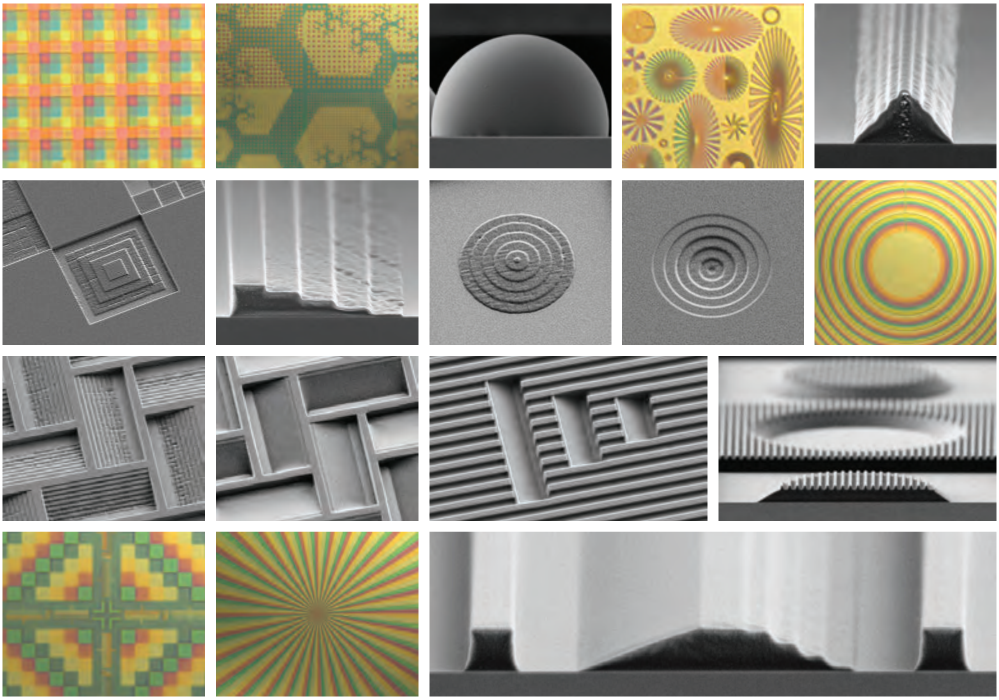

Library of Processes

Nanopatterning, Production and Applications based on Nanoimprint Lithography

Second edition with results of the NaPANIL-project, March 2012

Editor: H. Schift
Publisher: J. Ahopelto, NaPANIL Consortium

NaPANIL – Library of Processes

Nanopatterning, Production and Applications based on Nanoimprint Lithography

Second edition of the NaPa Library of Processes
with results from the NaPANIL-project, 2008 – 2012, status March 2012,
and with updated results from the NaPa-project, 2004 – 2008

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Disclaimer

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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 intented 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.

Acknowledgement

We thank all consortium partners of the NaPa and NaPANIL project for their valuable contributions to establish this Library of Processes. It would not have been possible without their technological and scientific achievements in both projects. In particular, we acknowledge all co-authors of Part II: Appendix - Process Library of the NaPa LoP (in 2008) as well as the NaPANIL LoP (in 2012).

NaPANIL - Library of Processes

Content

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 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 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 NanoImprinting Lithography”, 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 NaPa LoP can still be downloaded via the NaPANIL website.

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. Addtionally 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 variation 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 a 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 growths 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 extend. This collection of recipes is intented 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

This library is printed as a booklet in a limited number by the NaPANIL consortium and distributed by NaPANIL partners. It is not sold in bookshops or via internet. Information about how to get copies of this library will be placed on the NaPANIL web site [1] or elsewhere. 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 will not meet any more as a whole as it did frequently during the active time of the NaPANIL project and other projects, probably with fewer partners, will continue to collaborate. As the NaPa LoP, this library will be made available for download, to enable 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 "PAtterning 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) [online, 40 MB]. URL: http://www.NaPANIL.org.
[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. Schift, *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. Schift, 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. Schift, Paul Scherrer Institut. Please do not contact the editor for copies of this library.

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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.

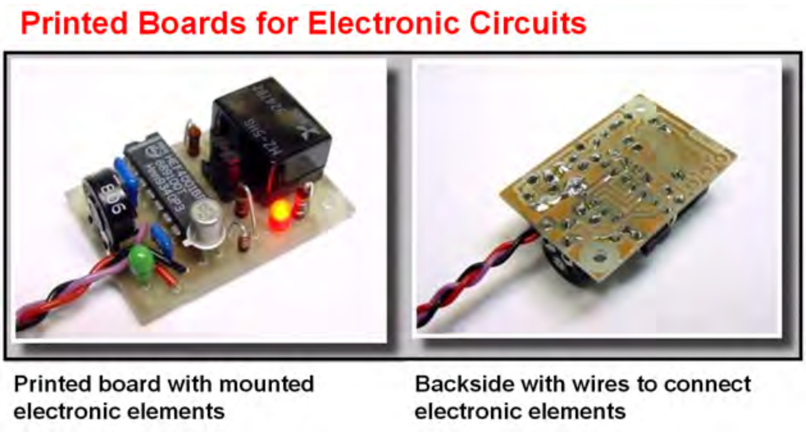


Figure 4.1: Photographs of a printed board after mounting of the discrete electronic elements (front and backside).

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 200 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.

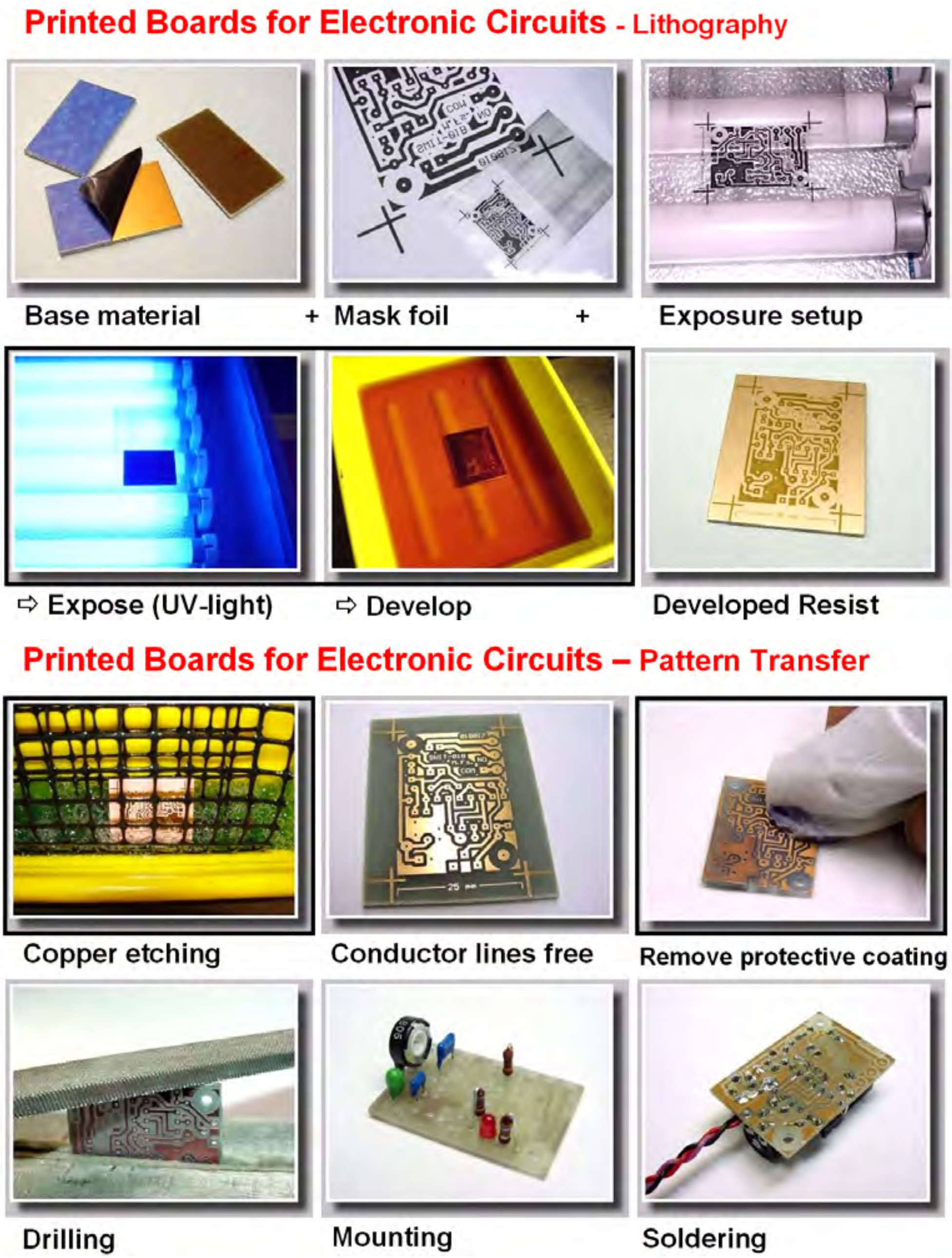


Figure 4.2: Photographs of printed board fabrication sequence: lithography and pattern transfer (http://www.kap-man.de/pcb01.htm).

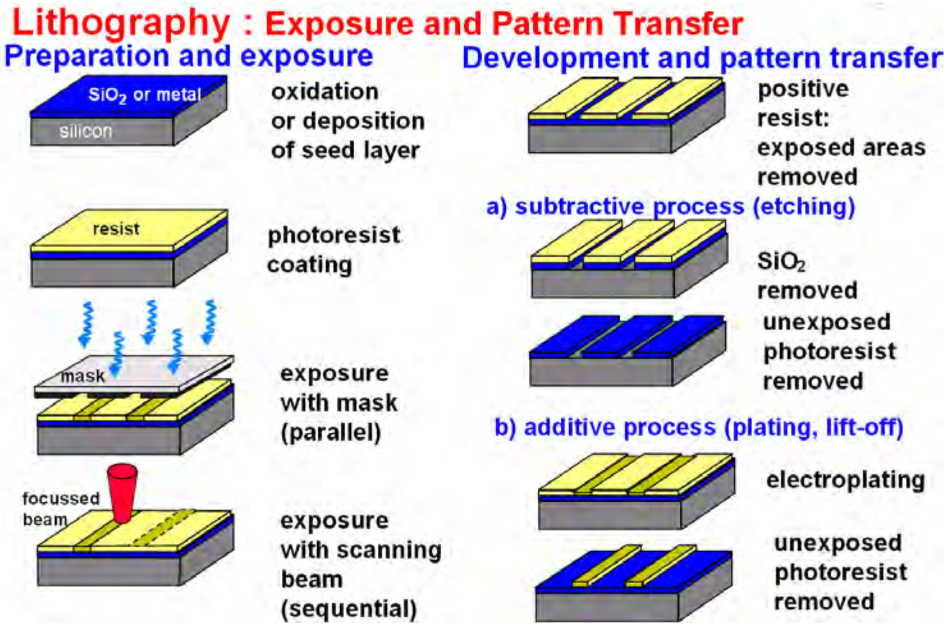


Figure 4.3: Example of standard photon and electron based lithography and pattern transfer.

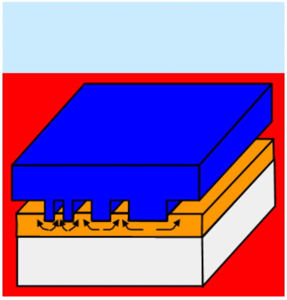
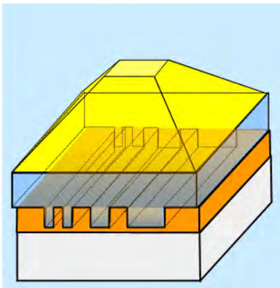
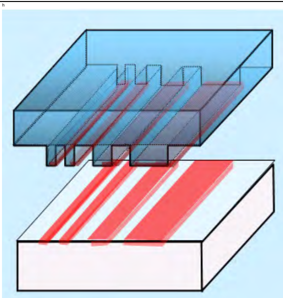
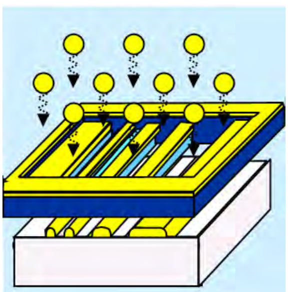
These schemes of lithography and pattern transfer are similar in the alternative patterning methods presented here, with some restrictions and variations.

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, accessability and reproducability. 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 cleanroom 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.

Pattering Process	Patterning Scheme	Process	Specific advantages	Industrial Activity
Thermal Nanoimprint Lithography (NIL, T-NIL) – Hot Embossing Lithography (HEL)		**Stamp:** hard, opaque (silicon wafers) **Process:** Thermoplastic molding at elevated temperature (100-200°C), demolding at low temperature (20-100°C) **Tools:** Hot presses (1-100 kN)	Similar to standard lithography (generating a thickness contrast of a resist) Maximum resolution: 2-5 nm Variety of thermoplastic materials Standard materials for stamps and substrates	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)		**Stamp:** a) transparent (quartz) b) elastomer with hard backplate **Process:** Molding of liquid resin and hardening by UV-exposure **Tools:** a) step and repeat tool with UV-lamp b) modified mask aligner	Similar to standard lithography (thickness contrast of a resist, UV-exposure of negative resist) Maximum resolution: 2-5 nm Fast, no heating involved	Fairly large research community with increasing activity, industry
Soft Lithography (SL) – Microcontact Printing (µCP)		**Stamp:** Elastomer, often backed by a hard plate **Process:** Transfer of an ink from the stamp surface (and from the bulk) **Tools:** chemical lab, modified mask aligner	Surface patterning of functional molecules possible (chemical contrast) Maximum resolution: 50 nm Easy stamp fabrication and printing Unexpensive	Beginning, first professional tools available
Stencil Lithography (STEN)		**Template:** hard, thin MEMS membrane (Si_3N_4) **Process:** Thermal evaporation in vacuum **Tools:** Physical vapor deposition combined with modified mask aligner	Patterning over topography possible (topological contrast) Maximum resolution: 50 nm	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 ciruits 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 adaptions 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 processs 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 complemetary 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.

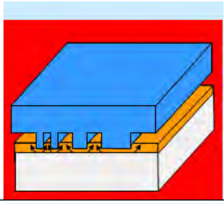
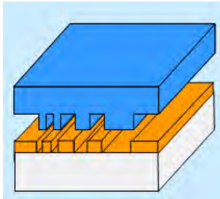
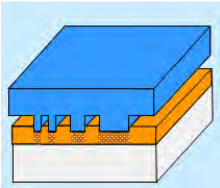
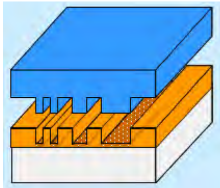
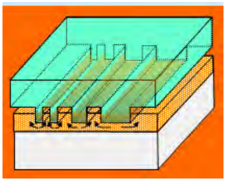
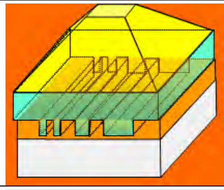
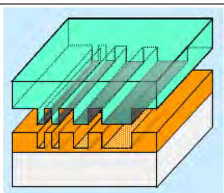
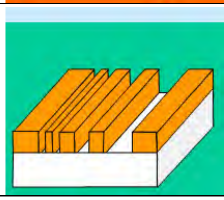
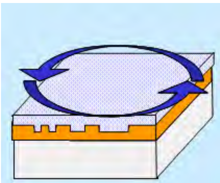
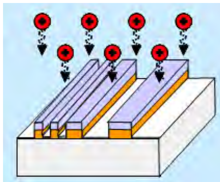
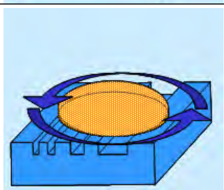
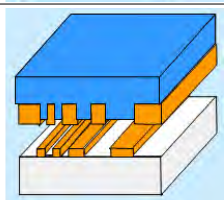
  b) Masking layer around an area of interest of a stamp, either on top of all structures or behind them (e.g. on the backside of the stamp or buried below the surface relief): Then the resist in the area of interest is crosslinked while the other areas can be removed in a wet developer. This is typically 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**. The 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**			**Process:** Self-limiting flow of a thin resist **Resolution:** lateral 200 nm, h_f nearly zero
RT– NIL **Room temperature NIL (hard stamp)**			**Process:** Resist compaction by high pressure under protrusions **Resolution:** 80 nm line with 300 nm spacing (100 nm deep)
Combined (hybrid) processes			
T+UV– NIL **Simultaneous thermoplastic and UV-NIL (e.g. STU)**			**Process:** Thermoplastic molding and UV curing **Resolution:** lateral <50 nm, h_f 20 nm
NIL+PL **Combined NIL and photolithography (e.g. CNP)**			**Process:** Exposure through semitransparent stamp and removal of unexposed residual layer **Resolution:** lateral 350 nm
Pattern transfer (reverse) processes			
NIL / R **Reverse tone NIL (e.g. SFIL / R) – Patterning over topo graphy**			**Process:** Overcoating of Si-containing etch barrier on prepatterned organic transfer layer, etch back and dry developing (window opening) **Resolution:** lateral <100 nm
R-NIL (T or UV) **Reversal NIL – With complete resist pattern transfer or "inking" mode** (partial transfer)			**Process:** Spincoating of resist onto stamp, complete or partial transfer to substrate by thermal bonding **Resolution:** lateral <100 nm, h_f nearly zero

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 a 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-assemby structural topographies in the micro- and and nanorange serve as guiding lines for the self-assembly of smaller entities such 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 **templated self-assemby of block-copolymers** (e.g. blocks consisting of a polymethylmetacrylate (PMMA) and of polystyrene (PS)), the 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 genate nodes or crystallization points for processes which are basically ordered in near-field, but will loose 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 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 processis 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 recombination of different stamps with limited size, from which thin metal shims are electroplated which are bent around rolls for replication into thin foils by roll-to-roll processing. The value chain is shown below.

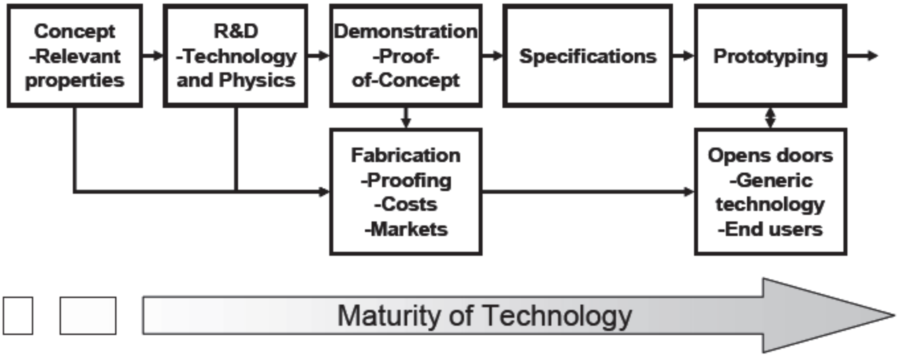


Figure 4.4: The value chain of the NaPANIL proposal. The chain extends from the concept, here controlling light at surfaces, via R&D step to demonstrating the proof-of-concept, checking the specifications followed by prototyping. To make this possible the manufacturing and qualification processes must be developed.

The applications contain **generic aspects** that can be regarded as common to the whole nanopatterning R&D field. The patterns utilised in these applications are truly 3-dimensional, ranging from 50 nm feature size up to several micrometers. The whole range of feature sizes is combined at the same surface location. The patterns can be created in an efficient manner using different nanoimprinting approaches: Step&Stamp, large area parallel, thermal, UV, soft UV or roll-to-roll approaches. The common feature here is that the fabrication and the subsequent duplication of the master stamp is crucial. Replicas will be created in hard and in soft surfaces. The former requires dry or wet etching steps after nanoimprinting, while in the latter case the patterns can be directly moulded using imprinting. Technologies such as sol-gel, plasma treatments, atomic layer deposition, among others, will be used to complement standard techniques. In addition to these well specified devices, development of exploratory processes for applications that are at in **embryonic state** but have potentially high impact, together with their manufacturing processes, will be carried out in the project. These include, in addition to advanced optical surfaces, applications in the fields of bioscience and health care. Example of a process chains, including measurement, can be found in the following areas:

a) **Compact Disc (CD) and Digital Versatile Disk (DVD) fabrication**: This is a standard industrial process where the original pattern is fabricated via laser patterning of a photosensitive resist, either by a focused laser or electron beam with rotating substrate table. From this original a metal copy is done via electroplating showing the inverse surface patterns. Using copying by electroplating, mothers sons and daughters can be copied from the original master. The mold is then placed into an injection molding machine for high speed replication of thin polymeric discs.
b) **Holograms for security devices**: As in CD manufacturing, a resist pattern is exposed on a glass plate. Due to the small size of patterns and the need to fabricate large area molds for roll-embossing (roll-to-roll and reel-to-reel), the patterns have to be recombining via step&repeat imprint processes (also called step&repeat embossing).
c) **Microfluidic devices**: The main difference to the processes described before is the combination of micro- and nanostructures. Large reservoirs and thin capillaries have to be integrated to guide fluids through plastic chips. Surface functionalization of channels using chemical or topographical patterning enables to fabricate valves and barriers. Injection molding, casting and hot plate embossing is used for replication.

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. A range of other processes have a hybrid character. However, often the term “hybrid” is also used for materials and tools and therefore should not be confused with the hybrid processes.

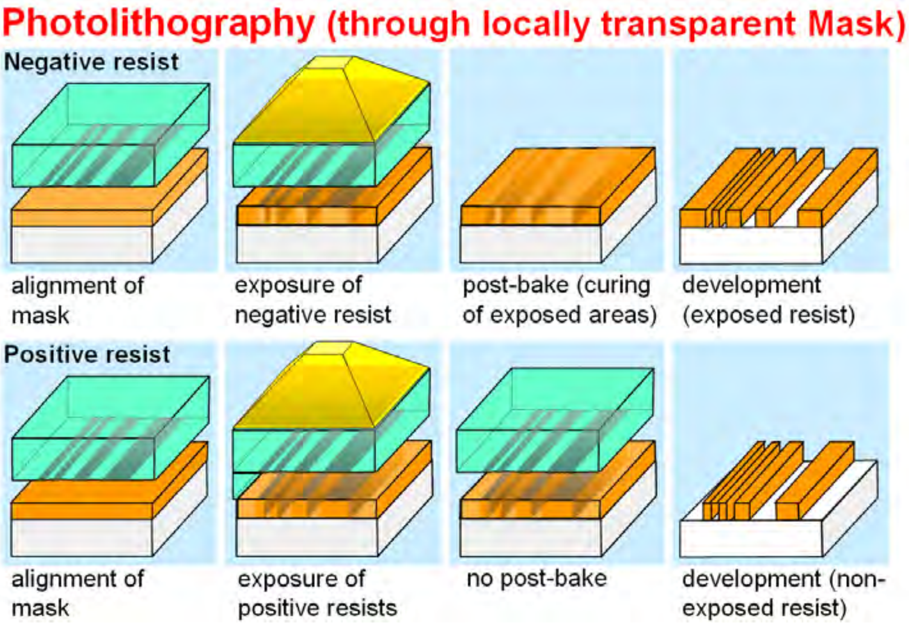


Figure 4.5: Process sequence for photolithography for top: negative resist and bottom: positive resist

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 orginal, 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. 20x20mm^2 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 € / lit.
- 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.

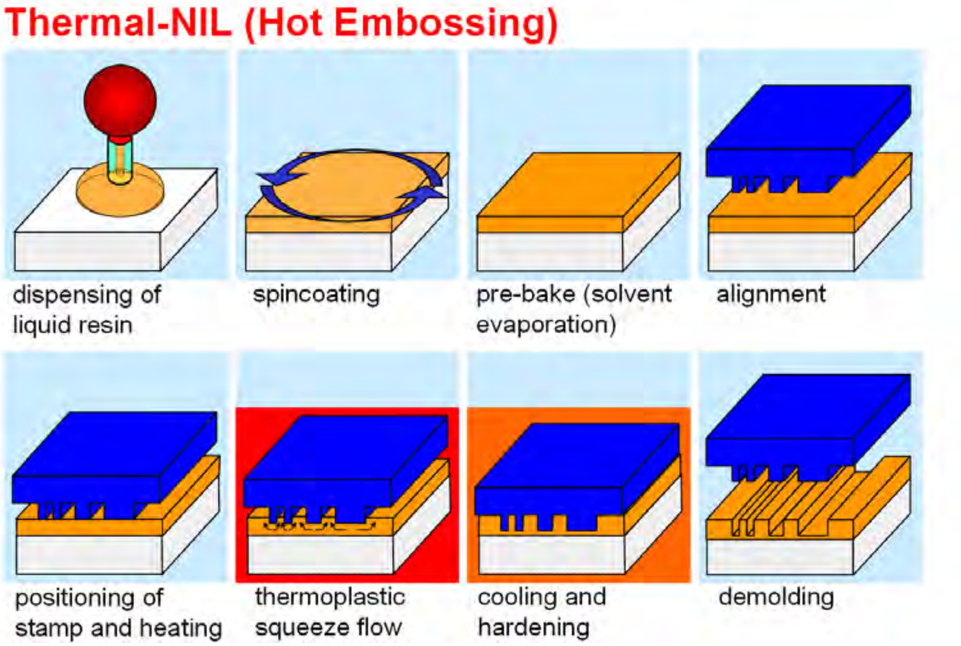


Figure 4.6: Process sequence for thermal nanoimprint lithography.

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. Schift 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. Schift, *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 100 €).
- 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 inkpad.
- 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

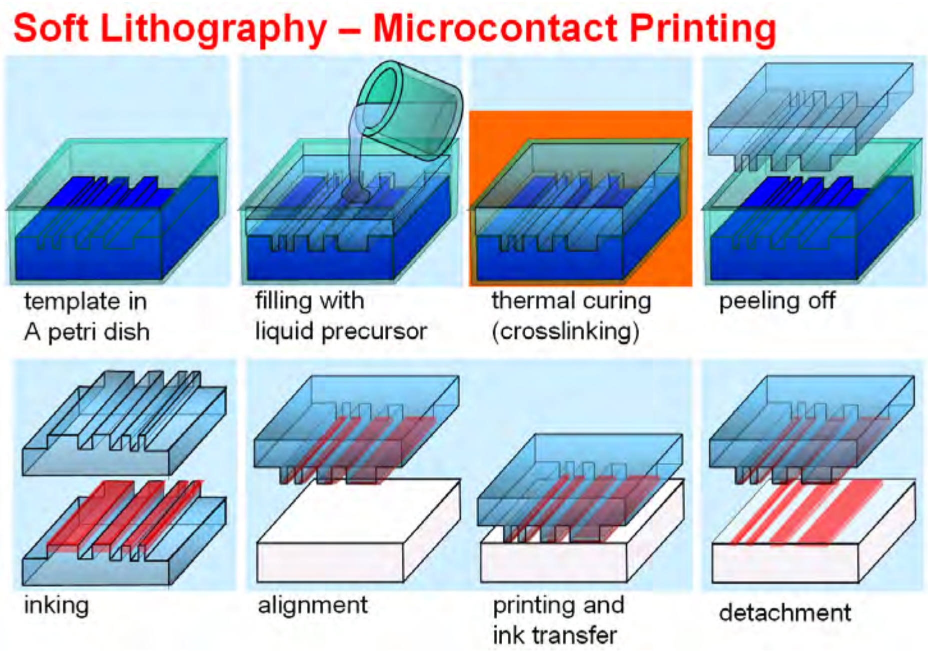


Figure 4.7: Process sequence for soft lithography – stamp manufacturing and microcontact printing.

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, 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, B. Michel, *Siloxane polymers for high-resolution, high-accuracy soft lithography*, Macromolecules **33**, 3042-3049 (2000).

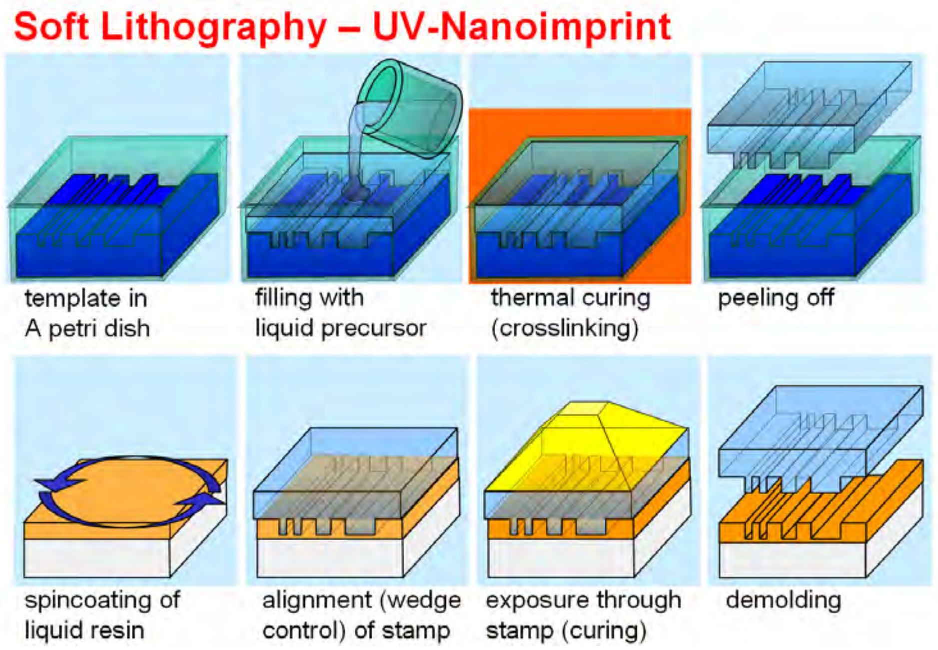


Figure 4.8: Process sequence for soft lithography – stamp manufacturing and UV-NIL.

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, 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, 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

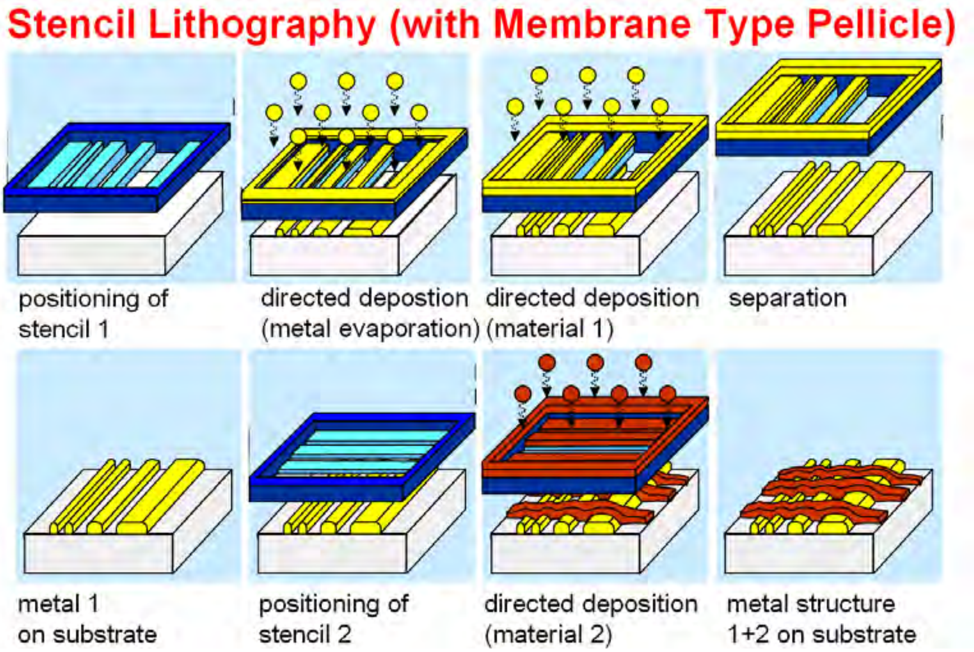


Figure 4.9: Process sequence for stencil lithography for two process steps (e.g. for metallization over non-flat surfaces).

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 definied 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 be become more complex if structure sizes and density varies over the surface of a stamp. A good example is shown in Figure 5.1.

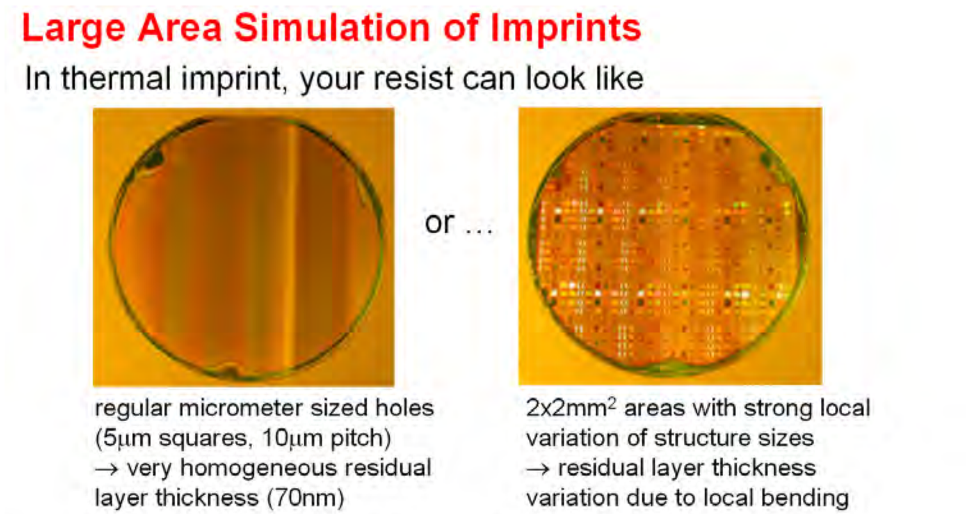
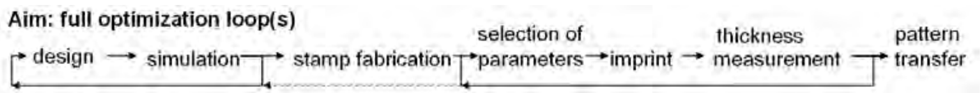


Figure 5.1: Photographs of typical resist patterns on a full wafer after imprint.

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:



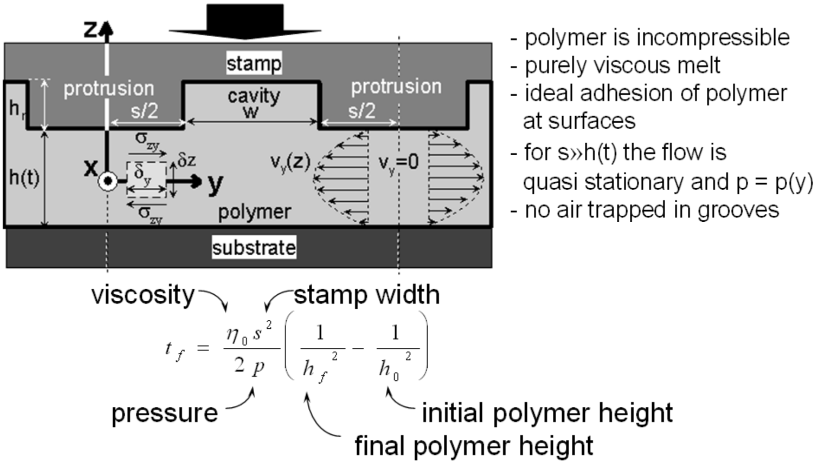
This process chain includes **two optimization loops**: The first loop includes a **simulation** step after the design, which means that the imprint of areas of a few mm up to the entire wafer area should be simulated and critical spots for molding and pattern transfer identified and avoided by adapting 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 consired. Simulation tools for large areas are currently been 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

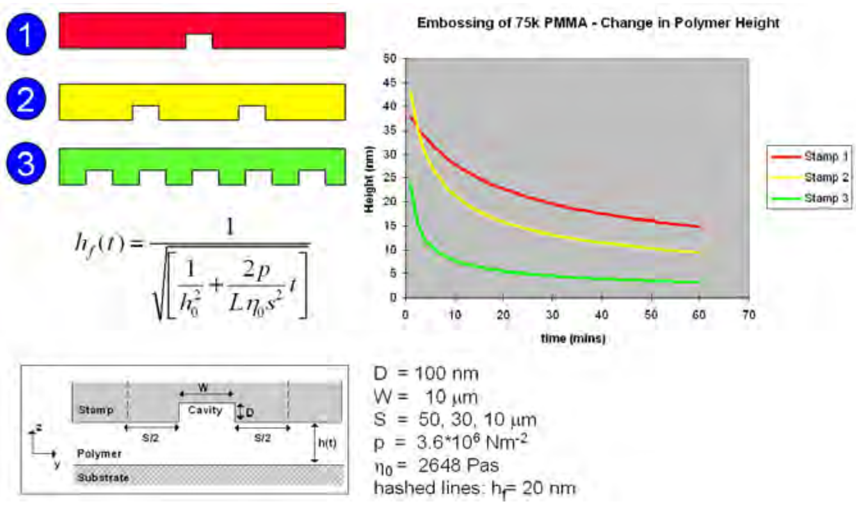
5.2.1 Introduction – the Stefan's equation

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:



$$t_f = \frac{\eta_0 s^2}{2p}\left(\frac{1}{h_f^2} - \frac{1}{h_0^2}\right)$$

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.



$$h_f(t) = \frac{1}{\sqrt{\left[\frac{1}{h_0^2} + \frac{2p}{L\eta_0 s^2}t\right]}}$$

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. Schift, 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. Schift 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 comparision 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 2x2 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 if 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. Schift, 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.

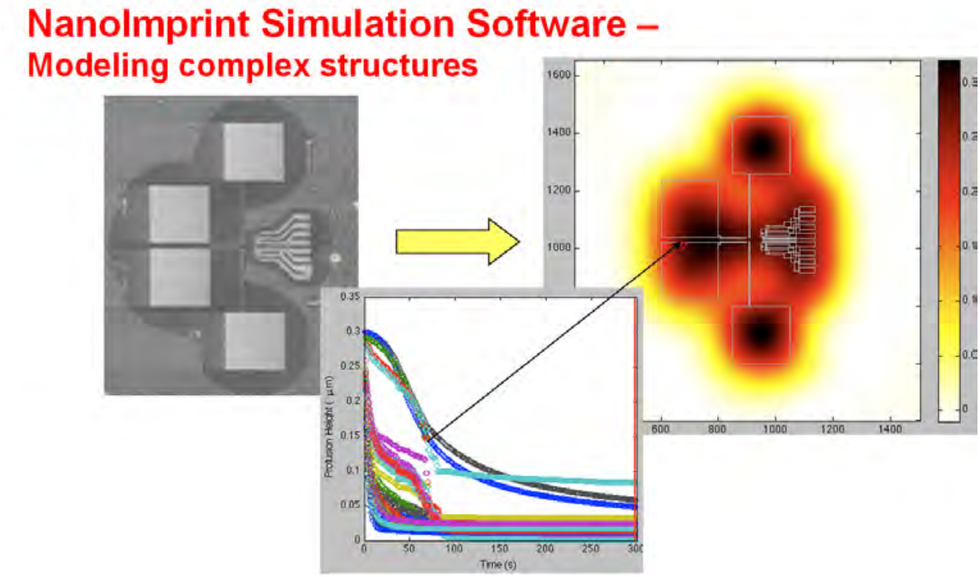


Figure 5.4: NIL Simulation Suite with example of a device consisting of large electrode pads and small wires, and the corresponding map of the residual layer thickness (left side: SEM micrograph of imprint, center: sinking of different protrusions, right side: simulation).

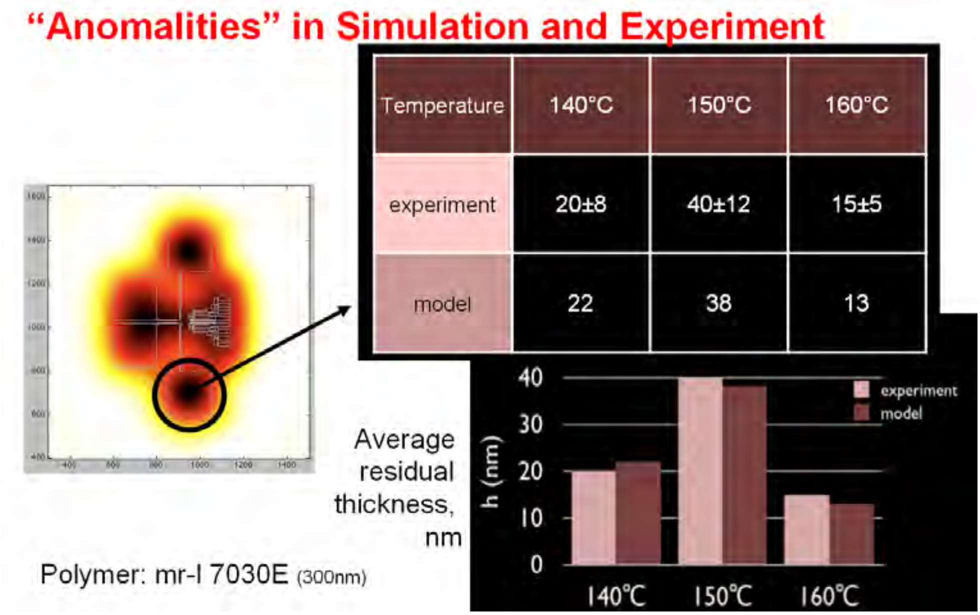


Figure 5.5: Example of residual layer optimization using the NIL Simulation Suite. Interestingly, for the given case an intermediate temperature imprint at 150°C is resulting in a higher residual layer thickness than with higher and lower temperatures.

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 squeenze 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 (avaoiding themal 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 constrat to Sic and Si_3N_4

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 microhardness** (kg mm^{-2})	**thermal conductivity** ($Wm^{-1}K^{-1}$)	**specific heat** $J{\cdot}kg^{-1}{\cdot}K^{-1}$
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_3N_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 easily 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

Resist (M_w)	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 from Dow Corning Inc., USA) used for stamp copying by casting, elongation at break 160
h-PDMS	four parts + solvent	tunable 8.2 MPa	improved mechanical stability for sub-1 µm features, elongation at break 7
UV-curable precursor (UV-initiated crosslinking after spincoating or casting)			
OrmoStamp*	UV-curable prepolymer, O_2 inhibitant	0.75 -1 Pa·s 0.650 GPa	organic-inorganic hybrid polymer for stamp copies used in T-NIL and UV-NIL, high mechanical stability for sub-50 nm dimensions, long stamp lifetime, release force optimized (fluorine-based modification)

***** 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 toolsbox 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.

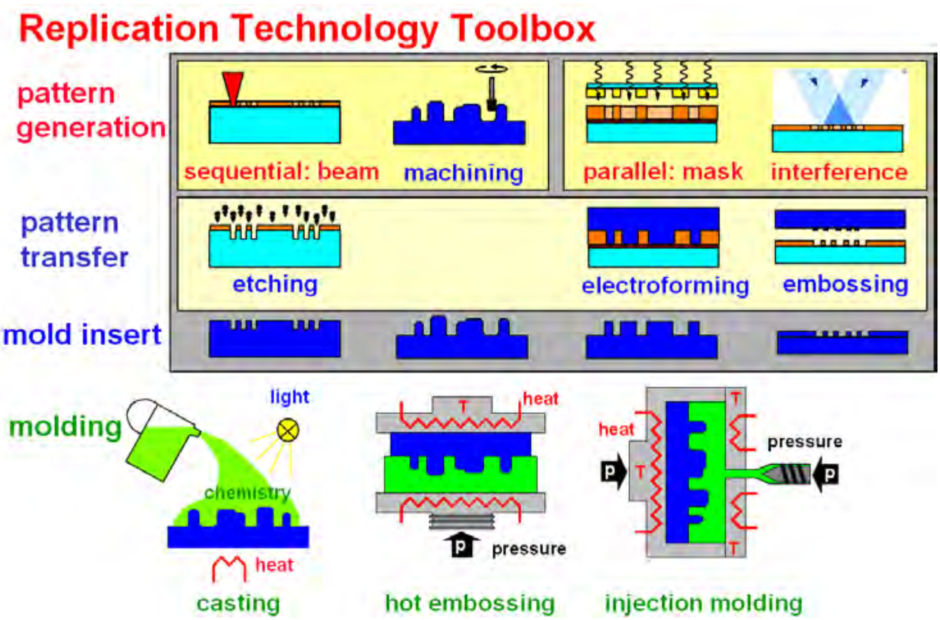


Figure 5.6: Process toolbox that summarizes a range of process variants from origination and tooling to molding.

5.4.1 Methods for stamp originination

Stamps are often made by serial or parallel methods. A typical serial method is a pattern generator based on a scanned focused beam 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 are used. Particulary interesting for regular patterns (dot or line arrays), interference 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 Stamps are often made by serial or parallel methods. A typical serial method is a pattern generator 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 stitchting errors.

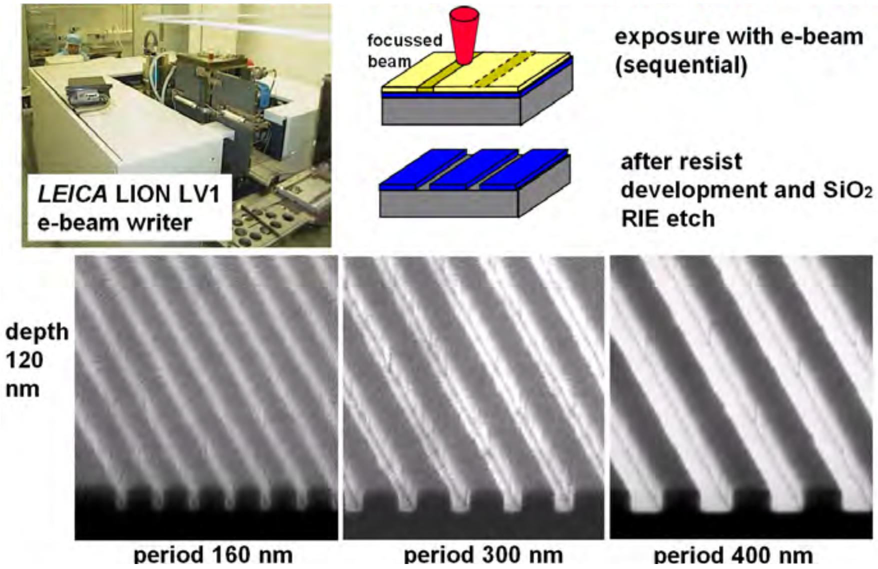


Figure 5.7: Exposure and pattern transfer for stamp fabrication by electron beam lithography and reactive ion etching.

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 continous profiles if thermal reflow techniques are used. These techniques are quite new and make use of the fact that not only the development condictions, 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 enables a selective reflow of exposed stuctures 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 follwing 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 µC/cm^2), the current I (in C/s) of the beam and the area A (in cm^2). For typical values of I = 1 nA and D = 300 µC/cm^2, a time of 5000 min = 40 h can be calculated for an area of A = 1 cm^2 (which would be fully covered by nanostructures with half the area exposed). For a moderate cost of 1'000 €/hour, this would result in result in a price of more than 40'000 € 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 know 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 loose 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. I 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.

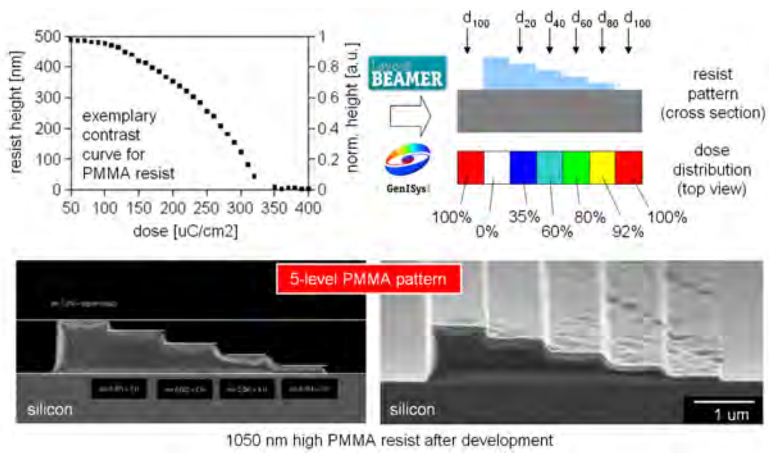


Figure 5.8: Grayscale electron beam lithography for generation of 3-D resist profiles using dose-modulation at a fixed development time. Only at the highest dose (dose-to-clear) a full development is achieved.

***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 brulée

***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 cm^2)
- Design errors due to proximity effects and stitching errors
- Charging effects and limited resist sensitivity (e.g. PMMA: 200 µC/cm^2 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 to 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 22 nm resolution for the fabrication of microprocessors. Since long the transition to alterantive pattering methods is expected, however, DUV has marked considerable success in developing optical enhancement techniques to push the resolution limites 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 schemces 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.

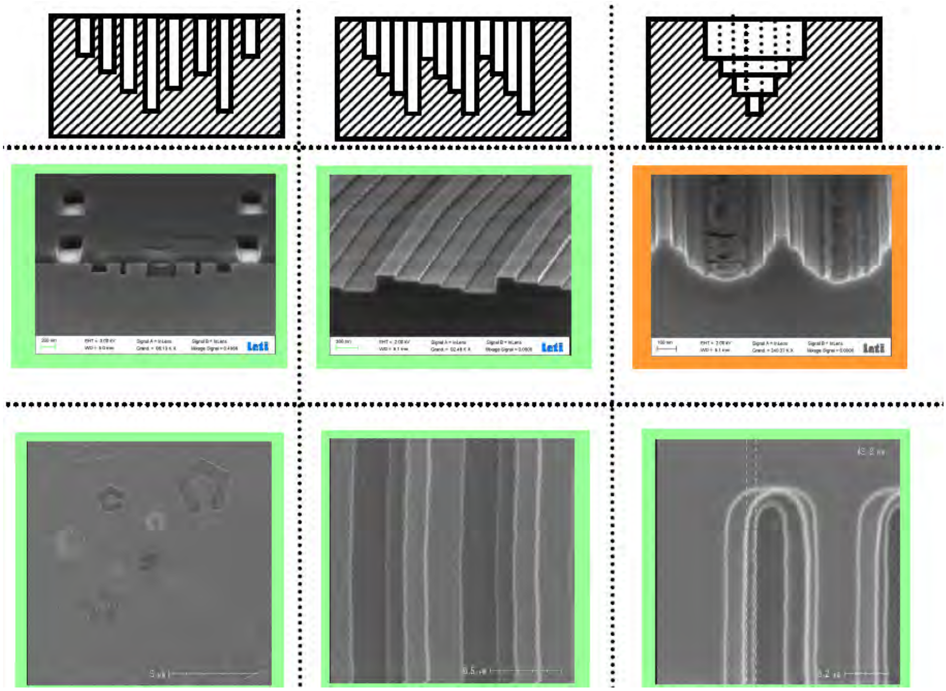


Figure 5.9: Multilevel stamp fabrication using DUV- projection lithography. Depending on the arrangement of the layers, different strategies for pattern transfer need to be applied.

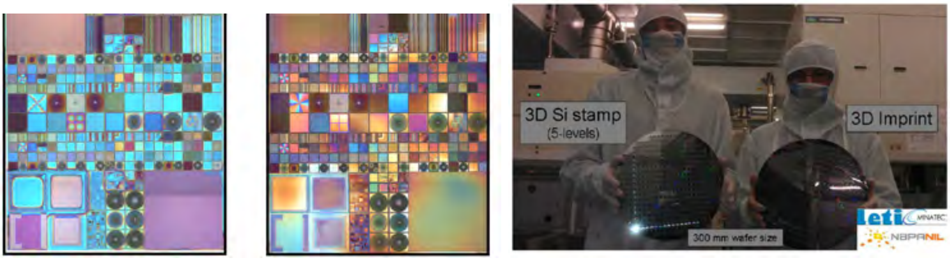


Figure 5.10: One area of the stepping field (24x18mm^2). Using the step and repeat mode of DUV-projection, stamps were fabricated from 300 mm wafers and replicated by thermal NIL.

5.4.5 Selective shape transformation by thermal reflow

Thermal reflow is a postprocessing of resist structures that melt upon heating. Due to lateral restictions, 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.

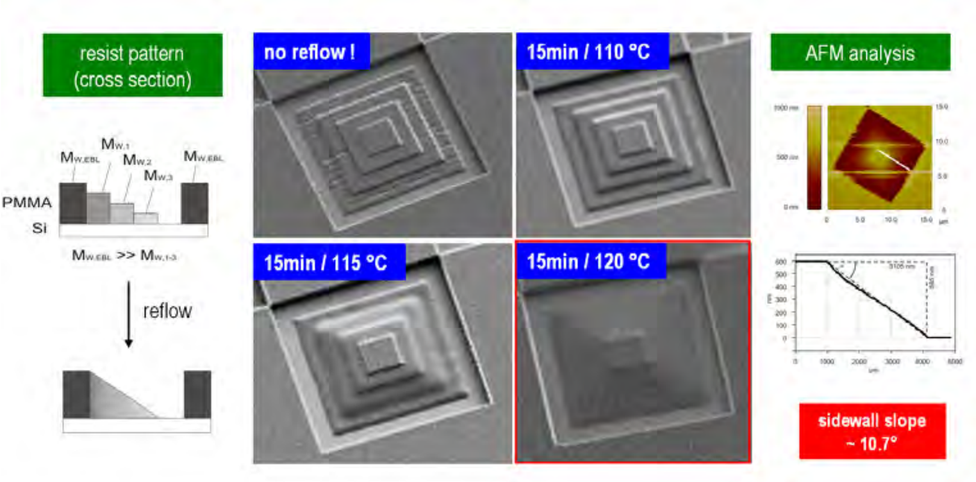


Figure 5.11: Thermal post-processing of 3-D PMMA patterns fabricated by grayscale electron beam lithography. Upon exposure, the molecular weight of the exposed areas and consequently the glass transition temperature is lowed, which allows a selective reflow of structures due to the thermal activated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

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 ORMOCERs (e.g. 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 profileration 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 reachtive 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 thoughput.

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 in the following conditions:

1) Solution of perfluoroalkytrichlorosilanes (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 perfluoroalkytrichlorosilanes 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 perfluoroalkytrichlorosilanes (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 (~2 µL of the chamber volume).
3) Leave the samples under this atmosphere for between 10 min and 1 hour (depending on set-up).
4) Rinse with toluene

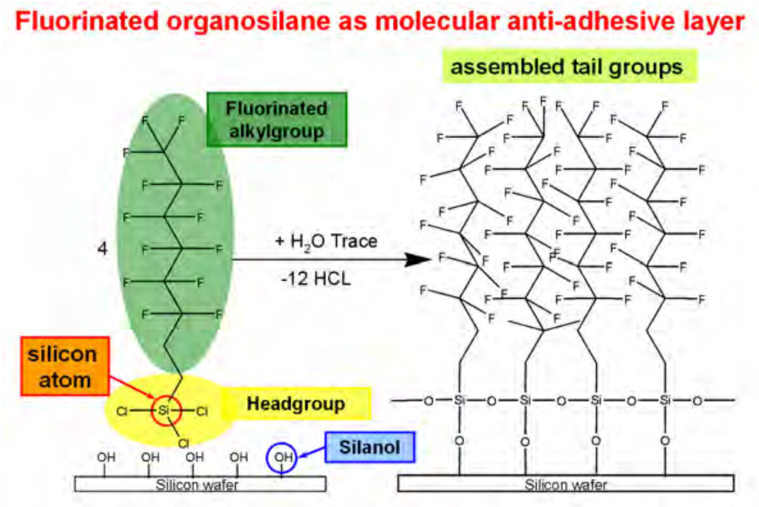


Figure 5.12: Silane binding on silicon dioxide.

Short description

Before wet or CVD coating, cleaning and activation is either done by so-called Pyranha etch, or by O2-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. Schift, S. Saxer, S. Park, C. Padeste, U. Pieles 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, L. Montelius, *Improving stamps for 10 nm level wafer scale nanoimprint lithography*, Microelectron. Eng. **61–62** (2002) 441–448.
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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. Meanwhile 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. However, the addition of organic components for release also reduces the T_g of a material, furthermore good adhesion to the substrate needs to be maintained. By adding silicon containing components etch selectivity for pattern transfer can be enhanced.

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 (°C), molecular weight M_w (kg/mol), viscosity η (Pa s) and Young's modulus E (Pa).

Resist (M_w)	T_g, $T_{imprint}$	η @ T and E	Comments
Thermoplastic (for variothermal molding)			
poly(methyl metacrylate) (PMMA)	T_g 100-120 °C, T_{im} 140 – 190 °C	10^5 – 10^7 Pa·s @ 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 Pa·s @ 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	< 3·10^4 Pa·s @ 120 °C	low T_g NIL polymer with very good flow ability and high plasma etch resistance, 40% lower release force than mr-I7000E, 12 nm resolution proved
mr-I 8000R*	T_g 105 °C T_{im} 150–180 °C	< 10·10^4 Pa·s @ 175 °C	NIL polymer with very good flow ability, good thermal stability and high plasma etch resistance, reduced release force over previous formulation
mr-I T85*	T_g 85 °C T_{im} 130–150 °C	300·10^4 Pa·s @ 140 °C	thermoplastic NIL polymer for micro optical and bio applications with high chemical stability and excellent UV and optical tranparency
SiPol*	T_g 63 °C T_{im} 110–130 °C		thermoplastic NIL polymer with high Si content used for aspect ratio enhancement (AR >> 3), has to be used with a thick organic transfer layer in bilayer systems
Thermocurable (crosslinking during heating – for demolding at nearly molding temp.)			
mr-I 9000M*	T_g 35 °C (before 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 after molding - for combined NIL and UV-photolithography)			
mr-NIL 6000E*	T_g 1 °C (before imprint) T_{im} 65–70 °C	< 0.2·10^4 Pa·s @ 100 °C	low T_g NIL resist for combined thermal and UV-based NIL (STU™ from Obducat), mix-and-match, multi-level patterning, reverse UV NIL

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

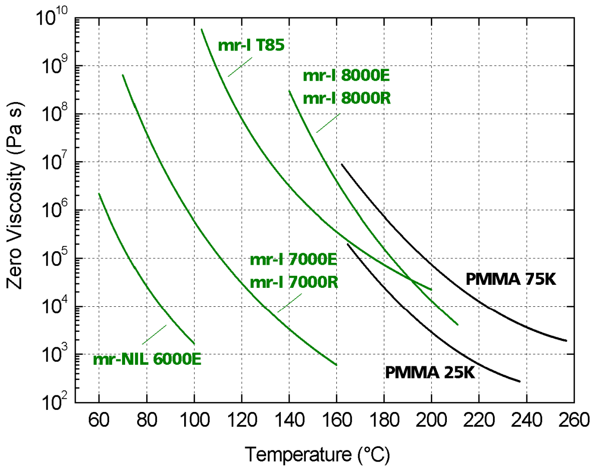

Figure 5.13: Viscosity of typical polymers for thermal NIL, e.g. the "classical" PMMA (poly methyl methacrylate) and commercial resists from *micro resist technology* GmbH: due to the strong dependence of the viscosity from temperature, small changes in imprint temperature can have a strong impact on resist flow and imprint times. Former materials mr-I 7000E, mr-I 8000E and mr-NIL 6000 have been replaced by the improved products mr-I 7000R, mr-I 8000R and mr-NIL 6000E, respectively.

5.6.2 UV-curable NIL-materials (UV-NIL)

UV-NIL is a combination of nanoimprint and UV-curing, therefore often called UV-assisted NIL. However, because UV-exposure is done in a flood exposure mode either through the transparent stamp or through substrate, it is different from combined processes using NIL and photolithography (see below). Resists for UV-NIL consist of different components for UV-initiation and crosslinking. Oxygen inhibitant materials do not cure in ambient condition that means that only the resist below a stamp will crosslink when exposed to UV light, while the material at the stamp borders will not cure. For oxygen "porous" stamps (such as PDMS), therefore non-inhibitant materials are of advantage. Oxygen inhibitant materials, in contrast, will 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. 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 Ormocers and resists with inherent antiadhesive properties.

Table 5.3. UV-curable resist materials for UV-assisted NIL and combined NIL and photolithography processes, preferably to be used with UV broad band or i-line exposure (@ 365 nm), all with specific adhesion promoter applied before spincoating

Resist	Characteristic	η	Comments
mr-UVCur21*	Purely organic, O_2 inhibitant, low viscosity	30 mPa·s	1. solvent version for broad film thickness range 40 nm up to 1 µm using spin-coating 2. solvent-free version (mr-UVCur21SF) for dispensing
XNIL26*	Purely organic, O_2 inhibitant,	139 mPa·s	1. fluorine-based formulation for imprints with bare stamps materials without anti-sticking layer due to inherent release properties 2. solvent-free version (XNIL26SF) for dispensing
AMONIL**	Si-containing, non-O_2 inhibitant	50 mPa·s	UV-NIL resist for soft (PDMS) stamps

***** 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 when imprinting reactive materials) 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, fluorinated components are mixed into standard resists. During spincoating and imprint, they segregate 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.

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.

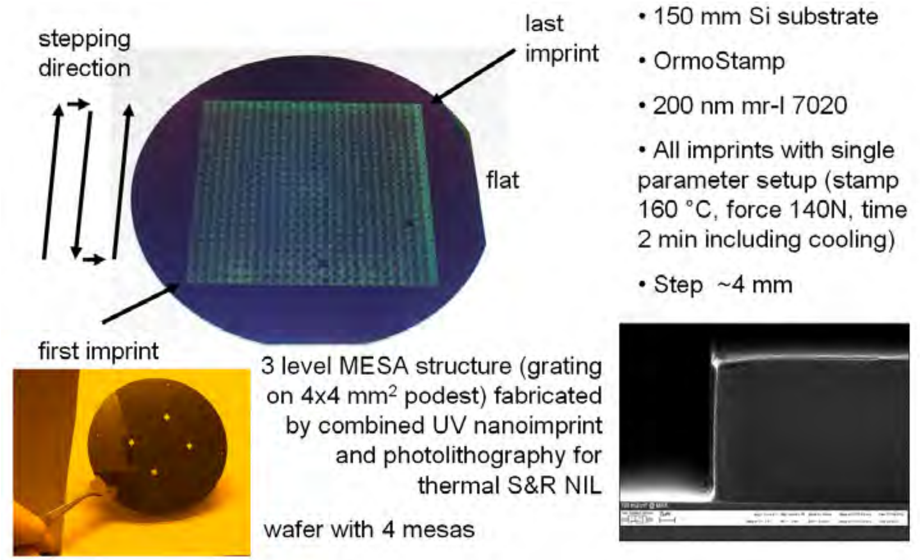

Figure 5.13: Large area S&R thermal NIL with OrmoStamp copy: In order to create a 4x4 mm^2 mesa on a base of a 10x10 mm^2 large stamp (to decouple the active area from the heated base), the imprint into the OrmoStamp layer was combined with a masked exposure of the 4x4 mm^2 wide mesa. Afterwards the non-crosslinked material was dissolved.

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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. Consequently, their mechanical, chemical and thermal properties are different from glassy materials. 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 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 OrmoStamp* is preserved after thermal treatment. Stamps can be coated using silane chemistry and used for several 10's or 100's of replicas before degradation sets in.

   (b) ORMOCER®s# are also very popular as imprintable coating materials with optical functionality. The commercialized materials OrmoComp* or OrmoClear* can be applied for the fabrication of micro-optical structures, diffractive optics, and waveguides.

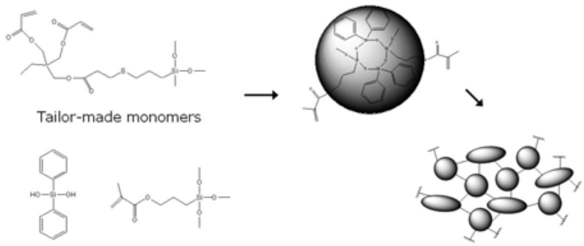

Figure 5.14: Chemistry: In a sol-gel process (simplified), organically modified silicic-acid derivate precursors and nanoscaled oligomers with organic backbone are completely crosslinked. OrmoStamp* is designed to be slightly elastic for improved imprint properties.

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

* commercially available from 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 intregrated 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.

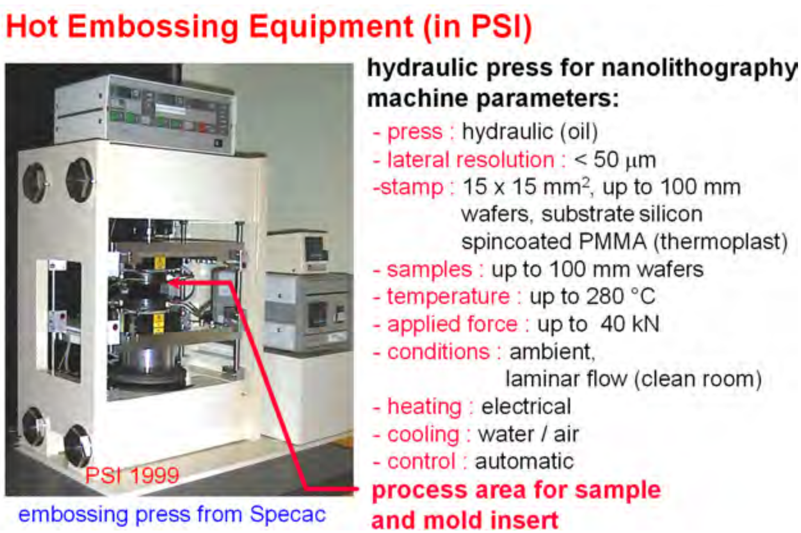


Figure 5.15: A simple (oil) hydraulic imprint machine.

Pressure Equilibration – Cushion / Compliance Layer

A thick (1 mm) sheet of standard silicone, called PDMS (Polydemethylsilane), 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. PMDS can be taken from any kind of workhop. 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.

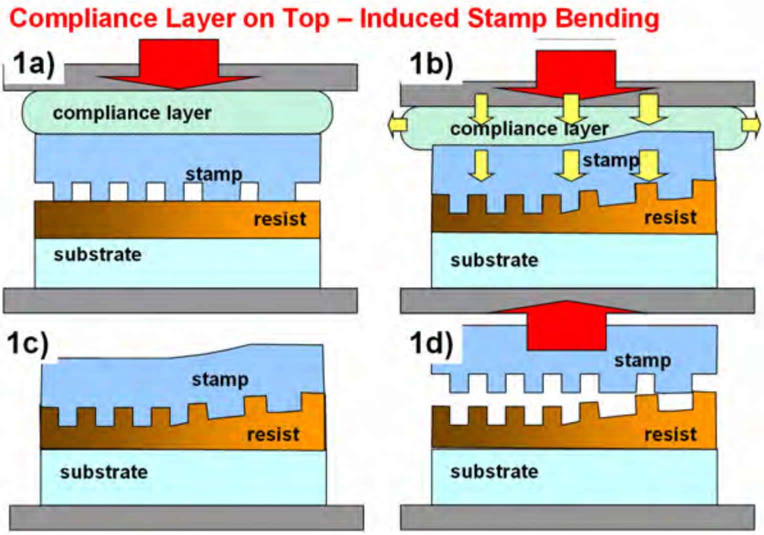


Figure 5.16: Principle of a cushion / compliance layer for pressure equilibration at the backside of the stamp. The bending of the stamp due to the variation of structure density in the stamp is exaggerated.

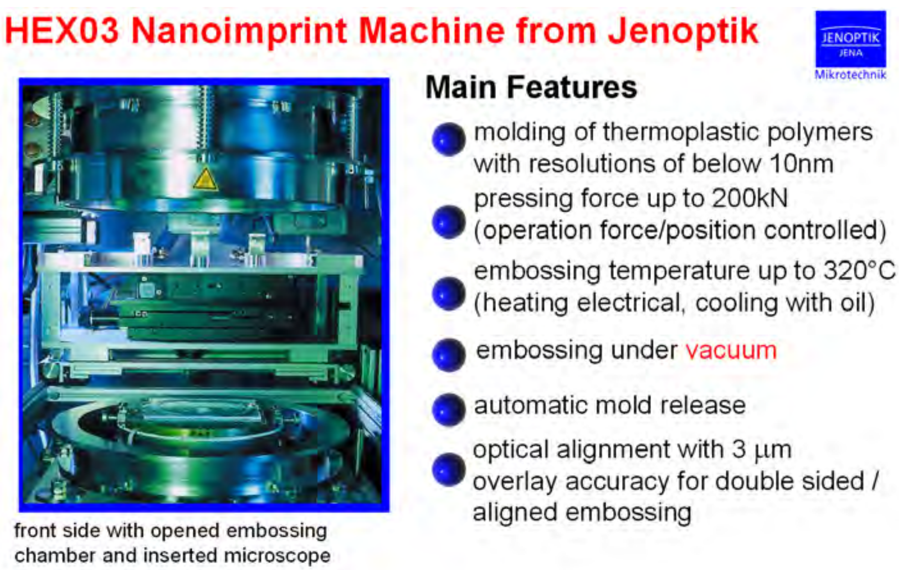


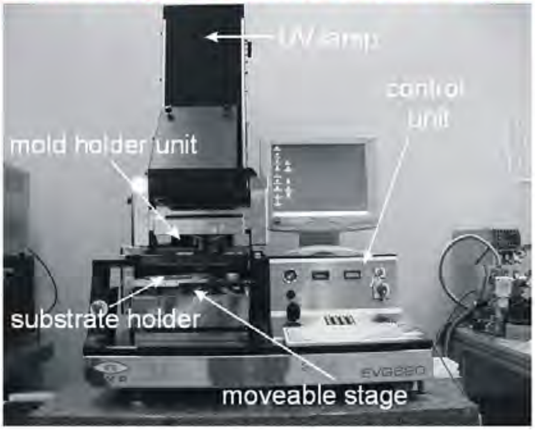
Figure 5.17: Integrated optical microscope in a hot embossing machine (Jenoptik HEX03).

Nanoimprint Machines from EVG: 520 HE

8" imprint bonder in LETI / Grénoble
• imprint under vacuum
• alignment separately in mask aligner
(+) good accessability, 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



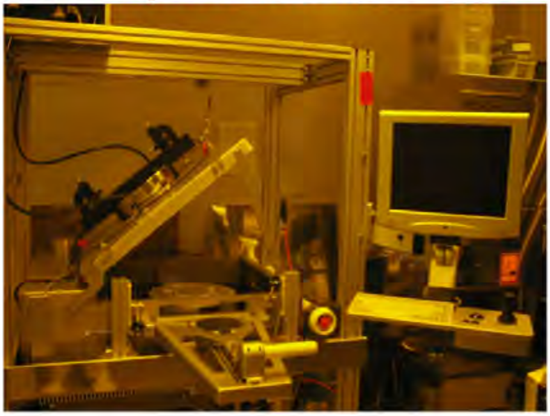
EVG-620
• Full wafer Soft-UV-NIL tool
• Semiautomatic tool
• Modified mask aligner
• 1000 W mercury lamp
• 6 inch exposure uniformity 4%
• 4 or 6 inch chuck system

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 an 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

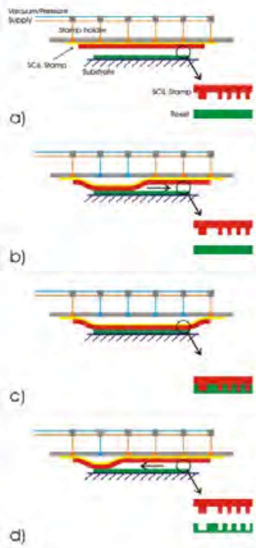
S&R UV imprint tool at AMO / Aachen
- imprint under vacuum
- alignment

(+) 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 an mask aligner for hybrid soft masks.

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

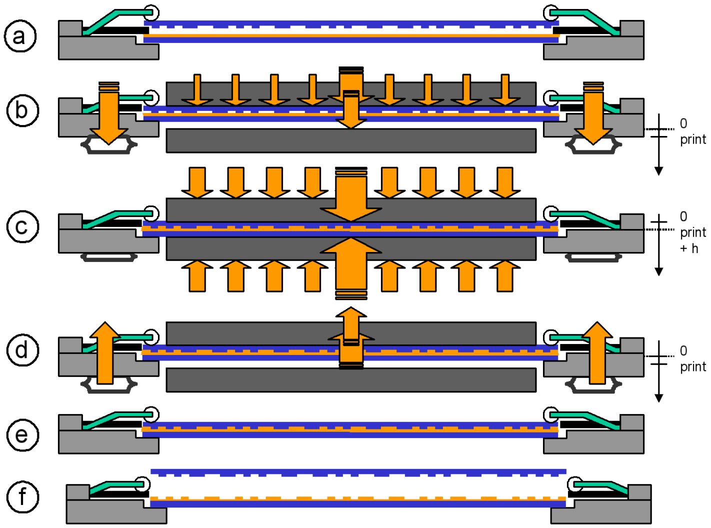


Figure 5.23: Schematic of a fast imprint with an alignment fixture: a) alignment and clamping of stamp (top) and substrate (bottom), b) contact of upper plate and down-movement, c) begin of molding upon contact to lower plate, d) pressure release and lift-up, e) cooling, f) manual demolding outside the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

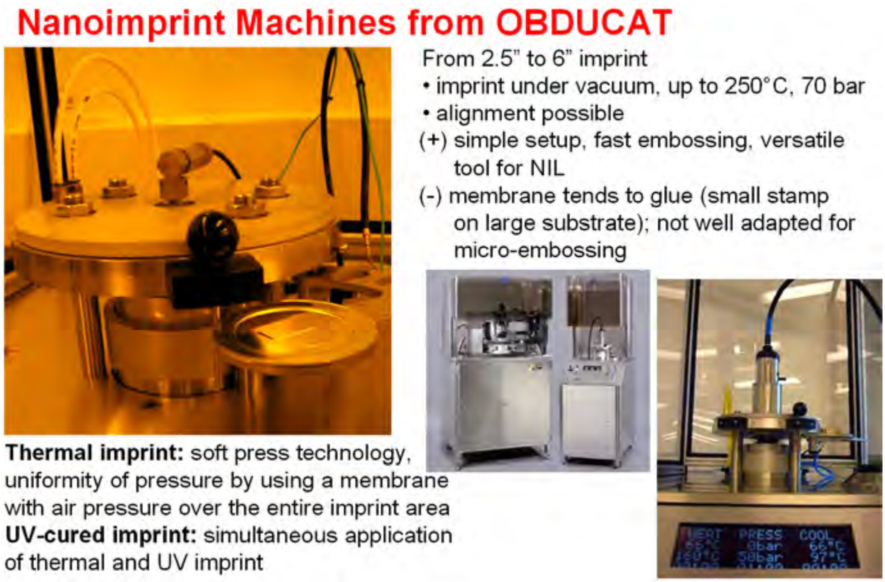


Figure 5.24: Nanoimprint machine from Obducat using a pressurized membrane on one side instead of a hard stamper (call soft imprint – not to be confused with soft lithography). By using a transparent membrane, thermal imprint can be combined with UV-curing.

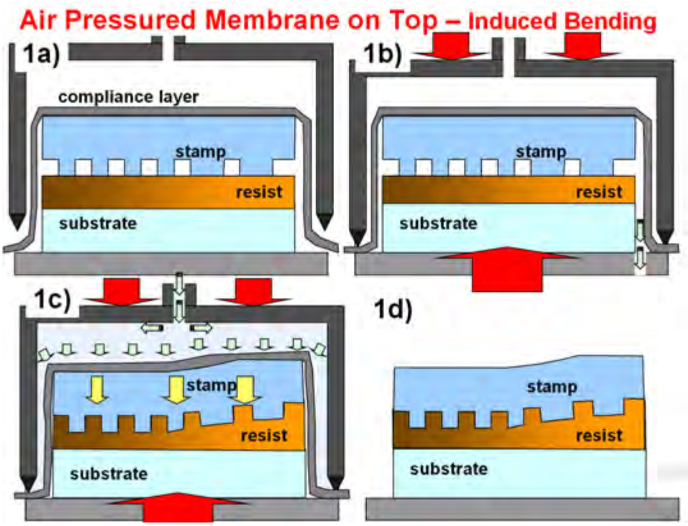


Figure 5.25: Principle of soft imprint approach by using a pressurized membrane (a compliance layer made from PDMS, a thin aluminium or plastic foil). By applying an air pressure on the sealed stack, a homogeneous pressure cushion is created at the backside of the stamp and maintained throughout the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

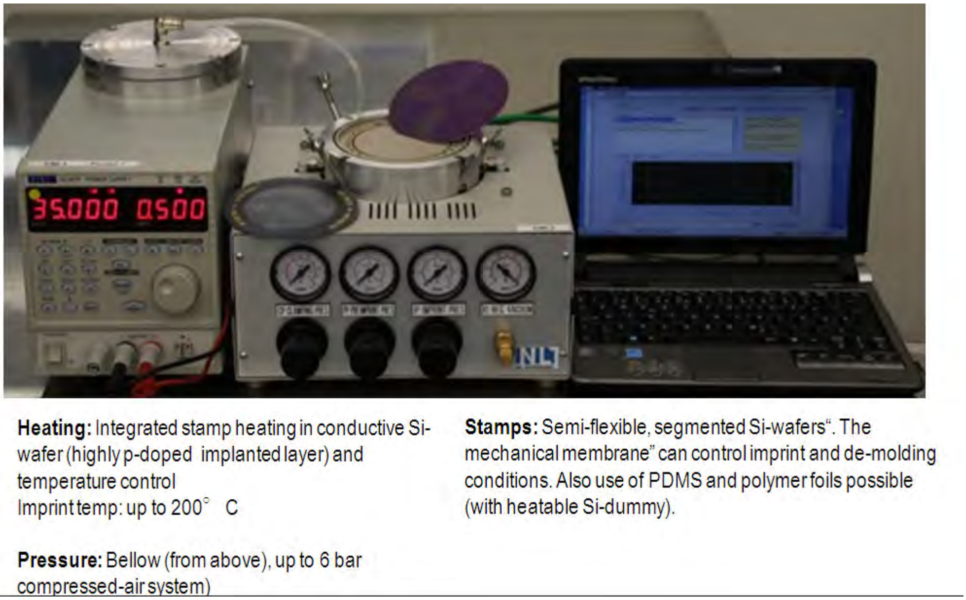


Figure 5.26: Compact NIL-2-GO nanoimprint machine from NILT using a pressurized membrane on one side instead of a hard stamper (call soft imprint – not to be confused with soft lithography). Additionally to this, segmented heatable silicon stamps can be used.

5.7.2 Roll-to-roll embossing tools (R2R)

Roll processing is a process in which a bent template is pressed agains 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.

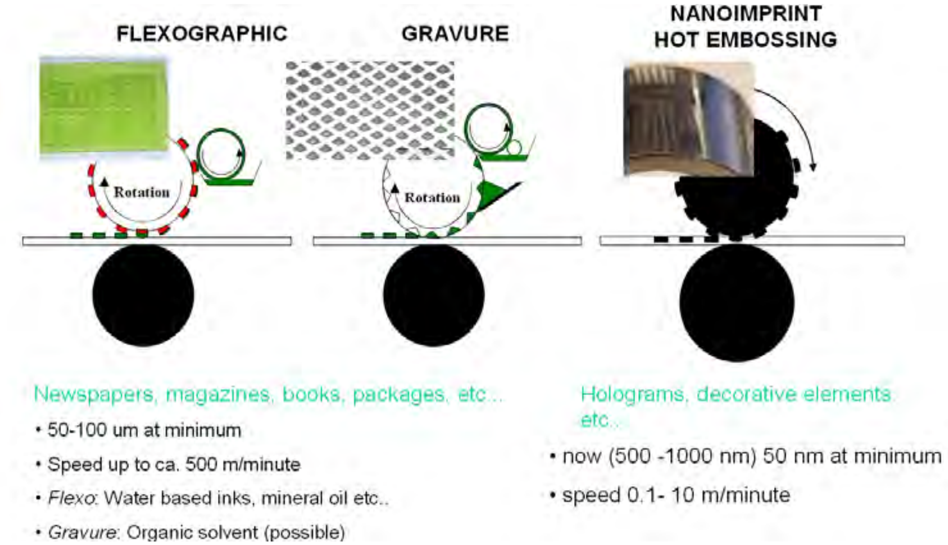
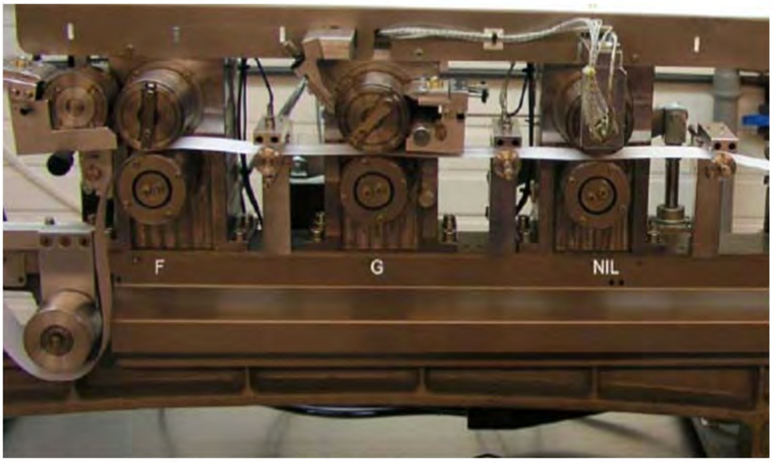


Figure 5.27: Schematic of different roll-to-roll processes.



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 tthermoplastic 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.

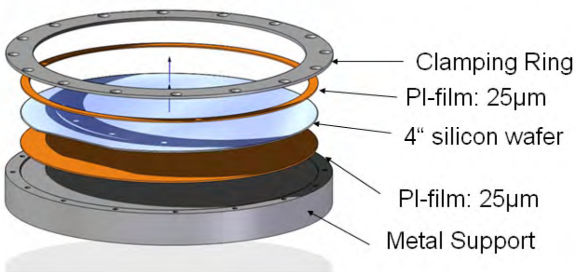


Figure 5.29: Left side: Clamping system for a 4“ wafer used as insert for injection molding. Right side: Tool with ejection side of the injection mold with structured 4“ silicon wafer.

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) anisotopic 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.

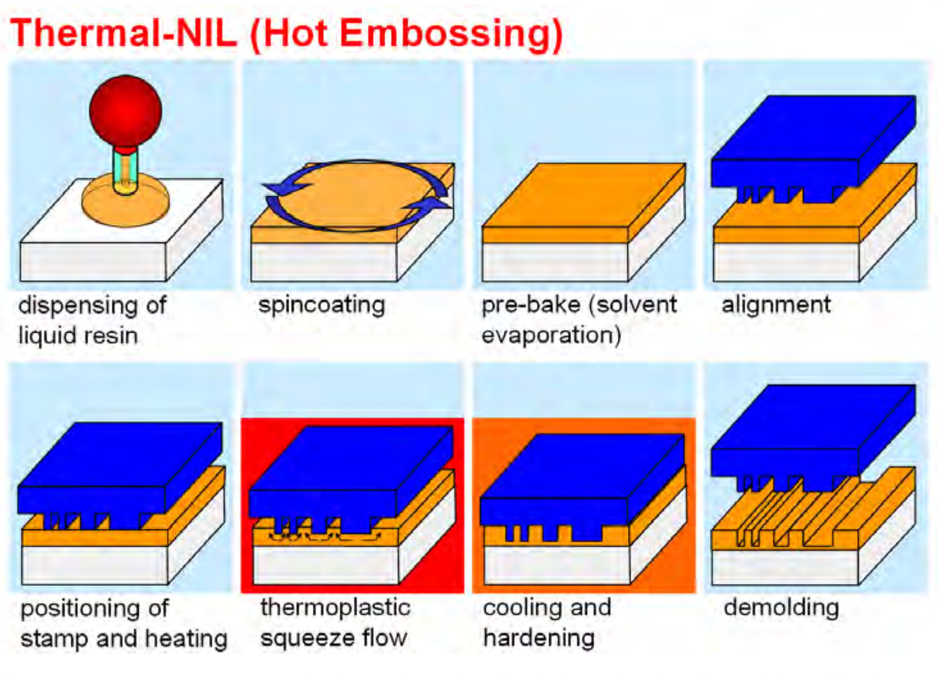


Figure 5.30: Process sequence for thermal nanoimprint (spincoating, imprint and demolding).

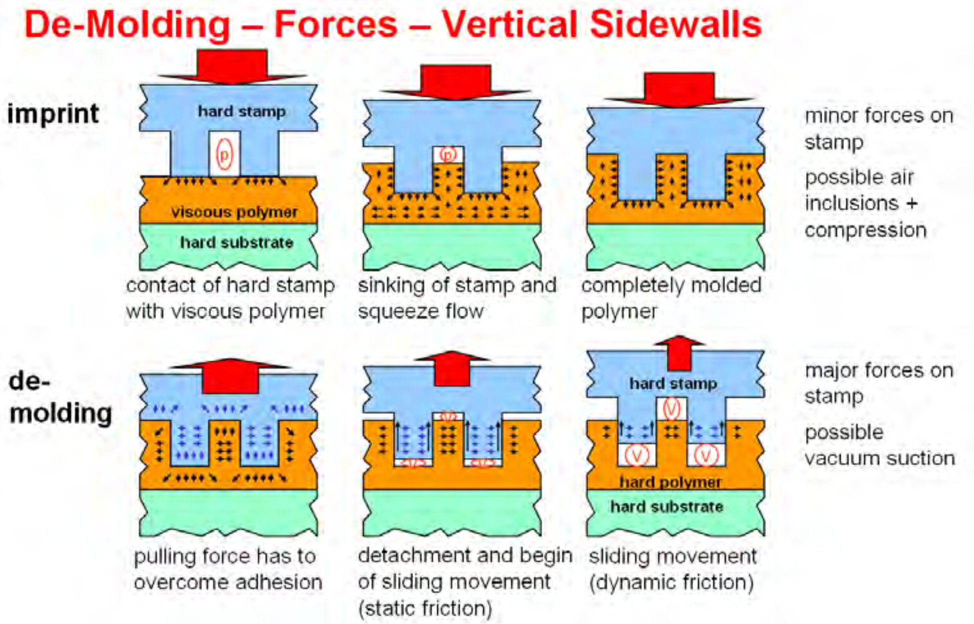


Figure 5.31: Forces present during the demolding of stamp structures.

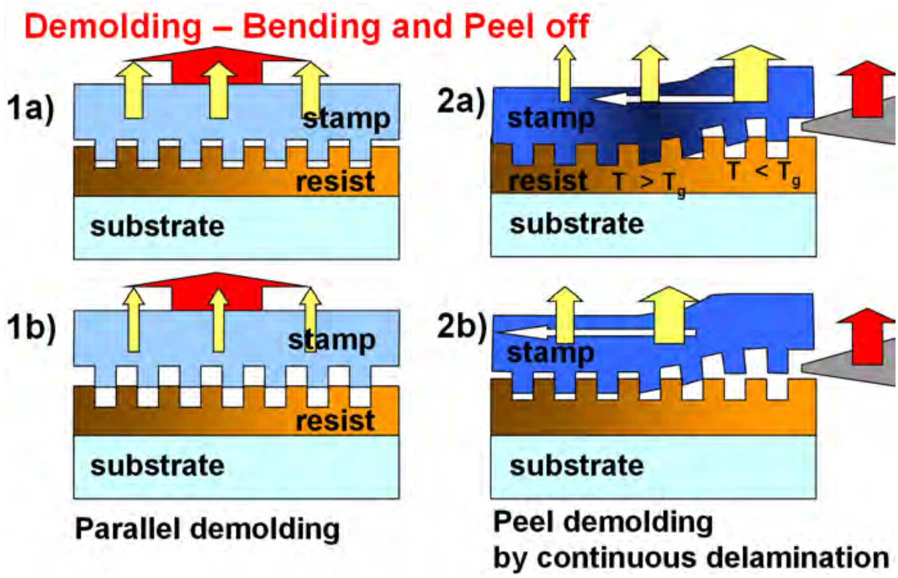


Figure 5.32: Principle for parallel and wedge induced demolding.

Residual Layer Etch (Substrate Window opening)

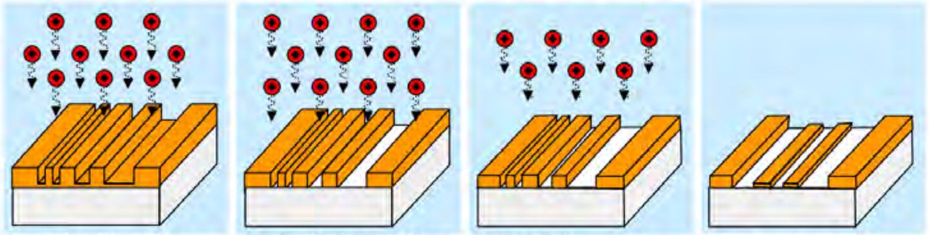


Figure 5.33: Process sequence for residual layer etching.

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, S.Y. Chou, *Pattern transfer fidelity of nanoimprint lithography on six-inch wafers*, Nanotechnol. **14** (2003) 33–36

[2] H. Schift, S. Park, J. Gobrecht, *Nano-imprint - molding resists for lithography*, J. Photopolym. Sci. Technol. (Japan) **16** (3) (2003) 435-438.

[3] H. Schift, 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.

Window Opening + Substrate Etching

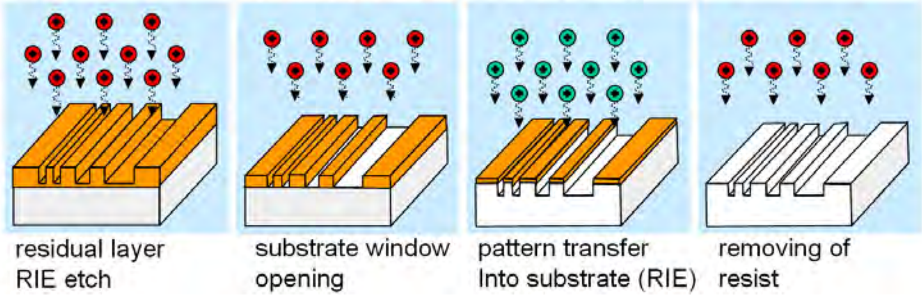


Figure 5.34: Process sequence for residual layer and substrate etching.

Short description

Etching of the substate 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. Schift, 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.

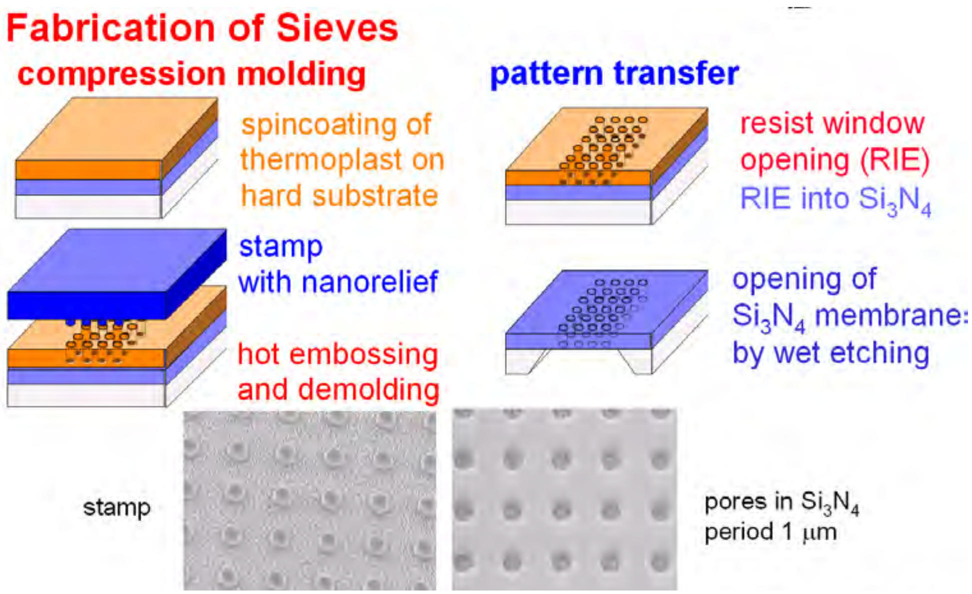


Figure 5.35: Example for etching as a pattern transfer process after NIL.

Lift-off

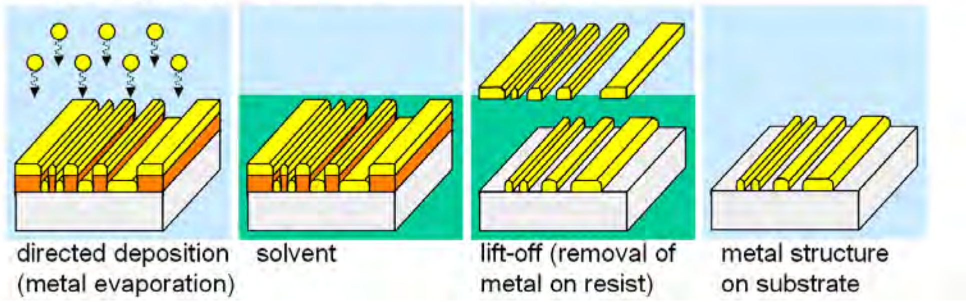


Figure 5.36: Example for lift-off as a pattern transfer process after NIL.

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. Schift, 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.

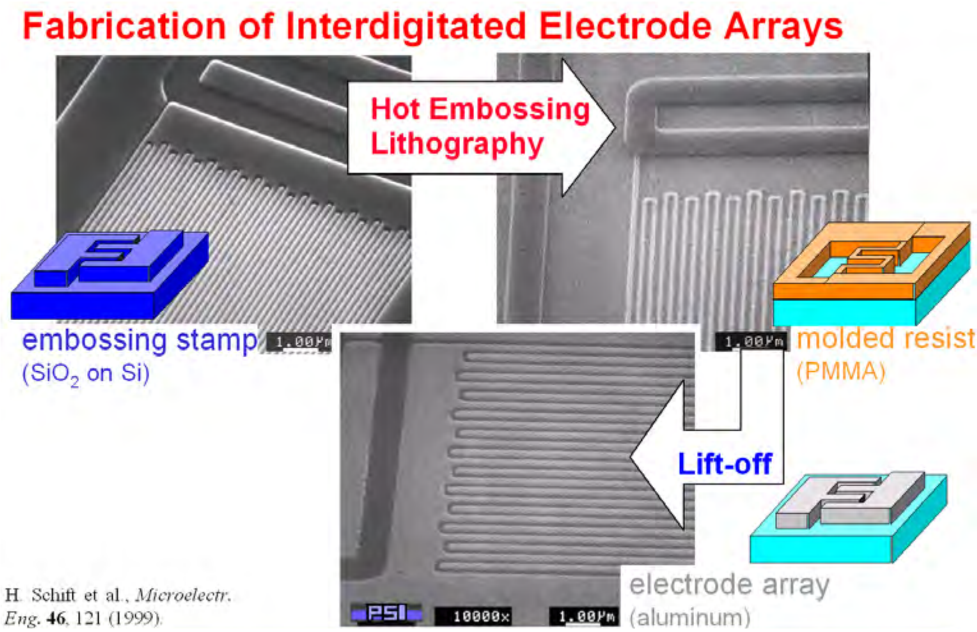


Figure 5.37: Example for lift-off as a pattern transfer process after NIL.

Electroplating

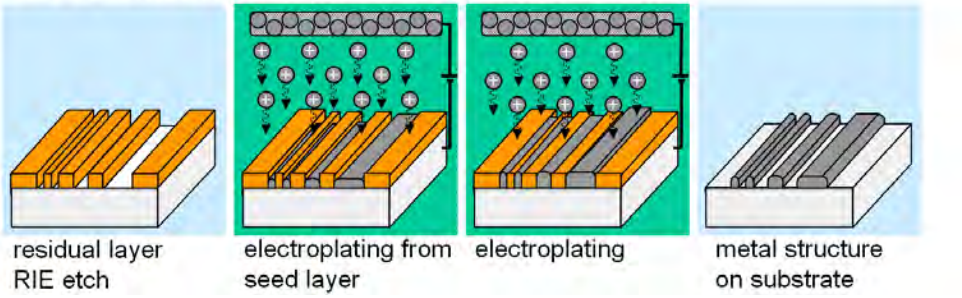


Figure 5.38: Example for electroplating as a pattern transfer process after NIL (with a conducting substrate).

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. Schift, 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.

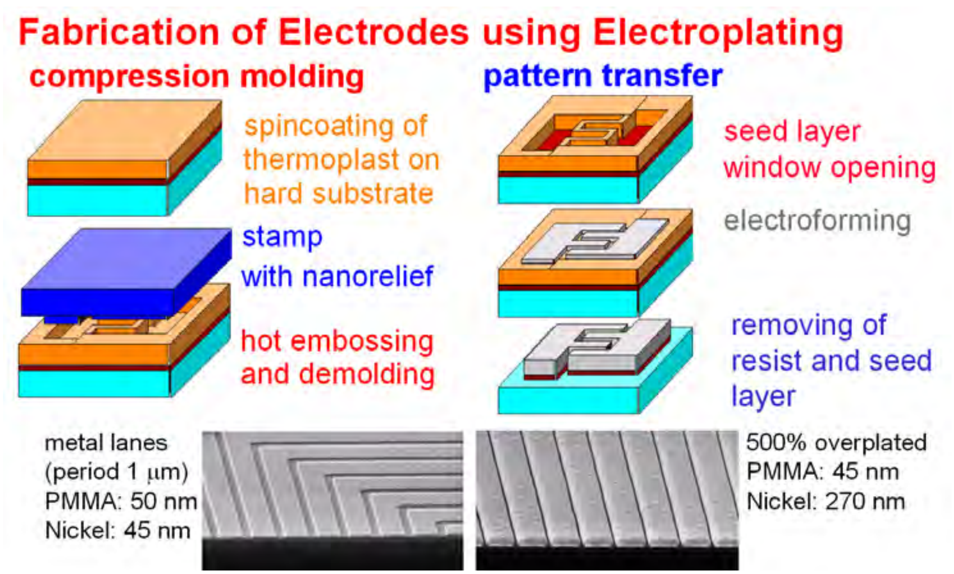


Figure 5.39: Example for electroplating as a pattern transfer process after NIL.

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. 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 hot embossing (NIL) and UV-imprint (UV-NIL), with typical parameters of current processes.

type of NIL / properties	**NIL** hot embossing	**UV-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°C	liquid, UV-curable
viscosity	10^3-10^7 Pa·s	10^{-3}-10^{-1} Pa·s
stamp material	Si, SiO_2 opaque	glass, SiO_2 Transparent
stamp area	full wafer, > 200 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	low viscosity, 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
Hybrid approaches	thermoset resists: embossing and curing before demolding	thermoplastic resists: hot molding and UV-curing before demolding
Advantage	low temperature variation cycle: demolding at high temperature possible	solid resist: full wafer single imprint possible

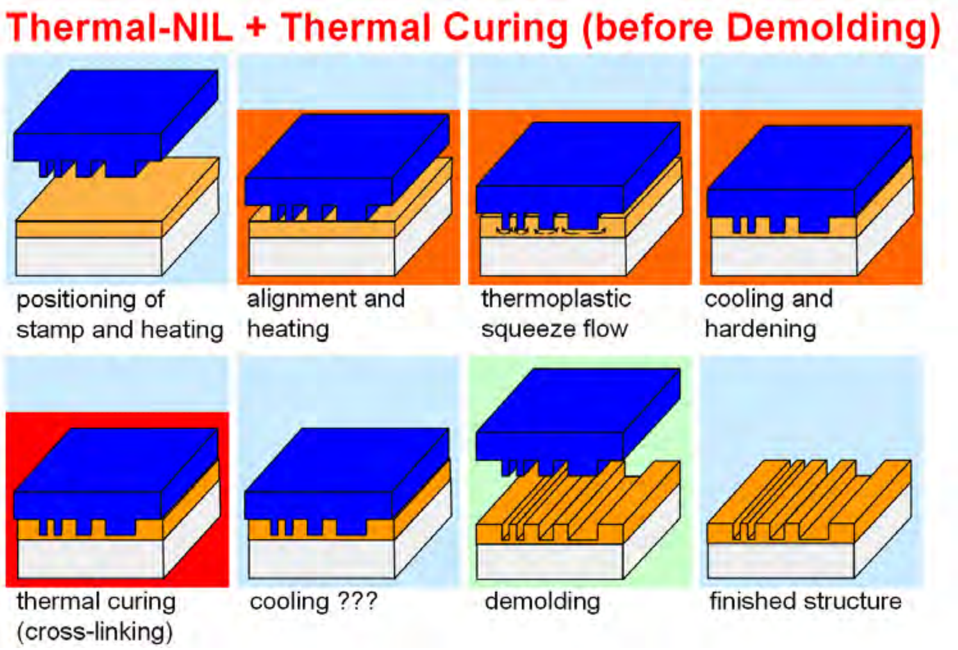


Figure 5.40: Process sequence for thermal NIL with a curable resist.

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. Lyebyedyev, H.-C. Scheer, K. Pfeiffer, G. Bleidiessel, G. Grützner, 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, H.-C. Scheer, *A comparison of thermally and photochemically cross-linked polymers for nanoimprinting*, Microelectron. Eng. **67**-**68** (2003) 266-273.

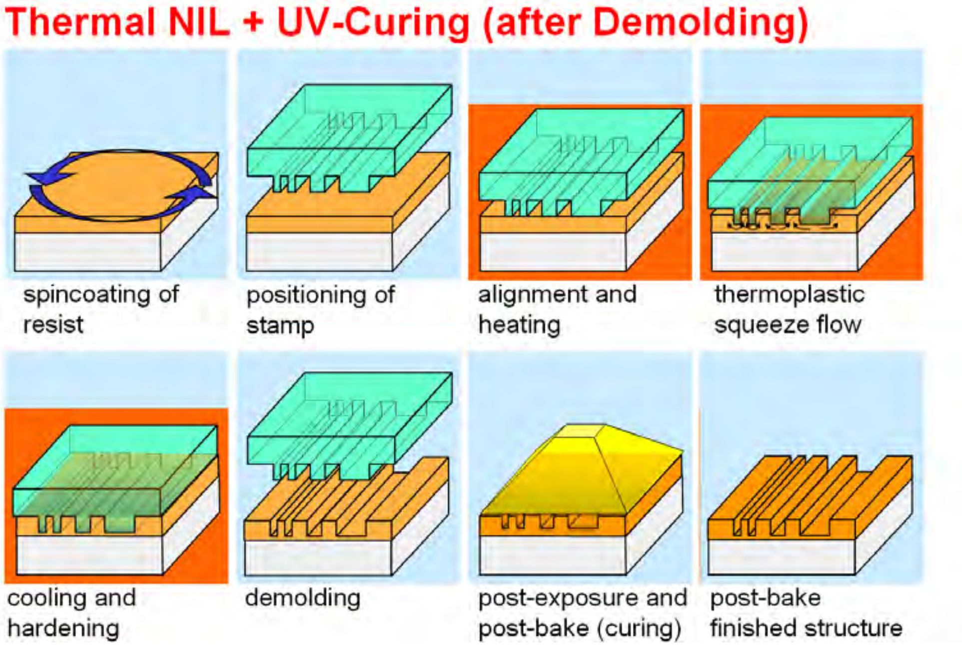


Figure 5.41: Process sequence for sequential thermal NIL into a low T_g thermoplastic material and subsequent curing.

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, 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, H.-C. Scheer, *Multistep profiles by mix and match of nanoimprint and UV-lithography*, Microelectron. Eng. **57**-**58** (2001) 381-387.

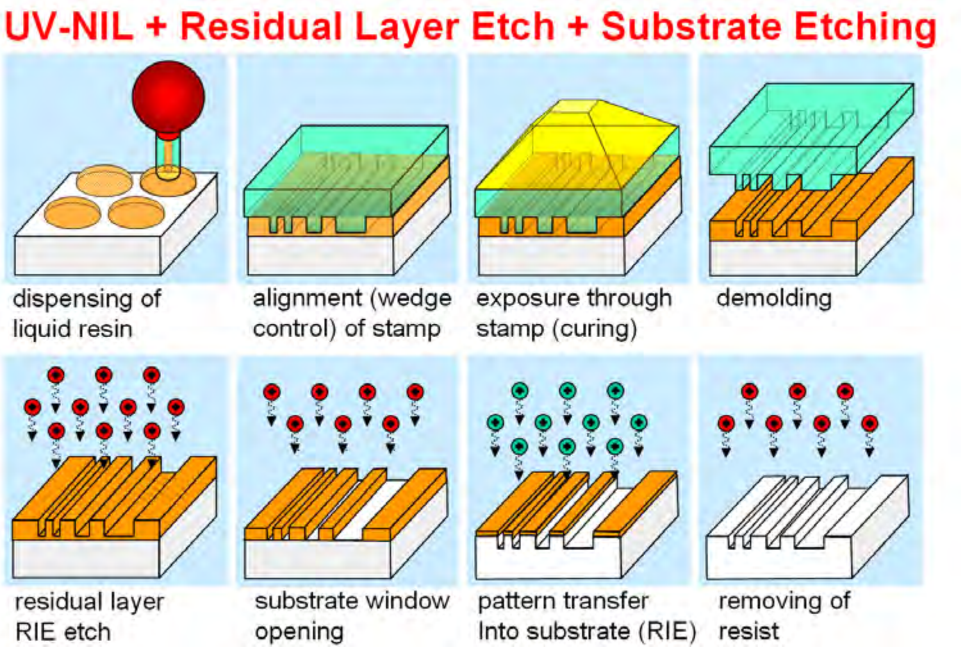


Figure 5.42: Process sequence for UV-NIL, residual layer etch and substate etching.

Short description

With the integration of light sources into imprint machines, UV-NIL was developed for curable 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 by curing..

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, 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, 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, C.G. Willson, *Step & flash imprint lithography*, Materials Today **8** (2005) 34-42.

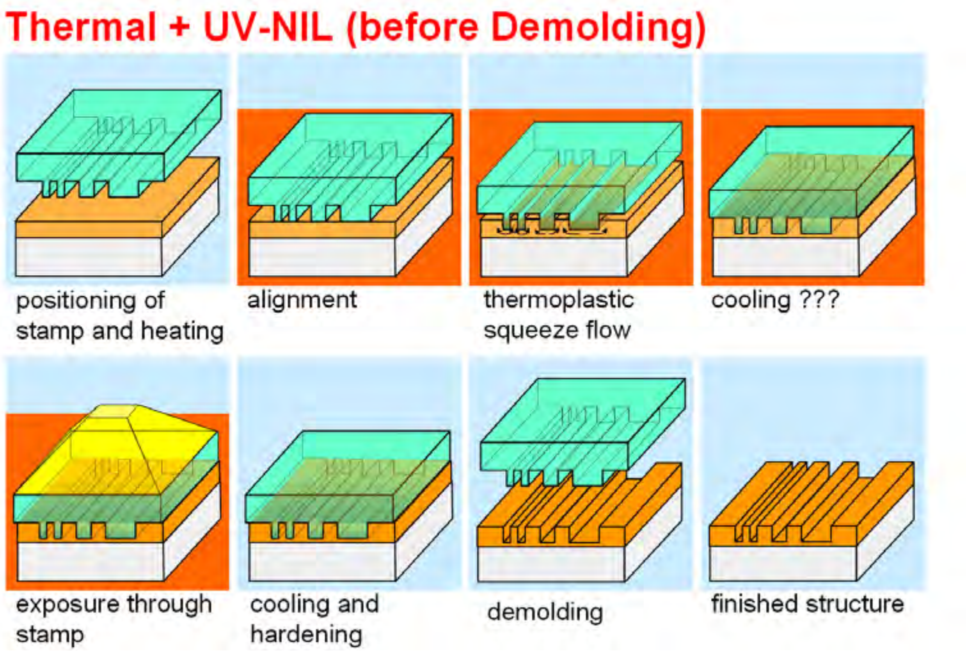


Figure 5.43: Process sequence for combined thermal and UV-NIL.

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, 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)

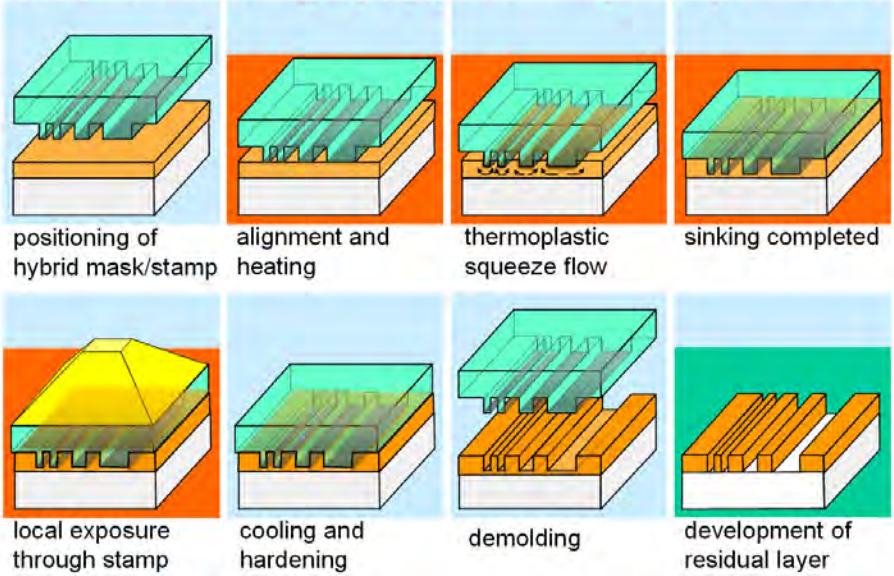


Figure 5.44: Process sequence for combined thermal and photolithography (CNP) with a semi-transparent stamp.

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, L.J. Guo, *A combined-nanoimprint-and-photolithography patterning technique*, Microelectron. Eng. **71** (2004) 277–282.
[2] X. Cheng, 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, 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. Schift, *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)

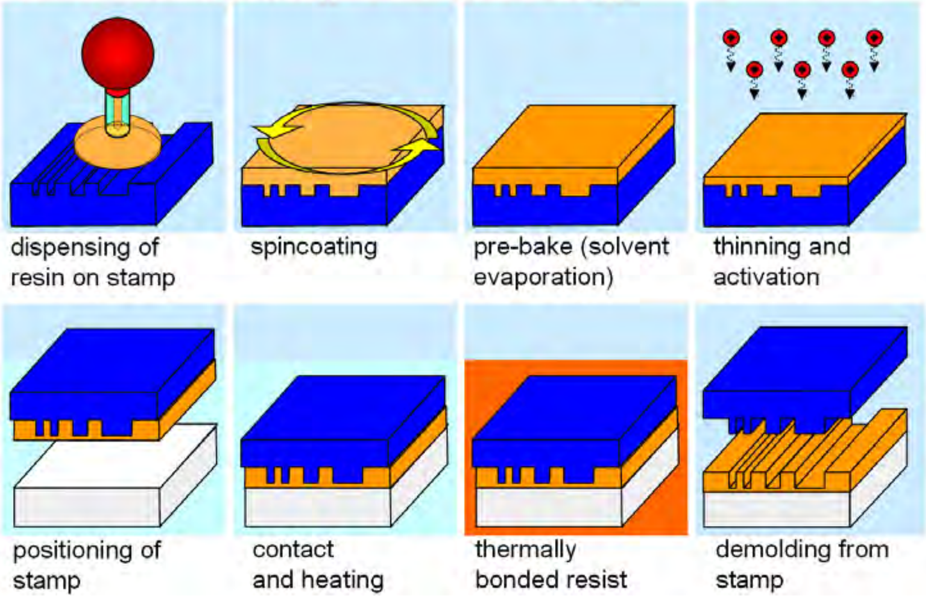


Figure 5.45: Process sequence for reveral imprint by thermal bonding of a resist layer from a stamp to a separate substrate.

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, 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, 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, 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, Y. Hirai, Yoshihiko, *Reproduction of fine structures by nanocasting lithography*, Microelectron. Eng. **84**(5-8) (2007) 909-911.

5.10 Processes – Part 3 : Hybrid processing

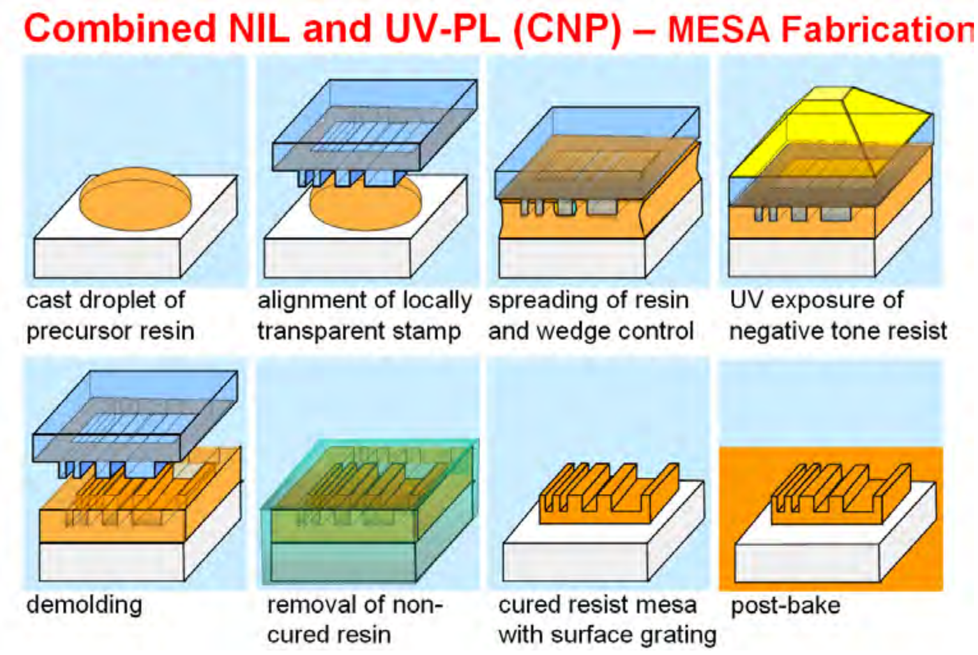


Figure 5.46: Process sequence for combined nanoimprint lithography and UV-photolithography (CNP) enables to combine surface patterning on mesas.

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, anostructures 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. Schift, *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.

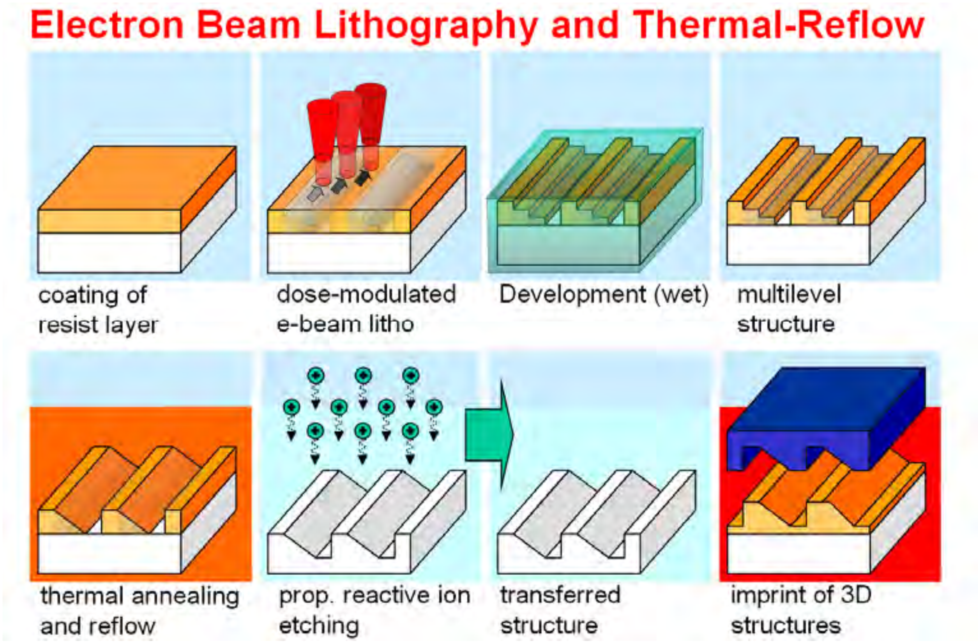


Figure 5.47: Process sequence for a TASTE (see below) process, here demonstrated for combination of dose-modulated (grayscale) electron beam lithography (here process variant with grayscale electron lithography for 3D patterning).

Short description

The TASTE process (Thermally Activated Selective Topography Equilibration) 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. Schift, *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. Schift, *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. Schift, *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. Schift, *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.

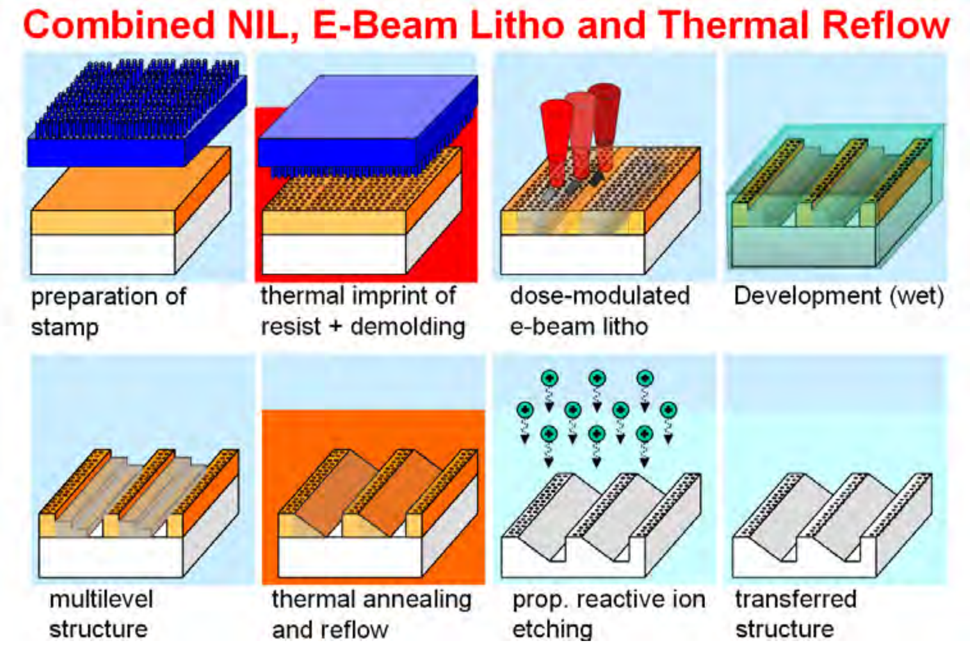


Figure 5.48: Process sequence for a hybrid TASTE process, by combining nanoimprint lithography, dose-modulated electron beam lithography, selective thermal reflow and proportional pattern transfer by reactive ion etching.

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

- Antireflexion (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. Schift, *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. Schift, *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.

5.11 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.

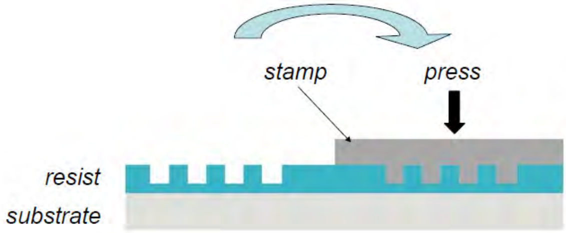


Figure 5.49: Process sequence for step and repeat imprint.

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 ^{o}C stamp temperature (in viscous state) and substrate temperature 0-10 ^{o}C above T_g.
- Pressure is applied until stamp and substrate are cooled 10-20 ^{o}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, K. Pfeiffer, *Step & stamp imprint lithography using a commercial flip chip bonder*, Proc. SPIE **3997** (2000) 874 – 880.
[2] T. Haatainen, J. Ahopelto, *Pattern Transfer using Step&Stamp Imprint Lithography*, Physica Scripta **67** (4) (2003) 357 – 360.

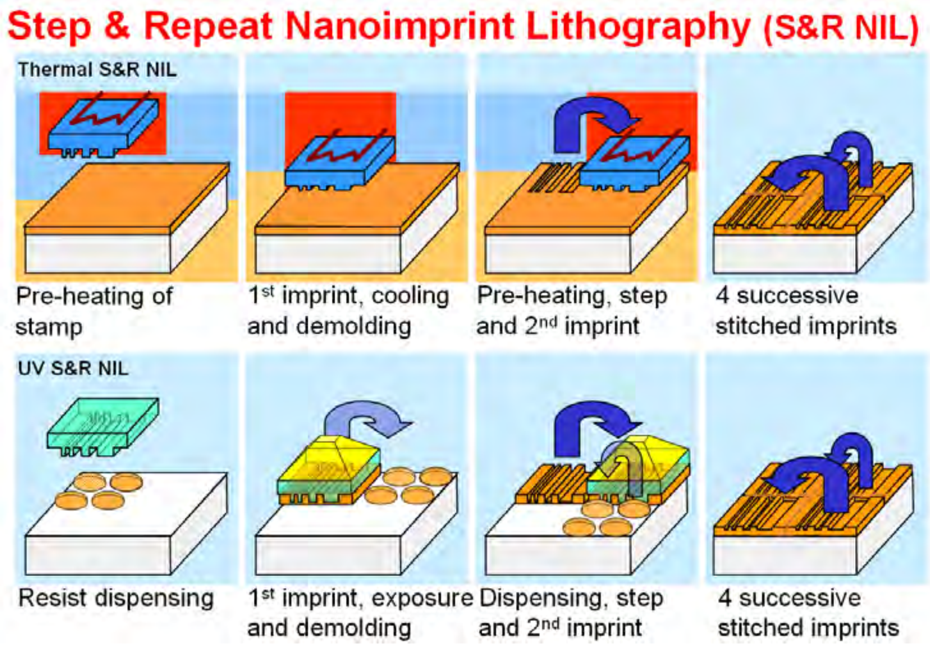


Figure 5.50: Step&Repeat imprint processes.

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

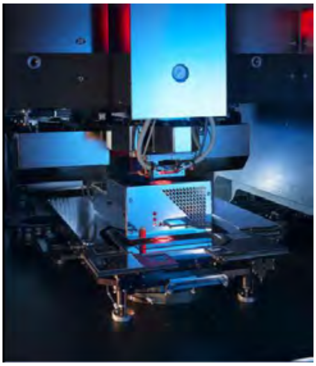
Advantages

- 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.

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.



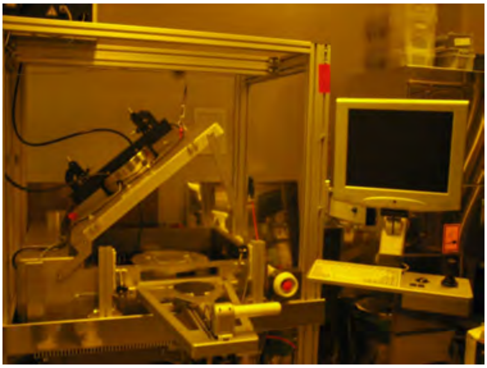


Figure 5.51: Left side: NPS300 from SET at VTT. Right side: EVG770 from EVG at AMO.

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 mimimum 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 is 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 andre 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 (^{K})	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.

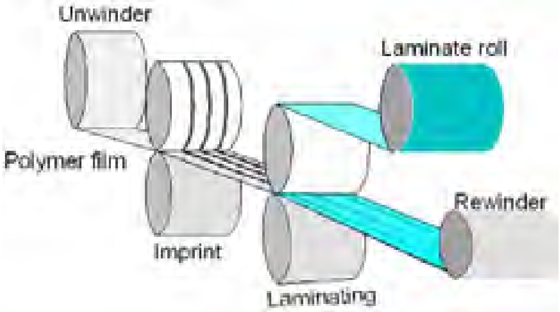


Figure 5.52: Schematic of roll-to-roll process using in-line imprint and lamination.

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 themal 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 oprimization 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. Schift, *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, 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: ptmtec@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).

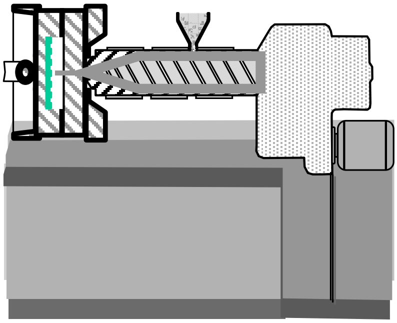


Figure 5.53: Schematic of an injection molding machine used for Compact Disk manufacturing.

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 protyping it is favorable to use silicon wafers or replicated stamps such as polymer foils or hybrid Ormostamp on glass molds.

Process parameters

- Typically tthermoplastic polymers are used which change their thermomechanical properties from solid to viscous. The mold is kept below or near to the Tg 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. Schift, 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. Schift, 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. Schift, *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 $\Psi = \arctan(\frac{r_p}{r_s})$ and $\Delta = \delta_p - \delta_s$, called scatterometric angles, linked to two intensities, I_s and I_c:

$$I_s = \sin(2\Psi).\sin(\Delta)$$
$$I_c = \sin(2\Psi).\cos(\Delta)$$

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.

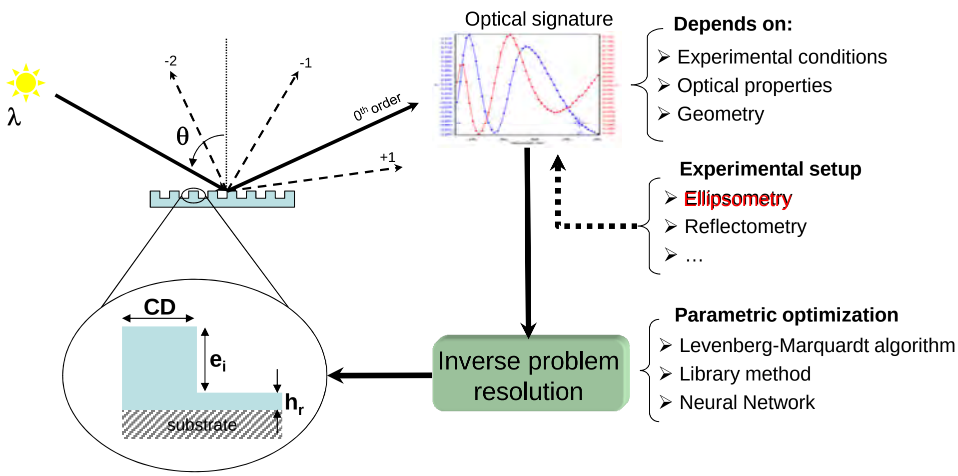
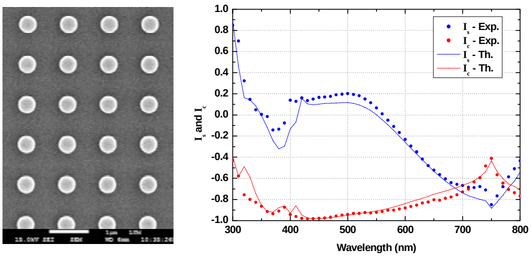


Figure 5.54: Schematic of scatterometry: From the diffraction pattern the shape of the original pattern can be determined by advanced mathematics.

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.

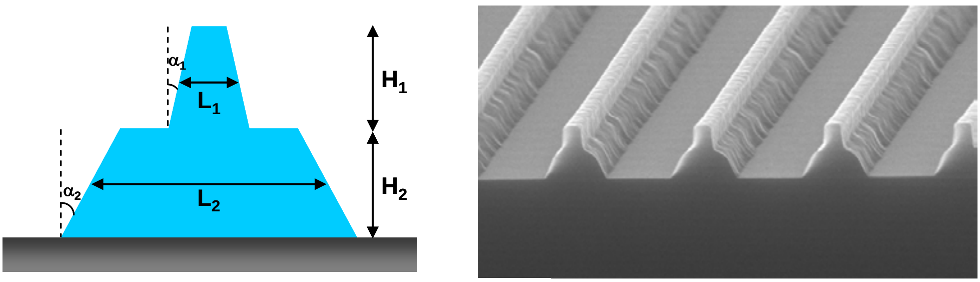


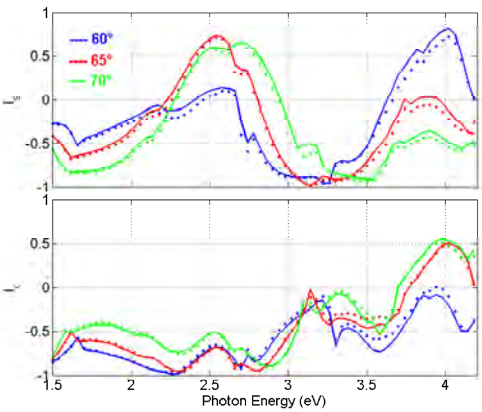
	Scatterometry	SEM
Diameter (nm)	410	423
Height (nm)	665	632
Residual thickness (nm)	81	82

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 stuctures: 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.





	Scattero.	SEM
L_1	185.5	182
L_2	461.8	462
H_1	243.8	225
H_2	251.4	246
α_1	7.55	-
α_1	30.6	-

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

5.15 References

An introduction into nanoimprint for engineers and scientists:

[1] H. Schift 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. Hard-bound, ISBN 0-306-47858-7, November 2003, 425 pp. (2003).

[3] NaPa Library of Processes, ed. H. Schift, 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. Schift, *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

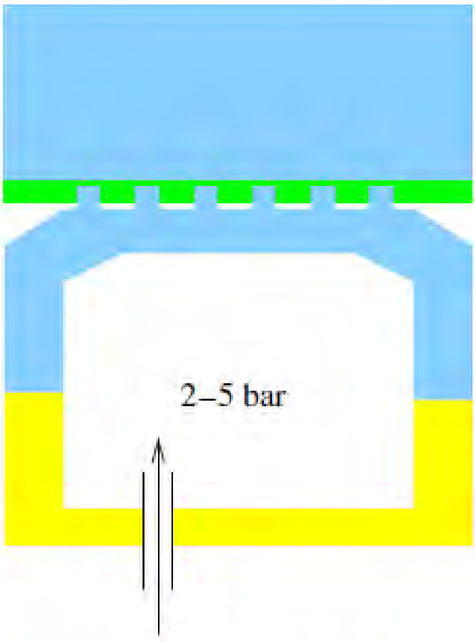
PTMTEC OY / Finland
Dr. Tapio Mäkelä

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

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

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

NILT - Denmark
Thedor 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)

Contact information:
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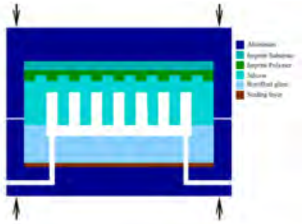
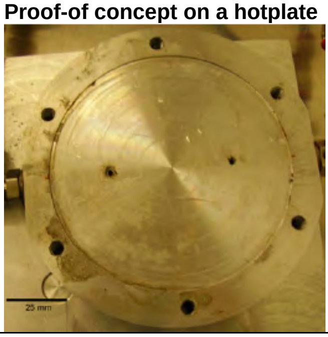
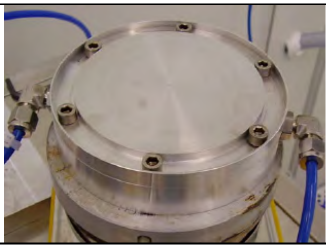
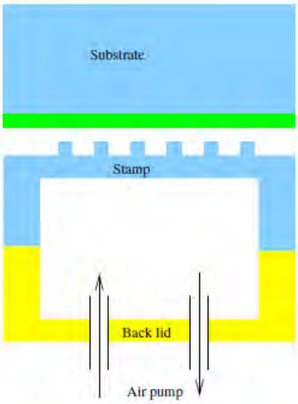
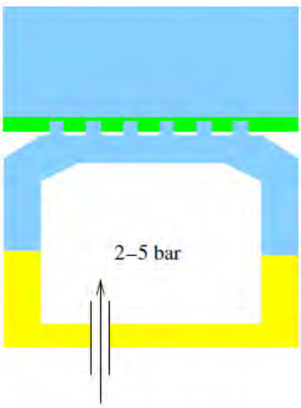
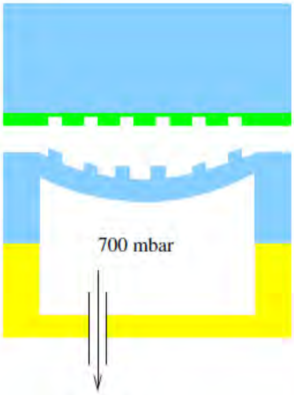
LoP2012_NIL001_CNI-Tool

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. $T_{imprint}$ ≈190 °C[a] $T_{separation}$ ≈23 °C[a]	

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

3.3	**Stamp concept (3)**  	**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 atmos-pheric at all times.	
	End of Process 3		
	End of Total Process		

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“. 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 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	**Process:** Step & Repeat thermal NIL
Address: Helsinki, FI	**Responsible:** Tomi Haatainen
Web-Address: http://www.vtt.fi	**E-mail:** tomi.haatainen @vtt.fi

Partner: S.E.T. SAS (Smart Equipment Technology)	**Process:** NPS300 Step&stamp Tool
Address: 74490 Saint Jeoire, France	**Responsible:** Gilbert Lecarpentier
Web-Address: http://www.set-sas.fr	**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 mm^2) and submicron scale features.
Purpose: The aim of this process is transfer periodical structures of stamp into thermoplastic polymer with low stitching eroors 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 elecments
References:

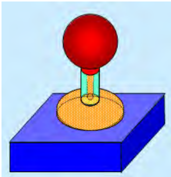
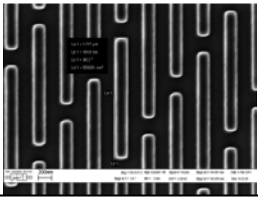
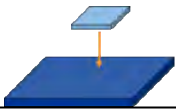
[1] T. Haatainen, J. Ahopelto, G. Grueztner, M. Fink, K. Pfeiffer, Step & stamp imprint lithography using a commercial flip chip bonder, Emerging Lithographic Technologies IV, Proceedings of SPIE, Vol. **3997**. SPIE-The International Society for Optical Engineering (2000), 874 – 880.
[2] T. Haatainen; 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.

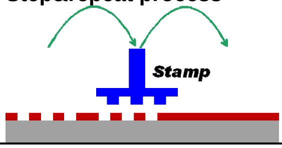
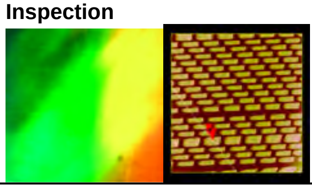
Contact information:
Dr. Tomi Haatainen
VTT Technical Research Centre of Finland
Tietotie 3
P.O.Box 1000
FI-02044 VTT, Finland

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**	*Height and profile control*
	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**	*Particle contamination*
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**	2µm thick layer of thermo-plastic polymer mr-I T85 1.0 µm	*Alternative resist as used in Figure 1 below:* *mr-I 7000R (high resolution)*
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	*Stamp-to-substrate parallelism. Feature profile due to thermal flow near adjacent imprints. Stitching accuracy.*
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.

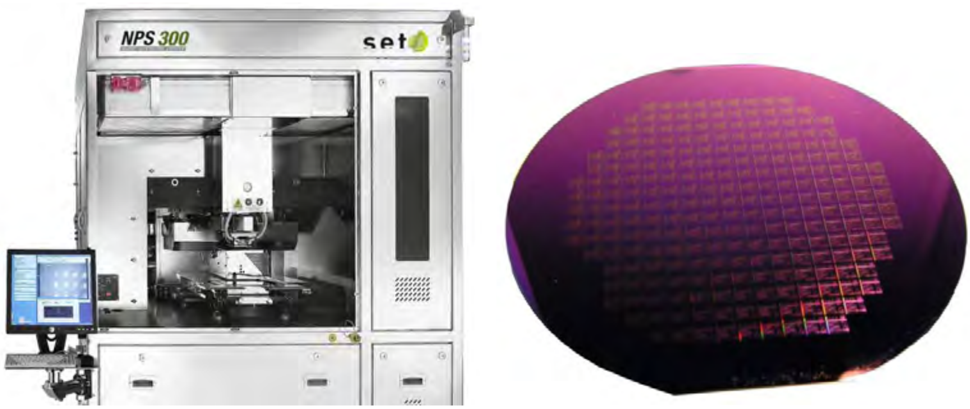
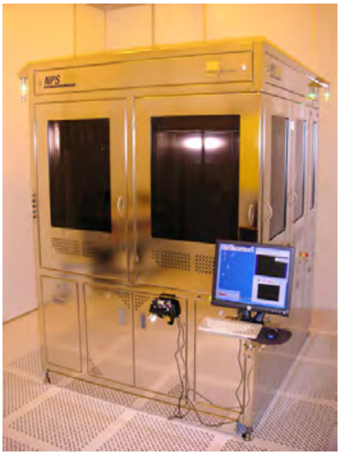


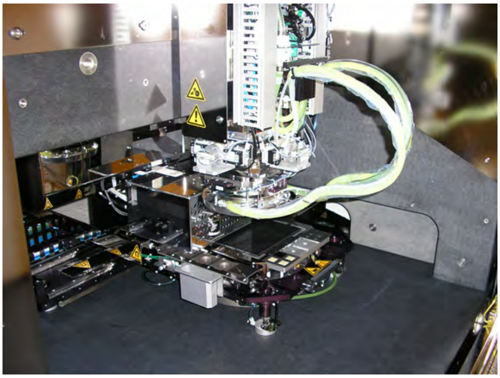
Figure 1: SET's NPS Step and Stamp machine for thermal and UV NIL used for these experiments (until 2007 SET was part of SÜSS Microtec), installed at VTT (left side), and example (right side) of a 237 consecutive thermal imprints into a 300 nm thick mr-I 7000R film (by *micro resist technology* GmbH) on a 100mm Silicon wafer. Stamp size 4x4mm^2, 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: ±90°
- Template / Stamp size up to 100 mm
- Substrate up to diameter 200mm (300mm option
- Pre-leveling accuracy 20 µradian
- 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 XYθ Stage
XY: 400 x 400 mm, resolution 10 nm (step 100nm)
θ: ± 5°, resolution 0.4 µradian
Top & Bottom Viewing Microscope
FoV: 870 x 690 µm (20X) – Pixel ~ 0.67 µm
Autocollimator for Pre-leveling
Sensitivity: 20 µradian

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 I 00740 Helsinki, Finland
Web-Address: 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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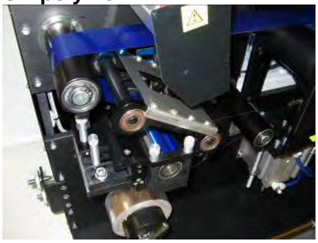
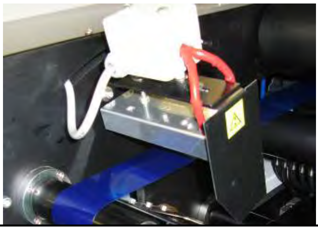
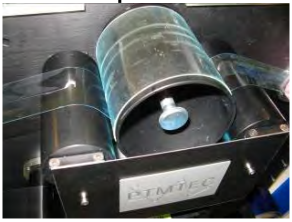
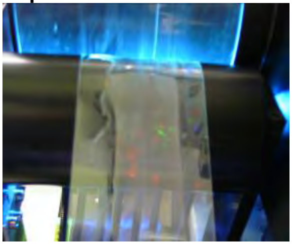
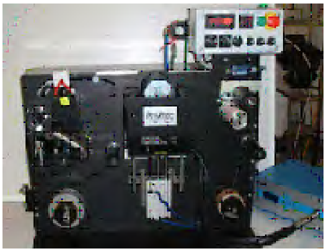
Finland

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	*good adhesion to polymer film sometimes difficult*
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.	*Web speed versus rod speed must optimize.*
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.	*Polymer can also be semi cured, but then adhesion to the mold is problem.*
	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.	*Higher aspect ratios might distort features.*
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 microsco-py/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

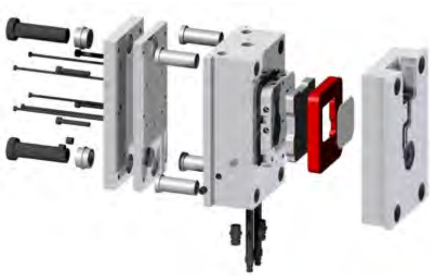


Figure:
Blow-up schematics of a variothermal injection molding tool

Process:
Variothermal injection molding requires sophisiticated 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 Schift
E-mail: helmut.schift@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 50x50mm^2.

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. Schift, 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. Schift, *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. Schift, 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. Schift, J. Gobrecht, and B. Müller, *Nano-mechanical transduction of polymer micro-cantilevers to detect bio-molecular interactions*, submitted to Biointerfaces **6**, SpringerOpen (2011).

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Institute of Polymer Nanotechnology
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CH-5210 Windisch, Switzerland

LoP2012_NIL004_variothermIM-Tool

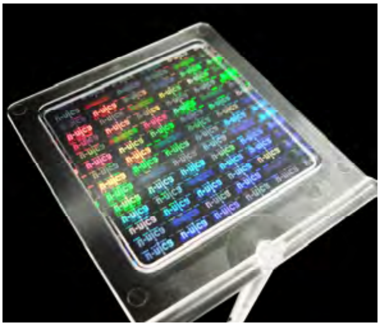

Figure 1: Versatile tooling for rapid variotherm injection molding (left) and sample of security feature replication (right).

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. $50x50mm^2$) 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 25 & 37) 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 demoling 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
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DTU - Lyngby/Denmark
Prof. Dr. Anders Kristensen

PSI/LMN - Villigen/Switzerland
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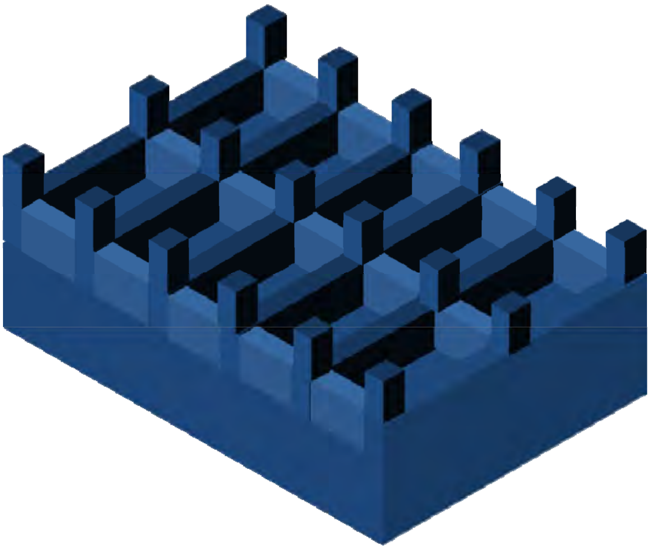
Christian Spreu

INFM TASC - 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

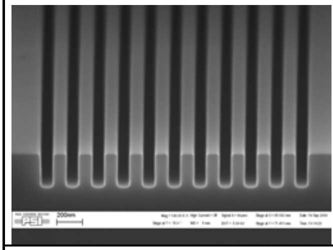


Figure:
SEM micrograph of a Grating with 100 nm period etched in Si using dry etching process (ICP) and PMMA resist as an etch mask.

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
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 Schift
E-mail: helmut.schift@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. Schift, S. Saxer, S. Park, C. Padeste, U. Pieles, 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. Schift, 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. Schift, 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.

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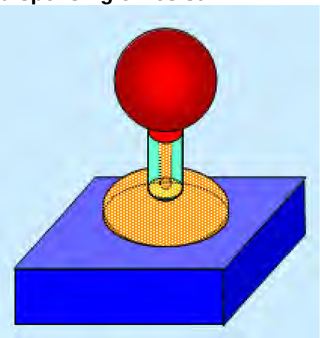
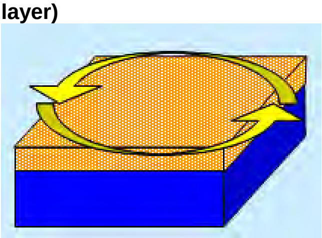
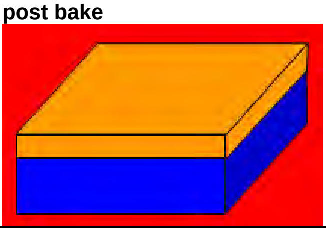
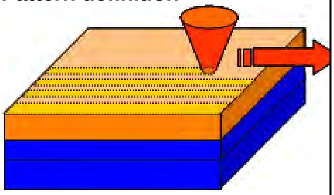
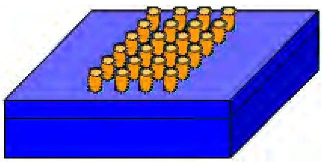
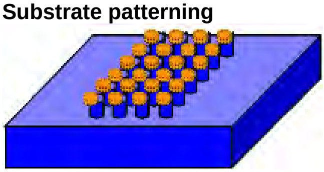
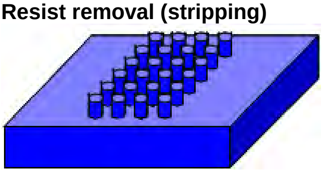
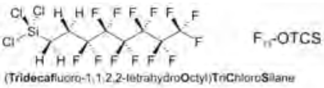
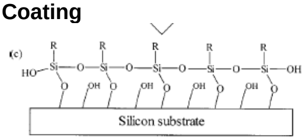
LoP2007_NIL001_Stamps for NIL

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)	*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.*
2.2	**coating resist (homogeneous layer)** 	**spincoating of PMMA** speed: 3000rpm, acceleration: 3000rpm/sec, time: 45 s -> ~200 nm thickness	*PMMA is known for its high resolution as a positive resist, but has a limited sensititivy 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.*
2.3	**post bake** 	**solvent evaporation** bake 1 min @ 170°C (hot plate)	*Alternative: convection oven at 180°C, for 30 min*
	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	*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.*
3.2	**Pattern definition** 	**serial exposure with focused beam** PMMA expose exposed to a 30 kV electron beam dose: 200 µC/cm^2	*For different resists datasheets are available with the range of exposure and development parameters.*
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**	**dry etching of silicon**	
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.	*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*
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-	

		tive solution is to dissolve the resist in a convenient solvent.	
4.3	**process control**	**optical and electron microscopy** *non-destructively*	*destructive (cleaving, metal coating) in SEM profilometry*
	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) for about 60 min. Alternatively, UV-ozone treatment can be used.	*Alternatively to dry treatment of the surface, the cleaning and activation of the surface can be done in a fresh solution of H_2O_2:H_2SO_4 (1:4). Attention: danger of explosion! Dip the silicon stamp for 5-10 min.*
5.2	**Solution preparation** 	**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.	*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*
5.3	**Coating** 	**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).	*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.*
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	*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*
	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

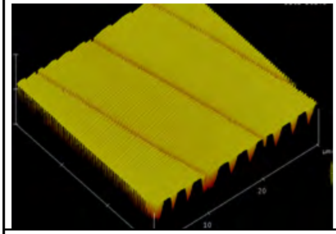


Figure:
AFM micrograph of a double grating with two distinct periods of 500nm and 10µm.

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 Aaachen, Germany
Web-Address: 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

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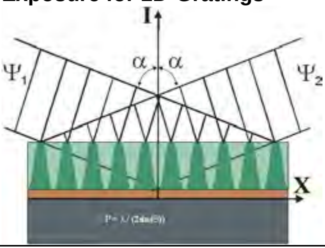
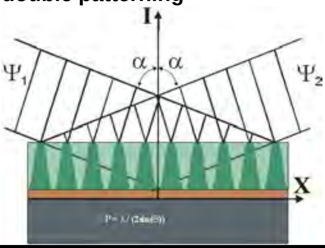
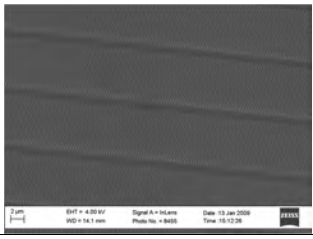
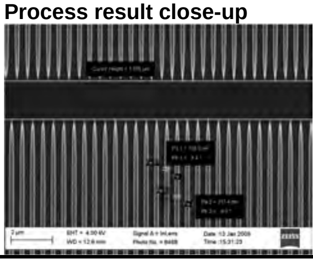
Otto-Blumenthal-Strasse 25
52074 Aachen
Germany

LoP2012_NIL005_LIL-Stamps

Laser Inferference 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	*BARC= bottom antireflec-tion coating*
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 -α=15.24° –> 500nm period	*p1=λ/(2sin(α))*
1.4	**Second exposure for Moiré double patterning**  	**2ne exposure** under rotated substrate angle β=2.86° –> 10µm period	*p2=p1/(2sin(β))*
1.5	**Development of double pat-terened grating**	**development of resist** in MF26@30sec.	
1.6	**Process result** 	After LIL process and standard etching into Sili-con 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

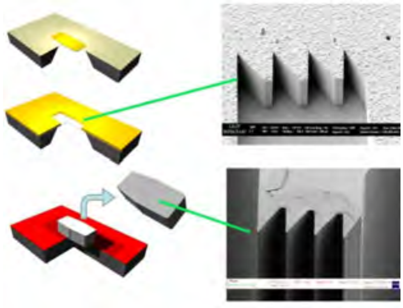


Figure:
Scheme of fabrication of a nickel master tool with a few-period saw-tooth grating. The released nickel shim is used for hot emboss the structure defined on its edge.

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 are 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	**Process:** XR-lithography, electroplat.
Address: 34012 Basovizza-Trieste, Italy	**Responsible:** Massimo Tormen
Web-Address: http:// www.tasc-infm.it	**E-mail:** tormen@tasc.infm.it

Partner: University of Glasgow (UG)	**Process:** EBL
Address: Glasgow, UK	**Responsible:** Nikolaj Gadegaard
Web-Address: http://www.gla.ac.uk	**E-mail:** n.gadegaard@gla.ac.uk

Partner: Modines Oy	**Process:** Design, application
Address: Helsinki, FI	**Responsible:** Kari Rinko
Web-Address: http://www.modines.com	**E-mail:** kari.rinko@modines.com

Partner: VTT Technical Research Centre of Finland, VTT	**Process:** Step & Repeat thermal NIL
Address: Helsinki, FI	**Responsible:** Tomi Haatainen
Web-Address: http://www.vtt.fi	**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 μm^2) are created with sawtooth structures. Finally, the structure is assembled and glued onto a 10x10 mm^2 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. Grenci, A.Pozzato, Paper in preparation

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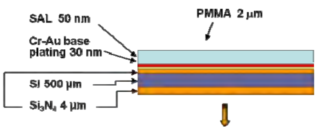
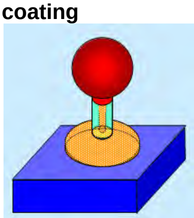
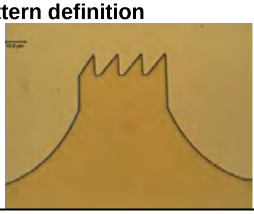
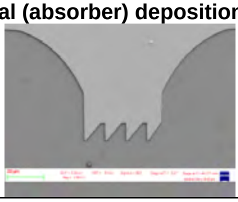
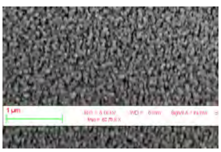
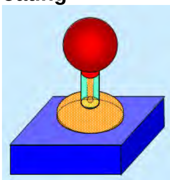
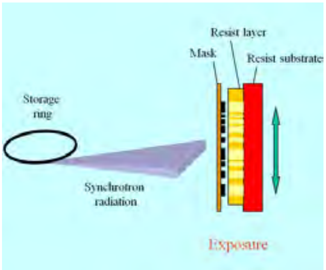
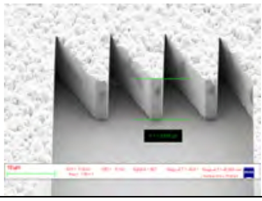
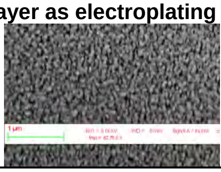
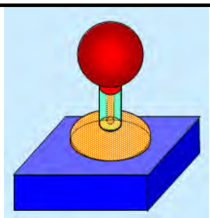
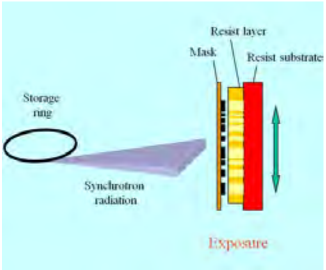
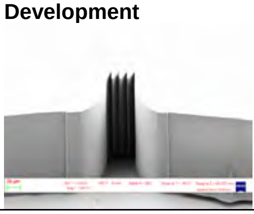
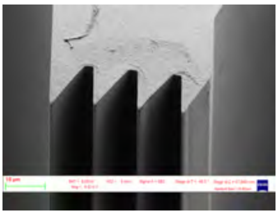
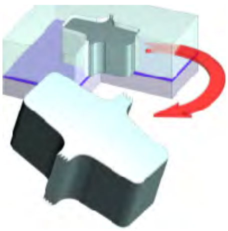
LoP2012_NIL006_Sawtooth-Stamps

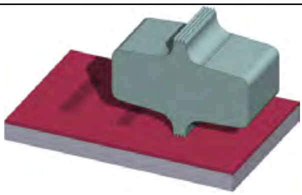
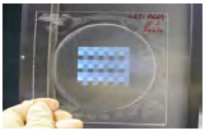
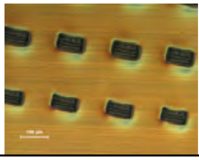
Saw-tooth stamps

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.	*No proximity correction required*
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.	*Adhesion issues solved by introducing nanorough titania*

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.	*Adhesion issues solved by introducing nanorough titania*
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	

		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	
3.5	**Deep X-ray Lithography** 	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/cm^3 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.	
3.6	**Development** 	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.	
3.7	**Electroplating of Nickel** 	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.	
3.8	**Release** 	The shims were finally released from the substrate by fully etching the silicon substrate and the titianium oxide in a 5 M KOH solution at 75 °C overnight.	
	End of Process 3		

4.0	**Process 4: Pattern enlargement**		
4.1	 **IMPRINTING TOOL: NPS300**	**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 (∅ 300mm).	
4.2		**Clamping** the nickel shim for step & repeat hot embossing.	*Replication into thermoplastic NIL materials (see page 34) or bulk polymer*
4.3	 	**Inspection:** Optical and electronic microscopy to characterize the results of the step & repeat hot embossing process.	
	End of Process 4		
	End of Total Process		

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

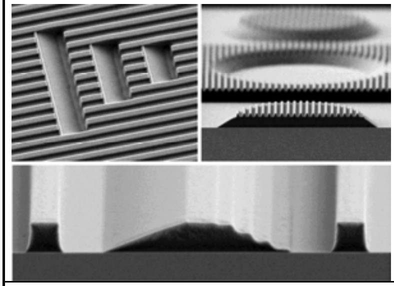


Figure:
Compilation of SEM micrographs illustrating the TASTE capabilities to manufacture sophisticated 3D surface structure with stepped, sloped and vertical sidewalls in close vicinity (here: 1 µm thick PMMA resist on silicon substrate).

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

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

Project leader: Paul Scherrer Institut (PSI)
Address: 5232 Villigen PSI, Switzerland
Web-Address: http:// www.psi.ch
Process: EBL, reflow, pattern transfer
Responsible: Helmut Schift
E-mail: helmut.schift@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: The 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.

References:

[1] A. Schleunitz et al., *Novel 3D micro- and nanofabrication method using thermally activated selective topography equilibration (TASTE) of polymers*, in preparation

[2] A. Schleunitz, C. Spreu, M. Vogler, H. Atasoy, and H. Schift, *Combining nanoimprint lithography and a molecular weight selective thermal reflow for the generation of mixed 3-D structures*, J. Vac. Sci. Technol. B **29** (2011) 06FC01

[3] A. Schleunitz, V.A. Guzenko, A. Schander, M. Vogler, and H. Schift, *Selective profile transformation of electron-beam exposed multilevel resist structures based on a molecular weight dependent thermal reflow*, J. Vac. Sci. Technol. B **29** (2011) 06F302

[4] A. Schleunitz and H. Schift, *Fabrication of 3D nanoimprint stamps with continuous reliefs using dose-modulated electron beam lithography and thermal reflow*, J. Micromech. Microeng. **20** (2010) 095002

Contact information:
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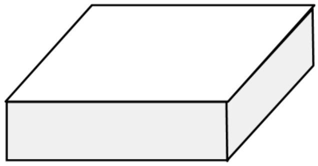
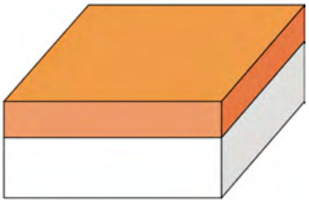
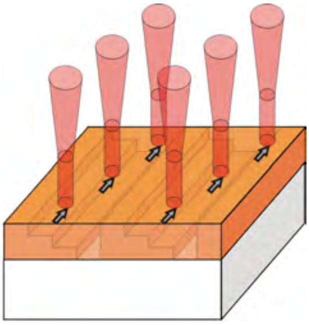
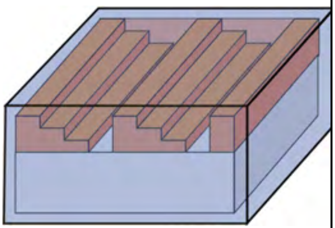
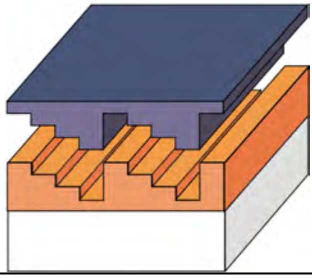
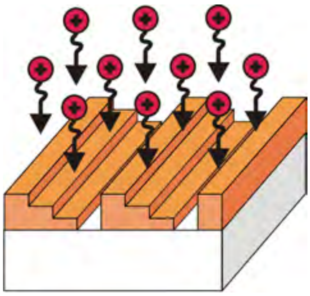
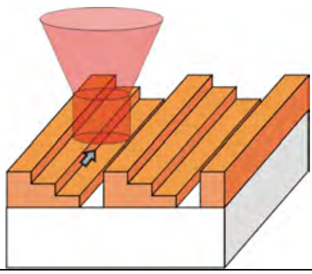
URL: http://www.psi.ch

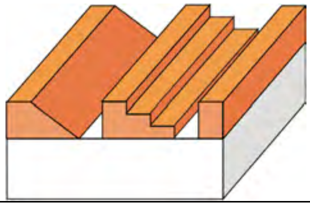
LoP2012_NIL007_3D-Stamps for NIL

Three-dimensional 3-D 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-caoting and pre-baking of PMMA resist** 	**Polymethyl (methacrylathe)** 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-back at 175 °C on hot plate (or oven)	*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.*
	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 uC/cm2 Dose-modulation is performed according to the **contrast curve** (i.e. etch depth vs. exposure dose)	*Dose modulation not only according to desired dose-depth variations, but also have to take the areal proximity effect into account.*

2.2a	… and wet etching 	**Development** of PMMA exposed to different doses leads to variations in the etching rates, thus stepped contours Developer: Methyl isobutyl ketone (MIBK) Rinse: IPA and DI water	*It is recommended to temperature control the developer bath to optimize the reproducibility.*
2.1b	**Topography origination** by 3D thermal NIL … 	**Alternative way** to generate stepped topographies is to replicate stepped stamps into PMMA by **thermal NIL.** Stamp: silicon or nickel PMMA molecular weight: ≤ 120 kg/mol Standard imprint parameter using Jenoptik HEX 03 press: 180 °C / 5 MPa / 15 min	*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.*
2.2b	… and residual layer etching 	Residual layer etching is a crucial step when the topography is generated by NIL in order to enables pinning point on the substrate inevitable for the formation of linear slopes. For concave and convex pattern, this step is less important. Exemplary etch recipe: Power: 20 W Pressure: 20 mtorr Oxygen: 20 sccm Resulting etch rate: 30 nm/sec	*Oxygen plasma might harm the stepped contours and thus lead to an unwanted pattern deviation.*
	End of Process 2		
3.0	**Process 3: flood exposure**	**Adjusting thermo-mechanical properties**	
3.1	**Precisely aligned high dose exposure to stepped contours** 	**Flood (EBL) exposure** with commercial lithography system, e.g. VISTEC or JEOL: Acceleration voltage: 100 keV Beam step size: 25 nm Beam current: 10 … 100 nA Dose range: > 250 uC/cm2	*Electron beam exposure reduces the glass transition temperature Tg of locally exposed PMMA resist, in particular if dose is higher than 250 uC/cm2. Here, the resulting molecular weight is below a Tg-critical value of 10 kg/mol.*

	End of Process 3		
4.0	**Process 4: topography equilibration**	**Controlled transformation os 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.	*Heating temperature according to modulation of thermal properties by previous flood exposure: For PMMA with reduced Tg below 90 °C (i.e. exposed to 400 uC/cm2), a reflow at 110 °C ideal since the original Tg of 120k PMMA is at 120 °C.*
	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).

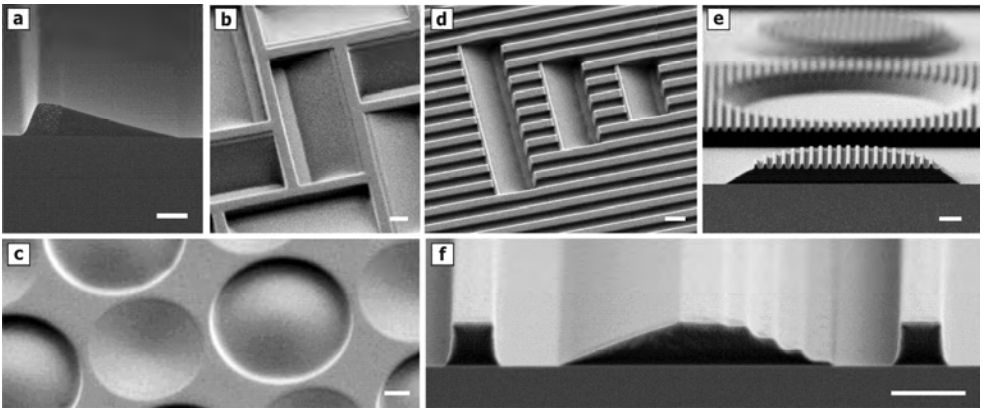


Figure 1: Compilation of exemplary 3D contours in a thin mr-I PMMA120k* film made by novel TASTE process. The SEM micrographs (angled views and cross sections) depict refined PMMA topographies after exposure of pre-patterned resist to high energy electrons and thermal annealing using hot-plate. Achievable 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

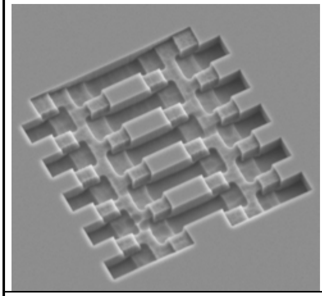


Figure:
SEM micrograph of a 3D structure fabricated with grayscale E-Beam lithography in PMMA and etched into silicon substrate.

Process:
Proportional pattern transfer with RIE of 3D resist structures

Application:
3D NIL stamps with stepped and continous slopes intended for optical, photonic, electronic or micro-/nanofluidic devices.

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

Project leader: Paul Scherrer Institut (PSI)
Address: 5232 Villigen PSI, Switzerland
Web-Address: http:// www.psi.ch
Process: Proportional RIE
Responsible: Helmut Schift
E-mail: helmut.schift@psi.ch

Partner: TASC Laboratory
Address: 34012 Basovizza-Trieste, Italy
Web-Address: http:// www.tasc-infm.it
Process: Proportional RIE
Responsible: Massimo Tormen
E-mail: tormen@tasc.infm.it

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.

References:

[1] H. Schift, S. Saxer, S. Park, C. Padeste, U. Pieles, J. Gobrecht: *Controlled co-evaporation of silanes for nanoimprint stamps*, Nanotechnology **16** (2005) S171-175

[2] H. Schift, 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

[3] A.Schleunitz, H. Schift, *Fabrication of 3D nanoimprint stamps with continuous reliefs using dose-modulated electron beam lithography and thermal reflow*, J. Micromech. Microeng. **20** (2010) 095002

[4] A. Schleunitz, C. Spreu, M. Vogler, H. Atasoy, H. Schift: *Combining nanoimprint lithography and a molecular weight selective thermal reflow for the generation of mixed 3D structures*, J. Vac. Sci. Technol. B **29** (2011).

[5] B. Morgan, C.M. Waits, J. Krizmanic, R. Ghodssi: *Development of a deep silicon phase Fresnel lens using gray-scale lithography and deep reactive ion etching,* J. Microelectromech. Syst. **13** (2004) 113 -120

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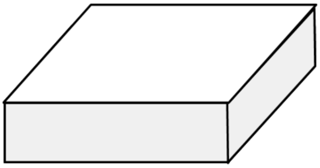
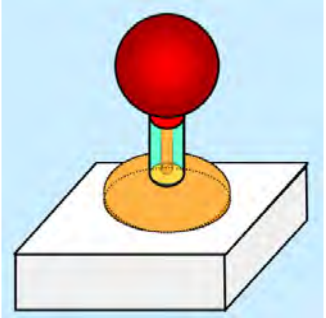
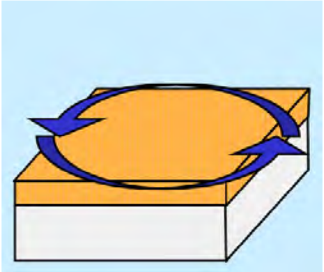
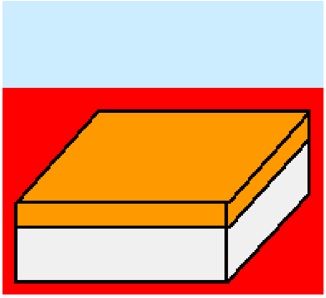
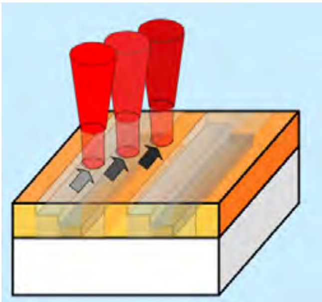
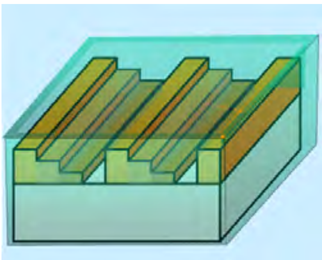
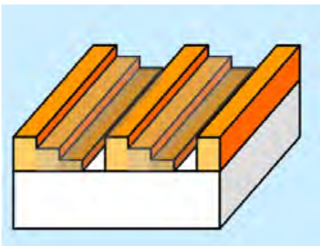
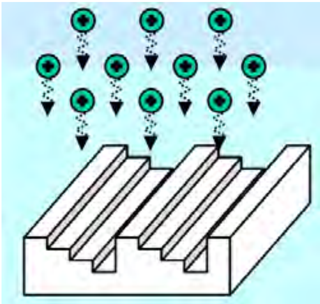
LoP2012_NIL008_3D RIE-Stamps

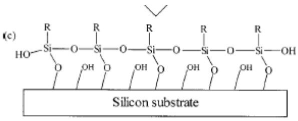
3-D stamps with proportional reactive ion etching

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 an 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: 1µm	*homogeneous layer*

2.3	**Pre bake** 	**solvent evaporation** bake 2 min @ 140°C (hot plate)	*Alternative: convection oven at 180°C, for 30 min*
	End of Process 2		
3.0	**Process 3: Lithography**	**E-Beam lithography**	
3.1		**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 uC/cm2 Dose-modulation is per-formed 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)	*It is recommended to tem-perature control the devel-oper bath to optimize the reproducibility.*
3.3		**Rinse**: Thorough rinsing in IPA and DI water removes diluted PMMA.	*Residues left on the resist surface might lead to con-tamination during dry etch-ing process, i.e. nucleation of polymer components during plasma step.*
	End of Process 3		

4.0	**Process 4: Pattern transfer**	**Reactive ion etching**	
4.1		A typical dry etch process for a depth from a few nanometers up to several micrometers uses a mixture of different gases e.g. (C_4F_8 50 sccm and SF_6 20 sccm, to stabilize the process noble gases like Ar could be added) The etch rate depends from the silicon load (means the exposed silicon) during the etch process and can change during the process. **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 Temperture: 0° C	*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.* *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.*
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**	**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)	*Alternatively to dry treatment of the surface, the cleaning and activation of the surface can be done in a fresh solution of H_2O_2:H_2SO_4 (1:2) at 90° C.* ***Attention:*** *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 SiO_2 layer on top of your substrate.*
5.2	**Solution preparation**  F_{13}-OTCS (Tridecafluoro-1,1,2,2-tetrahydroOctyl)TriChloroSilane	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.	*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*

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).	*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.*
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	*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*
	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 C_4F_8 makes a chamber clean step necessary.

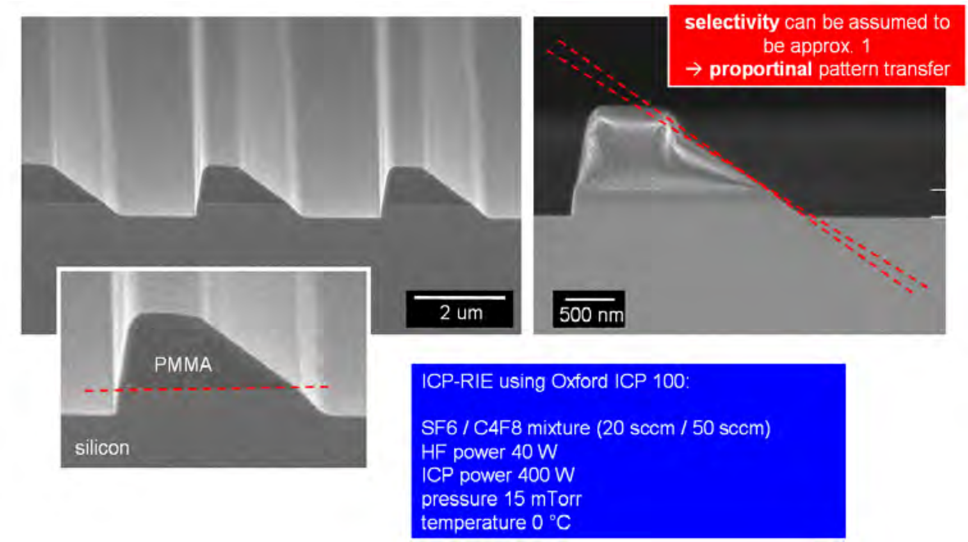


Figure 1: Demonstration of an almost proportional transfer of slopes in PMMA into the underlying silicon substrate using a RIE process. In the micrographs intermediate structures can be seen after stopping the etch procedure during RIE

2.6 Multilevel stamps

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

Process: Deep ultra violet photo lithography

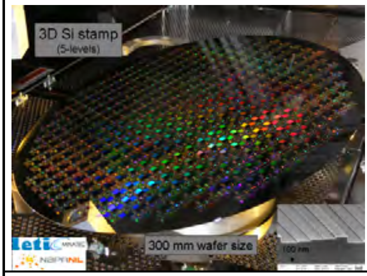


Figure:
SEM micrograph of a Grating with 100 nm period etched in Si using dry etching process (ICP) and PMMA resist as an etch mask.

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	**Process:** DUV 193 nm-Lithography
Address: 17 rue des martyrs 38054 Cedex 9	**Responsible:** Stefan Landis
Web-Address: http://www-leti.cea.fr/	**E-mail:** slandis@cea.fr

Partner: Paul Scherrer Institut (PSI)	**Process:** Thermal Nanoimprint
Address: 5232 Villigen PSI, Switzerland	**Responsible:** Helmut Schift
Web-Address: http://www.psi.ch	**E-mail:** helmut.schift@psi.ch

Partner: *TASC Laboratory*	**Process:** Isotropic wet etching / NIL
Address: S.S.14km 163,5; 34012 Basovizza (Trieste, Italy)	**Responsible:** Massimo Tormen
Web-Address: *www.tasc-infm.it*	**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 achieveable. Up to 5 levels in Si stamp can be manufactured.

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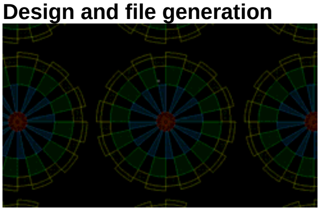
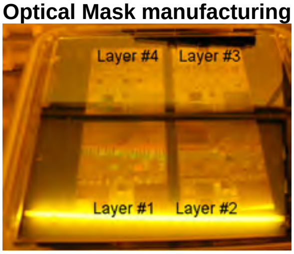
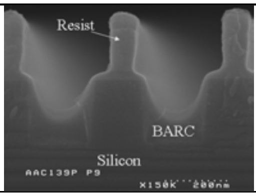
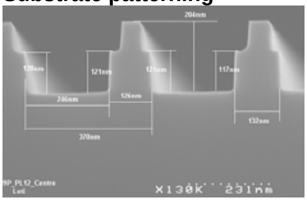
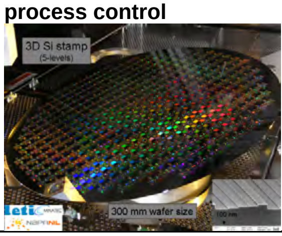
LoP2012_NIL009_Multilevel DUV-Stamps

Multilevel stamps

Process: DUV 193 nm photolithography

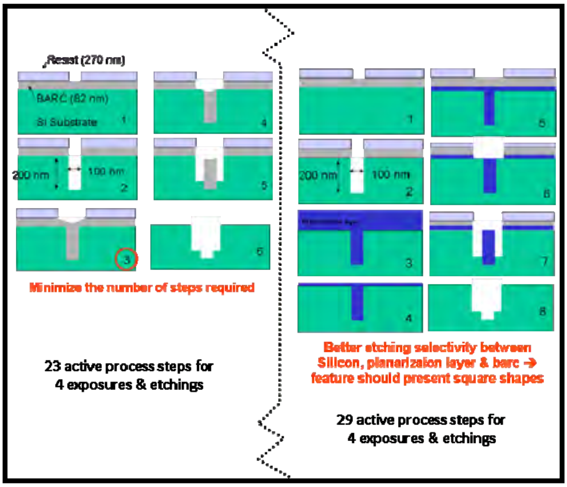
	Process	**Technical Parameters**	**Remarks**
	What	how it should work	critical issues
1.0	**Process 1: Wafer preparation**	**Silicon wafer format**	
1.1	**wafer selection and preparation**	standard Si substrate, 12“, <100>, thickness d=700-800 µm two side polished	
1.2	**substrate preparation**	no pretreatment 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)**	Commertial DUV193 nm resist and BARC, no priming, positive tone resist for optical lithography, process lab (clean room)	*These commercial resists use safe solvents.*
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)	*Automatic coating track or procedure is requested to optain a thin uniform film over 12” wafer.*
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 alignmet marks compatible with the alignment strategy of you optical stepper or scanner.	*The exposure strategy often depends on the preference for positive or negative resists and the pattern transfer process to be used.*
3.2	**Optical Mask manufacturing** 	Transfer complete GDS file to a maskshop to manufacture your exposure mask.	*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 expsed surface will be smaller.
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.	*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.*
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 fluoropolymere created during plasma treatments.	
4.3	**process control** 	**optical and electron microscopy** *non-destructively*	*destructive (cleaving, metal coating) in SEM profilometry*
	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 layeer**	Put the stamp in a hot (typically 70°) vapor contant 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 stiking mole-	

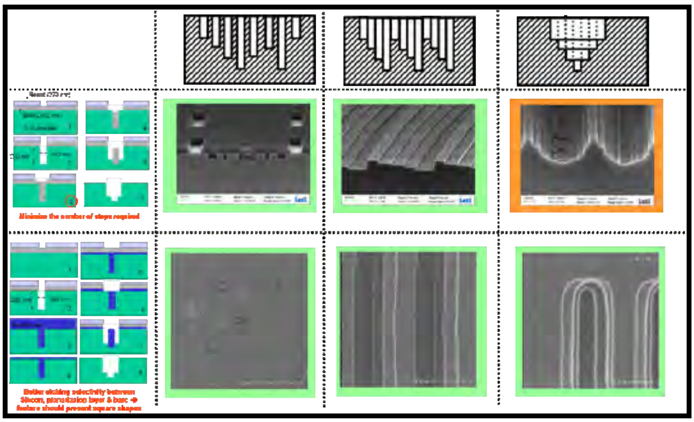
		cule (not grafted to the surface).	
5.6	**Process control**	**optical and electron beam microscopy** *non-destructively*	
	End of Process 5		
	End of Total Process		

General remarks:

To manufacture a multilevel stamp the processes from step 2 to 4 have to been repeted. Two processes flow may be used depending on the number of levels and control of the final excat shape. These two approaches are described belaow. 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

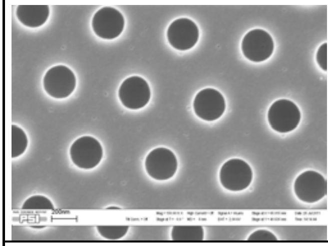


Figure:
SEM micrograph of a hexagonal hole pattern with a diameter of 200 nm replicated in OrmoStamp.

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 Schift
E-mail: helmut.schift@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]).

References:

[1] H. Schift, S. Saxer, S. Park, C. Padeste, U. Pieles, J. Gobrecht: *Controlled co-evaporation of silanes for nanoimprint stamps*, Nanotechnology **16** (2005) S171-175

[2] H. Schift, 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

[3] A. Klukowska, A. Kolander, I. Bergmair, M. Mühlberger, H. Leichtfried, F. Reuther, G. Grützner, R. Schöftner: *Novel transparent hybrid polymer working stamp for UV-imprinting*
Microelectronic Engineering, **86** (2009), Pages S 697-699

[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. Schift, *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

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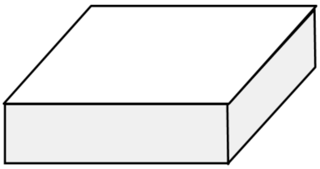
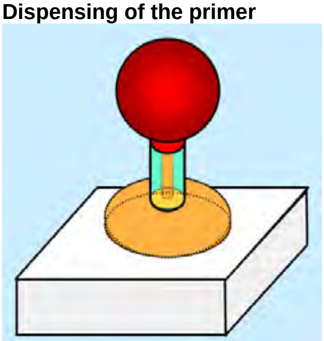
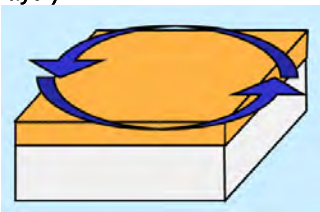
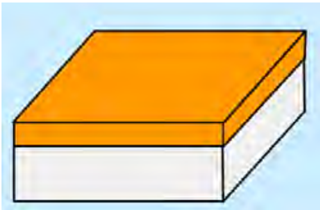
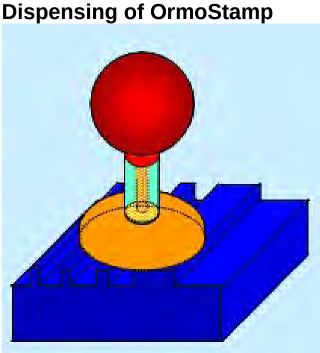
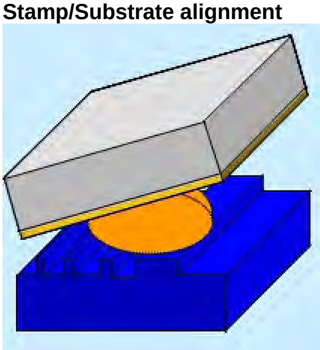
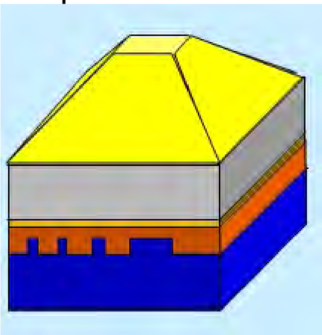
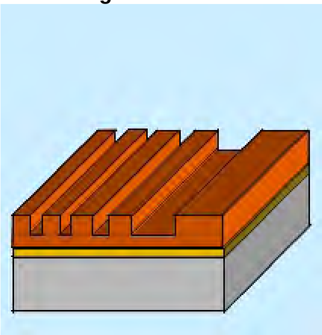
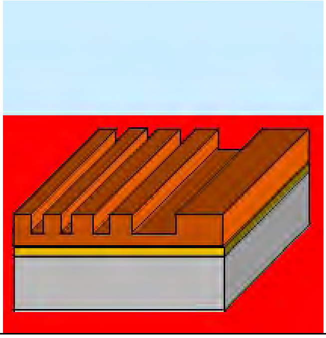
LoP2012_NIL010_OrmoStamp auxiliary stamps

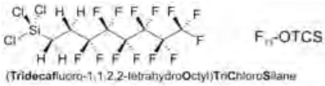
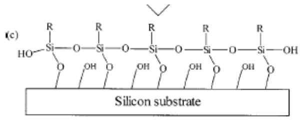
Standard fabrication process for OrmoStamp working stamps

Process: nanoimprint lithography

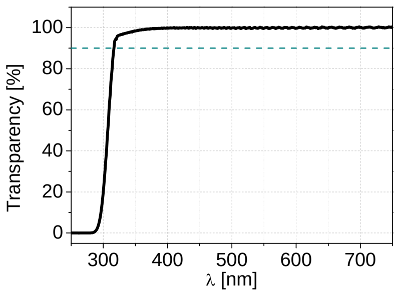
	Process	Technical Parameters	Remarks
	What	How it should work	Critical issues
1.0	**Process 1: Wafer preparation**	**Borofloat® Wafer**	
1.1	**Wafer selection and preparation**	**Borofloat® substrate** Glass substrate, 4“, thickness d = 700 µm	
1.2	**Substrate preparation** 	**Pretreatment** • Acetone 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** • H_2O_2:H_2SO_4 (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** • Oxygen plasma surface activation	*Wear safety glasses, gloves and clothes!* *The etch bath will grow a thin SiO_2 layer on top of your substrate*
	End of Process 1		
2.0	**Process 2: Primer coating**	**To improve the adhesion**	
2.1	**Dispensing of the primer** 	**Primer** OrmoPrime08	*The hybrid polymers adhesion to substrates like glass, fused silica, or Si surface can be increased by substrate pre-treatment using OrmoPrime.*

2.2	**Coating resist (homogeneous layer)** 	**Spincoating of OrmoPrime08** speed: 4000rpm, acceleration: 3000rpm/sec, time: 45 s	*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.: O_2/CHF_3). Residues would be left on the substrate after the treatment with pure oxygen plasma, since OrmoPrime08 contains silicon.*
2.3	**Pre bake** 	**solvent evaporation** bake 5 min @ 150°C (using hot plate)	*The prebake step removess 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*
	End of Process 2		
3.0	**Process 3: Lithography**	**UV-NIL**	
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.	*Alternatively, it is also possible to spin-coat the OrmoStamp onto substrate or stamp. For details, we refere to the data sheet by micro resist technology GmbH.*
3.2	**Stamp/Substrate alignment** 	• Carefully place the BOROFLOAT substrate with the primer upside down over the stamp origin with the OrmoStamp droplet on top. • Brind 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.	*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.*

3.3	**UV exposure** 	Jenoptik HEX03 UV-Module Intensity: 2.8 mW/cm² Wavelength: 365 nm Dose: 1000 mJ/cm²	*Alternative any UV source with a wavelength of 356 nm can be used e.g. UV oven or maskaligner.*
3.4	**Demolding** 	Separation of the stamp from the substrate with a razorblade or scalpel.	*OrmoStamp provides inherent antiadhesive properties for improved demolding process without damage of pattern origination and replica.*
3.5	**Hardbake** 	Hotplate at 130° C for a minimum time of 10 minutes	*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])*
	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!!!*** *Use a very short and gentle oxygen process otherwise porous silicondioxid will be formed.*

4.2	**Solution preparation** 	Prepare a solution 1-10 mM of perfluorotri-chlorosilane molecules in toluene. The preparation of the solution and the surface treatment is to be performed in an atmos-phere with low content of humidity. A convenient solution is to operate in glovebox.	*Alternatively, chemical vapor deposition methods have been developed which allow to generate the silane mono-layer from the gas phase. The coating should be done within about 1 hour after surface activation*
4.3	**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).	*In order to avoid the for-mation of a bulky deposit of molecules instead of a mon-olayer, washing of the stamp in acetone has to be per-formed in dry atmosphere.*
4.4	**Process control:**	**Optical microscope, AFM** The quality of the antis-ticking layer can be done by contact angle (CA) measurement, for per-fluorotrichlorosilane a CA 115° can be reached	*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*
	End of Process 4		
	End of Total Process		

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 fea-tures and the possibitlty to use standard lithography processeing equipment.



OrmoStamp copies can 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 are 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 sub-strate 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 sub-strate extreme conditions are necessary. A PGMEA solution at increased temperature (≈ 60° C) as-sisted by ultrasonification for several hours or hot piranha etch will usually (especially on glass) result in pealing off of OrmoStamp. Alternatively O_2 /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

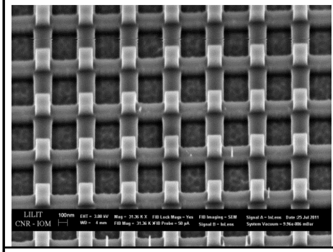


Figure:
SEM image of a nanopillars array self-aligned on a silicon mesh with a period of 500 nm.

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.

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Web-Address: http:// www.tasc-infm.it

Process: Thermal NIL
Responsible: Massimo Tormen
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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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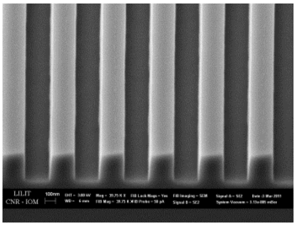
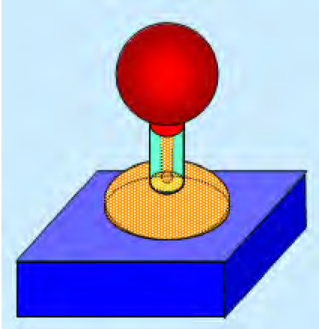
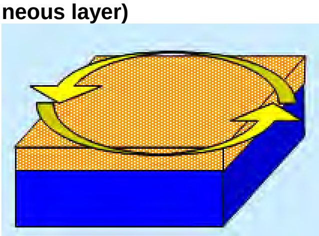
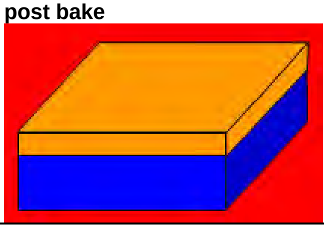
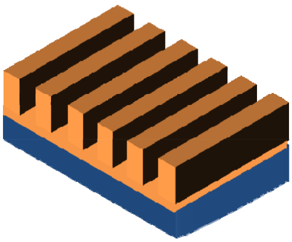
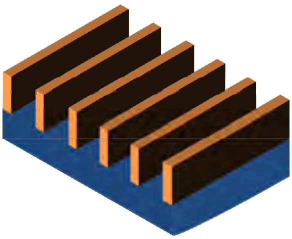
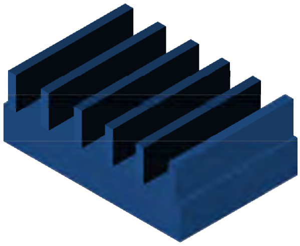
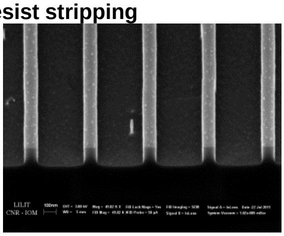
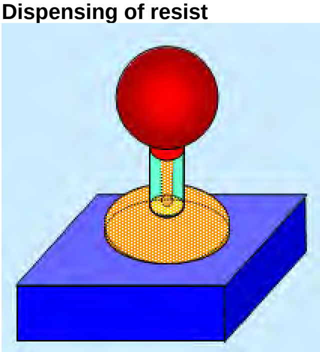
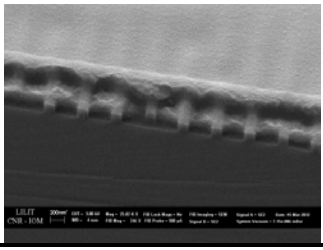
LoP2012_NIL011_Two-level Stamps

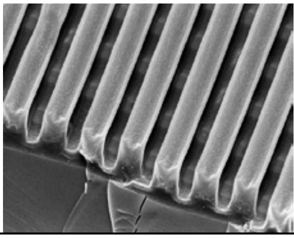
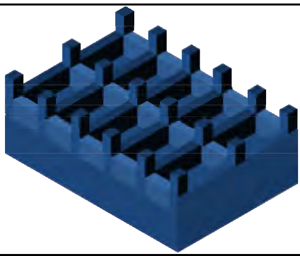
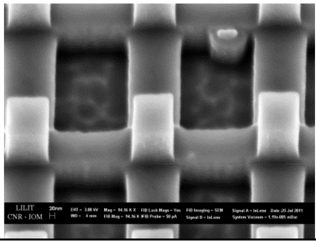
Iterative fabrication process for self-aligned nanopillars on silicon mesh for NIL applications

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)	*mr-I 7000E is a high resolution thermoplastic polymer resist (“E” series was replyed by “R”, i.e. mr-I 7000R, see Page 34/35)*

			
3.2	**first coating resist (homoge-neous layer)** 	**spincoating of mr-I 7010E** speed: 1000rpm, acceleration: 1000rpm/sec, time: 30 s -> ~140 nm thickness	
3.3	**post bake** 	**solvent evaporation** bake 2 min @ 140°C (hot plate)	
	End of Process 3		
4.0	**Process 4: Lithography**	**Nanoimprint lithography**	
4.1	**pattern definition** 	**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 re-leased at 50°C.	
4.2	**structures defini-tion** 	**shrinking of resist struc-tures** The residual layer after NIL is removed in an ICP reac-tor by oxygen plasma; this step is also used to obtain a controlled lateral shrink-ing of the lines.	*The etching parameters are usually strongly de-pendent on the equipment, thus dimensional shrink-age can be minimized under optimal etching con-ditions.*

4.3	**pattern transfer** 	**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 SF_6 30 sccm/ C_4F_8 60 sccm/ Ar 10 sccm, pressure of 8 mTorr, RF power 400 W (ICP RF source), 20 W (Platen RF source).	*The etching parameters are usually strong dependent on the tool.*
4.4	**resist stripping**  **End of Process 4**	**ICP resist ashing** Resist is removed by a isotropic oxygen plasma with low bias in the ICP tool.	
5.0	**Process 5: Resist coating**	**for nanoimprint lithography**	
5.1	**Dispensing of resist** 	**resist** no priming resist mr-I 7020E process lab (clean room)	*see step 3.1*
5.2	**Second coating resist**	**spincoating of mr-I 7020E** speed: 2000rpm, acceleration: 1000rpm/sec, time: 30 s -> ~210 nm thickness on flat substrates	
5.3	**Post bake** 	**solvent evaporation and partial planarization of resist layer** bake 5 min @ 140°C (hot plate)	*The actual thickness of the resist depends on the dimensions of underneath structures.*
	End of Process 5		
6.0	**Process 6: Lithography**	**Nanoimprint lithography**	

6.1		**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.	*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.*
6.2		**shrinking of resist structures** The resist lines are shrunk in the oxygen plasma process, which also removed completely the residual layers.	*After the oxygen plasma, silicon is exposed both on top of the first silicon lines and in the space between them.*
6.3		**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.	
6.4	**Resist stripping** 	**ICP resist ashing** Resist is removed by an isotropic oxygen plasma with low bias in the ICP tool.	
	End of Process 6		
	End of Total Process		

2.9 Microhollows for optical applications

Half hemi-cylindrical lenses for day lighting applications

Process: Wet etching

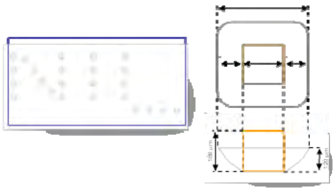


Figure:
CAD layout of the hollow lenses reproducing the "NIL" acronym, used as demonstrator for the process.

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

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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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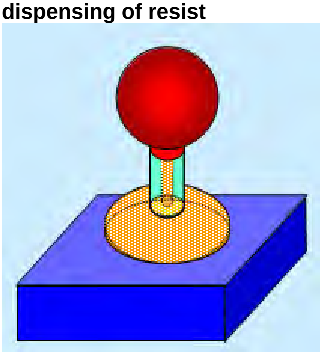
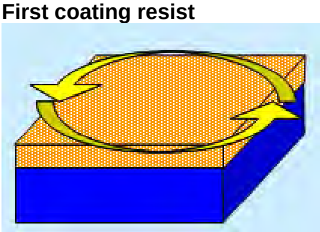
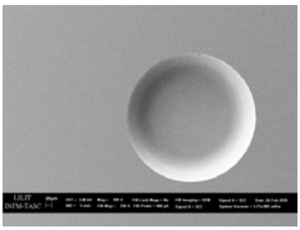
LoP2012_NIL012_Microhollow-Stamps

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.	*Quality of the deposited chromium film, that should be exempt from pin-holes*
	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)	*Loss of resolution due to wet etching of Chromium. The alternative is to use dry etching techniques*
	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 a oven and maintained at 500° C for 3-6 h. Ramps are applied both in heating and cooling steps.	*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.*
	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.	*Etching of holes through pin-holes in chromium leads to the formation of spherical cavities in undesired locations of the substrate.*
	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

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Dr. Nikolaj Gadegaard / Dr. Mathis Riehle /
Dr. Kris Seunarine / Johnny Stormonth-Darling /
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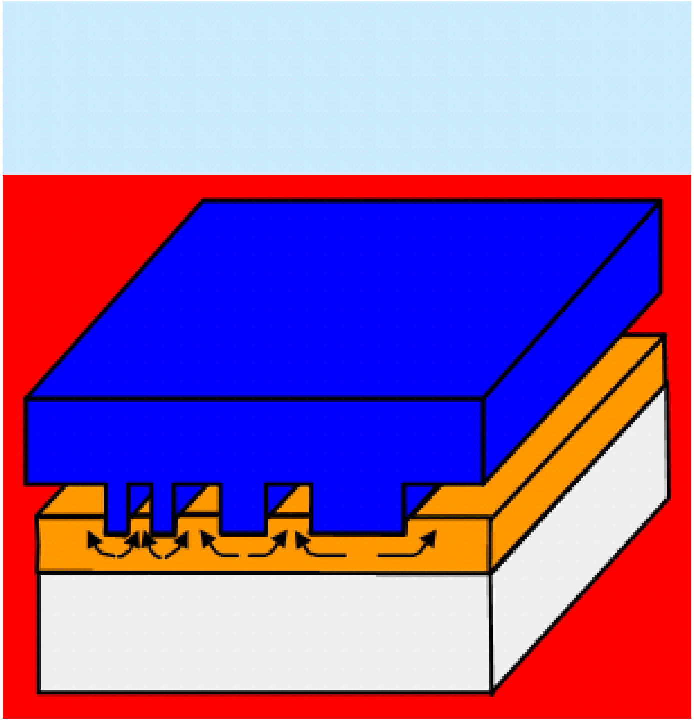

3.1 Nanoimprint Lithography of 3D structures

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

Process: nanoimprint lithography

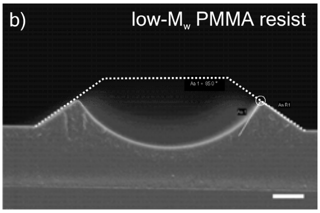

Figure:
SEM micrograph of pre-fill state in a symmetric cavity with sloped sidewalls (scale bar 500 nm). Due to surface energy of mold and material (PMMA 9k), a contact angle of around 98° is forming.

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
Responsible: Helmut Schift
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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 evolvement in 3D cavities.

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

References:

[1] H. Schift 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] H. Schift, G. Kim, J.J. Lee, and J. Gobrecht, *3D visualization of mold filling stages in thermal nanoimprint by white light interferometry and atomic force microscopy*, Nanotechnol. **20**, 355301 (2009)
[3] A. Schleunitz and H. Schift, *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.
[4] M. Altana, A. Schleunitz, H. Schift, Sidewall-angle dependent pre-filling of three-dimensional microcavities in thermal nanoimprint, contribution to EIPBN 2012, to be submitted to JVST (2012).

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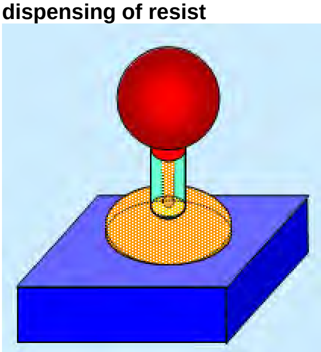
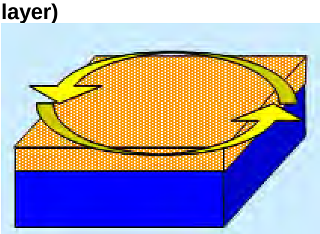
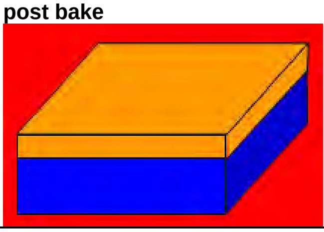
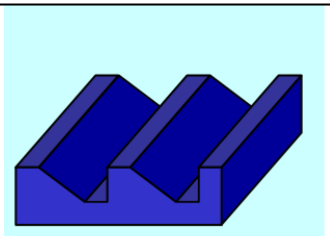
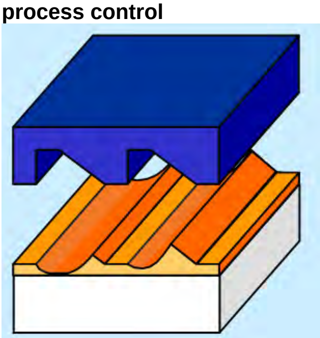
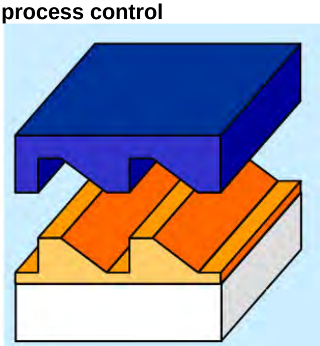
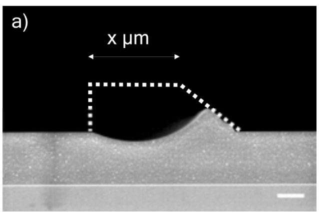
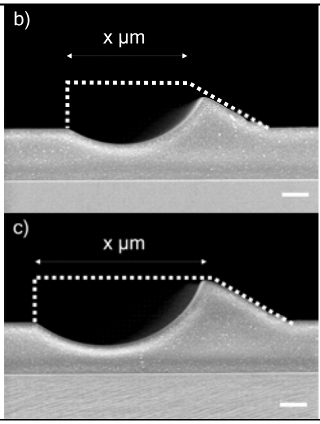
LoP2012_NIL013_3D NIL molding process

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	*Alternatively, 0.7 mm thick Borofloat glass has proven to be a good substrate (if transparency is needed)*
1.2	**substrate preparation**	**pretreatment** no pretreatment needed (if wafer is clean an 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 ethyllactate (safer solvent)	*Ethyllactate 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.* *Alternative materials: commercially availableresists from mirco resist technology GmbH, e.g. mr-I 8000E (see Page 34)*
2.2	**coating resist (homogeneous layer)** 	**spincoating of thermoplastic resist** **PMMA** -> ~990 nm thickness	*PMMA and mr-I 8000E are NIL resists with relatively high glass transition temperature* *T_g of …* *PMMA (low Mw): 120 °C* *mr-I 8000E: 115 °C*
2.3	**post bake** 	**solvent evaporation** bake 1 min @ 170°C (hot plate)	*Alternative: convection oven at 180°C, for 30 min*
	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	*Asymmetric structure*

		vertical sidewalls was pre-pared using grayscale elec-tron beam lithography and the TASTE process. With a fixed height of 1 µm and a varying footprint of 3 – 5 µm	*TASTE (thermally assisted selective topography equi-libration) – see Page 100.*
3.2	**Resist removal (stripping)** 	**Thermal imprint** A typical imprint process consists of a contact phase in which polymer is able to assume a surface of mini-mum energy due to the wetting of the sidewalls	
3.3a	**process control** 	**Incomplete molding** Stamp and resist show partially identical (opposite polarity) profiles but large areas where the surface profile of the resist is de-termined by a meniscus Capillary action completed and squeeze flow not yet completed	*Asymmetric structures are more prone to pinning at vertical sidewalls, while sloped enable a smooth filling without pinning* *Pinning at vertical sidewal and contact angle for-mation at sloped sidewall, meniscus forming with depth below initial resist level*
3.3b	**process control** 	**Complete molding** Stamp and resist show identical (opposite polarity) profiles	*Complete molding is achieved if squeeze flow of is enabled and enough material is flowing to fill the entire cavity*
3.4	**process control** 	**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	*non-destructive process control would be possible using profilometry*

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

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.

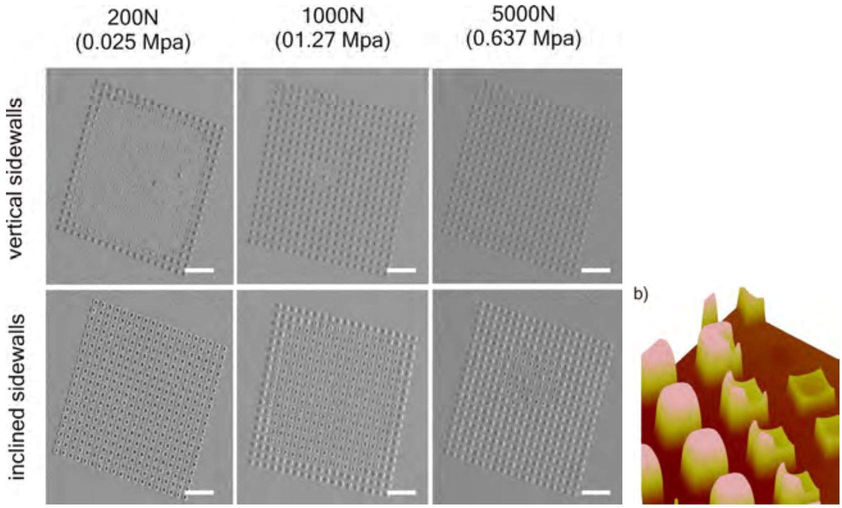


Figure 1: During imprint of extended arrays of microcavities (which are not too extended for the stamp to bend), transport of material for the filling of cavities is done by squeeze flow from the borders of the array. Due to the lack of material flow in the center, pre-fill states are generated in which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

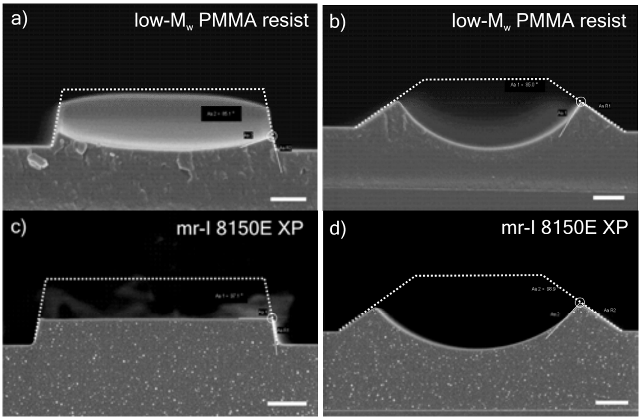


Figure 2: In case of (almost) vertical sidewalls, the filling is abrupt, i.e. the structures are filled by spontaneous wetting of sidewall surfaces (particularly at corners) and "jumps" up to the cavity top. In case of inclined sidewalls, a contact angle forms and results in the generation of a resist 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°.

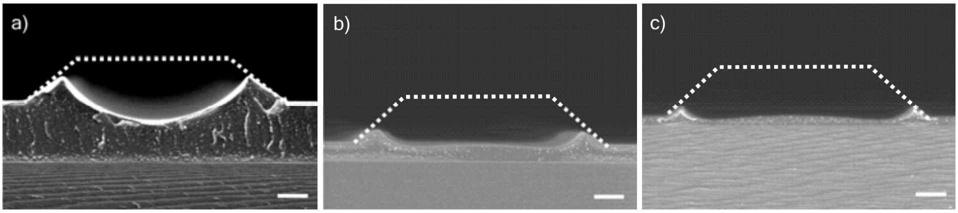


Figure 3: A lens- or cylinder-like depression below the cavity can only form for thick resist layers (PMMA), assuming the optimum contact angle. For thin resists, the same contact angle forms at the sidewalls, but instead of depletion down to the substrate, flow towards the borders is inhibited and the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

3.2 Suspended polymer membranes

Fabrication of suspended polymer membranes on LOR resist

Process: nanoimprint lithography

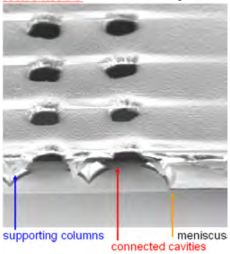


Figure:
SEM micrograph of a pore array in 1 µm thick polystyrene supported by 2 µm high pillars with 3 µm hole diameter and 5 µm period (cleaved sample)

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

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

References:

[1] H. Schift, S. Bellini and J. Gobrecht, *Perforated polymer membranes fabricated by nanoimprint lithography*, Microelectron. Eng. **83**, 873–875 (2006).

[2] H. Schift, S. Bellini, U. Pieles and J. Gobrecht, *Sustained polymer membranes fabricated by nanoimprint lithography*, J. Microlith., Microfab., Microsyst. **5**(1), 011010 (Jan–Mar 2006).

[3] C.-G. Choi, Y.-T. Han, J. T. Kim, and H. Schift, Air-suspended two-dimensional polymer photonic crystal slab waveguides fabricated by nanoimprint lithography, Appl. Phys. Lett. 90, 221109 (2007) doi: 10.1063/1.2744482.

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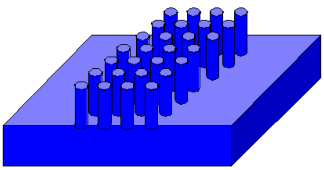
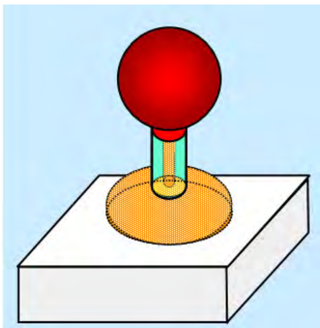
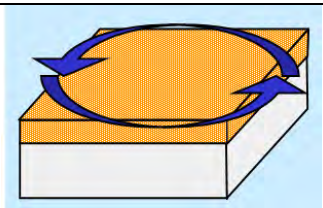
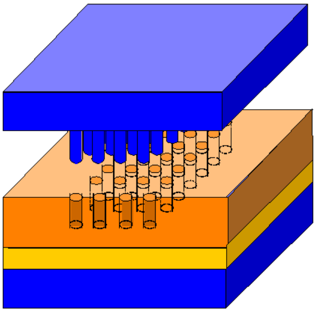
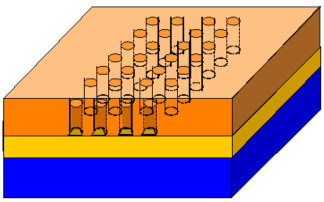
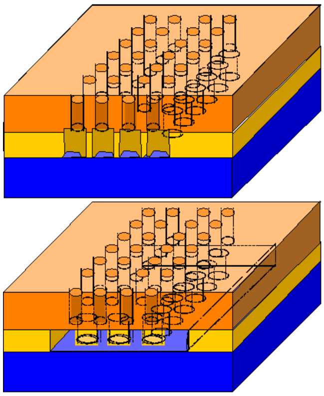
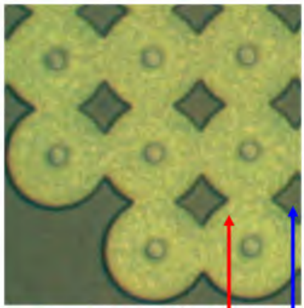
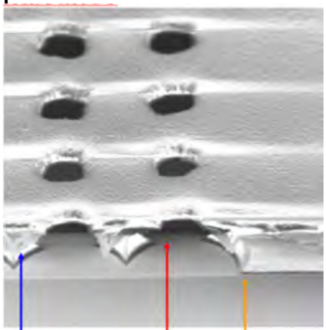
LoP2007_NIL002_suspended polymer membranes

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 $1 mm^2$ 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.	*microstructures are very good for the set-up of the process, because the process control can be done using optical microscopy*
2.2	**antiadhesive coating**	**silane CVD evaporation** standard process	*silane coating from gas phase is beneficial for sidewall coating*
	End of Process 2		
3.0	**Process 3: Lithography**		
3.1	**coating of layer 1 (sacrifical 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	*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*
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-	*PS was chosen because of its excellent optical and physiological properties.* *Resist with inherent anti-*

		ene 3000rpm, 60 s -> ~1000nm bake 1 min @ 170°C (hot plate)	*adhesive properties (by micro resist technology) have the potential to further improve the subsequent thermal NIL and demolding step with less defects.*
3.3	**Nanoimprint Lithography** 	**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 temperature.(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 temperature.(release)....70°C residual polymer thickness in grooves 150 nm	*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*
3.4		**demolding** pressure release at about 70°C demolding manually by applying a razor blade between stamp and substrate and inducing a wedge	*demolding of dense array of pillars more difficult reduction of thermal expansion by molding at low / demolding at high temperatures*
3.5	**process control**	**optical microscopy** *non-destructively*	*destructive (cleaving, metal coating) in SEM* *profilometry*
	End of Process 3		
4.0	**Process 4: Pattern Transfer**		
4.1	**Residual Layer (Breakthrough) Etching** 	**RIE Oxford Plasmalab 100:** thinning of resist PMMA etch with no cooling O_2.............20 sccm gas pressure 20 mtorr power 20 W temperature 300 K ecthing rates PS 30 nm/min, LOR 10B 48 nm/min	*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*
4.2	**process control**	**Profilometer /Microscope**	
4.3	**Sacrificial layer etching**	**LOR wet etching**	*The developer penetrates*

		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.*	*the pores and dissolves the LOR isotropically.* *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.* *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 1µm could be seen.*
4.4	**process control**  	**optical microscope** 100 x Connected cavities with supporting columns (PS 1 µm / LOR 1 µm, view size 30 x 30 μm^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	*online, without breaking substrate* *pores and undercuts with <0.4µm can be resolved, not suitable for nanopores (< 200nm)*
4.5	**process control**  	**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)	
	End of Process 4		
	End of Total Process		

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

3.3 Polymer multilayers by reverse UV-NIL

Fabrication of multiplayered woodpiles by reverse UV-NIL

Process: nanoimprint lithography

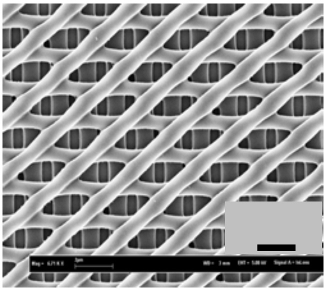


Figure:
SEM images of a three-layer woodpile-like structure fabricated by the reverse contact imprinting technique.

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	**Process:** Thermal nanoimprint
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Web-Address: http://www.tyndall.ie	**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 rending 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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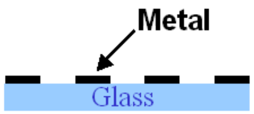
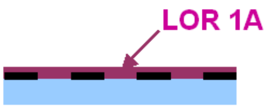
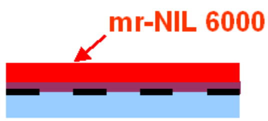
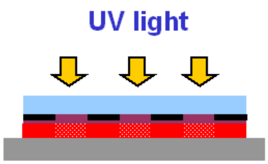
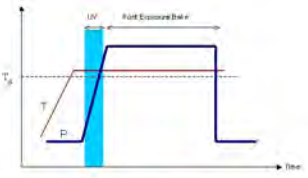
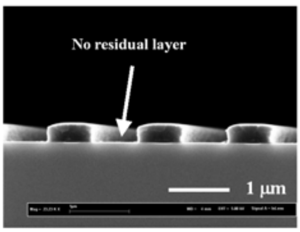
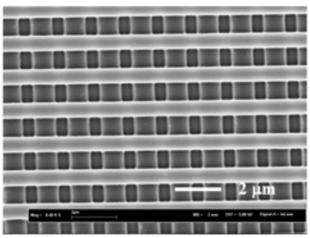
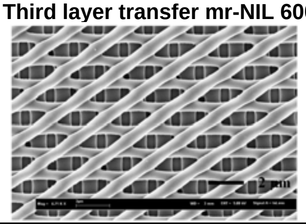
LoP2007_NIL003_RUVNIL woodpile

Polymer multilayeres 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 µm 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 pro-tusion	
2.1	**layout**  	**Functional structures** the stamp consist of gratings (about 5 mm^2 area) with a pitch variation from 200 nm to 10 µm 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 rpm for 1 min on the stamp and baked at 150 °C for 5 min. This sacrificial polymer layer is used as an adherence promoter, a pla-narization layer and to pro-tect the stamp from contam-ination by the photocuring resist.	*No antiadhesive coating needed*
2.3	Spin coat UV crosslinkable poly-mer  	A film of a UV crosslinkable polymer (mr-NIL 6000 from *micro resist technology* GmbH) is spin coated at 3000 rpm on the LOR layer and soft-backed at 120 °C for 5 min to evaporate the residual solvent	*mr-NIL 6000E is a low Tg NIL resist for combined thermal and UV-based NIL (see Page 34).*
	End of Process 2		
3.0	**Process 3: Lithography**		
3.1	**Reverse imprint**  Heat, pressure, UV light exposure apply	The polymer bilayer is re-verse imprinted onto a Si substrate. Stamp and substrate are then heated to a tempera-ture above the T_g of mr-NIL 6000 and exposed to UV radiation. Optimized imprint parame-ters on a non-flat substrate	*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 im-printed substrate. The control of the exposure dose can be done by*

	 Schematic of RUVNIL process showing the time at which point of UV light exposure occurs and the time of post exposure baking.	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.	*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.*
43.2	Separation and development. 	**Demolding** **Demolding in a developper 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.	*The oxygen plasma-etching step, usually necessary in standard NIL is avoided.*
	End of Process 3		
4.0	**Process 4: Pattern Transfer**		
4.1	**First layer transfer mr-NIL 6000** 	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.	*Due to the difference of surface energies between the stamp surface and the Si substrate, the polymers are successfully transferred onto the Si substrate.*
4.3	**Second layer transfer mr-NIL (** 	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.	*Surface patterned about 4 mm²*
4.4	**Third layer transfer mr-NIL 6000** 	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.	*Surface patterned less of 0.5 mm²*

4.5	**Process control**	**Optical microscopy** *non-destructively* **SEM** *destructive (cleaving, metal coating)*	
	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)

3.4 Combined Nanoimprint and Photolithography

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

Process: Combined Nanoimprint and Photolithography (CNP)

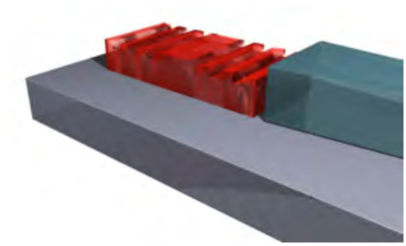


Figure:

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	**Process:** CNP
Address: DTU building 345E, 2800 Lyngby, Denmark	**Responsible:** Anders Kristensen
Web-Address: www.nanotech.dtu.dk	**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:

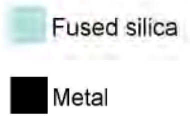
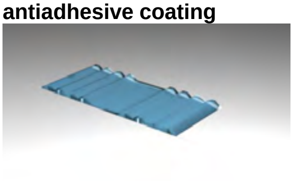
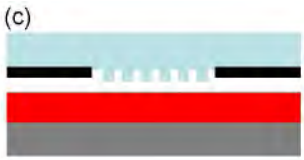
[1] M. B. Christiansen, M. Schøler, and A. Kristensen, "Integration of active and passive polymer optics", Optics Express 15(7) pp. 3931-3939 (2007)

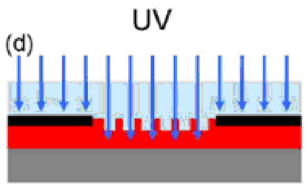
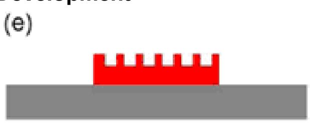
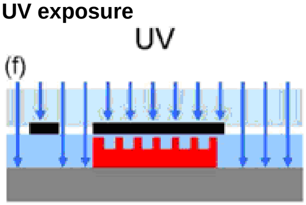
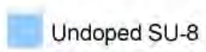
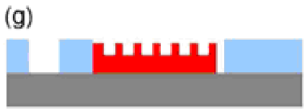
Contact information:
Prof. Dr. Anders Kristensen
Department of Micro- and Nanotechnology
Technical University of Denmark
DTU Nanotech, Building 345 East
2800 Kongens Lyngby
Denmark

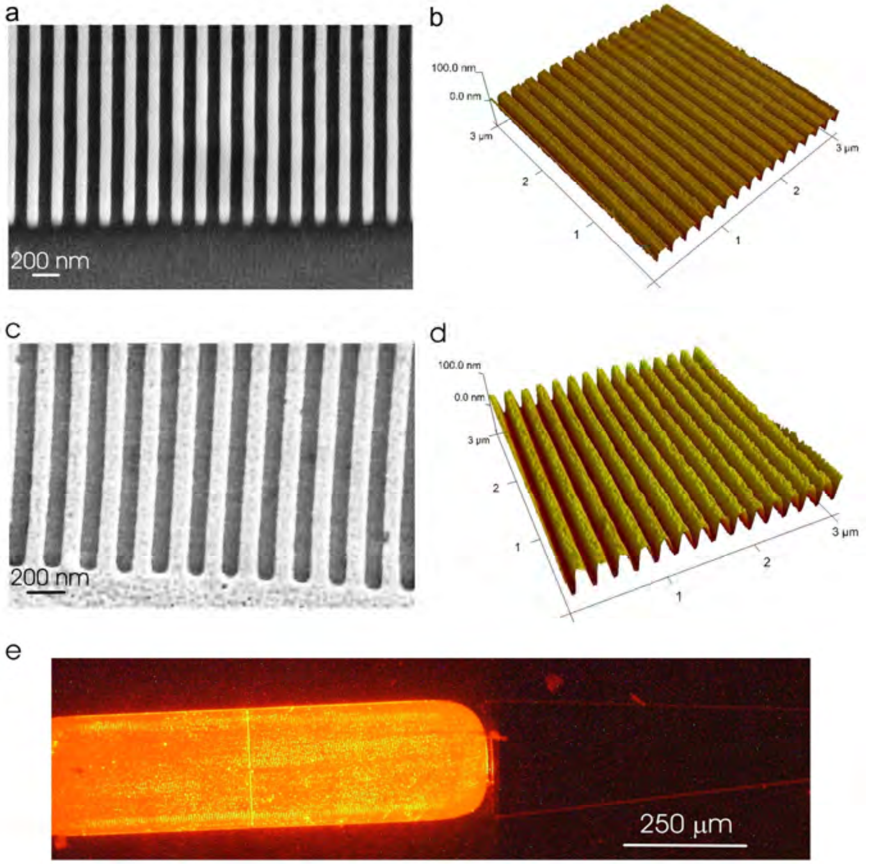
LoP2007_NIL004_CNP Combined NIL and PL process

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 with a width of approx. 100 nm and a period of approx. 200 nm are protruding.	
2.2	**antiadhesive coating**  *Stamp layout*	**FDTS coating** Standard recipe in MVD 100 molecular vapour deposition tool from Applied Microstructures Inc.	*Rather slow deposition is chosen to allow good sidewall coverage*
	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 mumol 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)	

		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	
3.3	**UV exposure**  	SÜSS mask aligner 9 mW/mm2 30 s x 11 with 15 s breaks PEB: 90°C, 2 min	
3.4	**Demolding**	Separation using scalpel	
3.5	**Development**  	PGMEA 30s IPA rinse N2 or spin dry	
3.6	**process control**	**SEM and AFM**	
	End of Process 3		
4.0	**Process 4: Waveguide defini-tion**		
4.1	**Spin coat**	**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	
4.2	**UV exposure**  	Cr Mask used. Aligned to laser layer SÜSS mask aligner 9 mJ/mm2 Hard contact 20 s PEB: 90°C, 2 min	
4.3	**development**  	PGMEA 3 min IPA rinse N2 or spin dry	
4.4	**process control**	Optical microscope, AFM and SEM, see figure below:	



SEM and AFM of hybrid stamp/UV mask (a-b) and imprinted structures (c-d). (e) is an optical microscope image of an operating SU-8/rhodamine 6G laser integrated with an SU-8 waveguide, where the pump light is filtered away.

	End of Process 4		
	End of Total Process		

3.5 Fast isothermal imprint

Fast isothermal imprint for full wafers

Process: nanoimprint lithography

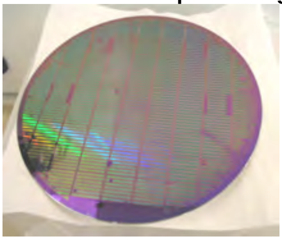


Figure:
Photograph of a 200 mm wafer imprinted using a 2 min process

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, 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. Schift, M. Tormen, S. Landis, C.M. Sotomayor-Torres, A. Kristensen, R.H. Pedersen, M.B. Christiansen, I. Fernandez-Cuesta, D. Mendels, L. Montelius, T. Haatainen, *Benchmarking of 50 nm features in thermal Nanoimprint*, J. Vac. Sci. Technol. B 25(6)(2007) 2373-2378

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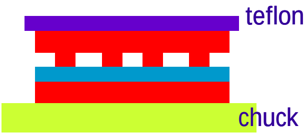
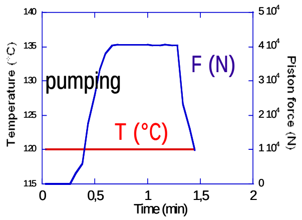
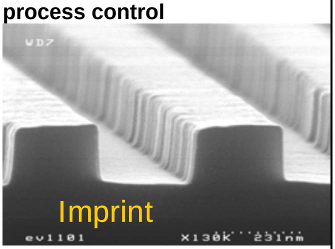
LoP2007_NIL010_Fast isothermal imprint

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	*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*
	End of Process 1		
2.0	**Process 2: imprint process**		
2.1	**Pumping and temperature uniformization**	**Pressure down to 100 mbars in 30 seconds**	*Limited by the pumping speed*
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	*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).*
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		

3.6 Pattern transfer optimization

Pattern transfer optimization for full wafer NIL

Process: development of anisotropic transfer processes

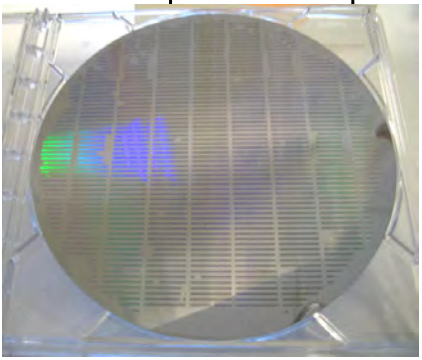


Figure:
Photograph of a 200 mm wafer imprinted and etched using an anisotropic process

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	**Process:** anisotropic pattern transfer
Address: 17 R. Martyrs, 38 054 Grenoble, France	**Responsible:** Cécile Gourgon
Web-Address: http://www.ltm-cnrs.fr/	**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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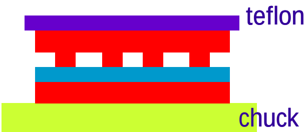
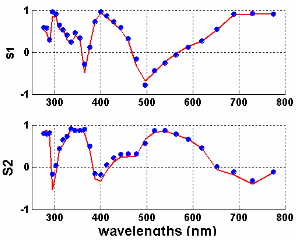
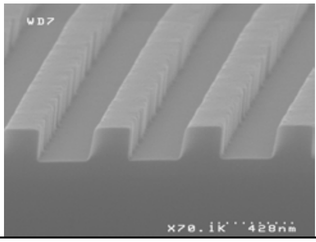
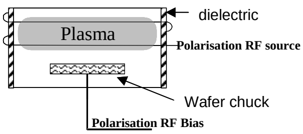
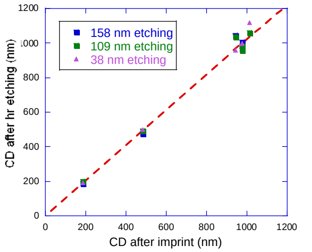
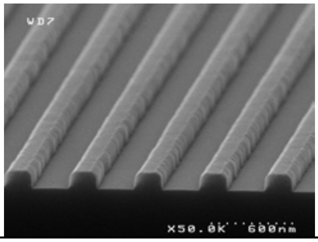
LoP2007_NIL011_Pattern Transfer Optimization

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	*A high accuracy measurement of n( ) and k( ) has to be performed before.* *Limitation : homogeneous pattern gratings with standard geometries*
2.3	**SEM characterization** 	Top-down SEM for pattern quality and homogeneity control, or cross-section SEM Line width: 209 nm	*test wafer needed if cross-section measurement*
	End of Process 2		
3.0	**Process 3: hr etching**		
3.1	**Loading of the imprinted wafer**	**Plateform 5200 from applied Materials, DPS ICP reactor**	
3.2	**Etching process** 	**$O_2/Cl_2/Ar$ plasma** O_2: 30 sccm, Cl_2: 40sccm, Ar:30sccm Pressure 10 mTorr Source power: 500 W Bias power: 60 W for NEB22 resist	*The anisotropy is mostly dependent on the bias power. Some resists, which are less resistant, require lower bias, and this limits the anisotropy control.*

3.3	**process control**  	**SEM and scatterometry** to measure the pattern size after the hr etching and compare it to the imprinted one Line width: 202 nm	
	End of Process 3		
	End of Total Process		

3.7 Liquid Transfer Imprint Lithography (LTIL)

Imprint process for rough and nonflat surfaces with an improved filling behaviour

Process: resist coating and UV-imprint

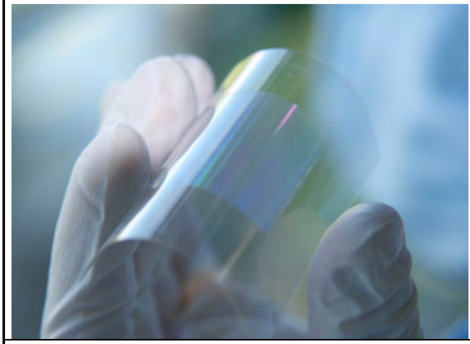


Figure:
Plastic foils with resist grating.

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	**Process:** LTIL
Address: 52074 Aaachen, Germany	**Responsible:** J.W. Kim
Web-Address: http:// www.amo.de	**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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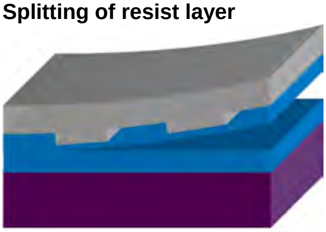
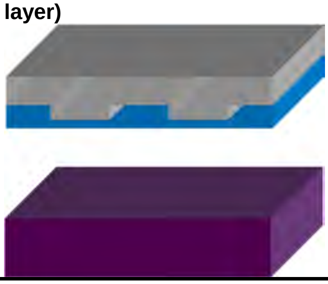
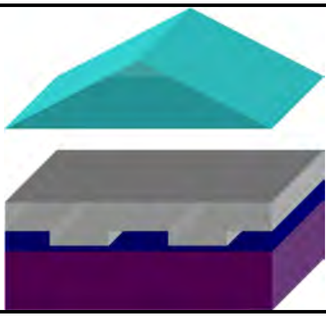
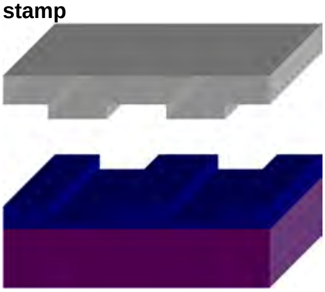
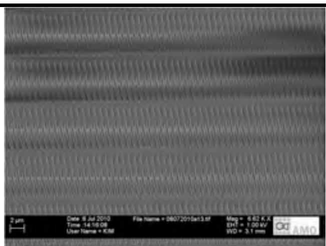
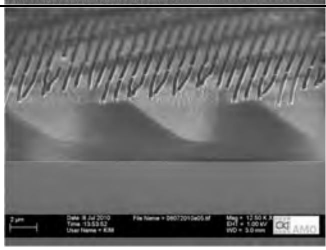
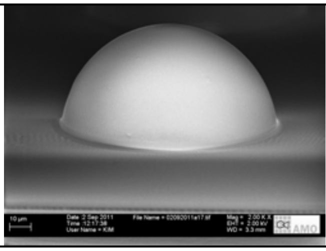
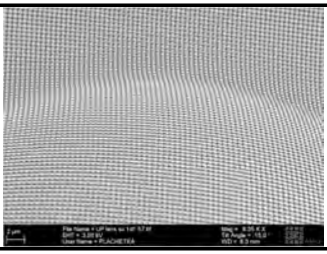
Germany

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** 	-Polmeric 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	

			
1.6	**Detachment of the stamp** 	-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		
2.0	**Process results**		
2.1		Top down view on µm-sized blazed grating with imprinted nanograting on top	
2.2		Cross section of µm-sized blazed grating with imprinted nanograting on top	.
2.3		Lens with 100µm diameter and imprinted nanopillars on top	

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.).

3.8 Nanoimprinting of hydrogels

UV and Thermal imprinting of hydrogels

Process: Thermal and UV-nanoimprint lithography

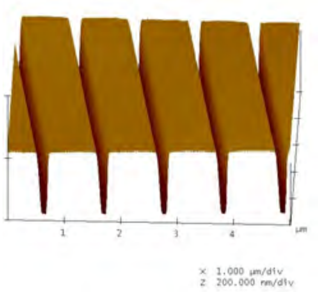


Figure:
AFM image of 250nm PEGDMA nanoimprinted by UV-NIL

Process:
UV and Thermal Nanoimprint

Application:
Biosensing, reconfigurable surfaces, lenses.

Keywords: thermal and UV nanoimprint, hydrogel

Project leader: TECNALIA
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Web-Address: www.tecnalia.com
Process: UV-NIL
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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

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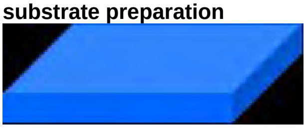
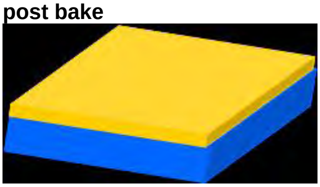
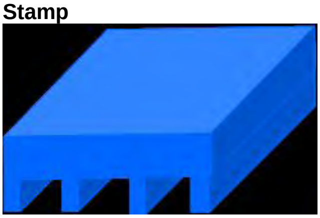
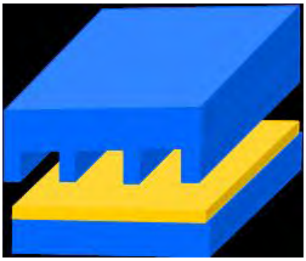
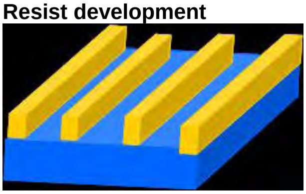
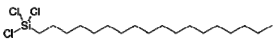
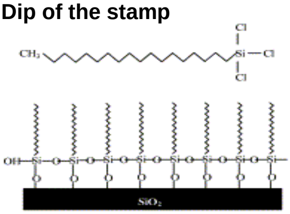
LoP2012_NIL015_Hydrogel imprint-process

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	*In samples without TPM treatment, hydrogel layer peels off the substrate when it swells*
	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.	*Less concentration than P30 (30%w) does not get uniform layers.*
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	

3.2	**Pattern definition** 	**NIL protocol** Pressure applied: depend on the stamp geometry. • For 2D structures <1bar • For 3D structures >3bars Time of exposure:600seg (wavelength 365nm -- 13mJ/cm^2)	
3.3	**Resist development** 	**Residual layer etch.** The residual layer is etched by RIE, using a combination of gases:Ar (1sccm) – O_2(5sccm) 100W and 40mtorr	
	End of Process 3		
4.0	**Process 4: Anti-adhesive coating**	**surface treatment**	
4.1	**Preparation of stamp surface**	**Surface activation** Not necessary	
4.2	**Solution preparation** 	**OTS solution** Prepare a solution 100:1 of octadecyltricholorosilane molecules in hexane. The preparation of the solution and the surface treatment have to be performed in an atmosphere with low content of humidity.	*Other SAMs work worse than OTS.*
4.3	**Dip of the stamp** 	The stamp is dipped into the silane solution for 5-8minutes. Afther that, rinse the stamp with hexane and then DI water.	
	End of Process:4		
	End of Total Process		

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
Prof. Dr. Anders Kristensen /
Dr. Morten Bo Mikkelsen

CNRS/Saint-Gobain, Unité Mixte (SVI) Aubervilliers - France
Dr. Elin Søndergård / Dr. Jeremie Teisseire

CRF Fiat - Orbassano/Italy
Dr. Vito Lambertini

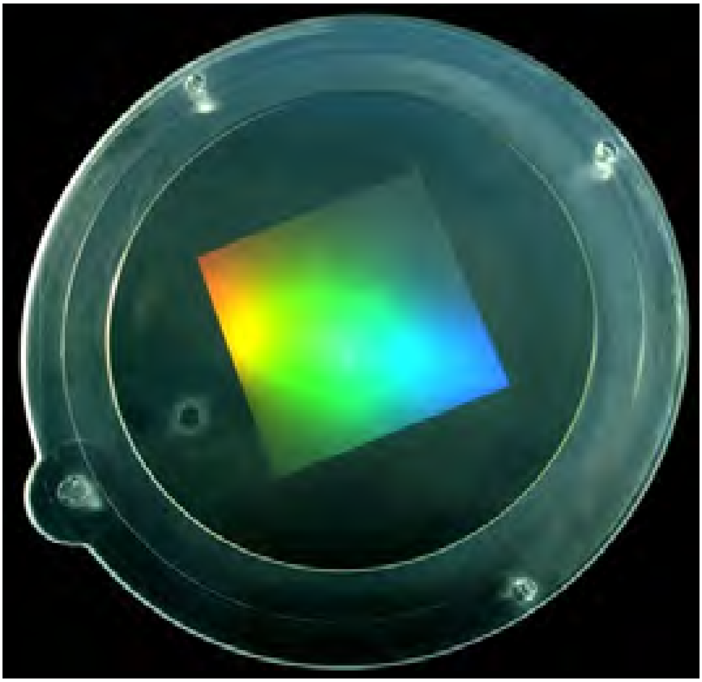
PSI/LMN - Villigen/Switzerland
Dr. Helmut Schift / Dr. Arne Schleunitz /
Christian Spreu / Konrad Vogelsang

INFM TASC - Trieste/Italy
Dr. Massimo Tormen / Dr. Gianluca Grenci

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

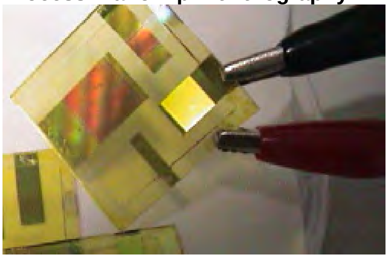


Figure:
Organic light emitting device with both side nanopatterned surfaces with squared shape (resolution 1 µm and height 300 nm).

Process:
OLED device fabrication on double side UV nanoimprinted substrate.

Application:
Lighting systems and displays.

Keywords: OLED, UV nanoimprint

Project leader: Centro Ricerche Fiat **Address:** Strada Torino 50, 10043, Orbassano (TO), Italy **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-wavelenght 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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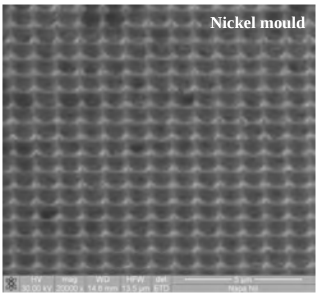
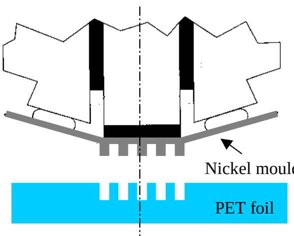
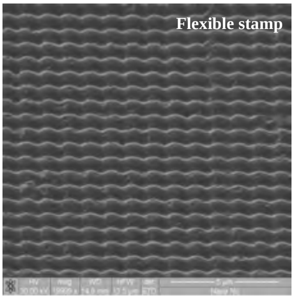
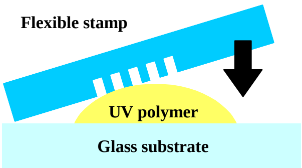
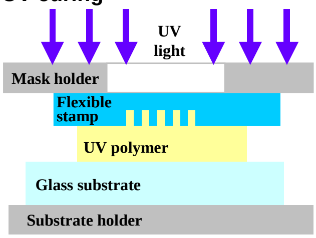
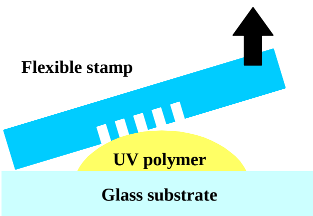
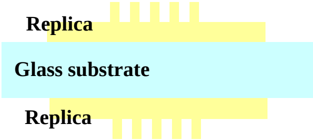
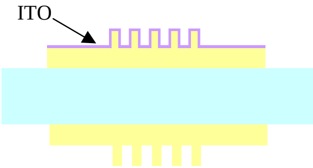
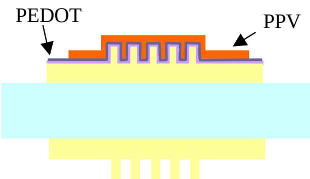
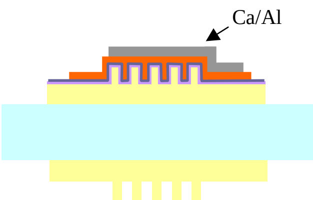
LoP2007_NIL005_Double_side_OLED

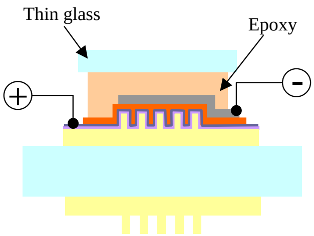
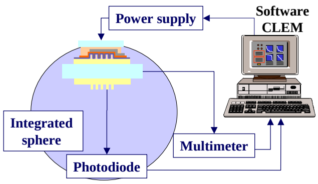
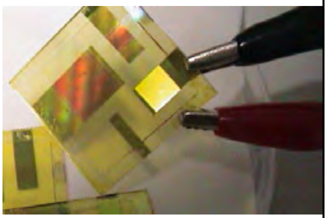
Double side patterned OLED

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 solition 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	

2.3	**Process control** 	**SEM**	
2.4	**antiadhesive coating**	**silane saturation chamber** 1 min	
	End of Process 2		
3.0	**Process 3: Double UV imprint-ing**		
3.1	**UV resin casting** 	**UV polymers:** UV acrylates (bisphenol-A-diglycidyl-ether-diacrylates BGEDA, bi-functional acrylates EBECRYL 210, 270, 600); organic modified alkoxysilanes (OrmoClad).	*No bubbles formation during flexible stamp positioning.* *OrmoClad is a com-mercially available hybrid polymer for optical waveguide fabrication (see Page 37 and www.microresist.com)* .
3.2	**UV curing** 	**EVG620 mask aligner** stack pre-assembled before UV exposition outside the machine. Exposition time 10 s.	
3.3	**Demolding** 	**Manual demolding HEX03 (PSI)** demolding manually by peeling the flexible stamps.	

3.4		**Repeat processes form 2.1 to 2.3 to get the second side pat-terned.**	*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** 	**DC/RF sputtering system** Target: Indium-tine oxide 10-90 (Lesker) 2 inches Vacuum 5x10-3 mbarr Current 300 mA	*Rotating sample holder to increase homogeneity; Alternating on/off of plasma to avoid over-heatinh of the polymer layer.*
4.1	**Process control**	Profilometer Thickness 250 nm UV/Vis spectra Transmittance 75% Multimeter Resistance 100 W/	
4.2	**Active layers deposition** 	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** 	**Thermal vacuum evaporation** AUTO306 coater Double layer: Ca Vacuum 9x10-6 mbarr 20-40 nm Al (capping layer) Vacuum 9x10-6 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:	*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*

		Thermal Tamb 2 hours UV (spot light) : 60 mW/cm2 10 s	*condition is to use a glove box.*
4.5	**Measurement**  	**Electro-optical analysis** I/V curves Efficiency curves (Lm/W) Software CLEM (CRF): power supply HP3432A multimeter HP34401 photodiode/integrated sphere IL1700 Characterization devices: four square shapes with different area (4, 16, 36,100 mm2)	
	End of Process 4		
	End of Total Process		

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

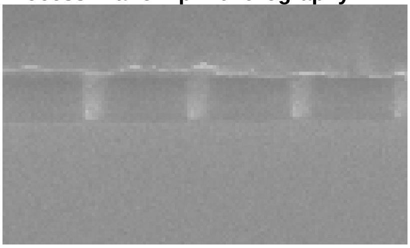


Figure:
Imprinted 180nm grating in 300 nm thick mr-I 7030 resist.

Process: Thermal SSIL to pattern thermoplastic polymer using Nano imprinting Stepper.

Application:
Optical grating

Keywords: thermal nanoimprint, Step&Stamp, SSIL

Project leader: VTT Technical Research Centre of Finland	**Process:** Step&stamp NIL
Address: FI-02044 VTT, Finland	**Responsible:** Tomi Haatainen
Web-Address: http://www.vtt.fi	**E-mail:** tomi.haatainen@vtt.fi

Partner: S.E.T. SAS (Smart Equipment Technology)	**Process:** NPS300 Step&stamp Tool
Address: 74490 Saint Jeoire, France	**Responsible:** Gilbert Lecarpentier
Web-Address: http://www.set-sas.fr	**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 mm^2) 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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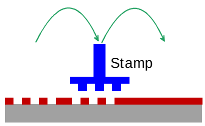
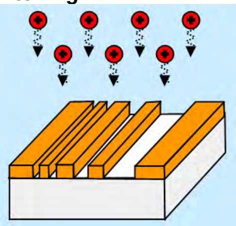
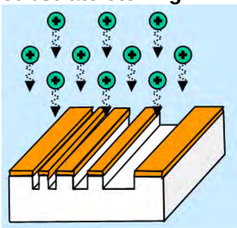
LoP2007_NIL007_Step and Stamp NIL for optical gratings

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	*Substrates up to 200 mm can be patterned by SSIL using NPS300*
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	*Thermally conductive adhesive must be used to ensure the stamp heating*
2.3	**antiadhesive coating**	**silane CVD evaporation** clean or silane vapour	*CVD evaporation preferred if available*
	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 ^{O}C (hotplate)	*The thermoplastic poylmer mr-I 7000R with excellent flow ability and high resolution capabilities.*
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	*SET is a former branch of the SÜSS company in Annecy, France*
3.4	**process control**	**AFM, SEM**	*Imprint depth measured by AFM*
	End of Process 3		

3.0	**Process 3: Pattern Transfer**		
3.1	**Residual Layer (Breakthrough) Etching** 	**O2 RIE:** O_2............40 sccm gas pressure 125 mtorr power 150 W time 5 sec temperature 300 K	*Plasmalab 80Plus RIE*
3.2	**process control**	**AFM**	*Before substrate etching residual removal confirmed by AFM*
3.3	**substrate etching** 	CF4+Ar RIE CF4………….20 sccm Ar……………..5 sccm gas pressure….20 mTorr power………..100 W time………….. temperature…..300K	*Plasmalab 80Plus RIE* *Selectivity Si:Resist(1:1.6)* *Etch rate (Si)=40 nm/min*
3.4	**process control**	**optical microscope** 100 x	
3.5	**process control**	**Ellipsometer**	*Resist thickness check*
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

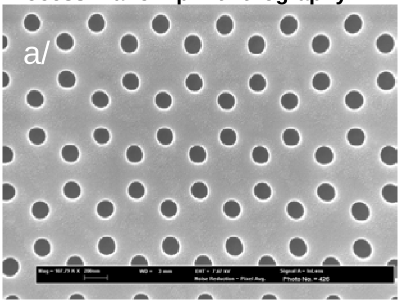


Figure: a) Scanning electron micrograph of a nanoimprinted two-dimensional PhC with a 380 nm lattice constant honeycomb array of holes (holes depth 350 nm), b) cross-section schematic of the studied system.

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	**Process:** Thermal nanoimprint
Address: Lee Maltings, Prospect Row, Cork, Ireland	**Responsible:** C.M. Sotomayor Torres
Web-Address: http://www.tyndall.ie	**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: Tthe 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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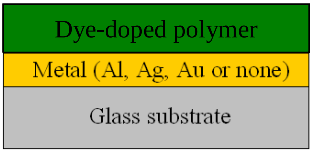
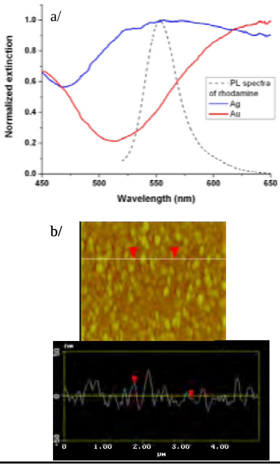
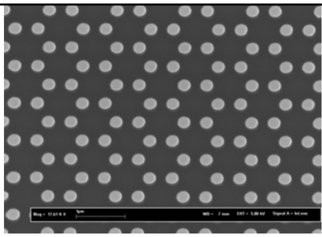
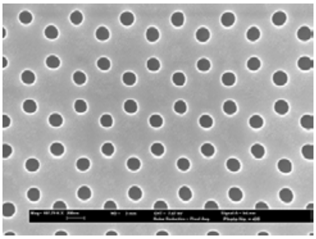
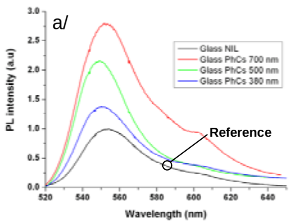
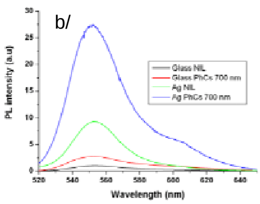
LoP2007_NIL008_photonic crystals

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 subrates.	*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).*
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).	

			
2.3	**Anti-adhesive coating**	The silicon stamp is treated with a self-assembled anti-adhesive monolayer (tride-cafluoro-1, 1, 2, 2-tetrahydrooctyl trichlorosilane deposited in vapour phase).	
	End of Process 2		
3.0	**Process 3: Nanoimprint Li-thography**		
3.1	**Process control :** **SEM top-view of the nanoim-printed photonic crystals** 	The stamp and the coated substrates are pressed to-gether 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.	
2.2	**Measurement:** **Optical characterization**  	Figure: a/ Photoluminescence spectra of a nanoimprinted unpatterned dye-doped poly-mer 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 im-printed 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).	
	End of Process 3		
	End of Total Process		

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 µC/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 5x10^{-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 ^{o}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 ^{o}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

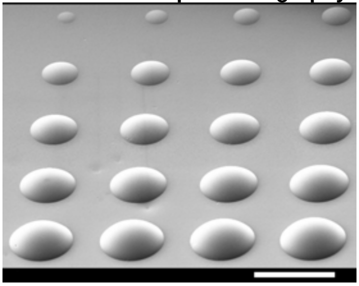


Figure:
Arrays of microlenses with different apertures (same radii of curvature) by polymer casting and UV exposure of SU8 resist. The unit bars correspond to 10 µm.

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

Process description: A process is described for the fabrication of polymeric arrays of microlenses or more complex systems of lenses (lenses on curved surfacecs, arrays of lenses with multiple radii of curvature) by means of a proceessof 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).

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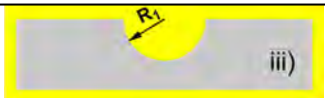
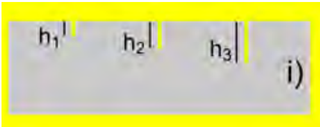
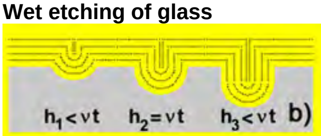
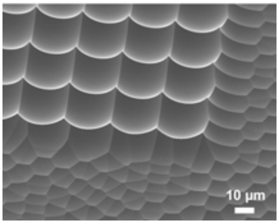
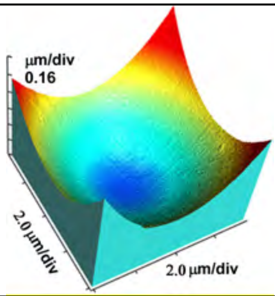
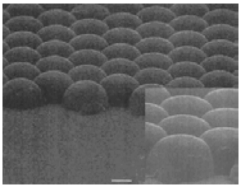
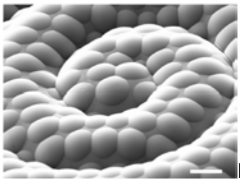
LoP2007_NIL009_Microlenses with spherical molds

Refractive microlenses

Process: nanoimprint lithography

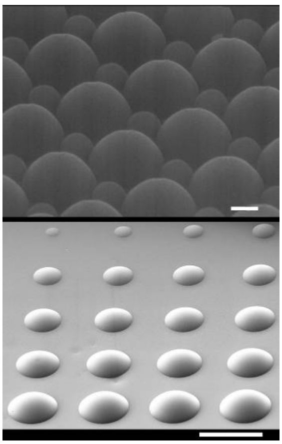
	Process	Technical Parameters	Remarks
	What	how it should work	critical issues
1.0a	**Process 1: Stamp preparation First option (a)**		
1.1a	**Stamp substrate preparation**	Sputter coating soda-lime glass with 100 nm chromium film.	Quality of the deposited chromium film, that should not have pin-holes
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 µC/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 ~1µm/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** 	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.	
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** 	Hholes are milled at different depths in a quartz substrate by focused ion (Ga+) beam at 30 KeV. Centers of curvature can be located atdifferent 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	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 nitrtogen atmosphere. The stamp is dip for 1-2 hours in the solution. Rinse in toluene before taking into air atmosphere	Safety precaution: pour H_2SO_4 into a beaker with H_2O_2, not vice-versa.

3.0	**Process 3: Embossing or polymer casting**		
3.1	**Different option for producing plastic microlenses.** **nanoimprinting** **hot embossing** **polymer casting**  Nanoimprinting in PMMA Hot embossing into Zeonex (see reference [1] and [2] for more details).	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. Nanoimprinting of relatively thick (>5 µm) polymethylmetacrylate (PMMA) films on silicon can be carried out at 210 ºC at a pressure of 5 MPa. Hot embossing of pellets of the polyolefin ZEONEX (Zeon Chemicals) can done at 160-190 ºC at a pressure of 2-10 MPa, to produce 50-100 µm thick polymer sheets with one or both patterned surfaces. 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.	Possible trapping of air in the cavities, leading to defects in hot embossed microlenses. Vacuum is helpful in removing defects created by air inclusion.
	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	**Process:** Nanoimprint Lithography
Address: Glasgow University	**Responsible:** M. Riehle
Web-Address: www.gla.ac.uk/centres/cellengineering	**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.

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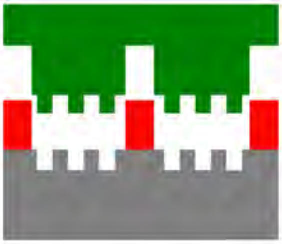
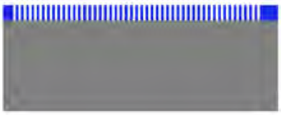
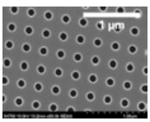
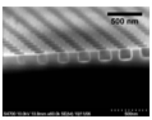
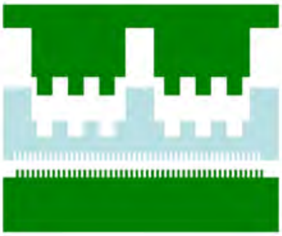
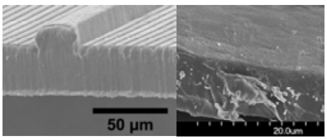
LoP2007_NIL012_Biodegradable polymer scaffold

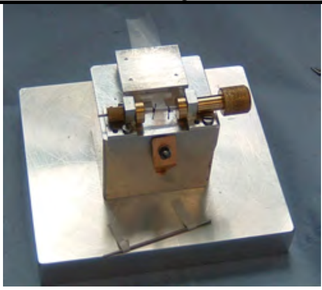
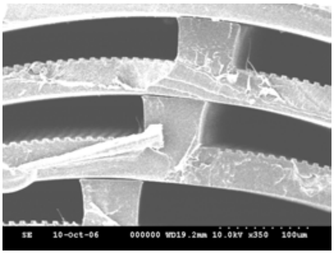
Biodegradable polymer scaffold

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^{o}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** 	**C_4F_8, SF_6**: 50 sccm, 40 sccm **Coil power**: 600 W **Platen power**: 10 W **Pressure**: 10 mT **Etch rate**: 825 nm/min 6 µm deep	
1.5	**Spacers** 	SU8 2050 @ 3 krpm (75 µm) 30 min at 95^{o}C MA6, 20 seconds PEB 95^{o}C for 7 minutes Develop in EC solvent for 7-10 minutes Rinse in IPA and dry in N_2 stream	*Low thermal cycling to prevent SU-8 cracking*
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 ($C_8H_4Cl_3F_{13}Si$) 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**  	**C_4F_8, SF_6**: 120 sccm, 40 sccm **Coil power**: 18 W **Platen power**: 525 W **Pressure**: 10 mT **Etch rate**: 100 nm/minute 100 nm deep	
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	*Piranha etch also oxidizes silicon prior to fluorination* *Warning – Piranha*

		silane ($C_8H_4Cl_3F_{13}Si$) from Gelest for 5-10 minutes. Rinse in heptane and dry in N_2 stream	*is a highly oxidizing solution*
2.6	**PDMS nano stamp** 	Cast 4:1 (pre-polymer:curing agent) Sylgard 184 to make inverse replica of stamp	*See also 5.3.2 Soft and hybrid layered stamps.*
	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 60-80µm.	
3.2	**Melt embossing**  	PCL film cut, aligned and sand-wiched 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	 	**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. 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. The roll is secured either by surgical suture thread or by the use of a biocompatible superglue, 2-Octyl Cyanoacrylate. After rolling and securing the pin clamps are loosened and removed. Excess film is trimmed and the scaffold is ready for use.	
	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

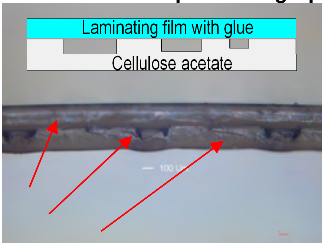


Figure:
Optical micrograph of a fluidics channels in 95 µm thick celluloseacetate sealed with ca. 90µm thick laminate foil. Fluidisc channel is 50 µm high and 150 µm width.

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	**Process:** Roll-to-roll NIL
Address: FI-02044 VTT, Finland	**Responsible:** Tapio Mäkelä
Web-Address: http://www.vtt.fi	**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 an laminate foil during the same printing cycle. In roll to roll NIL process a softening temperature of wed 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 possibilitity to manufacture fludics channels with continuous process. A specific reguirements of sequential process were shown.

Major challenges: In this novel process a many challanges 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

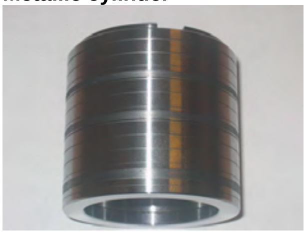
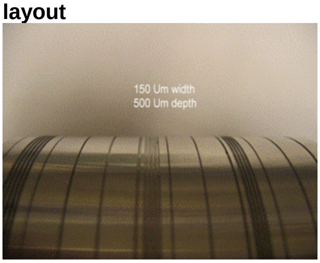
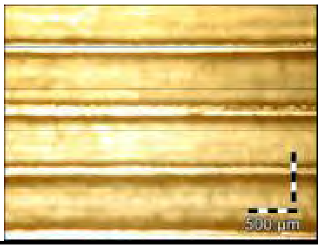
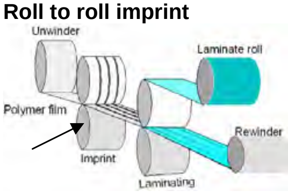
References:
[1] T. Mäkelä, T. Haatainen, P. Majander and J. Ahopelto, MNE07 (2007).
[2] T. Mäkelä, T. Haatainen, P. Majander and J. Ahopelto, Microelectr. Eng. 84 (2007) 877-879.
[3] T. Mäkelä et al. Unpublished data
[4] H. Schift, *Roll embossing and roller imprint*, Chapter (5) in "*Science and new 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).

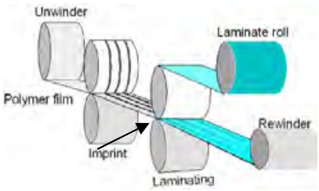
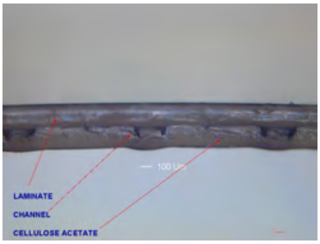
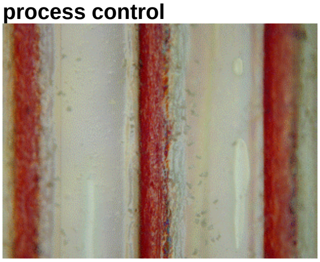
Contact information:
Ph.Lic. Tapio Mäkelä
VTT Technical Research Centre of Finland
Tietotie 3, Espoo
P.O.Box 1000, FI-02044 VTT
Finland

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** *Plastic roll*: 50 mm width , 95 um cellulose acetate , no pre-treatment *Laminate roll*: 50 mm width , 90 um 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 na-nomprinting**		
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	Tg 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 laminat-ing** 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 I 123 00740 Helsinki, FINLAND
www.ptmtec.com
Email: info@ptmtec.com

4.7 V-Grooves for plasmon confinement

Fabrication of V-groove waveguides for plasmon confinement by Nanoimprint Lithography

Process: nanoimprint lithography

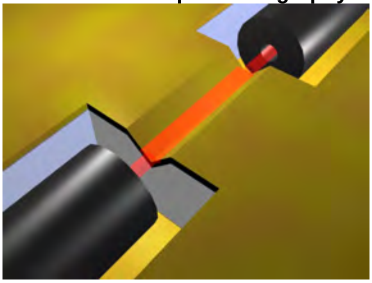


Figure:
Schematic illustration of the device: two deep channels (to place the optical fibers) are integrated with the v-groove (to confine the plasmon). The device is made in gold (200nm) onto a transparent and flexible substrate (OrmoComp®).

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).

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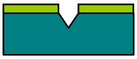
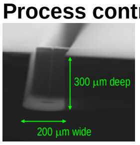
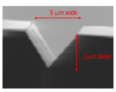
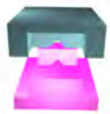
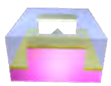
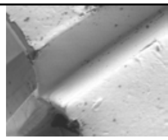
LoP2007_NIL014_V-Groove Waveguides

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 1100ºC (oxide thickness ~200nm)	
1.3	**Photolithography 1** 	Spin coating of UV resist (1.5µm of AZ5214B), UV exposure, and development.	
1.4	**RIE** 	RIE of 200 nm of SiO2. Stripping of the photoresist (acetone)	
1.5	**KOH to define de V** 	Anisotropic wet etching in KOH (wt 30%), at 80ºC, during 1h.	
1.6	**Oxide removing** 	HF 50%, 1 minute.	
1.7	**Photolithography 2** 	Spin coating of UV resist (1.5µm of AZ5214B), UV exposure, and development.	
1.8	**D-RIE to define the channels** 	Deep RIE of silicon, to define the channels (300 µm deep).	*Vertical and smooth sidewalls should be obtained, otherwise demolding would be difficult.*
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 1150ºC.	*For each size of the grooves, the oxidation time can be optimized (by simulations), to achieve the sharpest angle in the bottom.*

1.11	**Optional: improvement of the thickness of the stamp**	Anodic bonding of another silicon wafer to the bottom of the stamp.	*After etching 300um to create the deep channels, in a 500um thick wafer, it becomes very fragile.*
1.12	**Antisticking coating**	FDTS-layer (1H,1H,2H,2H-perflourodecyltri-chlorosilane) using a MVD system (Applied Microstruc-tures Inc.)	
	End of Process 1		
2.0	**Process 2: NIL**		
2.1	**Substrate preparation**	PMMA sheet, 5mm thick. Dehydrated in an oven, at 90ºC, 8hours.	
2.2	**NIL** 	Imprint with EVG imprinter: 180ºC, 10min, at 20kN. Demolding at 80ºC.	
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.	*A silicon wafer has to be stuck to the backside of the PMMA sheet, to avoid thermal gradients and bubbles formation.*
3.2	**OrmoComp deposition** 	Casting of OrmoComp® onto the gold layer. The sample is left for 10min. UV curing: 4 cycles of 30seconds.	*The OrmoComp has to be cured in short cycles, oth-erwise, internal stress appears and bends the structures.*
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 OrmoClear are commercially avbailable 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

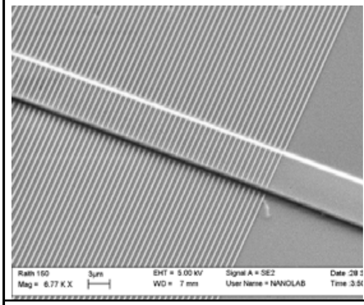


Figure:
SEM image of waveguide with crossed grating out-couple imprinted in hydrogel

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

Contact information:
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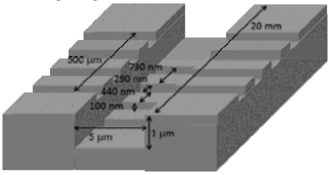
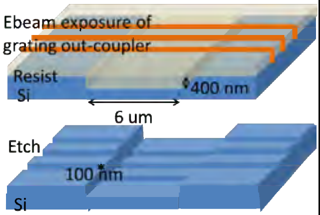
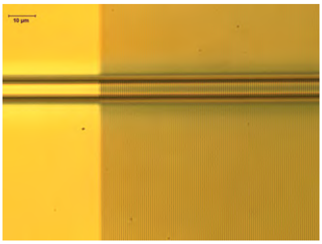
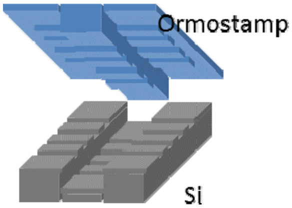
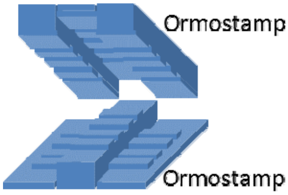
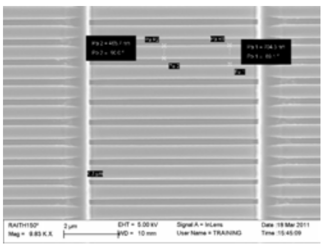
Catalan Institute of Nanotechnology,
Campus de la UAB, Edifici CM3,
08193 Bellaterra (Barcelona),
Spain

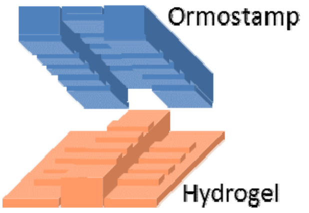
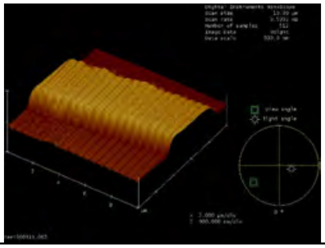
LoP2012_NIL016_Hydrogel waveguide-application

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 heigh 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 outcoupler **Reactive Ion Etch** to depth of 100 nm	*Ridge waveguides and outcoupler grating lines are at 90 degrees.*
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**	**Quartz substrate** Area 20mm x 20 mm, 0.5mm thick **Oxygen plasma** treatment to improve adhesion .	*OrmoSstamp will not adhere to quartz without oxygen plasma treatment*
2.2	**First replication: UV-NIL imprint** 	**Dropcast** inorganic-organic hybrid polymer such as OrmoStamp onto pretreated quartz substrate. Place quartz substrate on top of Si stamp to allow UV transmission. **Imprint** 3 bars, 2 minutes UV, 20 seconds at 3bars (using a UV radiation of 17.26 W/cm2 at 365 nm)	*Imprinting was performed on a home-made imprinting module.* *After imprinting, excess OrmoStamp should be trimmed away.*
2.3	**Anti-adhesion treatment**	**Optool** anti-adhesion treatment as for Step 1.5.	
2.4	**Second replication: UV-NIL** 	**Dropcast** organic-inorganic hybrid polymer such as OrmoStamp onto quartz substrate. Place quartz replica on top of quartz substrate. **Imprint** 3 bars, 2 minutes UV, 20 seconds at 3 bars (using a UV radiation of 17.26 W/cm2 at 365 nm)	*If anti-adhesion treatment is properly applied, OrmoStamp can be copied from OrmoStamp replicas, thus allowing to easily inverting the pattern polarity, if necessary.*
2.5	**Anti-adhesion treatment**	**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.	*Other SAMs (Optool, F13-TCS, FLKS10) work worse than OTS.*
2.6	**Process Control** 	**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	*In samples without TPM treatment, hydrogel layer peels off the substrate when it swells*
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/cm2 at 365 nm)	*Imprinting was performed on a home-made imprinting module.*
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 advantegous 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 Imprint of hybrid materials

All-silica micro and nanofluidic devices fabricated by imprint of sol-gel silica with silicon stamp

Process: Sol-gel imprint with silicon stamp

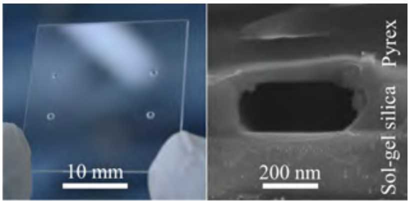


Figure:
Photo of all-silica nanofluidic lab-on-a-chip device fabricated by imprint of sol-gel silica. SEM micrograph of a cleaved nanochannel imprinted in sol-gel silica and fusion bonded to a Pyrex glass lid.

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:

[1] Morten Bo Mikkelsen, Alban A. Letailleur, Elin Søndergård, Etienne Barthel, Jérémie Teisseire, Rodolphe Marie, and Anders Kristensen, All-silica nanofluidic devices for DNA-analysis fabricated by imprint of sol-gel silica with silicon stamp, Lab on a Chip **12**, 262-267 (2012). DOI:10.1039/C1LC20689C

[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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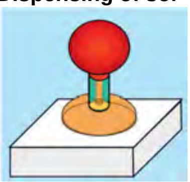
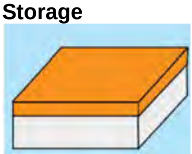
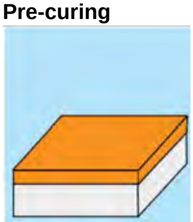
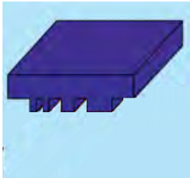
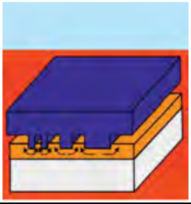
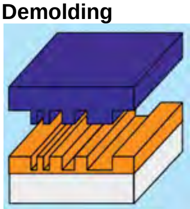
Denmark

LoP2012_NIL017_SVI hybrid materials

Imprint of hybrid materials

Process: All-silica micro and nanofluidic devices fabricated by imprint of sol-gel silica with silicon stamp

	Process	**Technical Parameters**	**Remarks**
	What	how it should work	critical issues
1.0	**Process 1: Material prepara-tion**		
1.1	**Mix sol-gel material**	**Sol preparation** Methyltriethoxysilane (MTES) is mixed with HCl (pH 2.0) at a molar mixing ratio MTES:H_2O of 1:14.	*Process described in Mikkelsen et al. Lab Chip 12, 262-267 (2012) [1].*
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 sensi-tive 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	*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 coat-ing and the storage and pre-curing steps must be changed.*
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.	*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.*
	Pre-curing 	**Reduction of water content before imprint** Prebake at 90°C for 5 min to pre-cure and further dry the gel.	*Reduction of water con-tent is necessary in order to avoid defects due to evaporating water. The prebake time can be used to tailor the material viscosity. A harder mate-rial may be convinient for imprint of, e.g., very low protrusion coverage nanostructures.*
	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. Perfluorodecyltri-chlorosilane (FDTS) is used as anti-sticking coating.	*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.*
3.2	**Imprint** 	**Imprint** Hot plates preheated to 60°C to assure reproducible tem-perature 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.	*Slow condensation at 60°C and reduced vis-cosity assures good fill-ing of the stamp cavities.*
3.3	**Demolding** 	**Demolding** Demolding with a razor blade.	*Triboelectric charging makes demolding of imprinted sol-gel silica on glass substrates more difficult than on silicon substrates.*
	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.	*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 di-mension. For imprinted pattern with large density of free surfaces the de-formation is very small.*
	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.	*Inlet holes fabricated by powder blasting as de-scribed in Mikkelsen et al. Lab Chip 12, 262-267 (2012) [1].*
5.2	**Prebonding**	**Prebonding** A weak bond is obtained when the two substrates are pressed together.	
5.3	**Annealing**	The bonding strength is in-creased 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

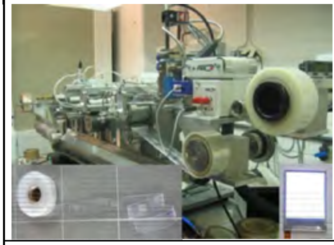


Figure:
A pilot scale Roll to Roll manufacturing process for backlight devices on Poly(methylmethacrylate) (PMMA) film.

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) 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. 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:
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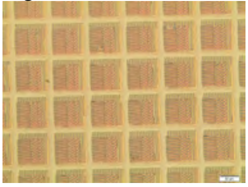
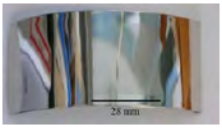
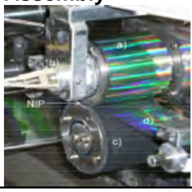
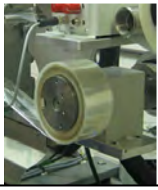
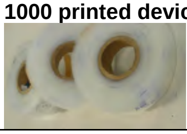
Tietotie 3, Espoo, FI-02044 Finland
Finland

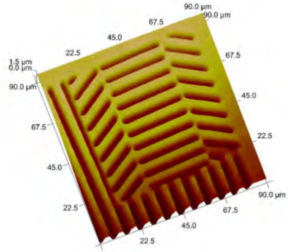
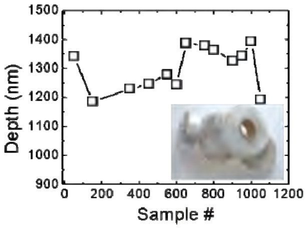
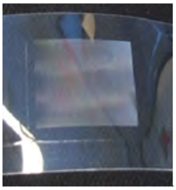
LoP2012_NIL018_R2R backlight-application

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 back-light 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 ^oC	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 unwind-er.	
3.2	**Thermal Roll to roll NIL** 	The mold is wrapped on metallic cylinder (width 60 mm) and heated to opera-tion temperature 115 ^{o}C. The printing speed 0.6 me-ter/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 quali-ty of the printed binary ele-ment 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		

4.0	**Process 4: LED connection and characterization of device**		
4.1	**Illumination element** 	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.	
4.2	**Depth variation** 	Depths of printed grooves are typically within 1.2-1.4 um. All printed devices are in the suitable range.	Variation in the height is due to the temperature control in the tool. This is due to the low thermal mass.
4.3	**Backlight device**  	**LED attachment and luminance measurement** Three LED connected to the device. Average luminance value was 120 cd/m^2. The standard deviation for the measured luminescence values for all devices was within 17 %.	
	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

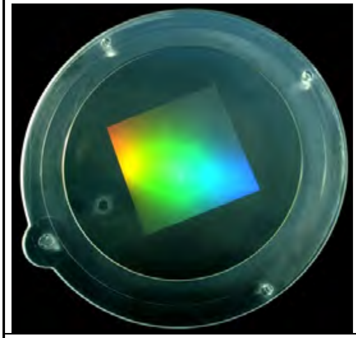


Figure:
Photograph of an injection molded specimen of an array (44x44mm^2) of pillars with 200nm diameter and 600 nm period, replicated directly from a 100mm silicon wafer usind a dedicated molding tool for wafer injection molding. This example was replicated in transparent polyamide

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 Schift
E-mail: helmut.schift@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 produe 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. Schift, 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)

Contact information:

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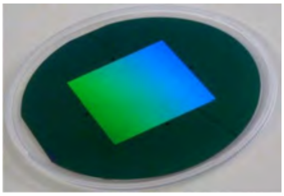
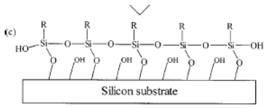
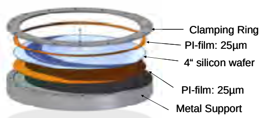
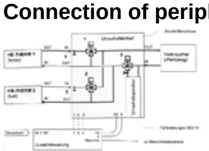
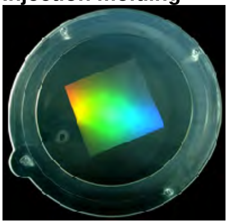
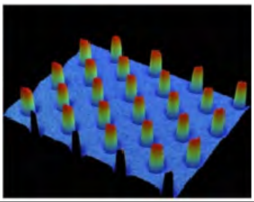
Institute of Polymer Nanotechnology
Klosterzelgstrasse 2
CH-5210 Windisch, Switzerland

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	*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*
1.2	**Application of antisticking coating** 	**Fluorosilane treatment** According to standard process described in NaPa LoP	*Application of antisticking coating is absolutely necessary to allow for demolding without damage of the replicated structure and more importantly to avoid wafer breakage*
	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	*Polyimide (Kapton) films are used as spacers to compensate for surface rougness of the metal support and to minimize the danger for*
2.2	**Material preparation** 	**Drying of polymer** Many thermoplastic materials need drying before processing	*Respective drying conditions can be found in respective product brochures*
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	*The process protocol needs to be adjusted to account for all necessary process steps. This is particularly important for the robot handling system*
	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 varation, handling system, …)	*This is typically straightforward to those skilled in the art of injection molding.*
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.	*This approach offers additional insight into the filling behavior of investigated nanostructures,in comparison to NIL filling studies.*
3.3	**Injection molding** 	**Replication** mold temperature close to Tg melt temperature: flexible pressure: depends on structure filling velocity: flexible	*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*
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. Schift, 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. Schift, *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. Schift, 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

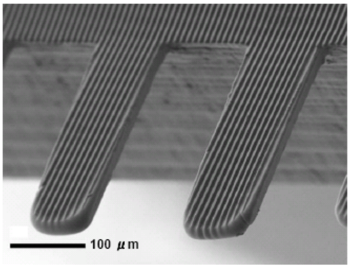


Figure:
Photograph of an injection molded microcantilever array featuring surface structures (here line grooves) achieved with embossed high-temperature polymer inserts. This example was realized in metallocene polypropylene using a structured PEEK foil as mold insert

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

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

Partner: University of Basel, Biomaterials Science Center
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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 produe 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 micro-cantilever 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

Contact information:
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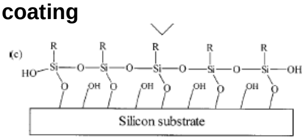
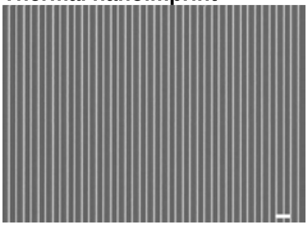
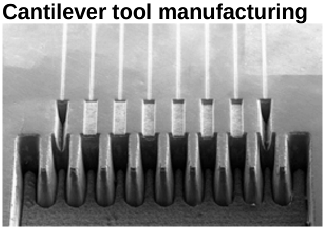
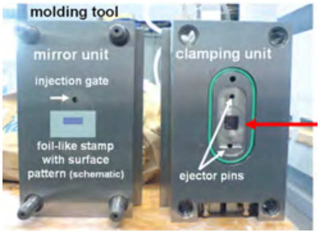
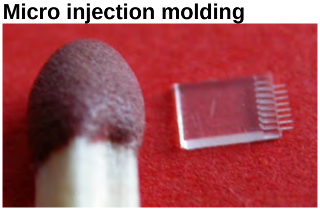
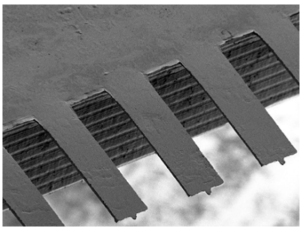
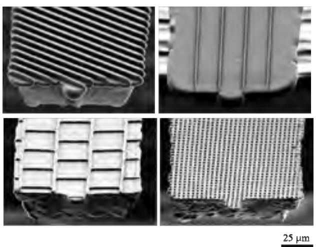
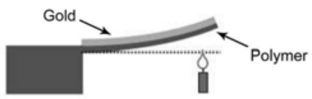
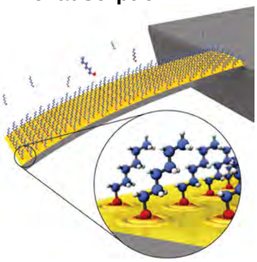
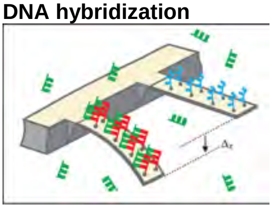
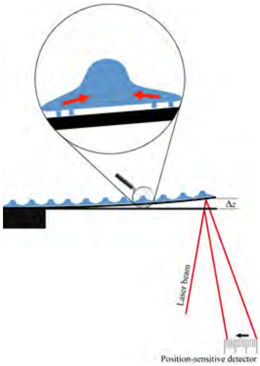
LoP2012_polymer micro cantilevers

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	*Alternative materials such as quartz wafers may also be used with the present setup*
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	*Very fine venting channels are needed at the tip of the microcantilevers to avoid diesel effect caused by compressed air*
	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	*Fixation of the structured polymer foil may be difficult for high temperatures and large sample volumes*
3.3	**Micro injection molding** 	**Proper molding conditions** Elevated mold temperature and high velocity filling of the mold	*Alternative: variothermal process control*
3.4	**Coating with gold**	**PVD coating**	*Not very strong adhesion of gold layer, depending on previous surface treatment*
	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	*High viscosity melts will not allow complete filling of the thin-walled cantilever beams, thus preventing reproducible cantilever geometries to be manufactured*
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	*Different cantilever beams may exhibit differences in deflection due to morphological differences*

		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

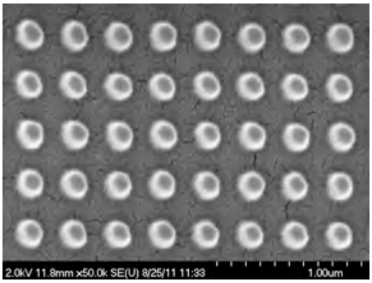


Figure:
Scanning electron micrograph of polycarbonate nanopillars produced by injection moulding with nanoimprinted hybrid polymer inlays.

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

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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

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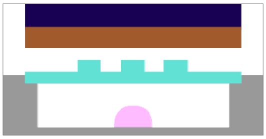
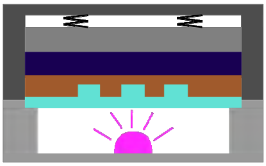
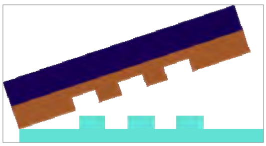
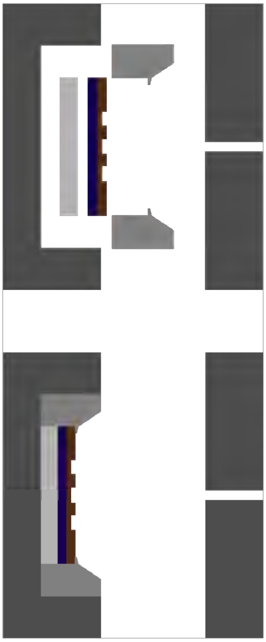
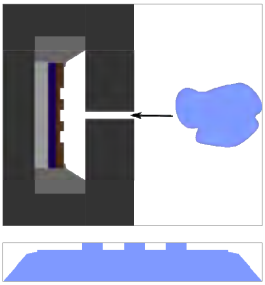
LoP2012_NIL020_inlay IM-process

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	*Samples size may be varied to better suit the final inlay size if required.*
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].	*Inclusion of anti-stick coating is critical to stamp performance.*
	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.	*Different thicknesses of PI film may be used. Kapton® comes in a range of thicknesses sown to ~25 µm*
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.	*Proceed directly to next step; do not leave a long delay.*
3.2	**coating resist** 	**Resist** No primer, SU-8 3000 series, apply with pipette evenly over surface	*With more viscous dilutions it may be easier to pour from the bottle than to use a pipette.*
3.3	**coating resist (homogeneous layer)** 	**Spin coating of SU-8** Thickness: 20-50 µm, spin speed depends on resist grade/dilution.	*Ensure prevention or removal of large edge beading.* *This process requires a wet resist so a soft bake is not required.*
	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	*This strengthens the SU-8 before injection moulding*
4.6	**process control**	**Optical, electron and atomic force microscopy** *non-destructively*	*destructive (cleaving, metal coating) in SEM profilometry.*
	End of Process 4		*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.*
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	*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.* *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.
5.2	**tool assembly** 	**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.	
5.3	**injection moulding** 	**perform injection moulding as normal**	
5.4	**process control**	**Optical, electron and atomic force microscopy** *non-destructively*	*destructive (cleaving, metal coating) in SEM profilometry.*
	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

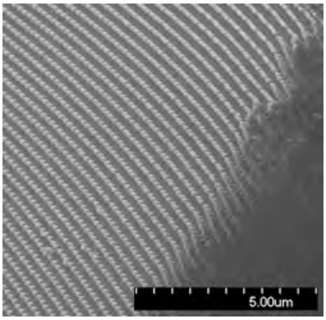


Figure:
Scanning electron micrograph of a regular array of 100 nm pillars on a sloped surface of a monolithic polycarbonate sample produced by injection moulding.

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

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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 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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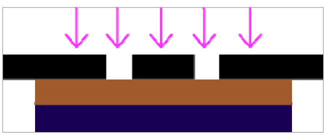
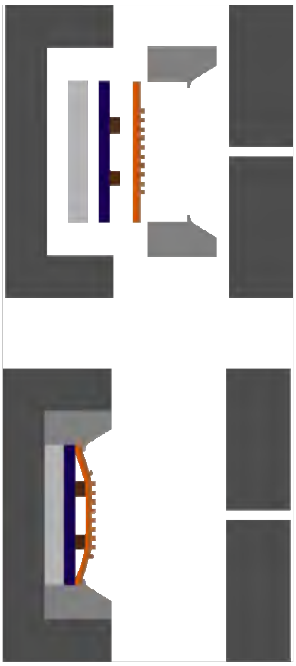
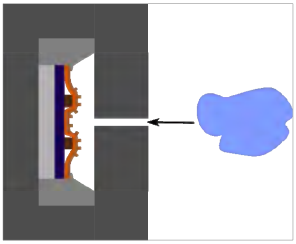
LoP2012_NIL021_non-flat IM-process

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.	*Choice of film thickness will depend on the planned feature size of the bottom layer (subtopography).*
1.2	**preparation and patterning** 	**Standard inlay process** fabricate naonpatterned stamp by the process described in Section X.X	*Very thin fims (less than 50 µm) can be very difficult to spin resist on to and pattern by NIL.*
	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.	*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).*
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	*Bake time may be extended for very thick layers*
2.5	**Photolithography** 	**Mask aligner** expose (i-line); time depends on feature size and resist thickness	*The minimum feature size should be greater than the film thickness.*
2.6	**post exposure bake**	**Curing** hot plate, 65°C, 1 minute 95°C 5 minutes	*Bake time may be extended for very thick layers*
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	*This strengthens the SU-8 before injection moulding*
	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	*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.* *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.*
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.	

3.3	**injection moulding**  	**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	*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.*
	process control	**Optical, electron and atomic force microscopy** *non-destructively*	*destructive (cleaving, metal coating) in SEM profilometry.*
	End of Total Process		

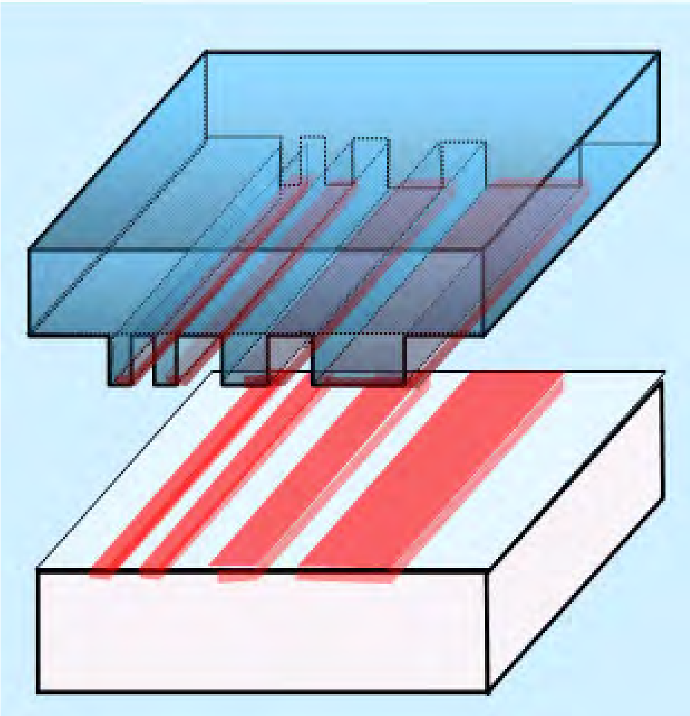
5. Soft Lithography and Microcontact Printing

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

Project leader: IBM Research Laboratory	**Process:** microcontact lithography
Address: CH-8803 Rueschlikon / Switzerland	**Responsible:** Heiko Wolf
Web-Address: http://www.zurich.ibm.com/	**E-mail:**

Process description: Microcontact printing (µCP, 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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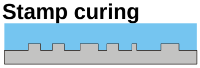
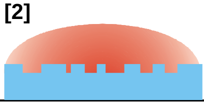
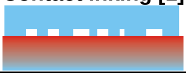
LoP2007_mCP001_microcontact printing alkalethiols

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	*ideal with smooth bottom surfaces and smooth vertical sidewalls*
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	*good mixing required for catalytic reaction,*
1.4	**Degasing**	Degas mixture to avoid air bubbles in stamp	*premixed aliquots can be stored at -20 ºC for 1-3 months*
1.5	**Stamp curing** 	Pour liquid prepolymer onto master inside of petri dish and cure at 60 ºC 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)	*higher molecular weight thiols decrease ink diffusion, but increase disorder of monolayer and tend to crystallize at the stamp surface*
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.	*purification removes low-molecular-weight thiols*
2.3	**Ink solution**	Prepare diluted thiol solution in ethanol, e.g. 0.1 mM	*changing the concentration allows to control the amount of ink transferred to the stamp*
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.	*only the average amount of ink transferred can be controlled.*
4a.1	**Inking**	Place two drops (~0.2 mL) of the freshly prepared (<1 h) ink solution on top of the stamp.	*make sure there's enough liquid to cover the surface.*

		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.	*quality of monolayer is less dependent on pattern geometry, diffusion is minimized.*
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.	*conformal contact allows transfer of thiols. Inking times control amount of thiols transferred.*
5	**Printing**		
5.1	**Making Contact** 	Place stamp onto gold substrate, monitor formation of conformal contact optically.	*conformal contact is made by the stamps own weight.*
5.2	**Detaching**	Remove the stamp after 10-20 s.	*the longer the printing time, the fewer the defects in the printed monolayer, but the higher the ink diffusion.*
6	**Etching [3]**		
6.1	**Preparation of etch bath**	Prepare a ferric nitrate etch bath (20 mM $Fe(NO_3)_3 \cdot 9H_2O$ and 30 mM thiourea in DI water, adjusted to pH 2.0 using HCL)	*the concentration of the ferric and thiourea in solution determine the etch rate*
6.2	**Etching** 	The bath should be operated at 23-25 ºC with moderate stirring and has an etch rate of ~ 10 nm min^{-1}.	*the granularity of the gold substrate limits the edge resolution to the size of the gold grains (15-30 nm).*

5.2 Optical resonators

Fabrication of optical resonators by soft UV-NIL

Process: soft lithography

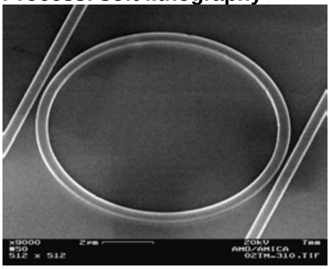


Figure:
SEM-image of an imprinted microring resonator.

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

Partner: *AMO GmbH*	**Process:** Soft UV-NIL
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Web-Address: *www.amo.de*	**E-mail:** plachetka@amo.de

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 youngs modulous.

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 silicom 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*

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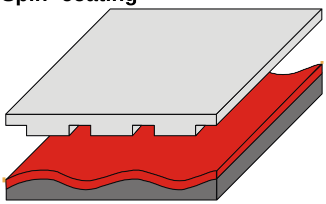
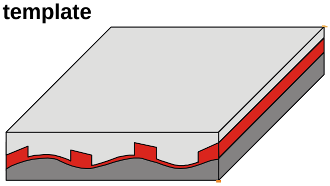
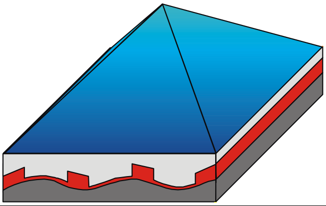
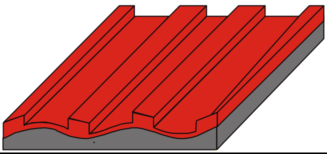
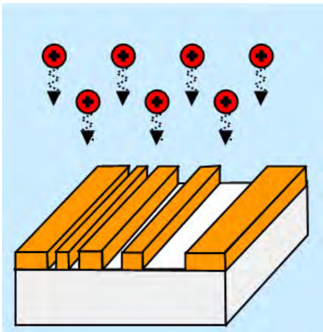
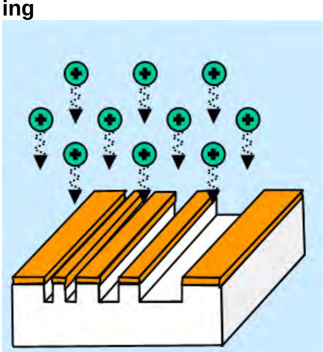
LoP2007_SoftNIL001_Resonators by SoftNIL

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 an detached from the silicon master.	
2.0	**Process 3: Lithography**		
2.1	**Spin -coating** 	spincoating of UV-curable resist onto an SOI-substrate (depending on the application other substrates amy be used freely) imprint resist: AMONIL MMS4 (3000rpm@30sec)	
2.2	**Soft imprinting with flexible template** 	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	

2.3	**UV-exposure** 	The AMONIL resist is cured directly through the flexible imprint template by UV-exposure in the EVG620 imprint tool	
2.4	**Detachment of template** 	After completely curing the resist the imprint template is removed from the pol-ymerized imprint resist; the moulded flexible imprint template can be used for other imprints	
	End of Process 2		
3.0	**Process 3: Pattern Transfer**		
3.1	**Residual Layer (Breakthrough) Etching** 	**BCl_3 –RIE (The plasma is used to open the SOI substrate)**	
3.2	**Substrate Etch-ing** 	**HBr-RIE (This plasma will stop perfectly on the BOX of an SOI-wafer)**	

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

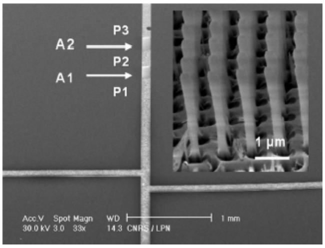


Figure:
Cross microfluidic channels with two integrated nanopillar arrays (A1 and A2) obtained using a mix-and-match approach based on i) soft UV nanoimprint lithography, ii) standard photolithography and iii) reactive ion etch techniques

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

Project leader: *LPN*
Address: CNRS-LPN, F-91460 Marcoussis, France
Web-Address: *www.lpn.cnrs.fr*

Process: soft UV nanoimprint
Responsible: Yong Chen
E-mail: yong.chen@lpn.cnrs.fr

Partner: *ENS*
Address: Ecole Normale Supérieure, F-75231 Paris
Web-Address: *www.ens.fr*

Process: soft UV nanoimprint
Responsible: Yong Chen
E-mail: yong.chen@ens.fr

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 coved 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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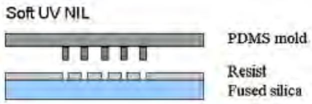
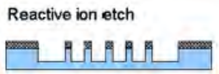
LoP2007_SoftNIL002_NIL Mix&Match

	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	*Including only nanostructures and alignment markers*
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**	*Including all large size features and alignment markers*
4.0	**Soft UV nanoimprint** 		
4.1	**Spin coating of layer 1 (sacrificial layer)**	**Spin-coating of PMMA** 300 nm thickness	*A thin quartz plate can be used for facilitating optical imaging of DNA migration.*
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)**	*Nanostructures alone can be easily replicated with large process latitude.*
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** 		
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	*With alignment*
	End of Process 6		
7.0	**Process 7: Second 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** 		
8.1	**Etch of micro and nanostruc-ture into the substrate**	**Reactive ion etch** SF_6 plasma	*Both micro and nanostruc-tures are etched simulta-neously.*
8.2	**Nickel mask removal**	**Chemical etch** HNO_3 for 1min	
	End of Process 8		
9.0	**Process 9: Device assembling** 		
9.1	**Preparation of PDMS cover slide**	**PDMS coasting (1:10)** Over a flat silicon wafer	*Other materials can also be used as cover layer*
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 Schift

6.1 Hot embossing of waffles

Fabrication process for waffles made with an 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 mobel 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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Web-Address: http://www.psi.ch
Process: Thermal Nanoimprint
Responsible: Helmut Schift
E-mail: helmut.schift@psi.ch

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 easy 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 pruposes they are connected with a hinge. **Prepare large and smaller bowl, electric hand beater and laddle**	***Different tool options*** *1. for fire* *2. for hot plate* *3. automated with integrated electrical heating and temperature control* *Waffles are different from so-called "Bretzel", which are thinner and often more ornamented (not to confuse with the pretzels made from sour dough)*
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 overmix! 4. Beat whites until moderately stiff. 5. Fold stiff egg whites into mixture.	***Alternatives:*** *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, buttermilk instead of while milk, and vanilla extract for flavoring.* *Wholemeal flour might need more liquid and time to soak.* *Pre-heat oven, if not served immediately after cooking.* *Prep Time: 15 minutes* *Cook Time: 30 minutes* *Total Time: 45 minutes* *The final batter should have a foamy, viscous appearance (but not liquid), which flows easily from the batter.*
	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.	*Butter of vegetable fat is normally used to guarantee the release of the baked waffle without damage* *Alternative: Spray both surfaces with cooking spray. State-of-the-art*

		 Fatal damage due to adhesion	*automated waffle irons are often coated with antiadhesive Teflon. In addition, the inherent fat content of the batter adds to the release properties.*
2.1	**Baking**  	**Baking** Ladle 120 to 180 g (½ to ¾ cup) batter on the hot waffle iron and close it. Press gently to enable spreading of the batter Bake 3 min @ hottest temperature 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. 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.	*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.* *Do not open too early, otherwise the incompletely cooked waffle will rip and parts will stick to the iron.* *Waffle should be crispy at the outside and slightly soft at the inside. This – along with the the thickness of the waffles (the "residual layer") – can be controlled by the amount of batter*
	End of Process 2		
3.0	**Process 3: Serving**	**Coating**	
3.1	**Serving example** 	**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.	*Cross-section of a thick (Belgium) waffle* 
	End of Process 3		
	End of Total Process		

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 eggs 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

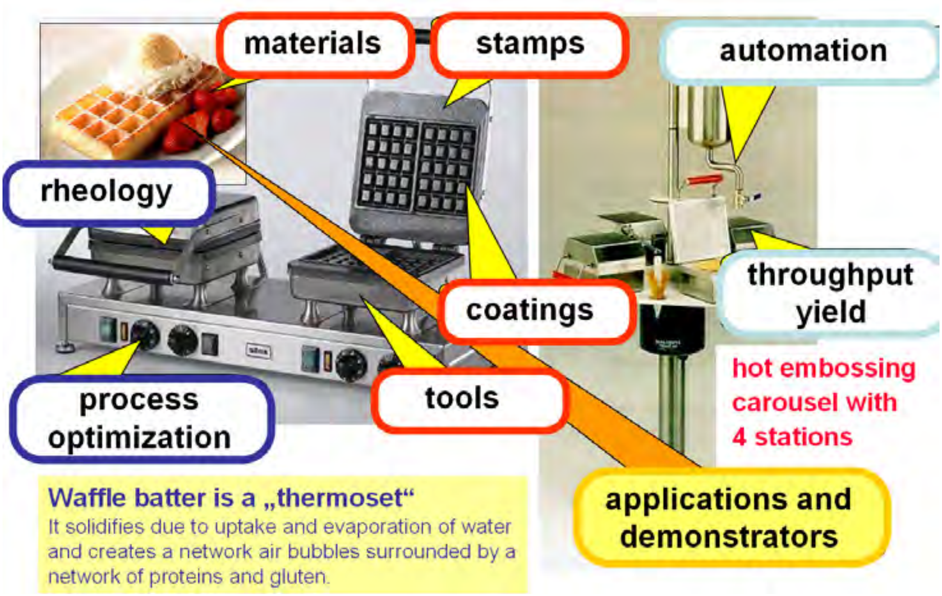

Figure 2: A typical presentation of aspects of molding which are helpful to understand the optimization of the thermal nanoimprint process.

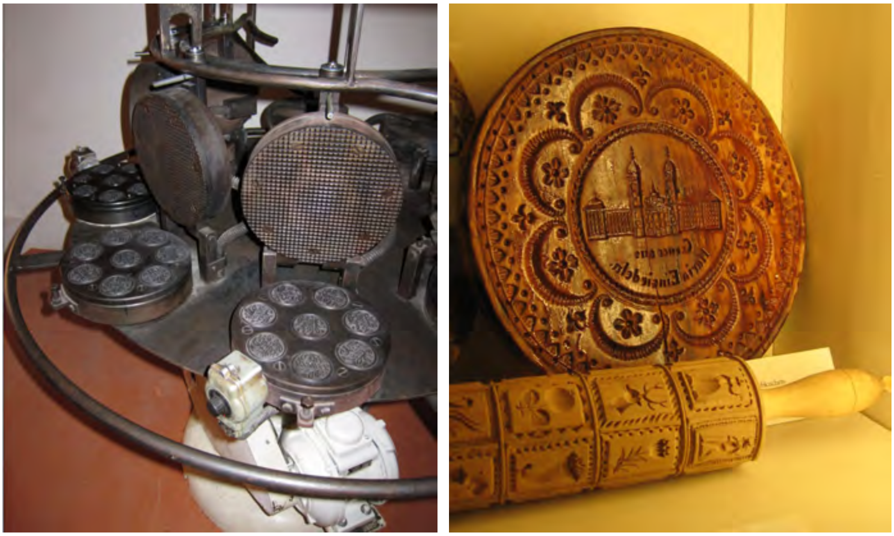

Figure 3: The Swiss traditional enterprise Kambly specializes in fabrication of Swiss Bretzeli (Bricelets), which are thin waffles without soft “interior”. The photograph (left) shows a machine in the Kambly museum in Trubschachen in Emmental, Switzerland. However, in contrast to waffles, the dough is not liquid and applied as soft balls. A range of old-fashioned wodden 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 wodden stampers and roll molds.

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