamp NIL

Process: Nanoimprint lithography



Figure:
Imprinted 180nm grat-
ing in 300 nm thick
mr-I 7030 resist.

Process: Thermal SSIL to pat-
tern thermoplastic polymer using
Nano imprinting Stepper.

Application:
Optical grating

Keywords: thermal nanoimprint, Step&Stamp, SSIL

Project leader: VTT Technical Research Centre of Finland
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Web-Address: <http://www.vtt.fi>

Process: Step&stamp NIL
Responsible: Tomi Haatainen
E-mail: tomi.haatainen@vtt.fi

Partner: S.E.T. SAS (Smart Equipment Technology)
Address: 74490 Saint Jeoire, France
Web-Address: <http://www.set-sas.fr>

Process: NPS300 Step&stamp Tool
Responsible: Gilbert Lecarpentier
E-mail: glecarpentier@set-sas.fr

Process description: This document contains a description of a general thermal imprint process for fabrication of periodical structures using sequential imprinting to pattern large areas. the parameters are valid for small stamps (< 5x5 mm²) and submicron scale features.

Purpose: The aim of this process is transfer periodical structures of stamp into thermoplastic polymer which can be used as an etch mask, lift-off or a mold for fabrication of metal templates by electroplating.

Major challenges: Uniformity of residual layer on the large substrates due to waviness and wedging of the stamp in the single imprints.

Application and state-of-the-art: Anti-reflection gratings etc.

References:

- [1] T. Haatainen, J. Ahopelto, G. Grueztner, M. Fink, K. Pfeiffer, Step & stamp imprint lithography using a commercial flip chip bonder, Emerging Lithographic Technologies IV, Proceedings of SPIE, Vol. **3997**. SPIE-The International Society for Optical Engineering (2000), 874 – 880.
- [2] T. Haatainen; J. Ahopelto, Pattern Transfer using Step&Stamp Imprint Lithography, Physica Scripta. Vol. **67** (2003) No: 4, 357 – 360.

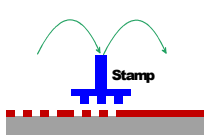
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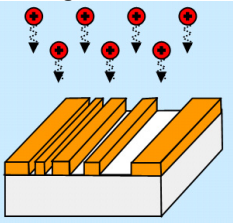
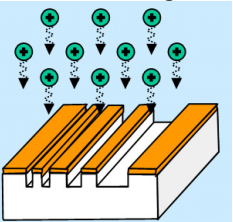
VTT Technical Research Centre of Finland
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LoP2007_NIL007_Step and Stamp NIL for optical gratings

Optical grating by step&stamp NIL

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Wafer preparation		
1.1	wafer selection and preparation	standard Si substrate Si substrate, 4", <100>, d=525 μm one side polished	<i>Substrates up to 200 mm can be patterned by SSIL using NPS300</i>
1.2	substrate preparation	oxidation RCA clean (Caros Acid)	
	End of Process 1		
2.0	Process 1: Stamp preparation		
2.1	layout	Functional structures the stamp consist of grating structure (linewidth <1μm)	
2.2	stamp preparation	Stamp attachment Stamp is glued to SiC-plate with silicone adhesive	<i>Thermally conductive adhesive must be used to ensure the stamp heating</i>
2.3	antiadhesive coating	silane CVD evaporation clean or silane vapour	<i>CVD evaporation preferred if available</i>
	End of Process 2		
3.0	Process 3: Lithography		
3.1	coating of layer 1 (NIL layer)	spincoating no priming mr-I 7000 series @3000 rpm bake 3 min at 140 °C (hotplate)	<i>The thermoplastic polymer mr-I 7000R with excellent flow ability and high resolution capabilities.</i>
3.3	Nanoimprint Lithography 	SET NPS300 temperature.(stamp).....140°C temperature (chuck).....70°C pressure.....(>10MPa) heating time (60-140°C)..10s cooling time (140-60°C)..60s hold time (140°C).....2min overall time.....20 min temperature.(demold)....60-65°C residual polymer thickness in grooves 10-20 nm	<i>SET is a former branch of the SÜSS company in Annecy, France</i>
3.4	process control	AFM, SEM	<i>Imprint depth measured by AFM</i>
	End of Process 3		

3.0	Process 3: Pattern Transfer		
3.1	Residual Layer (Breakthrough) Etching 	O2 RIE: O ₂40 sccm gas pressure 125 mtorr power 150 W time 5 sec temperature 300 K	<i>Plasmalab 80Plus RIE</i>
3.2	process control	AFM	<i>Before substrate etching residual removal confirmed by AFM</i>
3.3	substrate etching 	CF4+Ar RIE CF ₄20 sccm Ar.....5 sccm gas pressure....20 mTorr power.....100 W time..... temperature.....300K	<i>Plasmalab 80Plus RIE Selectivity Si:Resist(1:1.6) Etch rate (Si)=40 nm/min</i>
3.4	process control	optical microscope 100 x	
3.5	process control	Ellipsometer	<i>Resist thickness check</i>
3.6	measurement	AFM,SEM	
3.6	measurement	SEM LION video prints No.	
	End of Process 3		
	End of Total Process		

General remarks:

This process using mr-I 7000 series resist (by *micro resist technology* GmbH) is following the step & repeat thermal NIL process for master enlargement described in 1.2. *Step&repeat thermal NIL process with NPS300* on Page 77.

4.3 Photonic crystals for enhanced light extraction

Fabrication of nanoimprinted photonic crystals for light extraction enhancement via surface plasmons

Process: nanoimprint lithography

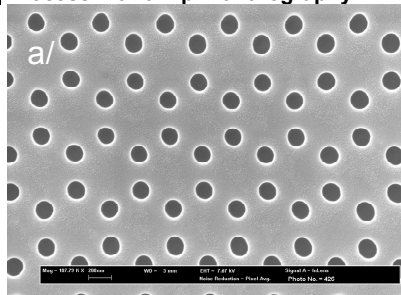


Figure: a) Scanning electron micrograph of a nanoimprinted two-dimensional PhC with a 380 nm lattice constant honeycomb array of holes (holes depth 350 nm), b) cross-section schematic of the studied system.

Process: A thermal NIL process is used to replicate the 2D periodic Si stamp in a dye-doped polymer. The dye-doped polymer is composed of rhodamine 6G directly dissolved in a printable polymer. The metallic substrates used have 50 nm thick layers of gold, aluminium and silver deposited by thermal evaporation on quartz substrates.

Application:
Light extraction applications (LEDs, OLEDs)

Keywords: thermal nanoimprint, photonic crystal, surface plasmon, light extraction

Project leader: Tyndall National Institute
Address: Lee Maltings, Prospect Row, Cork, Ireland
Web-Address: <http://www.tyndall.ie>

Process: Thermal nanoimprint
Responsible: C.M. Sotomayor Torres
E-mail:

Process description: A process is described for two-dimensional nanoimprinted polymer photonic crystal coupled to surface plasmons. A stamp with different lattice constant PhCs was fabricated in a silicon wafer by using electron-beam lithography and dry etching. A thermal NIL process is used to replicate these 2D periodic patterns in a dye-doped polymer.

Purpose: The aim of this process is to provide a method to enhance the photoluminescence of dye chromophores-loaded by coupling the emission to surface plasmons in nanoimprinted photonic crystals.

Major challenges: The major challenge in this process is to control clusters formation on the metallic film to allow the matching of the surface plasmon resonance wavelength with the emission wavelength of the dyes

Application and state-of-the-art: The combination of surface plasmons and nanoimprinted structures in an active layer can lead to a new class of cost effective and high efficiency OLEDs. Furthermore, the metallic surface could be used as an electrical contact.

References:

- [1] V. Reboud, N. Kehagias, M. Zelsmann, M. Fink, F. Reuther, G. Gruetzner and C. M. Sotomayor Torres, *Photoluminescence enhancement in nanoimprinted photonic crystals and coupled surface plasmons*, Optics Express, 15, 12, 7190, 2007.

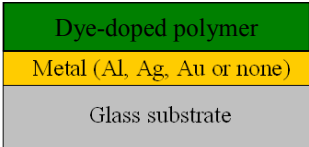
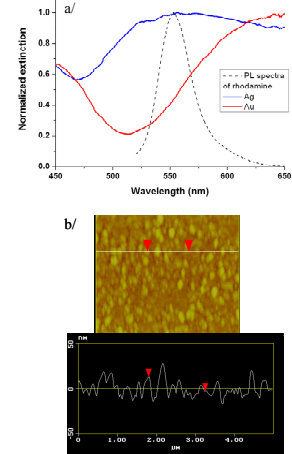
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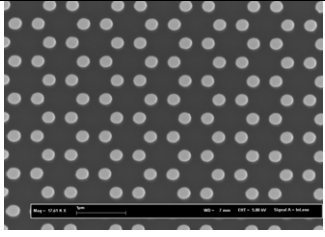
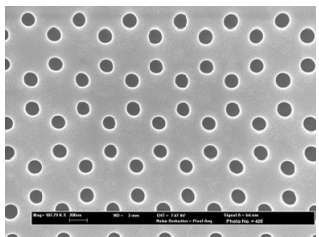
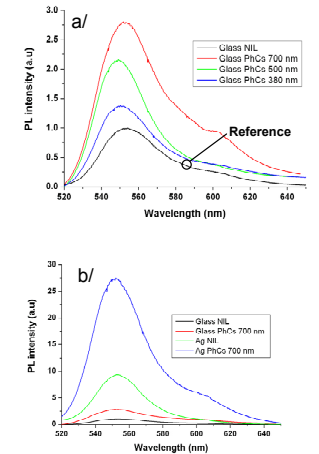
Prof. Dr. Clivia M. Sotomayor Torres
ICREA Research Professor
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Campus Bellaterra - Edifici CM3
08193 Bellaterra (Barcelona), SPAIN

LoP2007_NIL008_photonic crystals

Photonic crystals for enhanced light extraction

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Wafer preparation		
1.1	wafer selection and preparation	Standard glass or Pyrex substrate	
1.2	substrate preparation 	no pre-treatment of the substrate Evaporation of metal films deposited using NFC 2000 Temescal 6 kW electron beam guns with a deposition rate of 10 Angstroms per second. A 400 nm thick layer of this modified polymer is spun on substrates.	<i>The dye-doped polymer is composed of rhodamine 6G (from Sigma Aldrich) directly dissolved in an imprintable resist mr-NIL 6000 from micro resist technology GmbH (see description below).</i>
1.3	Process control 	Figure: a/ Normalized extinction spectra of the different used substrates, presenting the surface plasmon wavelength tunability. b/ right upper image: AFM images (5 x 5 μm ²) of a 50 nm thick Ag evaporated on quartz substrate, (black inset: the depth profile along the white line). To determine the plasmon resonance frequencies of the different substrates, normalized extinction spectra were measured.	The second advantage in using silver islands films apart from the tunability of the SP resonance wavelength is that the non-negligible surface roughness scatters the SP modes to radiated light.
End of Process 1			
2.0	Process 1: Stamp preparation		
2.1	layout	Functional structures The stamp consists of 10 arrays of pillars (350 nm height) on an area of 100x100 mm ² with a 100 mm pitch between arrays. The size of the Si is 2x2 cm ² .	
2.2	stamp preparation	wafer selection The stamp was fabricated in a silicon wafer by using electron-beam lithography and dry etching (for details, see introduction of this process).	

			
<p>2.3</p>	<p>Anti-adhesive coating</p>	<p>The silicon stamp is treated with a self-assembled anti-adhesive monolayer (tridecafluoro-1, 1, 2, 2-tetrahydrooctyl trichlorosilane deposited in vapour phase).</p>	
<p>End of Process 2</p>			
<p>3.0</p>	<p>Process 3: Nanoimprint Lithography</p>		
<p>3.1</p>	<p>Process control : SEM top-view of the nanoimprinted photonic crystals</p> 	<p>The stamp and the coated substrates are pressed together in a 2.5 inch <i>Obducat</i> nanoimprinter at 60 bar for 5 min at 90 °C. The pressure is sustained during the cooling phase until the temperature fell below 35 °C.</p>	
<p>2.2</p>	<p>Measurement: Optical characterization</p> 	<p>Figure: a/ Photoluminescence spectra of a nanoimprinted unpatterned dye-doped polymer film on a quartz substrate (black line), of a 2D photonic crystal with a 380 nm lattice constant (blue line), with a 500 nm lattice (green line) and with a 700 nm lattice (red line), b/ photoluminescence spectra of a flat surface imprinted on a quartz substrate (black line), of a 2D photonic crystal with a 700 nm lattice constant imprinted on a 50 nm Ag quartz substrate (blue line), of a 2D photonic crystal with a 700 nm lattice constant imprinted on a quartz substrate (red line), of a nanoimprinted unpatterned dye-doped polymer film on a 50 nm Ag quartz substrate (green line).</p>	
<p>End of Process 3</p>			
<p>End of Total Process</p>			

General remarks:

Process description: A process is described for two-dimensional nanoimprinted polymer photonic crystal coupled to surface plasmons. A stamp with different lattice constant PhCs was fabricated in a silicon wafer by using electron-beam lithography and dry etching. The electron-beam exposure was carried out on a Jeol 6000 equipment with a dose of $130 \mu\text{C}/\text{cm}^2$ under a beam current of 100 pA on single layer of a ZEP 520 resist (positive tone resist from *Zeon Corporation*). Development is carried out during 30 sec in a solution of ZED N50 (*Zeon Corporation*). The silicon stamp is then etched to a depth of 350 nm by inductively coupled plasma etching and treated with a self-assembled anti-adhesive monolayer (tridecafluoro-1, 1, 2, 2-tetrahydrooctyl trichlorosilane deposited in vapour phase). A thermal NIL process is used to replicate these 2D periodic patterns in a dye-doped polymer. The dye-doped polymer is composed of rhodamine 6G (from *Sigma Aldrich*) directly dissolved with a concentration of 5×10^{-4} mol/L in a printable polymer (mr-NIL 6000 from *micro resist technology GmbH*), which is optically transparent in the visible range. A 400 nm thick layer of this modified polymer is spun on a quartz wafer and on metal-coated quartz wafers and baked at 60 °C for 10 min before the NIL process. The stamp and the coated substrates are pressed together in a 2.5 inch *Obducat* nanoimprinter at 60 bar for 5 min at 90 °C. The pressure is sustained during the cooling phase until the temperature fell below 35 °C. The metal films were deposited using NFC 2000 Temescal 6 kW electron beam guns with a deposition rate of 10 Angstroms per second. The control of the deposition rate allows the tuning of the surface plasmon frequency of the film throughout the visible.

Purpose: The aim of this process is to provide a method to enhance the photoluminescence of dye chromophores-loaded by coupling the emission to surface plasmons in nanoimprinted photonic crystals. Two critical research issues in organic optoelectronics are to reduce the cost of organic LEDs and to improve their external efficiency. One approach to improve the extraction efficiency is to use two-dimensional (2D) photonic crystals (PhCs). A PhC structure enhances the light emitted from the active layer by slowing the propagation speed of the photons, thus increasing the coupling to the out-of-plane radiative modes. Another approach is to increase the spontaneous recombination rate of the emitters. This can be based on the energy transfer between light emitters and surface plasmons (SPs).

Major challenges: The major challenge in this process is to control clusters formation on the metallic film to allow the matching of the surface plasmon resonance wavelength with the emission wavelength of the dyes

Application and state-of-the-art: The two approaches mentioned above have been combined to enhance the light-emission efficiency of organic thin films. An active polymer film deposited on a metal surface is patterned by NIL and the SP energy is matched to that of the emitter in the PhC, reaching up to a x 27 enhancement. Our results indicate that nanoimprint lithography is a well suited process to fabricate these challenging photonic structures and that the combination of surface plasmons and nanoimprinted structures in an active layer can lead to a new class of cost effective and high efficiency OLEDs. Furthermore, the metallic surface could be used as an electrical contact.

4.4 Refractive microlenses

Fabrication of microlenses and complex refractive surfaces

Process: nanoimprint lithography

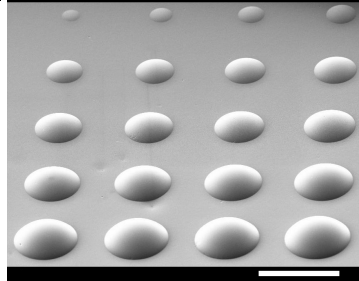


Figure:

Arrays of microlenses with different apertures (same radii of curvature) by polymer casting and UV exposure of SU8 resist. The unit bars correspond to 10 μm .

Process:

Isotropic wet etching of glass with patterned chromium mask. Hot embossing or polymer casting.

Application:

Spherical or cylindrical microlens arrays with full control on radii of curvature and diameter

Keywords: Isotropic wet etching, glass template, hot embossing, polymer casting

Project leader: TASC Laboratory

Address: S.S.14km 163,5;
34012 Basovizza
(Trieste, Italy)

Web-Address: www.tasc-ilm.it

Process: Isotropic wet etching / NIL
Responsible: Massimo Tormen

E-mail: tormen@iom.cnr.it

Process description: A process is described for the fabrication of polymeric arrays of microlenses or more complex systems of lenses (lenses on curved surfaces, arrays of lenses with multiple radii of curvature) by means of a process of wet etching of glass and hot embossing or polymer casting.

Purpose: The aim of this process is to produce large arrays of microlenses with a high control of geometrical parameters of the elements.

Major challenges: Accurate pattern definition in a chromium layer on glass with high etching resistance to concentrated hydrofluoric acid.

Application and state-of-the-art: Research process, light concentrators for CCD elements or photovoltaic cells,

References:

- [1] Massimo Tormen, Alessandro Carpentiero, Enrico Ferrari, Dan Cojoc and Enzo Di Fabrizio, *Novel fabrication method for three-dimensional nanostructuring: an application to micro-optics*, *Nanotechnology* **18**, 385301 (2007).
- [2] Massimo Tormen, Alessandro Carpentiero, Lisa Vaccari, Matteo Altissimo, Enrico Ferrari, Dan Cojoc, Enzo Di Fabrizio, *Fabrication of three-dimensional stamps for embossing techniques by lithographically controlled isotropic wet etching*, *Journal of Vacuum Science and Technology B* **23**, 2920 (2005).



Contact information:

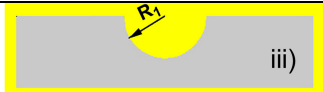
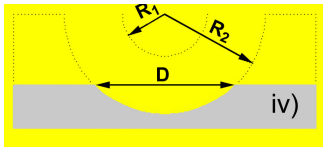
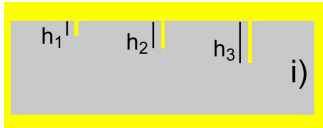
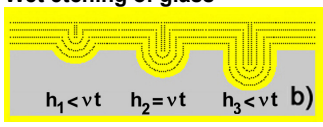
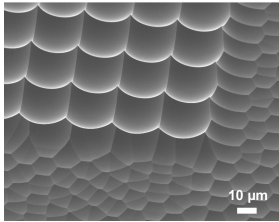
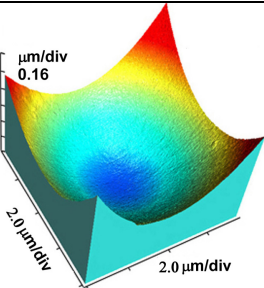
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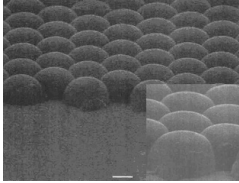
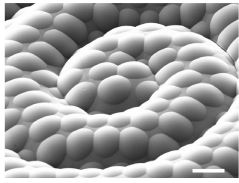
LoP2007_NIL009_Microlenses with spherical molds

Refractive microlenses

Process: nanoimprint lithography

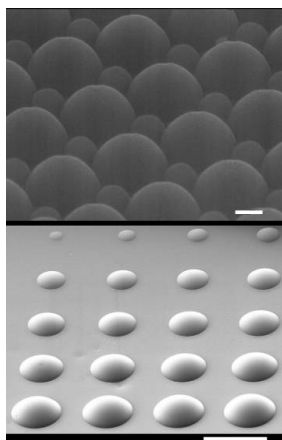
	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0a	Process 1: Stamp preparation First option (a)		
1.1a	Stamp substrate preparation	Sputter coating soda-lime glass with 100 nm chromium film.	Quality of the deposited chromium film, that should not have pin-holes
1.2a	Layout	Functional structures the pattern to be defined consists of dots or lines, corresponding to the centers of curvature of the spherical or cylindrical lenses in the plane of the glass surface.	
1.3a	Pattern definition by lithography	Standard electron beam or UV lithography can be used to define the pattern in a positive tone resist. For instance: Spin-coating 200 nm PMMA, expose exposed to a 30 kV electron beam 200 $\mu\text{C}/\text{cm}^2$ dose and develop developed in MIBK:IPA(1:3). Alternatively, UV lithography can be used for defining the center of curvature of microlenses larger than 5-10 μm	
1.4a	Chromium etching 	Open holes or trenches in the chromium layer by etching in aqueous solution of ammonium cerium (IV) nitrate (0.6 M) and acetic acid (1 M) for 1 min. The resist is stripped in solvents (e.g. acetone)	Loss of resolution due to wet etching of Chromium. The alternative is to use dry etching techniques
1.5a	Wet etching of glass 	Isotropic etching of quartz is performed in aqueous HF (48 wt.%) at room temperature, with an etching rate of $\sim 1\mu\text{m}/\text{min}$. The etching time is adjusted at each etching step in order to produce the required etching depth (=radius of curvature) in the glass substrate. For the etching of structures with fine details, more diluted HF solution (15 wt.%) is used to lower the etching rate to tens of nm/min.	Etching of holes through pin-holes in chromium lead to undesired spherical cavities .
1.6a	Chromium stripping	Stripping the chromium film by etching in aqueous solution of ammonium cerium (IV)	

		nitrate (0.6 M) and acetic acid (1 M) for 1 min.	
1.7a	Second step of wet etching of glass 	<p>Simple geometrical constructions show that for an etching time t_2 after the stripping of the mask, the surface results in a spherical cap with a diameter $D = 2v\sqrt{t_1^2 + 2t_1t_2}$ and radius of curvature $R = v(t_1 + t_2)$, where v is the etching rate.</p>	
1.0b	Process 1: Stamp preparation Second option (b)		
1.1b	Process 1: Stamp substrate preparation	Clean soda-lime glass surface is required as initial substrate.	
1.2b	Focused ion beam 	Holes are milled at different depths in a quartz substrate by focused ion (Ga+) beam at 30 KeV. Centers of curvature can be located at different coordinates (x,y,z), below the glass surface.	
1.3b	Wet etching of glass 	Different diameter (same radius of curvature) are obtained as a function of the height of the milled holes.	
1.8a and 1.4b	Process control: SEM, AFM 		
2.0	Process 2: Coating for anti-adhesion		
2.1	Coating with a hydrophobic monolayer of dodecyltrichlorosilane	<p>The glass stamp is immersed for 10min in freshly prepared solution of $H_2O_2:H_2SO_4$ (1:4). Dodecyltrichlorosilane 1-5 mM in toluene is prepared in glovebox under nitrogen atmosphere.</p> <p>The stamp is dip for 1-2 hours in the solution.</p> <p>Rinse in toluene before taking into air atmosphere</p>	<p>Safety precaution: pour H_2SO_4 into a beaker with H_2O_2, not vice-versa.</p>

3.0	Process 3: Embossing or polymer casting		
3.1	<p>Different option for producing plastic microlenses.</p> <p>nanoimprinting hot embossing polymer casting</p>  <p>Nanoimprinting in PMMA</p>  <p>Hot embossing into Zeonex (see reference [1] and [2] for more details).</p>	<p>Glass templates fabricated according to the processes outlined above can be used to microstructure a large selection of materials with various processes such as nanoimprint, hot embossing or casting processes with different polymers.</p> <p>Nanoimprinting of relatively thick (>5 μm) polymethylmetacrylate (PMMA) films on silicon can be carried out at 210 °C at a pressure of 5 MPa.</p> <p>Hot embossing of pellets of the polyolefin ZEONEX (Zeon Chemicals) can done at 160-190 °C at a pressure of 2-10 MPa, to produce 50-100 μm thick polymer sheets with one or both patterned surfaces.</p> <p>PDMS precursor can be cast on the template and baked can Examples of optics produced with these methods are shown in figure on the left.</p>	<p>Possible trapping of air in the cavities, leading to defects in hot embossed microlenses.</p> <p>Vacuum is helpful in removing defects created by air inclusion.</p>
End of Process 3			
End of Total Process			

General remarks:

Arrays of microlenses with two different radii of curvature hot embossed in PMMA (above) and arrays of microlenses with different apertures (same radii of curvature) by polymer casting and UV exposure of SU8 resist. The unit bars correspond to 10 μm.



4.5 Biodegradable polymer scaffold

Fabrication of a biodegradable micro- and nano-structured polymer scaffold for tissue engineering

Process: Nanoimprint, hot embossing



Figure:

Photograph of a 200 mm wafer imprinted and etched using an anisotropic process

Process:

Plasma etching processes are optimized to anisotropic pattern transfer, allowing the transfer of various densities of structures

Application:

Si devices with various patterns size and densities

Keywords: thermal nanoimprint, PDMS, rolling

Project leader: Glasgow University

Address: Glasgow University

Web-Address: www.gla.ac.uk/centres/cellengineering

Process: Nanoimprint Lithography

Responsible: M. Riehle

E-mail: m.riehle@bio.gla.ac.uk

Process description: Large surfaces require a high imprint uniformity, which is easier to achieve with residual layers in the 50-100 nm range. A anisotropic plasma etching process is developed to remove this residual polymer film. The anisotropy allows a high quality transfer into patterns with various densities, with a good fidelity of the pattern size. This process uses a $O_2/Cl_2/Ar$ plasma chemistry in a ICP reactor.

Purpose: The aim of this process is the development of etching processes which allow a high quality transfer in patterns with different densities or sizes, and therefore with different residual layer thickness.

Major challenges: A challenge of this process is the reduction of the resist budget which limits the Si depth that can be achieved finally. Indeed a high difference of the residual thickness implies longer etching processes. The fidelity of all the patterns is guaranteed by the anisotropy, but the polymer is still vertically etched in the features whose residual layer is opened first. The resist mask for the following Si etching is therefore reduced.

References:

- [1] N Gadegaard, S Thoms, D S Macintyre *et al.* Microelectronic Engineering 162 (2003) 67-68.
- [2] N. Gadegaard, E Martines, M.O.Riehle *et al.* Microelectronic Engineering 83 (2006) 1577-1581.
- [3] K. Seunarine, N. Gadegaard, M. Tormen *et al.* Nanomed. 1 (2006) 281-296.





Contact information:

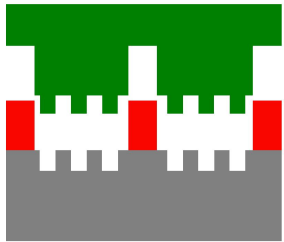


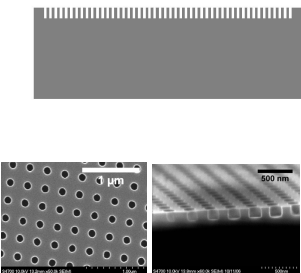
Dr. Mathis Riehle
Centre for Cell Engineering
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Glasgow G12 8QQ - UK



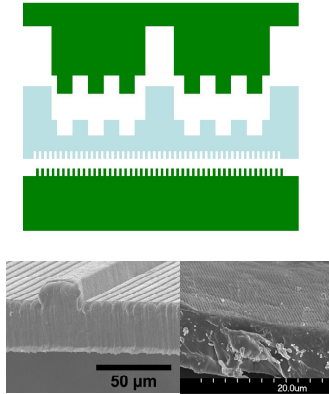
LoP2007_NIL012_Biodegradable polymer scaffold

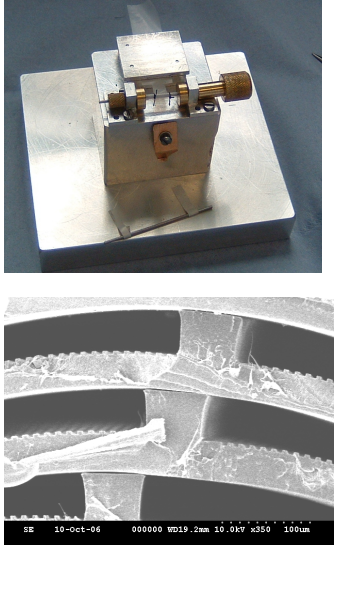
Biodegradable polymer scaffold

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks										
	What	how it should work	critical issues										
1.0	Process 1: Micro master fabrication	Micrograting: 6 μm pitch, 6 μm deep											
1.1	Wafer selection	standard Si substrate Si substrate, 4", <100>, d=525 μm one side polished											
1.2	Resist coating 	spin coat resist Primer at 5 krpm for 5 s S1818 @ 4 krpm for 60 s Bake 10 minutes @ 90°C (hot plate)											
1.3	Photolithography 	SÜSS Mask Aligner MA6 Expose (i-line) for 5 s Develop in 1:1 Microposit concentrate:RO water for 70 s Dry in N ₂ stream											
1.4	Dry etch - micro grooves 	<table border="1"> <tbody> <tr> <td>C₄F₈, SF₆</td> <td>50 sccm, 40 sccm</td> </tr> <tr> <td>Coil power</td> <td>600 W</td> </tr> <tr> <td>Platen power</td> <td>10 W</td> </tr> <tr> <td>Pressure</td> <td>10 mT</td> </tr> <tr> <td>Etch rate</td> <td>825 nm/min</td> </tr> </tbody> </table> <p>6 μm deep</p>	C₄F₈, SF₆	50 sccm, 40 sccm	Coil power	600 W	Platen power	10 W	Pressure	10 mT	Etch rate	825 nm/min	
C₄F₈, SF₆	50 sccm, 40 sccm												
Coil power	600 W												
Platen power	10 W												
Pressure	10 mT												
Etch rate	825 nm/min												
1.5	Spacers 	SU8 2050 @ 3 krpm (75 μm) 30 min at 95°C MA6, 20 seconds PEB 95°C for 7 minutes Develop in EC solvent for 7-10 minutes Rinse in IPA and dry in N ₂ stream	<i>Low thermal cycling to prevent SU-8 cracking</i>										
1.6	Anti-sticking layer	Ash in a O ₂ plasma (60W, 3 min) Immerse stamp in mixture of heptane with small drop of perfluoro silane (C ₈ H ₄ Cl ₃ F ₁₃ Si) from Gelest											

		for 5-10 minutes. Rinse in heptane and dry in N ₂ stream											
1.7	PDMS micro stamp 	Cast 4:1 (pre-polymer:curing agent) Sylgard 184 to make inverse replica of stamp											
End of Process 1													
2.0	Process 2: Nano master fabrication												
2.1	Wafer selection	standard Si substrate Si substrate, 4", <100>, d=525 μm one side polished											
2.2	Resist coating 	spin coat resist 60% ZEP520A @ 4 krpm for 60 s Bake 60 minutes @ 180°C (oven)											
2.3	e-beam lithography 	50 kV accelerating voltage 80 nm beam spot size 300 nm beam step size 42 μC/cm ² exposure dose for an array of 10 ⁹ spots/cm ² Develop O-xylene 60 s Rinse in IPA and dry in N ₂ stream	See[1]										
2.4	Dry etch 	<table border="1"> <tr> <td>C₄F₈, SF₆</td> <td>120 sccm, 40 sccm</td> </tr> <tr> <td>Coil power</td> <td>18 W</td> </tr> <tr> <td>Platen power</td> <td>525 W</td> </tr> <tr> <td>Pressure</td> <td>10 mT</td> </tr> <tr> <td>Etch rate</td> <td>100 nm/minute</td> </tr> </table> <p>100 nm deep</p>	C₄F₈, SF₆	120 sccm, 40 sccm	Coil power	18 W	Platen power	525 W	Pressure	10 mT	Etch rate	100 nm/minute	
C₄F₈, SF₆	120 sccm, 40 sccm												
Coil power	18 W												
Platen power	525 W												
Pressure	10 mT												
Etch rate	100 nm/minute												
2.5	Anti-sticking layer	Strip resist in Piranha etch (7:1 sulphuric acid:hydrogen peroxide) Immerse stamp in mixture of heptane with small drop of perfluoro	<i>Piranha etch also oxidizes silicon prior to fluorination</i> <i>Warning – Piranha</i>										

		silane ($C_8H_4Cl_3F_{13}Si$) from Gelest for 5-10 minutes. Rinse in heptane and dry in N_2 stream	<i>is a highly oxidizing solution</i>
2.6	PDMS nano stamp 	Cast 4:1 (pre-polymer:curing agent) Sylgard 184 to make inverse replica of stamp	<i>See also 5.3.2 Soft and hybrid layered stamps.</i>
End of Process 2			
3.0	Process 3: Polymer membrane fabrication and embossing		
3.1	Solvent casting 	Cast polymer mixture 1.25 g of PCL (Sigma, Poole, UK) dissolved completely in 25 ml of chloroform (Fisher scientific Inc., UK) left at room temperature for 2 hrs with frequent agitation 20 ml of PCL solution is deposited on a fluorinated 4" silicon wafer in a petridish. The solvent is evaporated overnight before the PCL film is demoulded. Average film thickness produced is between 60-80 μ m.	
3.2	Melt embossing 	PCL film cut, aligned and sandwiched between the PDMS micro and nano-stamps. Melt embossed (80°C) at a low pressure and allowed to cool.	
End of Process 3			

4.0	Process 4: Rolling		
4.1		<p>Custom built rolling jig Double side embossed film is trimmed into a manageable shape, the length of the film determines the subsequent number of layers that the scaffold will possess.</p> <p>The jig is a split pin configuration that clamps the edge of the film. The film is laid flat on a special 'runway' that is weighted by a special lid – this ensure that tension is exerted while the film is rolled providing a tight roll.</p> <p>The roll is secured either by surgical suture thread or by the use of a biocompatible superglue, 2-Octyl Cyanoacrylate.</p> <p>After rolling and securing the pin clamps are loosened and removed.</p> <p>Excess film is trimmed and the scaffold is ready for use.</p>	
End of Process 4			
End of Total Process			

4.6 Fluidic channels by roll-to-roll NIL

Fabrication for fluidics channels by using roll-to-roll NIL

Process: nanoimprint lithography, roll to roll printing, lithography

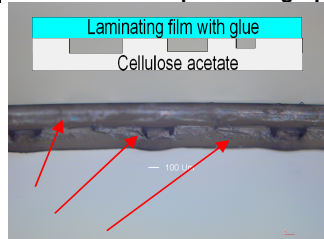


Figure:

Optical micrograph of a fluidics channels in 95 μm thick celluloseacetate sealed with ca. 90μm thick laminate foil. Fluidic channel is 50 μm high and 150 μm width.

Process:

Thermal roll to roll nanoimprint of a polymer film. Channels imprinted and sealed using custom made roll to roll device.

Application:

Microfluidic devices in high volume applications. Continuous processing.

Keywords: thermal nanoimprint, roll embossing, roll to roll NIL

Project leader: VTT Technical Research Centre of Finland

Address: FI-02044 VTT, Finland

Web-Address: <http://www.vtt.fi>

Process: Roll-to-roll NIL

Responsible: Tapio Mäkelä

E-mail: Tapio.Makela@vtt.fi

Process description: A process is based on continuous roll to roll manufacturing of fluidistic channels by using custom made manufacturing tool. Printing instrument consist two sequential units; thermal imprint lamination. In continuous manufacturing process; fluidics channels were imprinted on cellulose acetate web and sealed with a laminate foil during the same printing cycle. In roll to roll NIL process a softening temperature of web is higher than in a laminate film.

Purpose: The aim of this process is to demonstrate a high volume continuous roll to roll nanoimprinting process. In this process we show possibility to manufacture fluidics channels with continuous process. A specific requirements of sequential process were shown.

Major challenges: In this novel process a many challenges can be listed: Manufacturing methods for imprint master (on a roll) and optimal parameters for pressure, temperature and time. Suitable plastic materials on web is needed, since in roll to roll manufacturing typical imprint time is 1 s or shorter.

This process is developed by optimizing parameters suitable for cellulose acetate but PMMA, TOPAS, PS and other materials where softening or glasstransition temperature are below 200 C are possible to use. Aspect ratio in roll to roll process can not exceed much above 1:1 in rectangular shapes.

Application and state-of-the-art: Research process

References:

- [1] T. Mäkelä, T. Haatainen, P. Majander and J. Ahopelto, MNE07 (2007).
- [2] T. Mäkelä, T. Haatainen, P. Majander and J. Ahopelto, Microelectr. Eng. 84 (2007) 877-879.
- [3] T. Mäkelä et al. Unpublished data
- [4] H. Schiff, *Roll embossing and roller imprint*, Chapter (5) in "Science and new technology in nanoimprint". Volume editor Y. Hirai. Frontier Publishing Co., Ltd., Japan, ISBN4-902410-09-5, June 2006, 281 pp., English 74-89, Japanese translation (extract) 90-93 (2006).

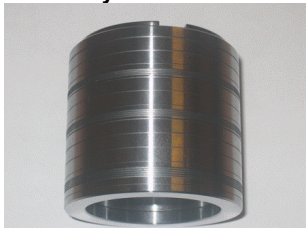
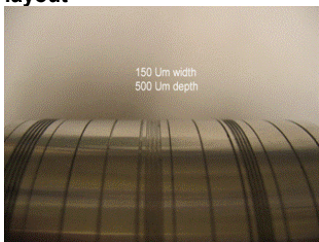
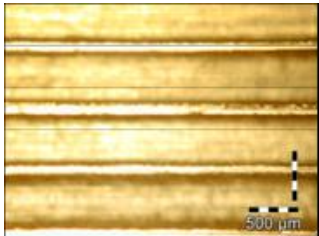
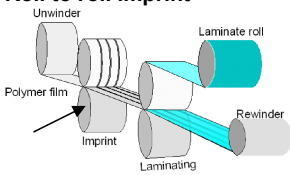
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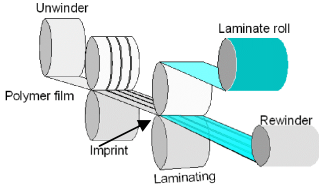
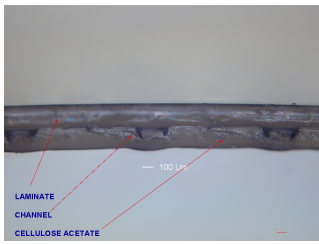
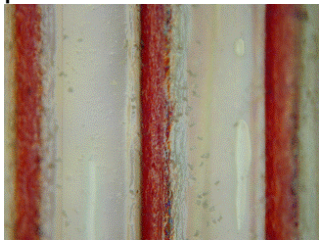
Ph.Lic. Tapio Mäkelä
VTT Technical Research Centre of Finland
Tietotie 3, Espoo
P.O.Box 1000, FI-02044 VTT
Finland

LoP2007_NIL013_RtoR for fluidics channels

Fluidic channels by roll-to-roll NIL

Process: nanoimprint lithography

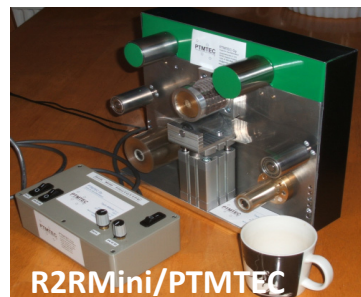
	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Master fabrication		
1.1	Metallic cylinder 	Metal roll and engraved channel structure on roll roll size 66 x 60 mm (diameter x width)	
1.2	Substrate preparation	Substrates <i>Plastic roll:</i> 50 mm width , 95 μm cellulose acetate , no pre-treatment <i>Laminate roll:</i> 50 mm width , 90 μm thick laminate with meltable glue	
	End of Process 1		
2.0	Process 2: Stamp preparation		
2.1	layout 	Functional structures Engraving of roll The stamp consist of 150 μm width and 500 μm depth grooves.	engraved grooves are relatively good but edges not clean
2.2	process control 	optical microscope 100 x	
	End of Process 2		
3.0	Process 2: Roll to roll nanomprinting		
3.1	Roll to roll imprint 	Thermal roll to roll imprint Pressure 8 MPa Temperature 105 C Speed 0.2 – 8 meter/minute 5 mm contact area between printing and backing rolls	T_g of cellulose acetate 120 C

3.2	Cooling/demolding	Cooling at room atmosphere (no blow) 30 cm distance between units	
3.3	process control	Optical microscope	
End of Process 3			
4.0	Process 3: Cover		
4.1	Laminated cover for fluidics 	Thermal roll to roll laminating Pressure < 0.1 MPa Temperature 80 C Speed 0.2 – 8 meter/minute 1 mm contact area between printing and backing rolls	
4.2	process control 	optical microscope cross section 100 x	
4.3	process control 	Channel test tested with water (+ dye)	
End of Process 4			
End of Total Process			

General remarks:

Further information on small scale R2R NIL and coating device for R&D, prototyping and pilot production (see 1.3 on page 81) is provided upon request by:

PTMTEC Oy
 Jousimiehentie 4 | 123 00740 Helsinki, FINLAND
 www.ptmtec.com
 Email: info@ptmtec.com



R2RMini/PTMTEC

4.7 V-Grooves for plasmon confinement

Fabrication of V-groove waveguides for plasmon confinement by Nanoimprint Lithography

Process: nanoimprint lithography

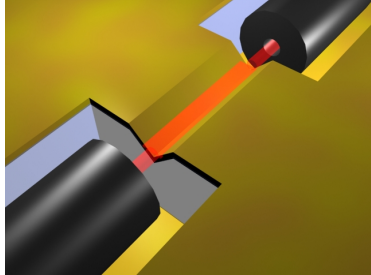


Figure:

Schematic illustration of the device: two deep channels (to place the optical fibers) are integrated with the v-groove (to confine the plasmon). The device is made in gold (200nm) onto a transparent and flexible substrate (OrmoComp®).

Process: The process is based on nanoimprint lithography, metallization, and casting of a UV curable hybrid polymer OrmoComp®, allowing to fabricate the same structures of the stamp in different materials.

Application: The v-grooves are used as subwavelength waveguides, where plasmons are confined and guided at the bottom. Further applications may be in the biosensing field.

Keywords: thermal nanoimprint, v-groove, plasmon confinement.

Project leader: DTU

Address: DTU building 345E, 2800 Lyngby, Denmark

Web-Address: <http://www.nanotech.dtu.dk/>

Process: Design and fabrication

Responsible: Anders Kristensen

E-mail: Anders.Kristensen@nanotech.dtu.dk

Partner: CNM-Barcelona

Address: Campus de la UAB, 08193 Bellaterra, Spain

Web-Address: www.cnm.es

Process: Sample fabrication

Responsible: Irene Fernandez Cuesta

E-mail:

Process description: A process is described for wafer scale fabrication of integrated devices, based on v-groove cavities for plasmon confinement. The process includes a double replication, thus, the final structures are equal to those fabricated in the initial stamp (silicon), but made in different materials. This goal is achieved by combining nanoimprint lithography, metallization and casting of a UV curable polymer (i.e. OrmoComp from *micro resist technology* GmbH) onto the imprinted structures, and finally dissolving the imprinted polymer. The stamp is fabricated in two steps: photolithography and wet etching in KOH, and photolithography and Deep RIE.

Purpose: The aim of this process is to fabricate cavities with V shape and smooth sidewalls (in gold onto a transparent and flexible substrate), and simultaneously two deep channels, integrated with the groove, where optical fibers can fit, to facilitate light coupling in the groove and measure output signal.

Major challenges: stamp fabrication: to achieve smooth and vertical sidewalls in the D-RIE step. Gold deposition is critical. Due to thermal expansion problems, the gold layer appears cracked sometimes.

Application and state-of-the-art: Research process, used for the fabrication of V-grooves, to study the confinement of plasmons in the bottom of the V-grooves.

References:

[1] S.I. Bozhevolnyi, et al. Nature, 2006. 440(7083): p. 508-511

[2] I. Fernandez-Cuesta, R. B. Nielsen, A. Boltasseva, et. Al., J. Vac. Sci. Technol. B 25(6), p. 2649 (2007).

Contact information:

Anders Kristensen

Department of Micro- and Nanotechnology

Technical University of Denmark

DTU Nanotech, Building 345 East









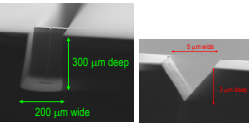
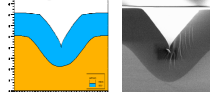
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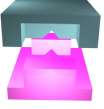

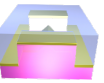
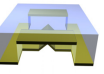
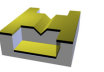
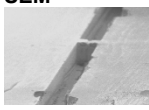
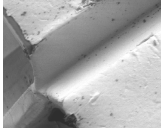
Denmark Email: Anders.Kristensen@nanotech.dtu.dk

LoP2007_NIL014_V-Groove Waveguides

V-grooves for plasmon confinement

Process: nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Stamp fabrication		
1.1	wafer selection	standard Si (100) substrate 4", d=500 μm double side polished	
1.2	substrate preparation 	Wet oxidation at 1100°C (oxide thickness ~200nm)	
1.3	Photolithography 1 	Spin coating of UV resist (1.5 μm of AZ5214B), UV exposure, and develop- ment.	
1.4	RIE 	RIE of 200 nm of SiO ₂ . Stripping of the photoresist (acetone)	
1.5	KOH to define de V 	Anisotropic wet etching in KOH (wt 30%), at 80°C, during 1h.	
1.6	Oxide removing 	HF 50%, 1 minute.	
1.7	Photolithography 2 	Spin coating of UV resist (1.5 μm of AZ5214B), UV exposure, and develop- ment.	
1.8	D-RIE to define the channels 	Deep RIE of silicon, to de- fine the channels (300 μm deep).	<i>Vertical and smooth side- walls should be obtained, otherwise demolding would be difficult.</i>
1.9	Resist stripping 	Acetone and ultrasounds, to remove the resist.	
1.9 b	Process control 	SEM	
1.10	Optional: improvement of the sharpness of the V. 	Wet oxidation, 6h at 1150°C.	<i>For each size of the grooves, the oxidation time can be optimized (by simu- lations), to achieve the sharpest angle in the bot- tom.</i>

1.11	Optional: improvement of the thickness of the stamp	Anodic bonding of another silicon wafer to the bottom of the stamp.	<i>After etching 300um to create the deep channels, in a 500um thick wafer, it becomes very fragile.</i>
1.12	Antisticking coating	FDTS-layer (1H,1H,2H,2H-perfluorodecyltri-chlorosilane) using a MVD system (Applied Microstructures Inc.)	
End of Process 1			
2.0	Process 2: NIL		
2.1	Substrate preparation	PMMA sheet, 5mm thick. Dehydrated in an oven, at 90°C, 8hours.	
2.2	NIL 	Imprint with EVG imprinter: 180°C, 10min, at 20kN. Demolding at 80°C.	
3.0	Process 3: pattern replication in Ormocomp and gold		
3.1	Gold deposition 	Evaporation of 200 nm of gold onto the imprinted face of the PMMA.	<i>A silicon wafer has to be stuck to the backside of the PMMA sheet, to avoid thermal gradients and bubbles formation.</i>
3.2	Ormocomp deposition 	Casting of OrmoComp [®] onto the gold layer. The sample is left for 10min. UV curing: 4 cycles of 30seconds.	<i>The OrmoComp has to be cured in short cycles, otherwise, internal stress appears and bends the structures.</i>
3.3	Releasing of the structures 	The sample is rinsed in acetone some hours, and cleaned afterwards in an O2 plasma.	
3.3b	process control 	SEM 	
End of Process 3			
End of Total Process			

General remarks:

Ormocomp and Ormocomp Clear are commercially available UV-curable hybrid polymers especially suited for the fabrication of micro-optical components. Further information on sol-gel materials and hybrid polymers can be found in on Page 37.

4.8 Hydrogel waveguide optical sensor structure

Fabrication of UV curable hydrogel waveguides with outcoupler

Process: Nanoimprint lithography

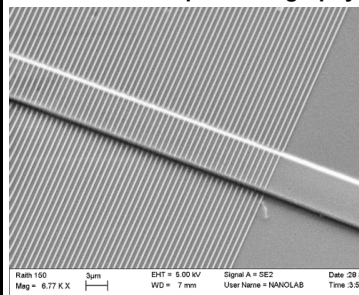


Figure:

SEM image of waveguide with crossed grating outcoupler imprinted in hydrogel

Process:

UV Nanoimprint

Application:

Environmental and chemical sensor, humidity, pH

Keywords: optical sensor, waveguide, outcoupler, UV nanoimprint, hydrogel

Project leader: Catalan Institute of Nanotechnology

Address: 08193 Bellaterra (Barcelona) SPAIN

Web-Address: <http://www.icn.cat>

Process: UV-NIL

Responsible: Timothy Kehoe

E-mail: tkehoe@icn.cat

Partner: TECNALIA

Address: Pº Mikeletegi 2, 20009 San Sebastian, Spain

Web-Address: www.tecnalia.com

Process: Material synthesis

Responsible: Isabel Obieta

E-mail: isabel.obieta@tecnalia.com

Partner: University of Glasgow

Address: James Watt South Building, Glasgow, Scotland

Web-Address: www.gla.ac.uk

Process: Master stamp fabrication

Responsible: Nikolaj Gadegaard

E-mail: Nikolaj.Gadegaard@glasgow.ac.uk

Process description: Fabrication of optical waveguide sensor structures comprising micro-scale ridge waveguides and nano-scale gratings on top of and perpendicular to the waveguides. The process involves the fabrication of master stamps in silicon with two levels of structures, using electron beam lithography and reactive ion etching, production of transparent replicas of the structures in Ormostamp by UV-NIL, and imprinting using UV-NIL in hydrogel materials.

Purpose: The aim of this process is to obtain optical sensor device structures in hydrogels sensitive to environmental stimuli such as humidity and pH, and of sufficient optical quality to enable coupling of light from an optical fibre, single-mode wave-guiding and outcoupling of light perpendicular to the surface. The hydrogel should absorb water and expand, thereby changing the measured optical signal.

Major challenges: Fabrication of a 2-level structure in a single stamp, with good optical quality over a range of 5 – 10 mm.

Application and state-of-the-art: Currently patterns below 50nm have been demonstrated and 3D nanostructures have been obtained

References (mainly on antiadhesive coatings):

- [1] A. Z. Khokhar, A. Gaston, I. Obieta et al., Compact LED based nanoimprinter for UV-NIL, *Microelectron. Eng.* 88(11) (2011) 3347-3352, DOI: 10.1016/j.mee.2011.06.023
- [2] A. Gaston, A.Z. Khokhar, L. Bilbao et al., Nanopatterned UV curable hydrogels for biomedical applications, *Microelectron. Eng.* 87(5-8) (2010) 1057-1061, DOI: 10.1016/j.mee.2009.11.089

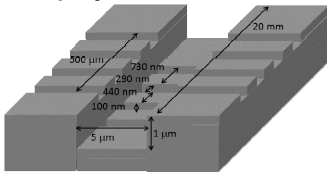
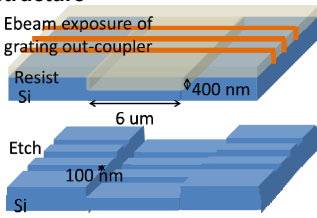
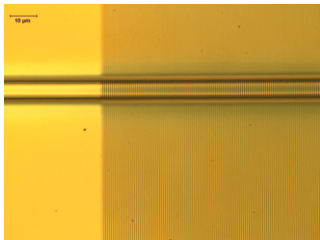
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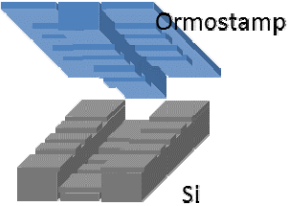
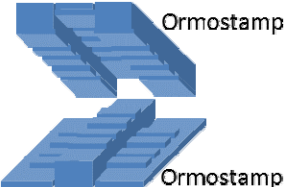
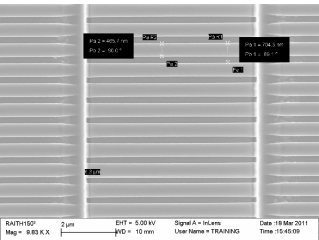
Prof. Clivia Sotomayor Torres
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Spain

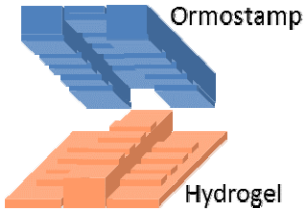
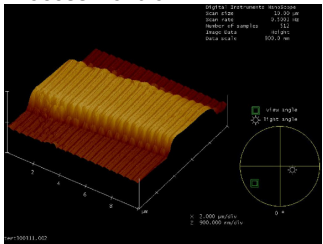
LoP2012_NIL016_Hydrogel waveguide-application

Hydrogel waveguide optical sensor structure

Process: E-beam lithography, RIE, UV nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	Process 1: Stamp preparation	E-beam lithography	
1.1	Wafer selection and preparation	standard Si substrate 100mm <100> Thickness 525 μm	
1.2	Stamp layout 	The pattern consists of 10 – 20 ridge waveguides of width 1 – 5 μm , length 20 mm and height 1 μm , and separated by 1 mm. Overlaid on this in the perpendicular direction is a grating pattern of period 750nm, line width 450 nm, and height 100 nm, covering an area of 10mm x 1mm.	
1.3	Pattern first level of structure	E-beam lithography of ridge waveguides Reactive Ion Etch to depth of 600 nm	
1.4	Pattern second level of structure 	Spin-coat over ridge waveguide structures E-beam lithography of grating out-coupler Reactive Ion Etch to depth of 100 nm	<i>Ridge waveguides and outcoupler grating lines are at 90 degrees.</i>
1.5	Anti-adhesion coating	Optool anti-adhesion treatment deposited in liquid phase. Solution of Optool in perfluorohexane, 1000:1. Submerge stamp for 1 minute, rinse with perfluorohexane, and shake dry. Heat stamp at 65degC for 1 hour with water bath. Finally rinsing with perfluorohexane for 10 minute	
1.6	Process control 	Optical microscopy SEM	
	End of Process 1		

2.0	Process 2: Stamp Replication	UV - NIL	
2.1	Substrate selection and preparation	<p>Quartz substrate Area 20mm x 20 mm, 0.5mm thick</p> <p>Oxygen plasma treatment to improve adhesion .</p>	<i>OrmoStamp will not adhere to quartz without oxygen plasma treatment</i>
2.2	<p>First replication: UV-NIL imprint</p> 	<p>Dropcast inorganic-organic hybrid polymer such as OrmoStamp onto pretreated quartz substrate. Place quartz substrate on top of Si stamp to allow UV transmission.</p> <p>Imprint 3 bars, 2 minutes UV, 20 seconds at 3bars (using a UV radiation of 17.26 W/cm² at 365 nm)</p>	<p><i>Imprinting was performed on a home-made imprinting module.</i></p> <p><i>After imprinting, excess OrmoStamp should be trimmed away.</i></p>
2.3	Anti-adhesion treatment	Optool anti-adhesion treatment as for Step 1.5.	
2.4	<p>Second replication: UV-NIL</p> 	<p>Dropcast organic-inorganic hybrid polymer such as OrmoStamp onto quartz substrate. Place quartz replica on top of quartz substrate.</p> <p>Imprint 3 bars, 2 minutes UV, 20 seconds at 3 bars (using a UV radiation of 17.26 W/cm² at 365 nm)</p>	<i>If anti-adhesion treatment is properly applied, OrmoStamp can be copied from OrmoStamp replicas, thus allowing to easily inverting the pattern polarity, if necessary.</i>
2.5	Anti-adhesion treatment	<p>OTS (Octadecyltrichlorosilane) Deposited in liquid phase. Solution of Optool in hexane, 100:1. Submerge stamp for 5-8 minutes, rinse with hexane and DI water.</p>	<i>Other SAMs (Optool, F13-TCS, FLKS10) work worse than OTS.</i>
2.6	<p>Process Control</p> 	Optical Microscopy and SEM	
End of Process 2			

3.0	Process 3: Lithography	UV-NIL	
3.1	Substrate selection	100 mm Si wafer with 400 nm thermal oxide layer	
3.2	Substrate preparation	pretreatment TPM (3-trichlorosilyl propyl methacrylate) coating	<i>In samples without TPM treatment, hydrogel layer peels off the substrate when it swells</i>
3.3	Imprint 	Deposit hydrogel onto treated SiO ₂ coated wafer, by drop-casting. Imprint conditions: 4 bars, 4 mins 4 mins UV at 4 bars (using a UV radiation of 17.26 W/cm ² at 365 nm)	<i>Imprinting was performed on a home-made imprinting module.</i>
3.4	Process Control 	Optical microscopy, SEM, AFM	
End of Process 3			
End of Total Process			

General remarks:

The generation of pattern copies in terms of working stamps can be advantageous for a wide range of reasons (see Page 30). Hybrid polymers like OrmoStamp used for working stamps are low-cost alternative to electroplated stamps (see Page 37) and thus are accessible for a wide range of engineers and researchers.

4.9 All-silica micro and nanofluidic device

Micro and nanofluidic devices fabricated by imprint of sol-gel silica with silicon stamp

Process: Sol-gel imprint with silicon stamp

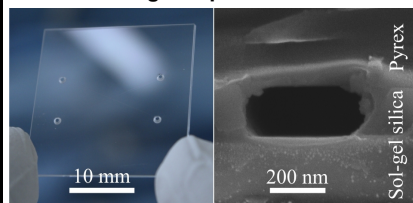


Figure:
Photo of all-silica nanofluidic lab-on-a-chip device fabricated by imprint of sol-gel silica. SEM micrograph of a cleaved nanochannel imprinted in sol-gel silica and fusion bonded to a Pyrex glass lid.

Process:
Imprint of micro- and nanochannels in sol-gel silica with hard stamp and fusion bonding to glass lid.

Application:
Micro- and nanofluidic lab-on-a-chip devices.

Keywords: sol-gel silica, nanoimprint, nanofluidics, lab-on-a-chip, fusion bonding

Project leader: Technical University of Denmark (DTU)
Address: Build. 345 B, DK-2800 Kgs. Lyngby, Denmark
Web-Address: <http://www.nanotech.dtu.dk>

Process: Sol-gel NIL with hard stamp
Responsible: Morten Bo Mikkelsen
E-mail: morten.mikkelsen@nanotech.dtu.dk

Partner Laboratoire Surface du Verre et Interfaces,
Unité Mixte CNRS/Saint-Gobain (SVI)
Address: F-93303 Aubervilliers Cedex, France
Web-Address: <http://www.saint-gobain-recherche.fr>

Process: Material development
Responsible: Elin Søndergård
E-mail: elin.sondergard@saint-gobain.com

Process description: A hybrid sol-gel silica material is imprinted with a multi-level silicon stamp, comprising micro- and nanofeatures, to produce channels of different depths in a single process step. Calcination of the imprinted hybrid sol-gel material produces purely inorganic silica, which has very low autofluorescence and can be fusion bonded to a glass lid.

Purpose: Providing a method for fabrication of combined silica micro- and nanochannels directly in an imprint process.

Major challenges: Reproducibility of the sol-gel material. Reduction of water content before imprint. Material shrinkage during calcination of organics.

Application and state-of-the-art: The process may be used as a simple and cheap method for fabrication of silica nanofluidic lab-on-a-chip devices for single-molecule studies.

References:

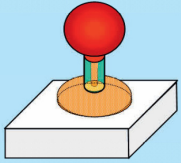
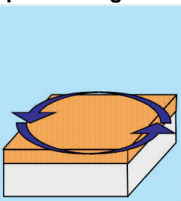
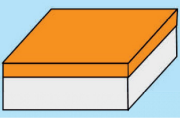
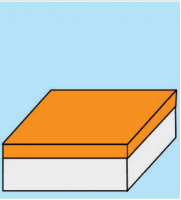
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- [2] L. H. Thamdrup, A. Klukowska and A. Kristensen, Stretching DNA in polymer nanochannels fabricated by thermal imprint in PMMA, *Nanotechnology* **19**, 125301 (2008). DOI:10.1088/0957-4484/19/12/125301

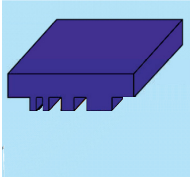
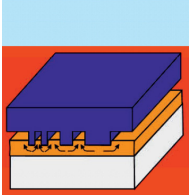
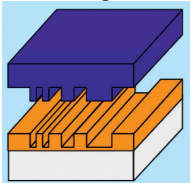
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Denmark

LoP2012_NIL017_SVI hybrid materials

All-silica micro and nanofludic device

Process: Thermal imprint

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Material preparation		
1.1	Mix sol-gel material	Sol preparation Methyltriethoxysilane (MTES) is mixed with HCl (pH 2.0) at a molar mixing ratio MTES:H ₂ O of 1:14.	<i>Process described in Mikkelsen et al. Lab Chip 12, 262-267 (2012) [1].</i>
1.2	Aging of sol	Aging The two-phased solution is vigorously stirred to obtain a single-phased sol, which is aged for 3.5 hours. Reaction kinetics and gel properties are highly sensitive to the pH of the solution.	
	End of Process 1		
2.0	Process 2: Spin-coating	Gel formation	
2.1	Dispensing of sol 	Dispensing of sol 1.5 – 2 ml of sol is deposited on the substrate (glass or silicon) through a 0.2 μm PTFE filter.	
2.2	Spin-coating 	Spin-coating to produce gel film Parameters for 700 nm gel film: Spin-speed: 1800 rpm Acceleration: 500 rpm/s Spin time: 50 s	<i>Sensitive to humidity during spin-coating. A relative humidity of 45 % is used. If the relative humidity drops to 25 %, the gel is hard after coating and the storage and pre-curing steps must be changed.</i>
2.3	Storage 	Storage and drying To assure reproducibility, the gel film must be stored in dry atmosphere immediately after spin-coating. Sol-gel films are dried for at least 30 min before imprint.	<i>A nitrogen flow-box or a silica gel dessicator can be used. Reproducible results are obtained for substrates stored at 0.0 %RH for 30 min to 5 hours.</i>
	Pre-curing 	Reduction of water content before imprint Prebake at 90°C for 5 min to pre-cure and further dry the gel.	<i>Reduction of water content is necessary in order to avoid defects due to evaporating water. The prebake time can be used to tailor the material viscosity. A harder material may be convenient for imprint of, e.g., very low protrusion coverage nanostructures.</i>
	End of Process 2		
3.0	Process 3: Imprint	Imprint	

3.1	Stamp 	Hybrid stamp A hybrid stamp with nanostructures defined in SiO ₂ and microstructures defined in OrmoComp on a silicon substrate is used for imprint. Perfluorodecyltrichlorosilane (FDTs) is used as anti-sticking coating.	<i>Fabrication of the stamp is described in Thamdrup et al. Nanotechnology 19, 125301 (2008) [2]. The same FDTs coating can be reused for more than 75 imprints of sol-gel silica.</i>
3.2	Imprint 	Imprint Hot plates preheated to 60°C to assure reproducible temperature profile. Imprint: 5 min at 10 kN, heating: to 120°C at 7°C/min, stay at 120°C for 20 min to fully cure the gel, cooling to 60°C and pressure release.	<i>Slow condensation at 60°C and reduced viscosity assures good filling of the stamp cavities.</i>
3.3	Demolding 	Demolding Demolding with a razor blade.	<i>Triboelectric charging makes demolding of imprinted sol-gel silica on glass substrates more difficult than on silicon substrates.</i>
End of Process 3			
4.0	Process 4: Annealing	Calcination of organics	
4.1	Annealing	Annealing Heating at 5°C/min to 600°C. Stay at 600°C for 4 hours to calcinate the organics and produce inorganic silica.	<i>Unstructured gel films shrink to 56% of initial thickness. Cracks appear in films of initial thickness > 700 nm. Imprinted nanostructures mainly deform in the lateral dimension. For imprinted pattern with large density of free surfaces the deformation is very small.</i>
End of Process 4			
5.0	Process 5: Fusion bonding	Sealing channels with a lid	
5.1	Surface activation	Surface activation The surfaces of the imprinted and annealed sol-gel silica and a Pyrex glass substrate are activated by subsequent RCA1 and RCA2 cleaning.	<i>Inlet holes fabricated by powder blasting as described in Mikkelsen et al. Lab Chip 12, 262-267 (2012) [1].</i>
5.2	Prebonding	Prebonding A weak bond is obtained when the two substrates are pressed together.	
5.3	Annealing	The bonding strength is increased when the bonded substrates are annealed at 550°C for 12 hours.	
End of Process 5			
End of Total Process			

4.10 Roll-to-roll NIL for backlight devices

Roll-to-roll pilot nanoimprinting process for backlight devices

Process: Thermal nanoimprint lithography

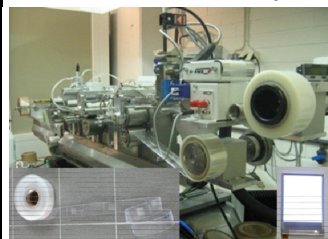


Figure:

A pilot scale Roll to Roll manufacturing process for backlight devices on

Poly(methylmethacrylate) (PMMA) film.

Main technologies required:

Roll to Roll NIL lithography, Flexible Ni-mold and assembly

Application:

Roll to roll NIL in high volume applications and continuous processing. R2R NIL for backlighting of flat panel displays

Keywords: Roll to roll nanoimprinting, thermal NIL, flexible Ni-mold, Roll to roll tools

Project leader: VTT Technical Research Centre of Finland

Address: Helsinki, FI

Web-Address: <http://www.vtt.fi>

Process: Roll to Roll thermal NIL

Responsible: Tapio Mäkelä

E-mail: tapio.makela@vtt.fi

Partner: Senidomia Oy

Address: Helsinki, FI

Web-Address: <http://www.senidomia.com>

Process: Design, application

Responsible: Leo Hatjasalo

E-mail: leo.hatjasalo@senidomia.com

Process description: Light illumination device is imprinted on PMMA web using a laboratory scale Roll to Roll imprinting machine. Backlight device (28 x 28) mm² consist more than 78 000 binary elements with different orientation. Each element has 40 trenches with 5 micron width and 1.3 micron thick, totally 3.1 million trenches in one device. Parameters were optimized in continuous roll-to-roll imprinting. More than 1000 device printed to demonstrate pilot production.

Purpose: The aim of this process is to demonstrate a pilot processing of display illumination device.

Major challenges: Printing quality of optical elements in Roll to Roll process and wearing of the mold.

Application and state-of-the-art: Partially standard process, but continuous high quality manufacturing not yet shown.

References:

- [1] T. Mäkelä, T. Haatainen; Roll-to-Roll pilot nanoimprinting proces. for backlight devices, Microelectron. Eng. 2012, accepted.
- [2] T. Mäkelä, T. Haatainen, J. Ahopelto; Roll-to-roll printed gratings in cellulose acetate web using novel nanoimprinting device, Microelectron. Eng. **88** (2011) 2045–2047

Contact information:

Dr. Tapio Mäkelä

VTT Technical Research Centre of Finland, VTT


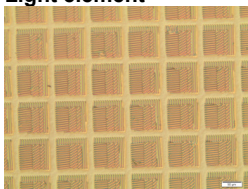


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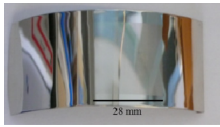
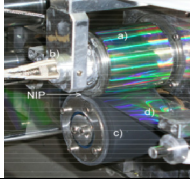
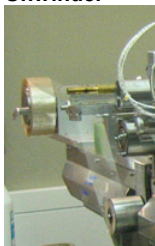
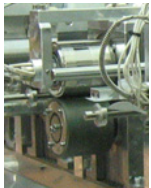
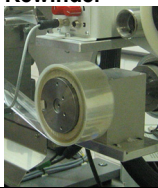

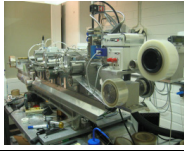
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LoP2012_NIL018_R2R backlight-application

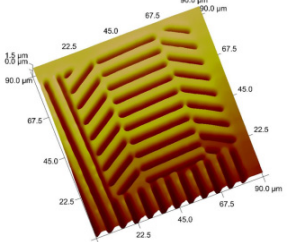
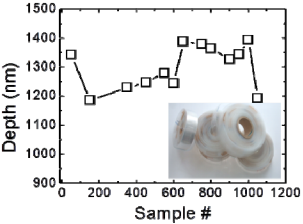
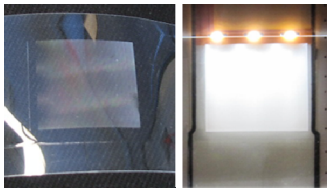
Roll-to-roll pilot nanoimprinting process for backlight devices

Process: Thermal nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Designing of backlight elements and materials	Designing	
1.1	Design of backlight device 	Display illumination device is designed using commercial design tool. Design based on three LED connected on the one side of device. Device will illuminate homogeneous light.	
1.3	Light element 	Backlight device (28 x 28) mm ² consist more than 78 000 binary elements with different orientation. Each element has 40 trenches with 5 micron width and 1.3 micron thick, totally 3.1 million trenches in one device.	
1.4	Device material 	375 micron thick PMMA with good optical parameters is be used to achieve optimum performance. optical transparency is 92 % refractive index 1.49 softening temperature 100 °C	PMMA quality critical
	End of Process 1		
2.0	Process 2: Flexible Ni-mold preparation and assembly to Roll to Roll machine	Electroplating and assembly	
2.1	Design transferring to polymer and seed metallization	Designed device transferred to the polymer using conventional UV process. Seed metals Mo (5 nm)+ TiW (10 nm) + Cu(300 nm) is sputtered on the top.	
2.2	Electroplating of Ni 	Ni-sulphamate bath is used and electroplating was obtained with AC current. +1.6 A (-1.6 A): 400 ms (100 ms) Growing speed: 5 um/h (ca. 100 um/20 h)	

2.3	Ni-mold 	300 micrometer thick mold is cut size 40 mm x 100 mm	
2.4	Assembly 	Ni-mold attached to the printing roll a) and placed in the printing tool. A thermal heating element b) is inside of the roll. Roll diameter 66 mm.	
End of Process 2			
3.0	Process 3: Pilot Roll to Roll production of 1000 device	Pilot process	
3.1	Unwinder 	PMMA substrate (50 mm wide) is located in unwinder.	
3.2	Thermal Roll to roll NIL 	The mold is wrapped on metallic cylinder (width 60 mm) and heated to operation temperature 115 °C. The printing speed 0.6 meter/minute and pressure 8 MPa.	Printing parameters are critical
3.5	Rewinder 	Printed devices were wrapped on rewinder roll.	Web tension accurately tuned
3.7	1000 printed device on roll 	The wearing of the mold does not effect to the quality of the printed binary element at least in a volumes up to 1000 pcs	Mold wearing in higher volumes
	Roll to Roll tool 	Web 50 mm width speed 0.2 m/min up to 20 m/min (NIL-unit) Pressure 125 N/cm up to 2510 N/cm Temperature RT- up to 200 C	
End of Process 3			

NaPANIL_Library of Processes

4.0	Process 4: LED connection and characterization of device		
4.1	Illumination element 	<p>The pattern replication to PMMA film is good and the depth of the imprinted structure is typically in the range of 1.2 - 1.4 μm. Limits for working device is ca. 1.0 μm.</p>	
4.2	Depth variation 	<p>Depths of printed grooves are typically within 1.2-1.4 μm. All printed devices are in the suitable range.</p>	<p>Variation in the height is due to the temperature control in the tool. This is due to the low thermal mass.</p>
4.3	Backlight device 	LED attachment and luminance measurement <p>Three LED connected to the device. Average luminance value was 120 cd/m². The standard deviation for the measured luminance values for all devices was within 17 %.</p>	
End of Process 4			
End of Total Process			

4.11 Replication by Injection Molding

Conventional injection molding with 100 mm full wafer tool

Process: Thermal injection molding

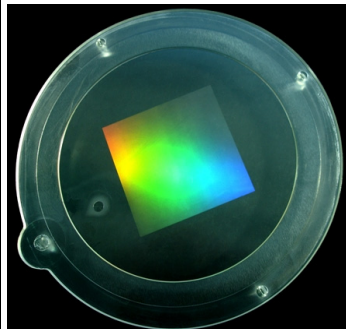


Figure:
Photograph of an injection molded specimen of an array (44x44mm²) of pillars with 200nm diameter and 600 nm period, replicated directly from a 100mm silicon wafer using a dedicated molding tool for wafer injection molding. This example was replicated in transparent polyamide

Process:
Conventional (isothermal) injection molding for micro- and nanostructure replication from silicon wafers

Application:
Microfluidics, DOEs, photonics, security features.

Keywords: thermal nanoimprint, PHABLE, plasma etching, surface coating

Project leader: Institute of Polymer Nanotechnology
Address: 5210 Windisch, Switzerland
Web-Address: <http://www.fhnw.ch/inka>

Process: Thermal Injection Molding
Responsible: Per Magnus Kristiansen
E-mail: magnus.kristiansen@fhnw.ch

Partner: Paul Scherrer Institut (PSI)
Address: 5232 Villigen PSI, Switzerland
Web-Address: <http://www.psi.ch>

Process: Thermal Nanoimprint
Responsible: Helmut Schiff
E-mail: helmut.schiff@psi.ch

Partner: Eulitha AG
Address: 5232 Villigen PSI, Switzerland
Web-Address: <http://www.eulitha.com>

Process: PHABLE technology
Responsible: Harun Solak
E-mail: harun.solak@eulitha.com

Process description: Direct replication of large area nanostructures from silicon wafers (or wafer-like replicas) by isothermal injection molding (mold kept at constant temperature); intended mainly for preliminary studies of replication

Purpose: The aim of this process is to produce high volume micro/nanostructured parts made out of bulk polymers, displaying a surface structure that adds functionality.

Major challenges: The durability of the silicon mold insert depends very much on the tool integration method as well as on the structures to be replicated and the quality of the antisticking coating. Filling of nanostructured cavities is challenging as the polymer melt freezes rapidly (within milliseconds) upon contact with the mold, usually held close to the T_g of the polymer.

Application and state-of-the-art: This dedicated tool is mainly used for preliminary studies on the replication behavior of nanostructures created by lithographic methods and transferred into silicon

References (mainly on antiadhesive coatings):

- [1] P.M. Kristiansen, C. Rytka, M.J. Cheung, H. Schiff, A. Schleunitz, C. Spreu, H. Solak: *Kleinste Strukturen in der Massenfertigung abformen*, *PlasticsNow!*, 20-21 (2011)
- [2] C. Bader, P.M. Kristiansen, *Hitting the nail on the head*, *Kunststoffe international*, 6, 6-11 (2011)

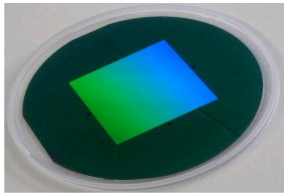
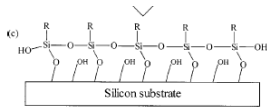
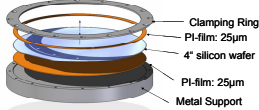


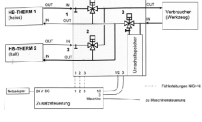
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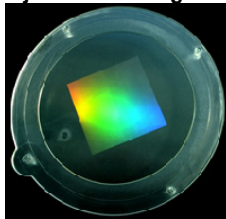
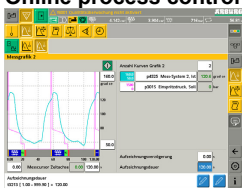
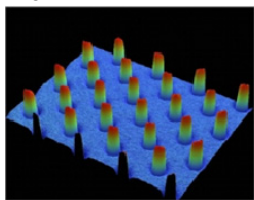
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University of Applied Sciences and Arts FHNW
Institute of Polymer Nanotechnology
Klosterzelgstrasse 2
CH-5210 Windisch, Switzerland

LoP2012_NIL019_full wafer injection molding

Conventional injection molding with 100 mm full wafer tool

Process: wafer injection molding

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Master generation	Silicon wafer format	
1.1	Structured wafer insert 	Master structure can in principle be manufactured by any silicon micromachining process described in the NaPa LoP/NaPANIL LoP Example master prepared by PHABLE technology of Eulitha AG	<i>For direct wafer injection molding, the pattern needs to be transferred into silicon; alternative materials such as structured quartz wafers, UV-imprinted OrmoStamp on Borofloat wafers, embossed polymer templates or direct structured metal inserts may be used accordingly</i>
1.2	Application of antisticking coating 	Fluorosilane treatment According to standard process described in NaPa LoP	<i>Application of antisticking coating is absolutely necessary to allow for demolding without damage of the replicated structure and more importantly to avoid wafer breakage</i>
	End of Process 1		
2.0	Process 2: Preparatory work	Tooling and materials	
2.1	Tooling preparation 	Dedicated molding tool integration of silicon wafer into tool insert by clamping	<i>Polyimide (Kapton) films are used as spacers to compensate for surface roughness of the metal support and to minimize the danger for</i>
2.2	Material preparation 	Drying of polymer Many thermoplastic materials need drying before processing	<i>Respective drying conditions can be found in respective product brochures</i>
2.3	Tool mounting and alignment 	Mounting of tool And proper alignment of molding tools	
2.3	Connection of periphery 	Suitable periphery includes Mold temperature control, Pressure- and temperature sensors, robot handling system for part removal	<i>The process protocol needs to be adjusted to account for all necessary process steps. This is particularly important for the robot handling system</i>
	End of Process 2		

3.0	Process 3: Injection molding	For direct wafer replication	
3.1	System setup and equilibration with starting parameters 	Process definition Involves programming the entire process cycle and corresponding periphery addressing (venting, mold temperature variation, handling system, ...)	<i>This is typically straightforward to those skilled in the art of injection molding.</i>
3.2	Filling study to determine optimum injection volume	Particularly important for unknown materials This step can be avoided when optimum process conditions have been established previously.	<i>This approach offers additional insight into the filling behavior of investigated nanostructures, in comparison to NIL filling studies.</i>
3.3	Injection molding 	Replication mold temperature close to T_g melt temperature: flexible pressure: depends on structure filling velocity: flexible	<i>The rheological behavior of the polymer plays quite an important role; it can be adjusted within boundaries by increasing the mass temperature but this causes additional shrinkage upon solidification</i>
3.4	Online process control 	The integration of pressure and temperature sensors Allows online monitoring of the injection molding process, including flow adjustment	
3.5	Inspection of replicated specimen 	Many methods are suitable SEM: requires metallization AFM: quite work-intensive Laserscanning confocal microscopy	
	End of Process 2		
	End of Total Process		

Further references:

- [1] H. Schiff, C. David, M. Gabriel, J. Gobrecht, L.J. Heyderman, W. Kaiser, S. Köppel, and L. Scandella, *Nanoreplication in polymers using hot embossing and injection molding*, Microelectron. Eng. 53, 171-174 (2000).
- [2] A. D'Amore, D. Simoneta, M. Gabriel, W. Kaiser, and H. Schiff, *Spritzgießen im Nanobereich - Kalibrierstrukturen für Rastersondenmikroskope*, Kunststoffe 90 (6/2000), 52-55 (2000). English version: *Nano injection moulding - calibration structures for scanning probe microscope*, Kunststoffe plast europe 90 (6/2000).
- [3] P.M. Kristiansen, C. Rytka, M.J. Cheung, H. Schiff, A. Schleunitz, C. Spreu, and H.H. Solak, Eulitha AG, *Kleinste Strukturen in der Massenfertigung abformen*, Plastics/Swiss Engineering STZ, Okt. (2011) 20-21.

4.12 Polymeric microcantilevers

Polymeric microcantilevers for bioanalytics applications

Process: Thermal thin-wall injection molding

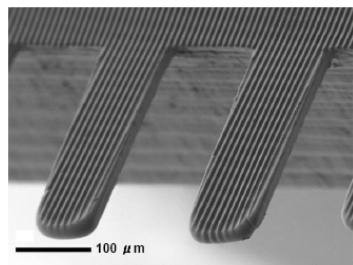


Figure:

Photograph of an injection molded microcantilever array featuring surface structures (here line grooves) achieved with embossed high-temperature polymer inserts. This example was realized in metallocene polypropylene using a structured PEEK foil as mold insert

Process:

Conventional injection molding for micro- and nanostructure replication from silicon wafers

Application:

Biosensing and cell force measurements

Keywords: thermal nanoimprint, polymer inserts, injection molding, microcantilevers

Project leader: Institute of Polymer Nanotechnology

Address: 5210 Windisch, Switzerland

Web-Address: <http://www.fhnw.ch/inka>

Process: Polymeric microcantilevers

Responsible: Per Magnus Kristiansen

E-mail: magnus.kristiansen@fhnw.ch

Partner: Paul Scherrer Institut (PSI)

Address: 5232 Villigen PSI, Switzerland

Web-Address: <http://www.psi.ch>

Process: Thermal Nanoimprint

Responsible: Helmut Schift

E-mail: helmut.schift@psi.ch

Partner: University of Basel, Biomaterials Science Center

Address: 4031 Basel, Switzerland

Web-Address: <http://www.bmc.unibas.ch>

Process: Biosensing

Responsible: Bert Müller

E-mail: bert.mueller@unibas.ch

Process description: Injection molding of microcantilevers with microstructured surfaces for bioanalytics and cell force measurements.

Purpose: The aim of this process is to produce high volume micro/nanostructured parts made out of bulk polymers, displaying a surface structure that adds functionality.

Major challenges: Manufacturing of the microcantilever mold with sufficient surface finish requires picosecond pulsed laser ablation. In view of the small dimensions of the molded cantilevers (thickness ~35 μm, length 500 μm and width 100 μm), large draft angles have to be used to allow for demolding without plastic deformation of the polymeric microcantilevers. Filling of the cavities is challenging as the dimensions are in the range of venting channels in classical injection molding.

Application and state-of-the-art: This dedicated tool is used for preparation of polymeric microcantilevers for biosensing – a joint research effort between PSI, FHNW and the University of Basel.

References:

- [1] P. Urwyler, H. Schift, J. Gobrecht, O. Häfeli, M. Altana, F. Battiston, and B. Müller, *Surface patterned polymer microcantilever arrays for sensing*, Sensors and Actuators A: Physical **172**(1) (2010) 2-8, doi:10.1016/j.sna.2010.12.007.
- [2] P. Urwyler, J. Köser, H. Schift, J. Gobrecht, and B. Müller, *Nano-mechanical transduction of polymer micro-cantilevers to detect bio-molecular interactions*, Biointerfaces **6**, SpringerOpen (2011), doi 10.1007/s13758-011-0006-6.
- [3] P. Urwyler, A. Pascual, P.M. Kristiansen, J. Gobrecht, B. Müller, H. Schift, *Mechanical and chemical stability of injection molded micro-cantilevers for sensing*, J. of Applied Polymer Science, (2012) in print

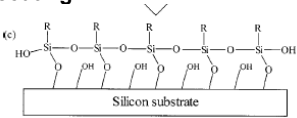
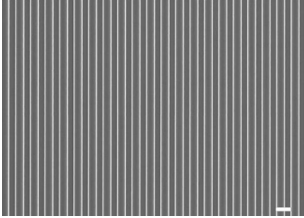
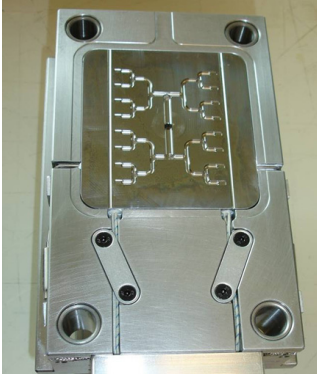
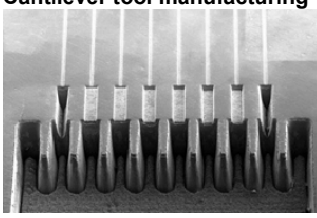
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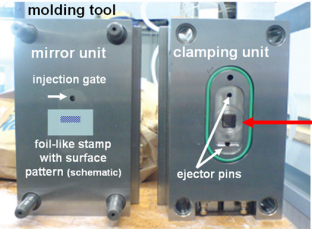
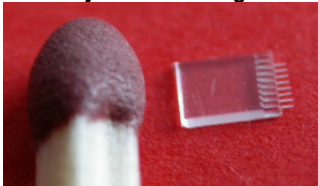
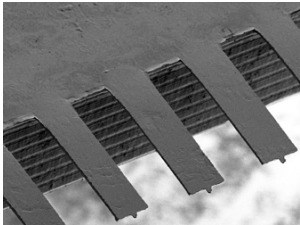
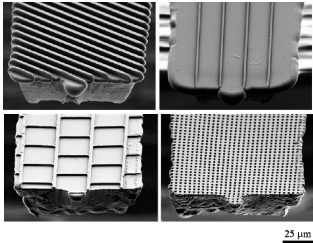
Prof. Dr. Per Magnus Kristiansen
University of Applied Sciences and Arts FHNW
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Klosterzelgstrasse 2
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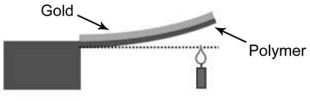
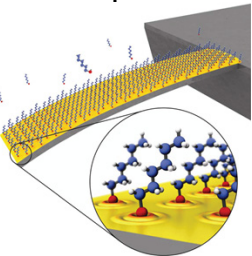
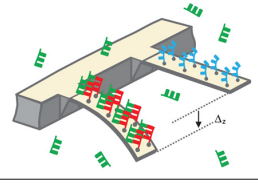
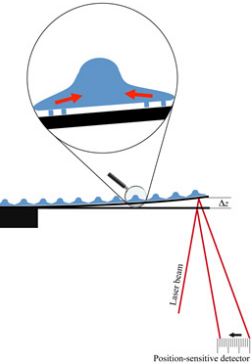
LoP2012_polymer micro cantilevers

Polymeric microcantilevers for bioanalytics applications

Process: wafer injection molding

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Polymer master inserts	e.g. PEEK	
1.1	Preparation of silicon master	Structure generation According to any suitable methods described in NaPa LoP or NaPANIL LoP	<i>Alternative materials such as quartz wafers may also be used with the present setup</i>
1.2	Application of antisticking coating 	Mandatory for allowing defect-free de-molding	
1.3	Thermal nanoimprint 	Structuring of the polymer film of choice is achieved through hot embossing with a silicon master with desired micro/nanostructure; Example: SEM picture of PEEK film with line grooves (scale bar 10 μm)	
End of Process 1			
2.0	Process 2: Tool manufacturing		
2.1	Mold manufacturing 	State of the art machining is used to manufacture the injection molding tool	
2.2	Cantilever tool manufacturing 	Pulsed laser ablation Is used to fabricate dedicated tool inserts for the manufacturing of microcantilevers	<i>Very fine venting channels are needed at the tip of the microcantilevers to avoid diesel effect caused by compressed air</i>
End of Process 2			

3.0	Process 3: Cantilever preparation	Injection molding	
3.1	Assemble tooling		
3.2	Mount structured polymer insert 	Fixation with scotch tape (tesa film) Sufficient for molding at melt temperatures up to 200°C for small	<i>Fixation of the structured polymer foil may be difficult for high temperatures and large sample volumes</i>
3.3	Micro injection molding 	Proper molding conditions Elevated mold temperature and high velocity filling of the mold	<i>Alternative: variothermal process control</i>
3.4	Coating with gold	PVD coating	<i>Not very strong adhesion of gold layer, depending on previous surface treatment</i>
End of Process 3			
4.0	Process 3: Biosensing	Cantisense research tool	
4.1	Inspection of cantilever quality 	SEM of bare cantilevers Complete filling of the cantilever beams is essential for reproducible biosensing experiments	<i>High viscosity melts will not allow complete filling of the thin-walled cantilever beams, thus preventing reproducible cantilever geometries to be manufactured</i>
4.2	Pattern check (if applied) 	SEM of structured cantilevers Different patterns can be replicated on cantilever beams depending on the inserted polymer foil and the location of the pattern	
4.3	Heat test	Temperature program Cantilever arrays are immersed in water (within Cantisense system) and temperature is raised from	<i>Different cantilever beams may exhibit differences in deflection due to morphological differences</i>

		25 to 30°C and deflection is monitored.	
4.4	Thiol adsorption 	Standard procedures Immersion in respective thiol solution to add functionality for detection of specific moieties	
4.5	DNA hybridization 	Detect complementary DNA strands in test solution Detection by differential signal between sensing MCs (Thiol-Sf162) and reference MCs (Thiol-NI4-3); sample DNA: 100µl of 1µM complementary Sf162	
4.6	Cell force measurements 	Cantilever deflection Is anticipated by the action of cell forces exhibited by cells aligned along line patterns of the cantilever	
End of Process 4			
End of Total Process			

General remarks:

Isothermal versus variothermal injection molding description: In contrast to isothermal injection molding, where the tool is kept at a constant temperature well below (and up to) the glass transition temperature of the injected polymer, variothermal molding is needed for the molding of high aspect ratio structures. Variothermal molding enables to inject the hot melt into a mold kept above the glass transition temperature. This way, freezing upon contact with the mold surface can be reduced and high aspect nanostructures molded. This requires either long cycle times, or new sophisticated heating and cooling system, in order to achieve short cycles with fast heating and cooling.

Application and state-of-the-art: Variothermal injection molding is increasingly used in industry but at present is not a standard process, since long cycle times are often prohibitive for mass fabrication.

4.13 Injection moulding with hybrid inlays

Standard fabrication process for nanostructured polymer inlays and guide for their use in injection moulding

Process: Thermal Injection Moulding

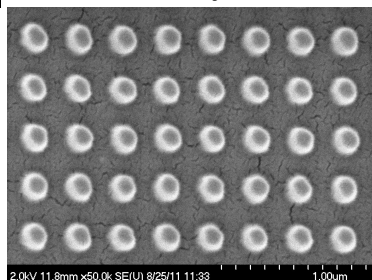


Figure:
Scanning electron micrograph of polycarbonate nanopillars produced by injection moulding with nanoimprinted hybrid polymer inlays.

Process:
UV-NIL using a quartz stamp in SU-8 resist on polyimide substrate & injection moulding guidelines.

Application:
Injection moulding traditionally difficult nanostructures, rapid mass prototyping of polymer samples with micro- and nanostructures, biology, optics, superhydrophobic surfaces, MEMs.

Keywords: UV, nanoimprint, injection, moulding, molding, photolithography

Project leader: University of Glasgow
Address: Oakfield Avenue, Glasgow, Scotland
Web-Address: [http:// www.glasgow.ac.uk](http://www.glasgow.ac.uk)

Process: Roll to Roll thermal NIL
Responsible: Nikolaj Gadegaard
E-mail: nikolaj.gadegaard@glasgow.ac.uk

Process description: Production of hybrid polymer inlays for injection moulding by imprinting into photocurable polymer film on a polymer substrate and a guide to their use in an existing injection moulding setup.

Purpose: This process provides a tooling solution which facilitates the reliable replication of pillar-like nanostructures as well as the rapid, high volume prototyping of micro- and nanostructured devices by injection moulding.

Major challenges: This process relies on high quality stamps being fabricated in advance. The nanoimprint steps and demoulding require a careful hand. Uncured photopolymer may stick to stamps.

Application and state-of-the-art: It is difficult (or impossible) to produce pillars and other raised structures with nanoscale dimensions by injection moulding with standard tooling materials such as nickel. This process provides a relatively uncomplicated and inexpensive way to achieve this as well as providing a useful process for the rapid prototyping of any structure required in large numbers within the boundaries of the mould tool's form factor.

References:

- [1] Stormonth-Darling and Gadegaard, *Macromolecular Materials and Engineering*, in publication, DOI = 10.1002/mame.201100397.
[2] Khokhar, Gaston, Obieta and Gadegaard, *Microelectronic Engineering*, 2011, 88, 11, 3347-3352, DOI = 10.1016/j.mee.2011.06.023






Contact information:

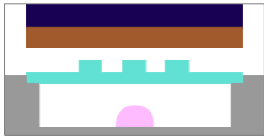
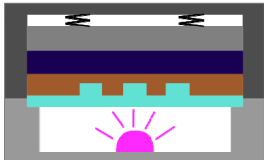
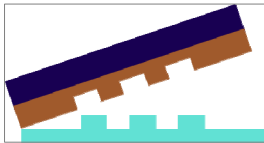

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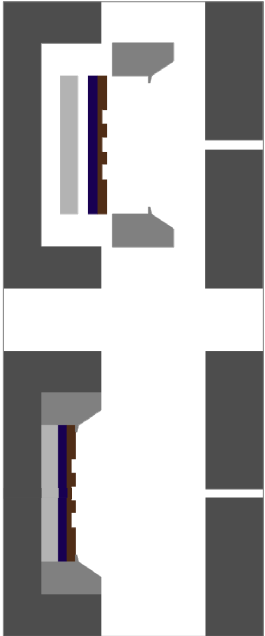
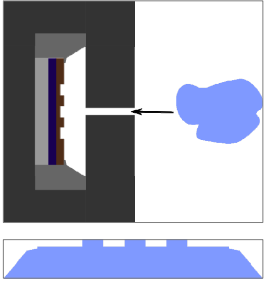
LoP2012_NIL020_inlay IM-process

Standard injection moulding process with polymer inlays

Process: Thermal injection moulding

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Stamp preparation	Quartz wafer format	
1.1	substrate selection and preparation 	standard quartz substrate 25 x 25 mm, 1 mm thick, polished on both sides	<i>Samples size may be varied to better suit the final inlay size if required.</i>
1.2	stamp fabrication 	Stamps fabricated by photolithography and RIE as described in NaPa Library of Processes section 3.15 (process 1) and [1-2].	<i>Inclusion of anti-stick coating is critical to stamp performance.</i>
	End of Process 1		
2.0	Process 2: Substrate preparation	Polyimide (PI) film	
2.1	sample selection 	Standard PI substrate Sample is cut or machined from 740µm thick Cirlex® sheet to the appropriate size for the injection moulder tool.	<i>Different thicknesses of PI film may be used. Kapton® comes in a range of thicknesses sown to ~25 µm</i>
2.2	sample cleaning	Prior to application of resist, sample must be cleaned in acetone, methanol and IPA with ultrasonic agitation for 5 minutes each. Nitrogen blow dry.	
	End of Process 2		
3.0	Process 3: Resist coating	For UV-NIL	
3.1	surface activation	Plasma treatment To enhance resist adhesion perform oxygen plasma treatment at 150-200 W for 15-20 s.	<i>Proceed directly to next step; do not leave a long delay.</i>
3.2	coating resist 	Resist No primer, SU-8 3000 series, apply with pipette evenly over surface	<i>With more viscous dilutions it may be easier to pour from the bottle than to use a pipette.</i>
3.3	coating resist (homogeneous layer) 	Spin coating of SU-8 Thickness: 20-50 µm, spin speed depends on resist grade/dilution.	<i>Ensure prevention or removal of large edge beading.</i> <i>This process requires a wet resist so a soft bake is not required.</i>
	End of Process 3		

4.0	Process 4: Imprinting	UV nanoimprint lithography	
4.1	prepare assembly 	Assemble samples Place stamp above light source, bring substrate into contact with stamp and apply weak pressure (~1 bar). Leave for 2 minutes.	
4.2	UV exposure 	Expose SU-8 Turn on UV source (ideally 356 nm wavelength) for 4 minutes	
4.3	demoulding 	Separate samples Turn off UV source, release pressure and carefully separate stamp from substrate	
4.4	curing 	Soft bake Hotplate, 65°C for 1 minute and 95°C for 5 minutes	
4.5	resist hardening	Hard bake oven, 180-300°C, 1-3 hours	<i>This strengthens the SU-8 before injection moulding</i>
4.6	process control	Optical, electron and atomic force microscopy <i>non-destructively</i>	<i>destructive (cleaving, metal coating) in SEM profilometry.</i>
	End of Process 4		<i>NB: It also possible to pattern solvent-free (soft baked) SU-8 by thermal NIL with a post imprint exposure and further bake (transparent stamp not required) or by thermal UV-NIL.</i>
5.0	Process 5: Injection moulding	Replicate structures	
5.1	preparation	Set up as normal prepare polymer (drying etc) and set up machine to your standard processing conditions	<i>NB if you normally use metal inlays you will probably want to adjust the following settings: tool temp: reduce by up to 20°C, melt temp: reduce by up to 20°C, cooling time: increase by 1-10 seconds.</i> <i>If such changes are not made you are likely to observe stretching of raised features (e.g. pillars). This effect can be tuned by</i>

			<i>adjusting tool temperature.</i>
5.2	<p>tool assembly</p> 	<p>Position inlay in tool The tool must contain a frame insert into which the inlay is placed with a back-plate of suitable thickness behind it.</p>	
5.3	<p>injection moulding</p> 	<p>perform injection moulding as normal</p>	
5.4	<p>process control</p>	<p>Optical, electron and atomic force microscopy <i>non-destructively</i></p>	<p><i>destructive (cleaving, metal coating) in SEM profilometry.</i></p>
	End of Process 5		
	End of Total Process		

4.14 Non-flat surfaces by injection moulding

Standard procedure for fabricating nanostructured non-flat surfaces by injection moulding

Process: UV Nanoimprint Lithography + Photolithography + Injection Moulding

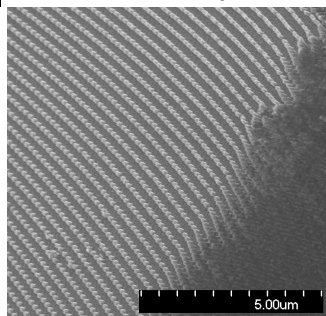


Figure:

Scanning electron micrograph of a regular array of 100 nm pillars on a sloped surface of a monolithic polycarbonate sample produced by injection moulding.

Process:

UV-NIL to define nanopattern in SU-8 resist on polyimide substrate, nonflat surface defined by photolithography & injection moulding guidelines.

Application:

Applications requiring mass production of multi length scale surface topographies, optics (e.g. non-reflective lenses), biology, superhydrophobic surfaces.

Keywords: UV, nanoimprint, injection, moulding, molding, photolithography

Project leader: University of Glasgow
Address: Oakfield Avenue, Glasgow, Scotland
Web-Address: [http:// www.glasgow.ac.uk](http://www.glasgow.ac.uk)

Process: Roll to Roll thermal NIL
Responsible: Nikolaj Gadegaard
E-mail: nikolaj.gadegaard@glasgow.ac.uk

Process description: Layering of patterned inlays to produce nanoscale surface topographies on non-flat injection moulded parts.

Purpose: It is advantageous for many potential applications to be able to pattern nanoscale features on curved surfaces. This small adaptation of an existing process facilitates this.

Major challenges: The limitation here lies in the ability of the top layer to conform to the surface of the bottom layer. As the bottom layer feature size approaches the top layer film thickness the translation of the bottom pattern is reduced. Furthermore, it is difficult to perform the imprint step on very thin substrates and they may also tear during the moulding process.

Application and state-of-the-art: Nanopatterns play an important role in the field of optics where it is often desirable to be able to place them on curved surfaces such as lenses. In biology there is a great deal of interest in the way cells and tissues respond to topographic structures at different length scales which may be simulated by devices fabricated with this technique.

References:

- [1] Johnny Stormonth-Darling and Nikolaj Gadegaard, Macromolecular Materials and Engineering, in publication, DOI = 10.1002/mame.201100397.
- [2] Khokhar, Gaston, Obieta and Gadegaard, Microelectronic Engineering, 2011, 88, 11, 3347-3352, DOI = 10.1016/j.mee.2011.06.023





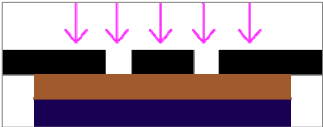
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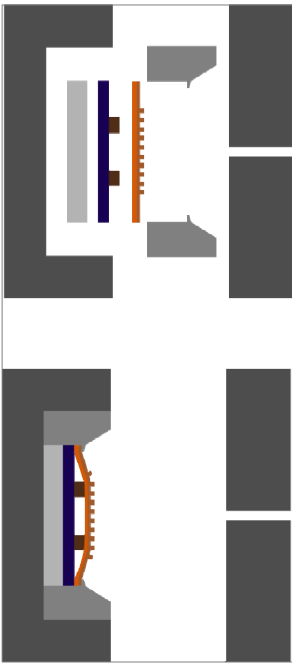
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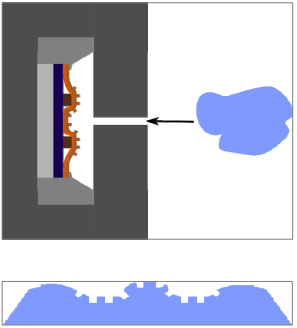
LoP2012_NIL021_non-flat IM-process

Non-flat nanostructured surfaces by injection moulding

Process: Thermal injection moulding

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Top layer preparation	Thin polyimide (PI) film	
1.1	sample selection 	Thin PI substrate Sample is cut from PI sheet (such as Kapton®) to the appropriate size for the injection moulder tool. Nominal film thickness: ~125 µm, but may be much thinner.	<i>Choice of film thickness will depend on the planned feature size of the bottom layer (subtopography).</i>
1.2	preparation and patterning 	Standard inlay process fabricate naonpatterned stamp by the process described in Section X.X	<i>Very thin films (less than 50 µm) can be very difficult to spin resist on to and pattern by NIL.</i>
	End of Process 1		
2.0	Process 2: Bottom layer preparation (photolithography example)	Polyimide (PI) film or any inlay material	
2.1	sample selection 	Standard PI substrate Sample is cut or machined from 740µm thick Cirlex® sheet to the appropriate size for the injection moulder tool.	<i>In this case we pattern SU-8 on a Cirlex inlay by photolithography, but it could be a different inlay material (e.g. steel) with any patterning technique desired (e.g. micro milling, millimeter scale drilling).</i>
2.2	sample cleaning	Prior to application of resist, sample must be cleaned in acetone, methanol and IPA with ultrasonic agitation for 5 minutes each. Nitrogen blow dry.	
2.3	resist coating 	Spin coating of resist Apply SU-8 resist as described in Section X.3.	
2.4	soft bake	Solvent evaporation hot plate, 95°C, 30 minutes	<i>Bake time may be extended for very thick layers</i>
2.5	Photolithography 	Mask aligner expose (i-line); time depends on feature size and resist thickness	<i>The minimum feature size should be greater than the film thickness.</i>
2.6	post exposure bake	Curing hot plate, 65°C, 1 minute 95°C 5 minutes	<i>Bake time may be extended for very thick layers</i>
2.7	pattern development	Developer EC Solvent, 5 minutes.	

		Rinse in IPA and blow dry with nitrogen	
2.8	resist hardening	Hard bake oven, 180-300°C, 1-3 hours	<i>This strengthens the SU-8 before injection moulding</i>
	End of Process 2		
3.0	Process 3: Injection moulding	Replicate structures	
3.1	preparation	Set up as normal prepare polymer (drying etc) and set up machine to your standard processing conditions	<i>NB if you are using 2 polymer inlays and normally use metal inlays you will probably want to adjust the following settings: tool temp: reduce by up to 20°C, melt temp: reduce by up to 20°C, cooling time: increase by 1-10 seconds.</i> <i>If such changes are not made you are likely to observe stretching of raised features (e.g. pillars). This effect can be tuned by adjusting tool temperature.</i>
3.2	tool assembly 	Position inlays in tool The tool must contain a frame insert into which the inlays are placed. The top (thin) inlay is inserted first with the bottom layer behind it. Place a back-plate of suitable thickness behind them.	

<p>3.3</p>	<p>injection moulding</p> 	<p>perform injection moulding as normal The top layer will conform to the topography of the bottom layer and the resulting moulded part will display its nanopattern on a non flat surface</p>	<p><i>Very thin top-layer films may be torn by the process. You may wish to start at a lower injection speed than usual or use a stronger/thicker inlay.</i></p>
	<p>process control</p>	<p>Optical, electron and atomic force microscopy <i>non-destructively</i></p>	<p><i>destructive (cleaving, metal coating) in SEM profilometry.</i></p>
<p>End of Total Process</p>			

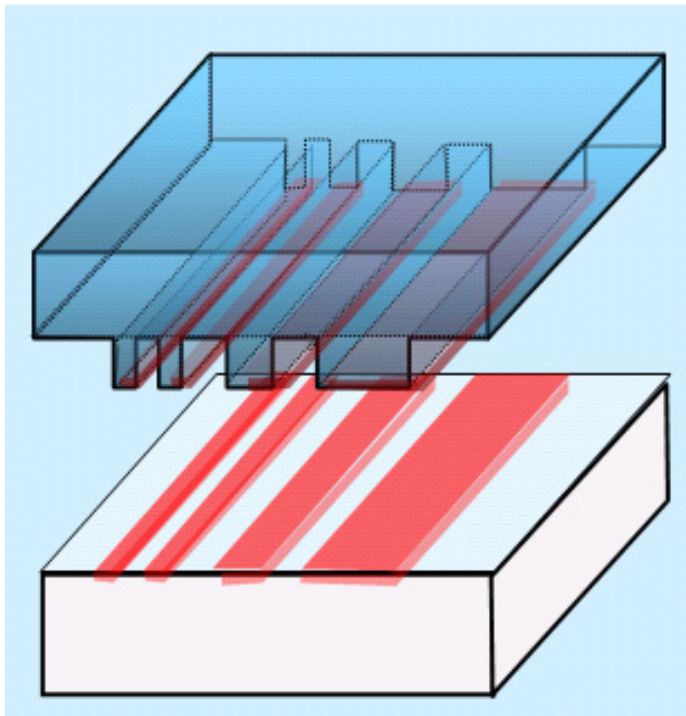
5. Soft Lithography and Microcontact Printing

Contributions to this section of the library are from

IBM ZRL - Zürich/Switzerland
Dr. Heiko Wolf

AMO - Aachen/Germany
Ulrich Plachetka

Ecole Normale Supérieure – Paris/France
Prof. Dr. Yong Chen



5.1 Soft stamp fabrication and alkanthiol printing

Microcontact printing of alkanethiols on gold

Process: microcontact printing lithography



Figure:

Casting PDMS (silicone) precursor onto a structured template in a Petri dish.

Process:

Casting PDMS (silicone) precursor (elastomer base and curing agent) onto a structured template in a Petri dish. Curing (hardening) by heat (60°C, 12-24 h).

Application:

Microfluidic devices
Photonic crystals

Keywords: microcontact lithography, soft lithography, protein patterning, PDMS

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Process: microcontact lithography
Responsible: Heiko Wolf
E-mail:

Process description: Microcontact printing (μ CP, mCP) of alkanethiols on gold

Purpose: A process is described for transferring a pattern from a silicon master via an elastomeric stamp onto a solid substrate.

Major advantages: In comparison to standard photolithography, microcontact printing is a low-cost, large-area, high-resolution patterning process.

References:

- [1] Libioulle, L.; Bietsch, A.; Schmid, H.; Michel, B.; Delamarche, E. *Langmuir* **1999**, *15*, 300-304.
- [2] Larsen, N. B.; Biebuyck, H.; Delamarche, E.; Michel, B. *Journal of the American Chemical Society* **1997**, *119*, 3017-3026.
- [3] Geissler, M.; Wolf, H.; Stutz, R.; Delamarche, E.; Grummt, U.-W.; Michel, B.; Bietsch, A. *Langmuir* **2003**, *19*, 6301-6311.




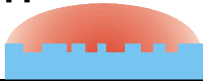
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LoP2007_mCP001_microcontact printing alkaethiols

Alkanethiol printing

Process: microcontact printing lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.	Stamp		
1.1	Master fabrication 	Fabricate patterned silicon master by photo- or E-beam lithography	<i>ideal with smooth bottom surfaces and smooth vertical sidewalls</i>
1.2	Master preparation	Coat master with fluorinated separation layer	hydro-phobic surface treatment to facilitate stamp separation
1.3	Mixing of PDMS	Mix precursor SYLGARD 184 elastomer base with curing agent 10:1	<i>good mixing required for catalytic reaction,</i>
1.4	Degasing	Degas mixture to avoid air bubbles in stamp	<i>premixed aliquots can be stored at -20 °C for 1-3 months</i>
1.5	Stamp curing 	Pour liquid prepolymer onto master inside of petri dish and cure at 60 °C for 12-24 hours.	
1.6	Stamp work-up	Cut and peel stamp off master. Rinse stamp three times with EtOH and dry under a flow of N ₂ for 30 s.	
2	Ink [1]		
2.1	Alkanethiols as ink	Chose an alkanethiol, e.g. dodecanethiol (DDT), hexadecanethiol (HDT) octadecanethiol (ODT) or eicosanethiol (ECT)	<i>higher molecular weight thiols decrease ink diffusion, but increase disorder of monolayer and tend to crystallize at the stamp surface</i>
2.2	Purification (optional)	Purify by chromatography using silica gel (20:1 hexane-ethyl acetate on Silica Gel 60, ~200 g per 0.5 mL of thiols), and degas by successive freeze-pump-thaw cycles at a pressure of <100 mTorr for 24 h.	<i>purification removes low-molecular-weight thiols</i>
2.3	Ink solution	Prepare diluted thiol solution in ethanol, e.g. 0.1 mM	<i>changing the concentration allows to control the amount of ink transferred to the stamp</i>
2.4	Storage	Store purified ink solution at 4 °C in the dark for up to one week.	
3	Substrate [1]		
3.1	Surface preparation	Evaporate ~1 nm Ti onto a Si/SiO ₂ wafer, e.g. with an e-beam evaporator at ~2x10 ⁻⁷ Torr and a rate of ~0.5 nm s ⁻¹ .	
3.2	Au deposition 	Immediately following, evaporate 15 nm gold (same evaporation parameters)	
4	Inking		
4a	Immersion inking [2] 	Inking by placing a drop of ink solution onto the stamp.	<i>only the average amount of ink transferred can be controlled.</i>
4a.1	Inking	Place two drops (~0.2 mL) of the freshly prepared (<1 h) ink solution on top of the stamp.	<i>make sure there's enough liquid to cover the surface.</i>

		After 30 s remove liquid quickly (<0.5 s) under a stream of N ₂ .	
4a.2	Drying	Continue the flow of N ₂ for 30 s after evident disappearance of the bulk drop to evaporate residual EtOH, use within 15 s.	
4b	Contact inking [1] 	Inking with an ink pad selectively directs the ink where it is needed.	<i>quality of monolayer is less dependent on pattern geometry, diffusion is minimized.</i>
4b.1	Ink pad fabrication	Prepare small blocks (~2 cm ² and 4mm thick) of cured PDMS as ink pads.	
4b.2	Impregnation	Immerse the ink pad in the thiol-solution for at least 12 h.	
4b.3	Drying and storage	Withdraw from the solution, dry in a stream of N ₂ for 10 s and store in a small glass flask.	
4b.4	Inking	Place the patterned stamp on the ink pad without applying pressure for 40s.	<i>conformal contact allows transfer of thiols. Inking times control amount of thiols transferred.</i>
5	Printing		
5.1	Making Contact 	Place stamp onto gold substrate, monitor formation of conformal contact optically.	<i>conformal contact is made by the stamps own weight.</i>
5.2	Detaching	Remove the stamp after 10-20 s.	<i>the longer the printing time, the fewer the defects in the printed monolayer, but the higher the ink diffusion.</i>
6	Etching [3]		
6.1	Preparation of etch bath	Prepare a ferric nitrate etch bath (20 mM Fe(NO ₃) ₃ •9H ₂ O and 30 mM thiourea in DI water, adjusted to pH 2.0 using HCL)	<i>the concentration of the ferric and thiourea in solution determine the etch rate</i>
6.2	Etching 	The bath should be operated at 23-25 °C with moderate stirring and has an etch rate of ~ 10 nm min ⁻¹ .	<i>the granularity of the gold substrate limits the edge resolution to the size of the gold grains (15-30 nm).</i>

5.2 Optical resonators

Fabrication of optical resonators by soft UV-NIL

Process: soft lithography

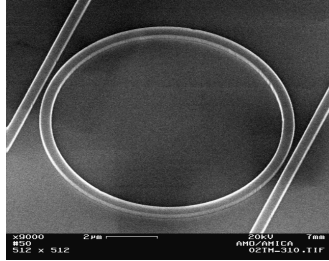


Figure:
SEM-image of an imprinted microring resonator.

Process: A polymeric imprint template is cast moulded from a master pattern and replicated by imprinting into a UV-curable resist. Afterwards the device is etched into the appropriate substrate.

Application:
Large scale patterning

Keywords: soft UV-NIL, PDMS stamps

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Process: Soft UV-NIL
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Process description: An imprint template is fabricated via cast moulding of from a pre-structured form and used during an imprint process. During the imprinting, first a thin layer of a low viscosity resist is spin coated onto the desired substrate followed by pressing the flexible imprint template into the liquid layer. Then the resist is polymerized by UV exposure, the template is removed and may be used for numerous other replications via Soft UV-NIL. Etching may be performed using standard RIE equipment

Purpose: This imprinting process can be used to pattern on large area scale with resolutions down to the 20nm regime. Due to the elastomeric properties of the imprint template patterning can also be performed on non-flat substrates, with very low imprint pressures and at room temperature. The major purpose for the development of this process is cost reduction.

Major challenges: The major challenge when using soft template materials is the adaptation of the young modulus.

Application and state-of-the-art: Products and prototypes that rely on large area nano-patterning at high resolutions at cheap costs. In this library it is used to fabricate photonic structures in silicon waveguide technology.

References:

- [1] U. Plachetka, M. Bender, A. Fuchs, T. Wahlbrink, T. Glinsner and H. Kurz; *Comparison of multilayer stamp concepts in UV-NIL, Microelectronic Engineering 83 (2006) 944-947*
- [2] M. Bender, A. Fuchs, U. Plachetka and H. Kurz; *Status and Prospects of UV-Nanoimprint Technology, Microelectronic Engineering 83 (2006) 827-830*

Contact information:

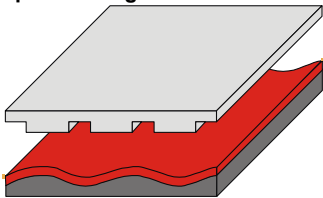
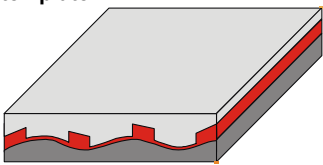
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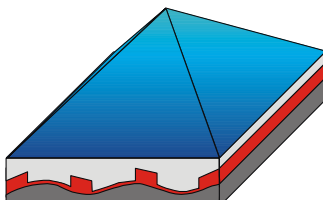
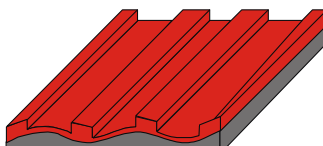
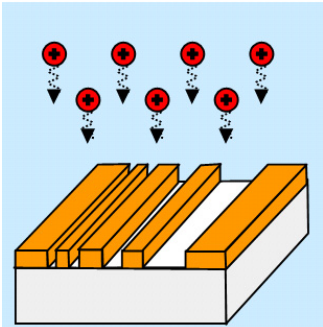
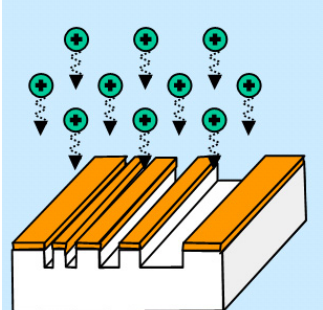
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LoP2007_SoftNIL001_Resonators by SoftNIL

Optical resonators

Process: soft lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0a	Process 1: Master preparation		
1.1	Master fabrication:	Si substrate, 6", <100>, one side polished, standard ebeam, followed by RIE (other substrates may also be used, i.e. metals, resist, etc.)	
1.2	Deposition of anti-adhesion layer:	Whatever the chosen master material is, an antiadhesion layer needs to be deposited onto its surface by plasma deposition (i.e. in an etching chamber); CxFx-plasmas works (standard passivation settings for your tool)	
	End of Process 1		
1.0b	Process 2: Stamp preparation		
1.1	Elastomeric template material:	A 10:1 (base:curing agent) mixture of Sylgard 184 (Dow Corning) is prepared and degassed in a vacuum	
1.1	Cast moulding of imprint template:	The mixture is poured onto the master, degassed in a vacuum and afterwards cured on a hotplate (110°C@30min)	
1.2	Detachment	The template is then cut and detached from the silicon master.	
2.0	Process 3: Lithography		
2.1	Spin -coating	 <p>spincoating of UV-curable resist onto an SOI-substrate (depending on the application other substrates may be used freely) imprint resist: AMONIL MMS4 (3000rpm@30sec)</p>	
2.2	Soft imprinting with flexible template	 <p>The flexible imprint template is pressed into the liquid resist at an imprint pressure of 50mbar; the template adjusts to the non-flat parts of a substrate The used tool may be a EVG620 custom modified mask aligner</p>	

<p>2.3</p>	<p>UV-exposure</p> 	<p>The AMONIL resist is cured directly through the flexible imprint template by UV-exposure in the EVG620 imprint tool</p>	
<p>2.4</p>	<p>Detachment of template</p> 	<p>After completely curing the resist the imprint template is removed from the polymerized imprint resist; the moulded flexible imprint template can be used for other imprints</p>	
<p>End of Process 2</p>			
<p>3.0 Process 3: Pattern Transfer</p>			
<p>3.1</p>	<p>Residual Layer (Breakthrough) Etching</p> 	<p>BCl₃ -RIE (The plasma is used to open the SOI substrate)</p>	
<p>3.2</p>	<p>Substrate Etching</p> 	<p>HBr-RIE (This plasma will stop perfectly on the BOX of an SOI-wafer)</p>	

5.3 Mix- and match of soft-NIL and photolithography

Soft UV nanoimprint and optical lithography based mix-and-match technique

Process: soft lithography, optical lithography

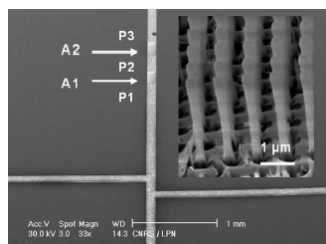


Figure:

Cross microfluidic channels with two integrated nanopillar arrays (A1 and A2) obtained using a mix-and-match approach based on i) soft UV nanoimprint lithography, ii) standard photolithography and iii) reactive ion etch techniques

Process:

Soft UV nanoimprint lithography

Application:

The mix and match approach can be applied for any type of micro and nanostructures patterning as well as their device integration. In the case of microfluidics, the nanopillar are used as sieving gels for DNA molecule separation

Keywords: soft UV nanoimprint lithography

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Process: soft UV nanoimprint

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Partner: ENS

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Process: soft UV nanoimprint

Responsible: Yong Chen

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Process description: Soft UV NIL is used to pattern only high density nanostructures. Then, after lift-off, the mould pattern is defined on the substrate with alignment markers. A standard photolithography is applied to define patterns with large size features, followed by the second lift-off. Afterwards, both micro and nanoscale features are etched into the substrate by reactive ion etch. Finally, the pattern structures are covered by a PDMS layer, forming a microfluidic device with integrated high density nanopillars arrays. Such a mix-and-match process is highly parallel which can be used for large scale manufacturing of many other types of nano-devices.

Purpose: To integrate high density nanostructures into micro-devices. A particular example is given for the fabrication of microfluidic chips for large size DNA molecule separation but other types of micro-devices can also be obtained in a similar way.

Major challenges: Integration of high density nanostructures into functioning microfluidic devices with parallel process

Application and state-of-the-art: The proposed process has been validated by demonstration of microfluidic device with integrated high density nano-pillars arrays for large size DNA molecule separation. The same device has already been fabricated by electron beam lithography based techniques but this is the first demonstration of highly parallel process for such microfluidic devices.

References:

- [1] J. Shi, A. P. Fang, L. Malaquin, A. Pépin, and D. Decanini, J. L. Viovy and Y. Chen, *Highly parallel mix-and-match fabrication of nanopillar arrays integrated in microfluidic channels for long DNA molecule separation*, Appl. Phys. Lett. **91**, 153114 (2007)

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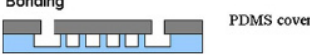
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LoP2007_SoftNIL002_NIL Mix&Match

	Process	Technical Parameters	Remarks
1.0	Process 1: Master fabrication		
1.1	Pattern definition of by electron beam lithography	Standard EBL Silicon substrate PMMA resist	<i>Including only nanostructures and alignment markers</i>
1.2	Pattern transfer	40nm Nickel evaporation Lift off Reactive ion etch with SF ₆ gas	
1.3	Surface treatment	Evaporation of anti-sticking reagent In TMCS vapour during 1 min	
	End of Process 1		
2.0	Process 2: Soft stamp preparation		
2.1	Thin layer PDMS deposition	Spin coating Approximately 10µm thickness	
2.2	Soft PDMS layer deposition	Casting and curing 5-10mm thick and baked at 80°C for 30min	
2.3	PDMS stamp separation	Manual	
2.4	Surface treatment	Evaporation of anti-sticking reagent In TMCS vapour during 1 min	
	End of process 2		
3.0	Process 3: Photolithography mask		
	Mask design and fabrication	Standard photolithography	<i>Including all large size features and alignment markers</i>
4.0	Soft UV nanoimprint Soft UV NIL 		
4.1	Spin coating of layer 1 (sacrificial layer)	Spin-coating of PMMA 300 nm thickness	<i>A thin quartz plate can be used for facilitating optical imaging of DNA migration.</i>
4.2	Spin coating of layer 2 (UV-NIL layer)	Spin coating of AMONIL 100 nm thickness	
4.3	Soft UV Nanoimprint	Imprint at low pressure UV expose (1 min)	<i>Nanostructures alone can be easily replicated with large process latitude.</i>
4.4		De-moulding	
4.5	Residual Layer (Break-through) Etching	Reactive ion etch O ₂ plasma	
	End of Process 4		
5.0	Process 5: First lift-off		

			
5.1	Lift-off	Ni thin film E-beam evaporation (40nm) Dissolution of AZ resist	
	End of Process 5		
6.0	Process 6: Photolithography Photolithography 		
6.1	Resist deposition	Spin coating AZ 5215E Resist pre-bake at 125°C for 1min	
6.2	UV exposure	UV exposure 1min with a standard aligner	<i>With alignment</i>
	End of Process 6		
7.0	Process 7: Second lift-off Lift-off 		
7.1	Lift-off	Ni thin film E-beam evaporation (40nm) Dissolution of AZ resist	
	End of Process 7		
8.0	Process 8: Pattern transfer Reactive ion etch 		
8.1	Etch of micro and nanostructure into the substrate	Reactive ion etch SF ₆ plasma	<i>Both micro and nanostructures are etched simultaneously.</i>
8.2	Nickel mask removal	Chemical etch HNO ₃ for 1min	
	End of Process 8		
9.0	Process 9: Device assembling Bonding 		
9.1	Preparation of PDMS cover slide	PDMS coating (1:10) Over a flat silicon wafer	<i>Other materials can also be used as cover layer</i>
9.2	Access hole drilling	Manuel	
9.3	Surface activation	Plasma treatment 1 min in a plasma cleaner for both PDMS and etched sample	
9.4	Device assembling	Thermal bonding In an oven of 70°C for 30min	
	End of process 9		

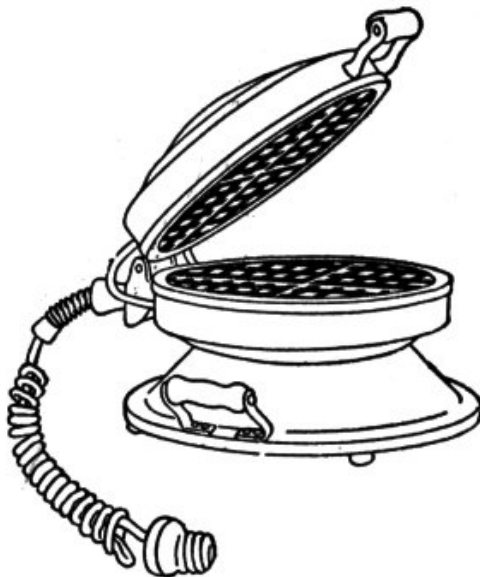
General remarks:

Since only nanoscale features are replicated by nanoimprint lithography, the fabrication process latitude can be largely enhanced. In addition, both lift-off and reactive ion etch steps can be replaced by other pattern transfer techniques. Therefore, the above mix-and-match process is highly parallel and versatile not only for microfluidic device fabrication but also for manufacturing of other types of nano-devices at low cost and high throughput.

6. Nanoimprint Lithography in Daily Life

Contributions to this section of the library are from

PSI/LMN – Villigen PSI/Switzerland
Dr. Helmut Schiff



6.1 Hot embossing of waffles

Fabrication process for waffles made with a waffle iron

Process: thermal nanoimprint (hot embossing)



Figure:

Photograph of a waffle made from apple batter. The waffle iron consists of two round cast iron plates with long handles. Here it is placed onto a mobile electrical cooking plate.

Process:

Hot embossing of batter with high content of eggs.

Application:

Afternoon coffee and birthday celebration with children.

Keywords: thermal nanoimprint, batter, waffle, surface coating

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Process: Thermal Nanoimprint

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Process description: A batter made from eggs, flour, milk and sugar is cast onto a hot waffle iron and baked into crispy waffles. The iron gives the waffle its distinctive characteristics, its shape and the little pits that trap your preferred topping.

Purpose: Waffle baking is a heat-assisted molding process of a thermoset material in which all aspects of nanoimprint are present ranging from material issues, tools, stamps, rheology, residual layer minimization, surface coating. This is also the reason why it is often presented as an introduction to NIL processing and particularly in this NaPANIL library of processes.

Major challenges: The science of baking is difficult to describe with simple scientific descriptions due to its complexity. Furthermore, the waffle batter is not thermoplastic (it is a thermoset and during curing generates porous waffles). Therefore resolution limitations cannot be easily assessed.

Application and state-of-the-art: Waffle baking is a well known process that is established in many households since centuries.

References (you will find tons of recipes in the internet):

- [1] http://en.wikipedia.org/wiki/Waffle_iron
- [2] <http://www.waffle-recipe.com/>
- [3] http://www.exploratorium.edu/cooking/icooks/article_5-03.html
- [4] <http://allrecipes.com/recipe/classic-waffles/>
- [5] Swiss waffle recipe with high content of eggs – private source





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LoP2012_NIL022_baking of waffles

Fabrication process for waffles made with an waffle iron

Process: thermal nanoimprint lithography

	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0	Process 1: Preparation	Silicon wafer format	
1.1	Preparation of tools  Often iron molds are round, 150-200 mm in diameter and consisting of 4 to 6 heart like sections	Waffle iron Waffle irons typically consist of two thick metal (cast iron) plates that are flat at one and structured on the other side. Both structures are designed to yield structures with constant thickness (also disc and rims) and allow space for 2-5 mm. For alignment and handling purposes they are connected with a hinge. Prepare large and smaller bowl, electric hand beater and ladle	Different tool options 1. for fire 2. for hot plate 3. automated with integrated electrical heating and temperature control <i>Waffles are different from so-called "Bretzel", which are thinner and often more ornamented (not to confuse with the pretzels made from sour dough)</i>
1.2	Preparation of batter (dough)  	Ingredients (for 4 persons) butter: 250 g granulated sugar: 100 g eggs (separated): 6 whole milk (3.5 %): ¼ liter all-purpose flour: 300 g lemon zest: 1 tea spoon salt: 1 pinch (dash) Directions 1. Separate eggs into yolk and whites, set whites aside in a small mixing bowl. 2. Put butter, sugar and yolks into a large mixing bowl, whisk them together with hand beater until fluffy. 3. Add flour, milk, and finally the lemon zest to the ingredient mixture, and mix gently until combined. Don't over-mix! 4. Beat whites until moderately stiff. 5. Fold stiff egg whites into mixture.	Alternatives: <i>In the internet different recipes for waffles can be found, including such with vegetable oil instead of butter, baking powder or yeast instead of high number of eggs, butter-milk instead of whole milk, and vanilla extract for flavoring.</i> <i>Wholemeal flour might need more liquid and time to soak.</i> <i>Pre-heat oven, if not served immediately after cooking.</i> <i>Prep Time: 15 minutes</i> <i>Cook Time: 30 minutes</i> <i>Total Time: 45 minutes</i> <i>The final batter should have a foamy, viscous appearance (but not liquid), which flows easily from the batter.</i>
	End of Process 1		
2.0	Process 2: Fabrication of waffles	Baking of waffles	
2.1	Coating and pre-heating of iron 	Coat the waffle irons generously with fat or vegetable oil (using a brush) should be repeated every time – or every second time Pre-heat your waffle iron to its hottest setting.	<i>Butter of vegetable fat is normally used to guarantee the release of the baked waffle without damage</i> <i>Alternative: Spray both surfaces with cooking spray. State-of-the-art</i>

		 <p>Fatal damage due to adhesion</p>	<p>automated waffle irons are often coated with antiadhesive Teflon. In addition, the inherent fat content of the batter adds to the release properties.</p>
<p>2.1</p>	<p>Baking</p>  	<p>Baking Ladle 120 to 180 g (½ to ¾ cup) batter on the hot waffle iron and close it.</p> <p>Press gently to enable spreading of the batter</p> <p>Bake 3 min @ hottest temperature</p> <p>Cook until until no more steam comes out of the waffle iron, or if the iron's indicator light shows that cooking is complete. The finished waffle should be golden brown and crispy.</p> <p>Lift the waffle out of the iron with a pair of tongs and either serve right away or transfer it to the oven to keep warm.</p>	<p>Placing a cookie-sheet under the iron can help catch any batter drippage during cooking. It's not unusual for a bit of batter to seep out of the edges of the iron. If there is excessive leakage, use less batter for the next waffle.</p> <p>Do not open too early, otherwise the incompletely cooked waffle will rip and parts will stick to the iron.</p> <p>Waffle should be crispy at the outside and slightly soft at the inside. This – along with the thickness of the waffles (the “residual layer”) – can be controlled by the amount of batter</p>
	<p>End of Process 2</p>		
<p>3.0</p>	<p>Process 3: Serving</p>	<p>Coating</p>	
<p>3.1</p>	<p>Serving example</p> 	<p>Decoration There are lots of different variations on the shape of waffles, the actual recipe for making waffles and what you put on top of or eat along with waffles. Some ideas include butter and syrups, powdered sugar, chocolate, strawberries, blue berries and meat.</p>	<p>Cross-section of a thick (Belgium) waffle</p> 
	<p>End of Process 3</p>		
	<p>End of Total Process</p>		

General remarks:

Traditional waffle irons are attached to tongs with wooden handles and are held over an open flame, or set on a stove. Most modern waffle irons are self-contained tabletop electrical appliances, heated by an electric heating element controlled by an internal thermostat. Many have a light that goes off when the iron is at the set temperature. Most modern waffle irons are coated with a non-sticking coating (Teflon) to prevent the waffles from sticking to them.

Modern waffle iron makers offer a large variety of choices. Some waffle irons can make a very thin waffle, capable of making waffle cones. While there is no set standard of classification for waffle shapes or thicknesses, models that fall within the most common shapes and thicknesses are often labeled as "traditional" or "classic". Models that make thicker and/or larger pocketed waffles are often labeled as "Belgian" waffle makers. In the USA, the most commonly used determining factor of whether a waffle is a "Belgian waffle" or not is the thickness and/or pocket size, although the recipes between Belgian waffles and American waffles do differ.



Figure 1: This is an example of waffles made from apple batter on the veranda of our home in Switzerland. The waffle iron consists of two round cast iron plates with long handles without thermal insulation (cast iron is a bad thermal conductor) that are connected by a hinge. Here it is placed onto a mobile electrical cooking plate.

The science/physics behind waffle baking is the following:

Egg whites are 88 percent water, yolks nearly 50 percent. So, together with the milk, the high ratio of eggs contributes liquid to batters and doughs. As flour absorbs liquid in baking, starch granules swell to form the framework that becomes a cake. Eventually moisture converts to steam, a leaven so powerful that just one part liquid explodes into 1,600 parts steam. On a smaller scale, the steam created from the liquid in just one or two eggs works quietly in most batters and doughs to boost rising.

The proteins in eggs also enable them to act as leavens but in a completely different manner. Proteins unwind and stretch to form the flexible, elastic film that encases air bubbles. When eggs are beaten, they can expand to foam that is up to eight times their original volume. Beaten egg whites hold millions of tiny air bubbles, which lift sponge cakes and souffles. Even in batters containing baking powder, beaten egg whites are an additional source of leavening.

Starch, a carbohydrate that makes up about 70% of flour by weight, also plays an important role. Starch reinforces gluten and absorbs water during baking, helping the gluten to contain the pockets of gas, e.g. produced by the yeast or present due to the egg foam. During baking, the gas in the batter continues to expand. As the temperature of the cooking dough rises, the gluten hardens, and the dough solidifies.

Ref.: http://www.exploratorium.edu/cooking/icooks/article_5-03.html

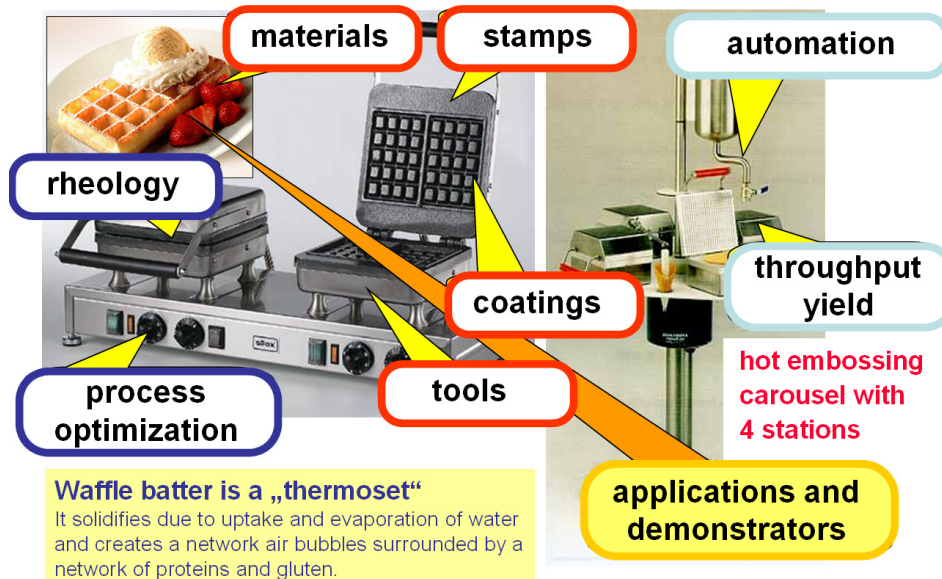


Figure 2: A typical presentation of aspects of molding which are helpful to understand the optimization of the thermal nanoimprint process.

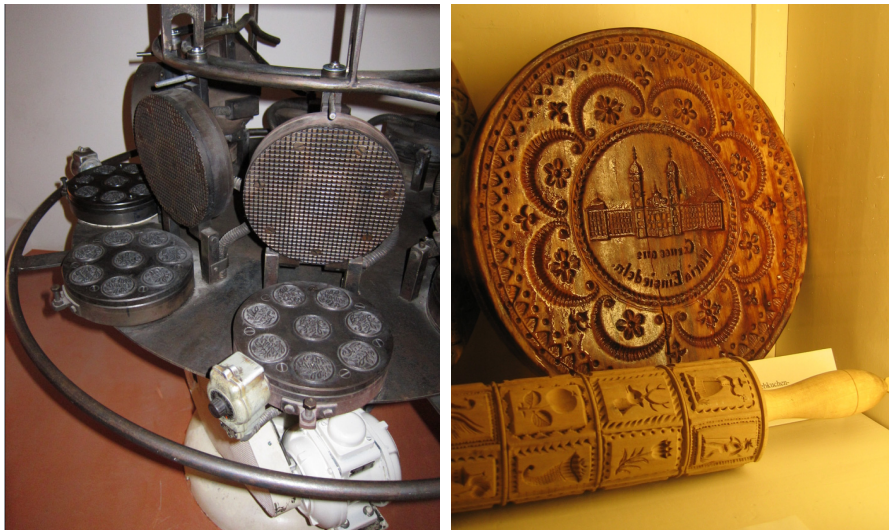


Figure 3: The Swiss traditional enterprise Kambly specializes in fabrication of Swiss Bretzeli (Bricelets), which are thin waffles without soft “interior”. The photograph (left) shows a machine in the Kambly museum in Trubschachen in Emmental, Switzerland. However, in contrast to waffles, the dough is not liquid and applied as soft balls. A range of old-fashioned wooden molds can also be found in Einsiedeln, Switzerland, in the Lebkuchen museum. Since Einsiedeln was one of the most important Benedictine monasteries from medieval ages up to today, the ginger bread making was well connected with the technique to pattern bread for holy mass. The photograph shows flat wooden stampers and roll molds.

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