NaPANIL – Library of Processes
Nanopatterning, Production and Applications based on Nanoimprint Lithography

Third edition of the NaPa Library of Processes
with results from the NaPa-project, 2004 – 2008,
and from the NaPANIL-project, 2008 – 2012
revised and updated, August 2014

IMPRINT

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A. Kristensen, H. Schift, D. Mendels, and G. Grützner

Edited by: H. Schift, Paul Scherrer Institut, Switzerland

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

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

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

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

The project NaPANIL, from 2008 to 2012, can be considered as the natural follow-up to NaPa. Although different in the range of processes and the orientation towards industrial applications, it takes up the impetus generated by NaPa and adds some essential ingredients in terms of the value chain of manufacturing, which goes further than the original NaPa sub-project “Nanoimprint Lithography” with its workpackages Stamps, Processes and Applications. In NaPANIL, a Large Scale Integrating Collaborative Project on “Nanopatterning, Production and Applications based on Nanolprinting 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 con-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.

For more information about NaPANIL, please contact:

Prof. J. Ahopelto, project coordinator: jouni.ahopelto@vtt.fi
WEB site: The NaPa LoP can be downloaded via http://www.psi.ch/lmn/helmut-schift
The NaPANIL project

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

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

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

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

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

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

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

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

**3D patterning and moulding of complex shapes:** If you need to mould 3D instead of 2D surface structures, as needed for saw-tooth, multi-level, lens-like structures, in most cases you need a more complex stamp and continue as used in 2D patterning. But you need also a way to fabricate the stamp – in a reproducible way. Often there is only a limited set of processes suitable for 3D patterning, and they are less reproducible than the more established 2D processes. If 3D stamps are saw-tooth like (symmetric or asymmetric), i.e. with sloped walls, there are a few ways to do this, by gray tone lithography, ion-beam etching or lithography with inclined beam. Often these techniques do not allow a var-
iation of the slope within the pattern. Multilevel structures are fabricated by multiple, aligned lithography. With each level, overlay issues will become more prominent. A stamp with a defined 3D shape with different levels is self-aligning, i.e. all levels are fixed and every replication will mould exactly the same shape as the previous one. Tolerances are therefore more relaxed. Lens-like structures are fabricated using reflow or isotropic etching processes. Large areas are often not possible because the initial structures have to be fabricated by high-resolution techniques. In addition, here, a mould with a defined structure needs to be replicated in S&R for devices.

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

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

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

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

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

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

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

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

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

<table>
<thead>
<tr>
<th>Institution</th>
<th>Contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technical Research Centre of Finland (VTT) - Finland</td>
<td>Jouni Ahopelto</td>
</tr>
<tr>
<td>Institut Català de Nanotecnologia (ICN) - Phononic and Photonic Nanostructures Group - Spain</td>
<td>Clivia Sotomayor-Torres</td>
</tr>
<tr>
<td>Technical University of Denmark (MIC) - Denmark</td>
<td>Anders Kristensen</td>
</tr>
<tr>
<td>Paul Scherrer Institut (PSI) – Switzerland</td>
<td>Helmut Schift</td>
</tr>
<tr>
<td>Cognoscens - France</td>
<td>David Mendels</td>
</tr>
<tr>
<td><em>micro resist technology</em> GmbH (MRT) - Germany</td>
<td>Gabi Grützner</td>
</tr>
<tr>
<td>C.R.F. Società Consortlie per Azioni (CRF) - Italy</td>
<td>Vito Lambertini</td>
</tr>
<tr>
<td>AMO GmbH Gesellschaft für Angwandte Mikro- und Optoelektronik mbH (AMO) – Germany</td>
<td>Ulrich Plachtetka</td>
</tr>
<tr>
<td>Tecnalia - Spain</td>
<td>Isabel Obieta</td>
</tr>
<tr>
<td>Commissariat à l’Energie Atomique (LETI) - France</td>
<td>Stefan Landis</td>
</tr>
<tr>
<td>LTM-CNRS Laboratoire des Technoloquies de la Microélectronique, Délégation Régionale Rhône-Alpes (LTM) - France</td>
<td>Cecile Gourgon</td>
</tr>
<tr>
<td>Modines – Finland</td>
<td>Kari Rinko</td>
</tr>
<tr>
<td>Saint Gobain Recherche – France</td>
<td>Elin Sondergard</td>
</tr>
<tr>
<td>Istituto Officina dei Materiali (CNR-IOM) - Italy</td>
<td>Massimo Tormen</td>
</tr>
<tr>
<td>University of Glasgow (UG) - United Kingdom</td>
<td>Nikolaj Gadegaard</td>
</tr>
<tr>
<td>NILT – Denmark</td>
<td>Theodor Kamp Nielsen</td>
</tr>
<tr>
<td>SET - France</td>
<td>Gilbert Lecarpentier</td>
</tr>
</tbody>
</table>

## Contributions to this library

Special thanks for editing this library go to:

**AMO GmbH – Aachen/Germany**  
Dr. Ulrich Plachtetka

**CEA-LETI – Grenoble/France**  
Dr. Stéfan Landis

**DTU Nanotech – Lyngby/Denmark**  
Prof. Dr. Anders Kristensen

**PSI – Villigen/Switzerland**  
Dr. Arne Schleunitz / Christian Spreu

**CNR-IOM – Trieste/Italy**  
Dr. Massimo Tormen

**micro resist technology GmbH**  
Berlin/Germany  
Gabi Grützner / Dr. Marko Vogler / Dr. Arne Schleunitz / Thomas Endrulat
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 grows steadily. While the number of research groups building up NIL processes is continuously increasing, nanoimprint is now moving into industry. Not all these people have a platform for comparison, or exchange.

3.2 How this library is structured

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

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

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

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

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

It can serve as the basis for lectures and courses on nanopatterning. The NaPa project organized a series of Summer Schools in Toulouse each year in July called PANAMA. The concept of this training was a “hands-on” approach of nanotechnologies focused on nanopatterning. PANAMA stands for “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].

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.

NaPANIL Project Coordinator and Publisher
Prof. Dr. Jouni Ahopelto
Research Professor
VTT Information Technology
P.O. Box 1208
02044 VTT
Finland
e-mail: jouni.ahopelto@vtt.fi
www: http://www.vtt.fi

Laboratory for Micro- and Nanotechnology
Paul Scherrer Institut (PSI)
5232 Villigen PSI
Switzerland
e-mail: helmut.schift@psi.ch
www: http://www.psi.ch/lmn

Editor and NaPANIL Library of Processes
Manager for this edition
Dr. Helmut Schift
3.5 Beyond the NaPANIL project (Update 2014)

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

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

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

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

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

In conclusion, the most important factors for the success of NIL in production are throughput, defectivity and reliability – thus cost-efficiency. In this context, NIL gains maturity in all these fields. The basic requirements are still the same: stamps with high resolution and good surface quality, tools and materials that enable high volume fabrication and the use of NIL as a simple alternative to other costly lithographies. For these areas, the LoP will be a valuable tool.
Figure 3.1: Nanoimprint lithography (NIL) consists of the three major steps origination, replication and pattern transfer.
Figure 3.2: NIL process chain including feedback loops for process and device requirements.

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

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

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

4.1 Processes and process chains

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

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

Printed Boards for Electronic Circuits

Printed board with mounted electronic elements

Backside with wires to connect electronic elements

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

The methods of printed circuit board fabrication were much refined in photolithography and scaled down by many orders of magnitude. The mask fabrication, first by gluing patches of opaque tape on a transparent carrier, was then fabricated by plotters and photographic printers, and finally glass masks were fabricated by focused laser or electron beam lithography of resist with a thin opaque chromium layer as masking layer for UV light. Mask aligners for 100 to 300 mm glass mask and silicon substrates are now precision tools with sub-µm alignment and leveling. The pattern transfer processes have been equally developed, and apart from etching processes, electroplating and lift-off methods are now widely used. An overview is given in Fig. 4.3.
Figure 4.2: Photographs of printed board fabrication sequence: lithography and pattern transfer (http://www.kap-man.de/pcb01.htm).
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 clean-room facilities. In addition, if patterning has to be done over topography, a soft stamp or stencil method is predestined for use – stencil is very adapted to pattern different kinds of materials, too. However, there are many intersections where different techniques may be used with similar results. A first comparison can be seen in Tab. 4.1.
## Table 4.1. Comparison of different alternative patterning methods.

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

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

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

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

- **Combined processes**, e.g. combined nanoimprint and photolithography (CNP). Basically, UV-light assisted NIL or UV-NIL is a combination of photolithography and nanoimprint lithography. Instead of heating to change the thermo-mechanical properties of the resist, a liquid resist is used which is cured and hardened by light before demolding. In CNP, additionally to the imprint of the surface profile a masking layer on or below the surface profile is used to block the light in UV-light assisted NIL from different areas.
  a) Masking layer on the protrusions of the stamp: Then the resist area below the protrusions (the residual layer) is inhibited to crosslink and can be removed after demolding in a wet developer.
  b) Masking layer around an area of interest of a stamp, either on top of all structures or behind them (e.g. on the backside of the stamp or buried below the surface relief): Then the resist in the area of interest is crosslinked while the other areas can be removed in a wet developer. This is typically done to generate waveguides or mesas.
  c) Masking layer within an area of interest of a stamp, either on top of all structures or behind them (e.g. on the backside of the stamp or buried below the surface relief): Then the resist around the area of interest is crosslinked while the resist in the center of interest can be removed in a wet developer. This is only done if the structure below the resist (e.g. a grating) has to be replicated and the replica should act as generate waveguide or mesas.

- These processes, dealing with the same resist but using two different properties, are often called mix and match. 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:

<table>
<thead>
<tr>
<th>Process</th>
<th>(1) Pattern generation</th>
<th>(2) Curing or transfer</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>NIL</td>
<td>Partial mold filling and zero residual NIL</td>
<td>Process: Self-limiting flow of a thin resist</td>
<td>Resolution: lateral 200 nm, ( h ), nearly zero</td>
</tr>
<tr>
<td>NIL</td>
<td>Room temperature NIL (hard stamp)</td>
<td>Process: Resist compaction by high pressure under protrusions</td>
<td>Resolution: 80 nm line with 300 nm spacing (100 nm deep)</td>
</tr>
<tr>
<td>NIL+PL</td>
<td>Simultaneous thermostatic and UV-NIL (e.g. STU)</td>
<td>Process: Thermoplastic molding and UV curing</td>
<td>Resolution: lateral &lt;50 nm, ( h ), 20 nm</td>
</tr>
<tr>
<td>NIL+PL</td>
<td>Combined NIL and photolithography (e.g. CNP)</td>
<td>Process: Exposure through semitransparent stamp and removal of unexposed residual layer</td>
<td>Resolution: lateral 350 nm</td>
</tr>
<tr>
<td>NIL / R</td>
<td>Reverse tone NIL (e.g. SFIL / R) – Patterning over topology</td>
<td>Process: Overcoating of Si-containing etch barrier on prepatterned organic transfer layer, etch back and dry developing (window opening)</td>
<td>Resolution: lateral &lt;100 nm</td>
</tr>
<tr>
<td>R-NIL (T or UV)</td>
<td>Reversal NIL – With complete resist pattern transfer or “inking” mode (partial transfer)</td>
<td>Process: Spincoting of resist onto stamp, complete or partial transfer to substrate by thermal bonding</td>
<td>Resolution: lateral &lt;100 nm, ( h ), nearly zero</td>
</tr>
</tbody>
</table>
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-assembly structural topographies in the micro- 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 directed self-assembly (DSA) of block-copolymers (e.g. blocks consisting of a polymethylmetacrylate (PMMA) and of polystyrene (PS)), templates of lithographically defined structures (e.g. a grating consisting of hydrophilic and hydrophobic lines with distances of several 10s of nm) enable the ordering of several blocks of the polymer chain between two lines of same property (i.e. the PMMA on the hydrophilic and the PS on the hydrophobic lines). Thus, the orientation of entire polymer chains can be achieved. The periodicity of the grating has to be chosen in a way that full numbers of blocks can order between two lines of same property. Thus a near-field ordering can be achieved and a doubling or tripling of periods. If one entity can be selectively etched away (e.g. the PS etches faster than the PMMA in oxygen plasma), the remaining PMMA can serve as a masking layer for the substrate. This process is used to enhance the density of patterned media. The original surface pattern is generated via the imprint of a stamp with dense nanopillars (e.g. with 100 nm period), and the resulting structure after block-copolymer coating will have half periods and thus four times density and dot numbers due to the ordering. The pattern is then transferred into the substrate and a stamp can be fabricated for high-density nanoimprint.

c) Imprint of surfaces can also generate nodes or crystallization points for processes which are basically ordered in near-field, but will 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 upscaleable 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 process is used for setting up tools for replication, either for small scale or for large scale production. Particularly important is the surface enlargement by step and repeat processes, a process well known in holography industry, where large area molds are fabricated using recombin-
tion 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.

![Value Chain Diagram]

**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 micrometres. 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 an **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.
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:
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. 20x20mm² or entire wafers), or smaller stamps

**Beginners’ “kit” for Nanoimprint Lithography**
- Manual hydraulic press with up to 1 tons force and heating platens. Temperature range up to 200 °C. Cost: > 1000 €. Simpler (for demonstration) is a metal clamp which is heated in an oven. However, efficient cooling (e.g. with nitrogen gas is beneficial) is needed.
- Resist (e.g. PMMA with molecular weight 25k-75k, or mr-I 8000R series). Thickness 300 nm.
- 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.
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:
4.6 Soft Lithography (SL) – for beginners

**What is Soft Lithography? – Short description**

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

**Soft Lithography in daily life? – Examples**

- Printing of ink by rubber stamp.
- Fingerprints

**When do you use Soft Lithography? – Main applications**

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

**Advantages**

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

**Restrictions**

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

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

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

**Beginners’ “kit” for Soft Lithography**

**Stamp fabrication:**

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

**Pattern Transfer:**

For µ-CP:

- Ink stamp with alkanethiol from solution or PDMS 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.
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:**


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:**

4.7 Stencil Lithography (STEN) – for beginners

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

Stencil Lithography in daily life? – Examples
- Patterning sugar (icing / powdered sugar) by means of a pellicle onto a cake.
- Airbrush through mask (on cars or walls)

When do you use Stencil Lithography? – Main applications
- Mix- and match applications by patterning on already patterned substrates.
- Dots

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

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

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

Beginners’ “kit” for Stencil Lithography
- Place stencil on substrate and clamp it
- Install it at the top of the evaporation chamber opposite to the evaporation source.
- Evaporate metal (no rotation)
- Detach stencil from substrate
- Clean stencil
Stencil Lithography: Process description

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

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

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

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

References:

5. Nanoimprint Lithography

5.1 Overview

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

![Large Area Simulation of Imprints](image)

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

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

- **Aim:** full optimization loop(s)
- **Process Chain:**
  - design → simulation → stamp fabrication
  - selection of parameters → imprint → thickness measurement
  - pattern transfer

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:

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

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

References:


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 mm² 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.

References:

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
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.

![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).](image)

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).

![“Anomalies” in Simulation and Experiment](image)

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

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

5.3.1 Hard stamps

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

<table>
<thead>
<tr>
<th>Material</th>
<th>Young’s modulus (GPa)</th>
<th>Poisson’s ratio</th>
<th>thermal expansion (10⁻⁶ K⁻¹)</th>
<th>Knoop microhardness (kg mm²)</th>
<th>thermal conductivity (W m⁻¹ K⁻¹)</th>
<th>specific heat (J kg⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>silicon</td>
<td>131</td>
<td>0.28</td>
<td>2.6</td>
<td>1500</td>
<td>170</td>
<td>705</td>
</tr>
<tr>
<td>fused silica (SiO₂, bulk)</td>
<td>73</td>
<td>0.17</td>
<td>0.6</td>
<td>500</td>
<td>1-6</td>
<td>700</td>
</tr>
<tr>
<td>quartz (SiO₂, fused)</td>
<td>70-75</td>
<td>0.17</td>
<td>0.6</td>
<td>&gt;600 (8 GPa)</td>
<td>1.4</td>
<td>670</td>
</tr>
<tr>
<td>silicon nitride (Si₃N₄)</td>
<td>170-290</td>
<td>0.27</td>
<td>3</td>
<td>1450</td>
<td>15</td>
<td>710</td>
</tr>
<tr>
<td>Diamond</td>
<td>1050</td>
<td>0.104</td>
<td>1.5</td>
<td>8000-8500</td>
<td>630</td>
<td>502</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>200</td>
<td>0.31</td>
<td>13.4</td>
<td>700-1000</td>
<td>90</td>
<td>444</td>
</tr>
<tr>
<td>Tita nitride (TiN)</td>
<td>600</td>
<td>0.25</td>
<td>9.4</td>
<td>2000</td>
<td>19</td>
<td>600</td>
</tr>
</tbody>
</table>

Table 5.1. Comparison of different materials for hard stamps.

5.3.2 Soft and hybrid layered stamps

Soft stamps are often made from silicone or rubber. Particularly popular is Sylgard 184, a poly(dimethoxy siloxane) (PDMS), which is transparent in UV-light and can be used for UV-NIL. Replicas can be easily made of silicon or PMMA originals. Since PDMS is considered as too soft for sub-µm resolution, harder silicone (h-PDMS) is often used. For better handling, hybrid solutions have been
developed, e.g. by casting of PDMS on glass wafer-like substrates. Furthermore, hybrid polymer based molds (e.g. OrmoStamp®) combine ultra-high resolution capabilities (due to mechanical stability in sub-50 nm regime) and sufficient bulk flexibility.

Table 5.2: Comparison of different materials for polymeric working stamps

<table>
<thead>
<tr>
<th>Material</th>
<th>Characteristic</th>
<th>$\eta$ @ T and E</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-PDMS</td>
<td>precursor + initiator, fully cross-linked after curing</td>
<td>4.575 Pa·s, 1.8 MPa</td>
<td>elastomeric, thermocurable silicone (Sylgard 184 from Dow Corning Inc., USA) used for stamp copying by casting, elongation at break 160, significant porosity ($O_2$ absorbance, reduced life-time)</td>
</tr>
<tr>
<td>h-PDMS</td>
<td>four parts + solvent</td>
<td>tunable</td>
<td>improved mechanical stability for sub-1 μm features, elongation at break 7, moderate porosity (less $O_2$ absorbance, slight life-time improvement)</td>
</tr>
<tr>
<td>UV-curable precursor (UV-initiated crosslinking after spincoating or casting)</td>
<td>OrmoStamp®</td>
<td>0.4 ± 0.2 Pa·s, 0.650 GPa</td>
<td>organic-inorganic hybrid polymer for stamp copies used in T-NIL and UV-NIL, sub-10 nm resolution, high mechanical stability for aspect ratio $\geq 5$, long stamp lifetime (cf. PDMS), release force optimized (fluorine-based modification), high material-network density (insignificant $O_2$ absorbance)</td>
</tr>
</tbody>
</table>

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

5.4 The Replication technology toolbox

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

![Replication Technology Toolbox](image-url)

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

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

5.4.2 Serial patterning methods – Electron Beam Lithography (EBL)

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

![Figure 5.7: Exposure and pattern transfer for stamp fabrication by electron beam lithography and reactive ion etching.](image)

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

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

\[ \text{time} = \frac{\text{dose} \cdot \text{area}}{\text{current}} \]

in which the time \( t \) (in s) is calculated from the dose \( D \) required to expose the resist (in \( \mu \text{C/cm}^2 \)), the current \( I \) (in C/s) of the beam and the area \( A \) (in cm\(^2\)). For typical values of \( I = 1 \text{ nA} \) and \( D = 300 \mu \text{C/cm}^2 \), a time of 5000 min = 40 h can be calculated for an area of \( A = 1 \text{ cm}^2 \) (which would be fully covered by nanostructures with half the area exposed). For a moderate cost of 1'000 €/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.
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 17 nm resolution for the fabrication of microprocessors (2014: 14 nm). Since long the transition to alternative patterning methods is expected, however, DUV has marked considerable success in developing optical enhancement techniques to push the resolution limits beyond typical diffraction limits. New developments are immersion techniques and double exposure strategies. For the next generation of microchips, Extreme UV photolithography using 13.6 nm wavelength is expected to be mature to meet the requirements given by modern chip manufacturing. Although DUV tools are normally reserved for high throughput manufacturing, in NaPANIL we were able to use state-of-the-art equipment for the fabrication of multilevel stamps. The processes for generation multiple layers of exposures had to be developed because they deviate from the typical patterning schemes for transistor manufacturing. In total, a 4-level stamp with resolutions down to 100 nm and a total depth of 200 nm was manufactured. Masks for DUV-processes cost between 20'000 € and 40'000 €. The process is described in more detail in the second part of the Library of Processes.

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

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

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

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

References:

5.4.6 Working stamp fabrication

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

1) Improper handling or extensive use may damage masks and stamps, which need to be replaced. Some processes therefore spare the original and use it only for the generation of
working masks or stamps. Then only copies are used for processing and backups are generated to plan for damage when damage occurs or yield drops due to damage of single structures.

2) Scale-up of processes may need multiple identical masks and stamps for parallel use.

3) Stamps need to be made in different materials, with different hardness, material composition, flexibility or optical properties. E.g. transparent stamps in quartz may be needed for UV-NIL while originals are easier to be made on opaque silicon substrates. The same strategy is needed for masks used for X-ray lithography, where thick gold absorber structures instead of thin chromium layers are needed. For roll-to-roll processes, bendable stamp with metal or polymer backbone may be needed and are better to be fabricated by copying from flat wafer-like stamp substrates than using the flexible backbone in electron beam writers or mask aligners. Also for non-fast devices bendable stamps are needed and can be used in processes e.g. by crowning and thermoforming to generated nanostructure reliefs on on lens-like structures and calottes.

4) Working stamps in materials such as Hybrid Polymers (e.g. ORMOCER®-based OrmoStamp® commercially available from NaPANIL partner micro resist technology GmbH) are low-cost alternative to electroplated stamps. They can be used for several 10's or 100's of replicas before degradation sets in. In some cases, disposable strategies (“lost mold” or one time stamp) are employed to avoid any cross-talk and proliferation of defects from one replication to the next (e.g. to encapsulate particles which are on the substrate).

5) Copies can be fabricated on special substrates, e.g. with a pre-machined mesa (i.e. an elevated area defining the stamp area which is separated from the stamps' holder), which may be needed for S&R processes.

6) Inverse tone of masks may be needed to facilitate processing, e.g. using NIL and reactive ion etching (RIE) the stamp copy automatically has the inverse polarity. Therefore for generation of polarities identical of the original (the second generation), the copying process has to be repeated with the first generation copy.

7) Stamp copies can exhibit modified structures, e.g. with different line width, sidewall inclination and reduced roughness for easier demolding. This can be done by overetching or modified reflow techniques, e.g. the so-called structure perfection by liquification (SPEL). Particularly interesting is aspect ratio enhancement. This enables to use originals with low aspect ratio and transform them into stamps with higher aspect ratio which are difficult to fabricate or more prone to defects and demolding errors.

8) Copies can also simply be reserved for process characterization and comparison with replicated structures. E.g. if replicas are made in brittle materials (e.g. sol-gel), they can be cleaved and used to examine cross-sections of structures while the original is preserved. Also different antiadhesive coating strategies can be tested and comparisons between stamps of the same generation can be made.

9) Multiple stamp copies can be used to recombine them to a large area stamp. Instead of aligning and assembling different stamps in a matrix, step & repeat imprint techniques have been developed to stitch stamp fields together on the same substrate or resist. The replicated large area structure can then be directly used for pattern transfer or to manufacture a large area stamp, e.g. for roll-to-roll embossing. Particularly interesting are step&repeat NIL processes where stamps are not just stitched together in a orthogonal manner, but with a defined pattern of rotated imprints.

10) Any kind of adding structures, e.g. frames, large area patterns such as antireflective gratings or macroscopic alignment structures (e.g. with holes or registration marks), auxiliary cavities for residual layer equilibration can be achieved by mix and match techniques. This can be done by double imprint (nano after micro) with different stamps, by additional scanning laser or electron beam lithography or by photolithography. Backside patterning of the stamp or generation of stamps with surface reliefs on both sides may also help to improve process conditions, increase yield, functionality or throughput.

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

In the past mask shops using advanced electron beam patterning services have been established for the fabrication of masks. This activity has also been extended to special services for non-standard processes such as thick resists or direct writing on silicon wafers. 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 structures, 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]

5.5.1 Treatment in liquid phase

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

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

![Fluorinated organosilane as molecular anti-adhesive layer](image)

**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:**
5.6 Resists, substrates and tools

5.6.1 Thermoplastic NIL-materials (thermal-NIL)

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

<table>
<thead>
<tr>
<th>Resists (( M_w ))</th>
<th>( T_g, T_{im} )</th>
<th>( \eta @ T ) and ( E )</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(methyl methacrylate) (PMMA)</td>
<td>( T_g 100-120 , ^oC ), ( T_{im} 140-190 , ^oC )</td>
<td>( 10^5 - 10^7 ) Pas @ 170 , ^oC; 380-540 MPa</td>
<td>the “classic” NIL resist, also suitable for grayscale electron beam lithography</td>
</tr>
<tr>
<td>poly(styrene) (PS)</td>
<td>( T_g 100 , ^oC ), ( T_{im} 120-180 , ^oC )</td>
<td>( 10^7 - 10^8 ) Pas @ 170 , ^oC;</td>
<td>integrated optics, bio-applications</td>
</tr>
<tr>
<td>NEB22 (3k)</td>
<td>( T_g 80 , ^oC )</td>
<td></td>
<td>negative EBL resist, high etch resistance in fluoro- and chloro-based plasmas</td>
</tr>
<tr>
<td>mr-I 7000R*</td>
<td>( T_g 50 , ^oC ), ( T_{im} 120-140 , ^oC )</td>
<td>( &lt; 3 \times 10^4 ) Pas @ 120 , ^oC</td>
<td>low ( T_g ) NIL polymer with very good flow ability and high plasma etch resistance, effective release force reduction due to fluorinated additives, 12 nm resolution proved</td>
</tr>
<tr>
<td>mr-I 8000R*</td>
<td>( T_g 105 , ^oC ), ( T_{im} 150-180 , ^oC )</td>
<td>( &lt; 10 \times 10^5 ) Pas @ 175 , ^oC</td>
<td>NIL polymer with very good flow ability, good thermal stability and high plasma etch resistance, effective release force reduction due to fluorinated additives</td>
</tr>
<tr>
<td>mr-I T85*</td>
<td>( T_g 85 , ^oC ), ( T_{im} 130-150 , ^oC )</td>
<td>( 300 \times 10^8 ) Pas @ 140 , ^oC</td>
<td>thermoplastic NIL polymer for micro optical and bio applications with high chemical stability and excellent UV and optical transparency</td>
</tr>
<tr>
<td>SIPOL*</td>
<td>( T_g 63 , ^oC ), ( T_{im} 110-130 , ^oC )</td>
<td></td>
<td>thermoplastic NIL polymer with high Si content used for aspect ratio enhancement (AR &gt;&gt; 3) using a bilayer system with organic transfer layer UL1</td>
</tr>
<tr>
<td>mr-I 9000M*</td>
<td>( T_g 35 , ^oC ) (before imprint, no ( T_g ) after imprint), ( T_{im} 90-100 , ^oC )</td>
<td></td>
<td>low ( T_g ) thermally curable NIL resist allowing almost isothermal imprint (demolding at 100(^o)C) with high plasma etch resistance, particularly suited for demanding sub-100 nm patterns</td>
</tr>
<tr>
<td>mr-NIL 6000E*</td>
<td>( T_g 1 , ^oC ) (before imprint, no ( T_g ) after imprint), ( T_{im} 65-70 , ^oC )</td>
<td>( &lt; 0.2 \times 10^{10} ) Pas @ 100 , ^oC</td>
<td>low ( T_g ) NIL resist for combined thermal and UV-NIL (STU™ from Obducat), mix-and-match, multi-level patterning, reverse UV-NIL</td>
</tr>
</tbody>
</table>

* Commercially available from NaPANIL partner *micro resist technology* GmbH, Berlin, Germany
5.6.2 UV-curable NIL materials (UV-NIL)

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

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

<table>
<thead>
<tr>
<th>Resist</th>
<th>Characteristic</th>
<th>η (film)</th>
<th>Comments</th>
</tr>
</thead>
</table>
| mr-UVCur21* | 100% organic, sensitive to O$_2$, low viscosity | 30 mPas | 1. Solvent containing version for broad film thickness range (40 nm up to 1 μm) using spin-coating  
2. Solvent-free version (mr-UVCur21SF) for dispensing |
| mr-XNIL26*  | 100% organic, sensitive to O$_2$ | 140 mPas | 1. formulation with high amount of fluorinated components for imprints with bare stamps without anti-sticking layer due to inherent release properties  
2. solvent-free version (mr-XNIL26SF) for dispensing |
| AMONIL**    | Si- and Zr-containing, not sensitive to O$_2$ | 50 mPas | UV-NIL resist for soft (PDMS) stamps  
Not compatible to oxygen plasma |
| mr-NIL200*  | 100% organic, not sensitive to O$_2$ | >200 mPas | Processable using soft stamps (PDMS, PFPE) |
| mr-UVCur26SF XPC* | 100% organic, sensitive to O$_2$ | 16 mPas | Formulation for inkjet dispensing at room temperature |

* from NaPANIL partner micro resist technology GmbH, Berlin, Germany  
** from NaPANIL partner AMO GmbH, Aachen, Germany
5.6.3 Resists with inherent antiadhesive properties

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

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

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

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

References:
5.6.5 Sol-gel materials and hybrid polymers

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

1) Protective coatings made from sol-gel materials are hard films on glass or polymer substrates. The aim is to imprint a pattern into a still viscous sol-gel precursor that will be transferred into a hard film with high fidelity by the following process route: Drying, thermal annealing, sintering (vitrification). The removal of the remaining liquid (solvent) phase is typically accompanied by a significant amount of shrinkage and densification. The thermal treatment, or firing process, is often necessary in order to favor further polycondensation and enhance mechanical properties and structural stability via final sintering, densification and grain growth. One of the distinct advantages is that densification is often achieved at a much lower temperature than with other techniques. Due to their complex chemistry, the lifetime of its precursors is often restricted.

2) Hydrogen silsesquioxane (HSQ) by Dow Corning has been successfully used as high-resolution resist used for exposure with electrons or photons (EUV 13.6 nm) but can also be patterned by NIL. After cross-linking and developing, the HSQ material becomes a layer of SiO₂. This mechanically tough coating is stable in vacuum, at extremely high temperatures, and against the effects of radiation. Also here, the precursor lifetime is often restricted.

3) Inorganic-organic hybrid polymers such as the ORMOCER®s are designed to be used without firing step, which means that the organic component is not removed (low shrinkage). Consequently, their mechanical, chemical and thermal properties are different from glassy materials. Furthermore, they exhibit optimized chemical stability and thus increased lifetime (at least 6 months). The application of hybrid polymers in NIL is twofold:

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

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

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

References:

* ORMOCER® is a registered trademark of the Fraunhofer-Gesellschaft zur Förderung der Angewandten Forschung in Deutschland e.V.
* OrmoStamp®, OrmoClear®, and OrmoComp® are registered trademarks of NaPANIL partner micro resist technology GmbH.
5.7 Machines and tools using molding processes

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

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

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

Pressing mechanism

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

![Hot Embossing Equipment](image)

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

Pressure Equilibration – Cushion / Compliance Layer

A thick (1 mm) sheet of standard silicone, called PDMS (polydimethylsilane), is sufficient to equilibrate any kind of unevenness, e.g. caused by substrate undulations or even dust particles. The stamp can bend around these particles and leaves some “halo”, where the imprint is not complete. PMDS can be taken from any kind of workshop. When made hot, it tends to glue, which is an advantage to
keep the substrate or stamp fixed, but if not wished, a polyimide layer can be used as an intermediate layer for separation. The cushion layer can be placed at the backside of the stamp (or the substrate). Normal PDMS will expand when pressed (e.g. some cm over the borders of a 100 mm wafer). The initial size should be slightly bigger than the stamp.

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

Figure 5.19: Nanoimprint machine from EV Group based on a mask aligner.
Figure 5.20: Nanoimprint machine from EV Group for S&R UV-NIL.

Figure 5.21: Nanoimprint machine from SÜSS based on a mask aligner for hybrid soft masks.
Figure 5.22: Jenoptik HEX03 nanoimprint machine with and integrated adapter for a Süss alignment fixture for an anodic bonder. Alignment is possible by using the appropriate mask aligner.

Figure 5.23: Schematic of a fast imprint with an alignment fixture: a) alignment and clamping of stamp (top) and substrate (bottom), b) contact of upper plate and down-movement, c) begin of molding upon contact to lower plate, d) pressure release and lift-up, e) cooling, f) manual demolding outside the press. For fast processing, the press plates are kept at constant (molding) temperature.
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.
5.7.2 Roll-to-roll embossing tools (R2R)

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

Figure 5.27: Schematic of different roll-to-roll processes.
5.7.3 Micro injection molding tools (IM)

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

Figure 5.29: Left side: Clamping system for a 4” wafer used as insert for injection molding. Right side: Tool with ejection side of the injection mold with structured 4” silicon wafer.
5.8 Processes – Part 1: Thermal Nanoimprint with simple pattern transfer

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

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

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:
Window Opening + Substrate Etching

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

<table>
<thead>
<tr>
<th>Short description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching of the substrate can be done as in normal resist processes. There is no major difference to optical or electron beam lithography.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Advantages with respect to other pattern transfer processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Etching is the process of choice in industry because the pattern transfer is more precise than in additive processes.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suitable etching gases have to be found for RIE with high selectivity.</td>
</tr>
</tbody>
</table>

References:


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:**


**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:
5.9 Processes – Part 2: Process variants for resist patterning

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

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

<table>
<thead>
<tr>
<th>type of NIL / properties</th>
<th>thermal NIL hot embossing</th>
<th>UV-assisted NIL UV-imprint</th>
</tr>
</thead>
<tbody>
<tr>
<td>basic process sequence</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1) spin-coat thermoplastic film</td>
<td>1) dispense liquid resin</td>
<td></td>
</tr>
<tr>
<td>2) place stamp on film</td>
<td>2) parallel alignment of stamp with defined gap</td>
<td></td>
</tr>
<tr>
<td>3) heat until viscous</td>
<td>3) imprint at low pressure</td>
<td></td>
</tr>
<tr>
<td>4) emboss at high pressure</td>
<td>4) expose with UV-light through stamp and crosslink</td>
<td></td>
</tr>
<tr>
<td>5) cool until solid</td>
<td>5) demold stamp</td>
<td></td>
</tr>
<tr>
<td>6) demold stamp</td>
<td></td>
<td></td>
</tr>
<tr>
<td>pressure $p$</td>
<td>20-100 bar</td>
<td>0-5 bar</td>
</tr>
<tr>
<td>temperature $T_{mold}$</td>
<td>100-200°C</td>
<td>20°C (ambient)</td>
</tr>
<tr>
<td>temperature $T_{demold}$</td>
<td>20-80°C</td>
<td>20°C (ambient)</td>
</tr>
<tr>
<td>Resist</td>
<td>solid, thermoplastic</td>
<td>liquid, UV-curable</td>
</tr>
<tr>
<td>$T_g \approx 60-100°C$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>viscosity</td>
<td>$10^3-10^7 \text{ Pa}\cdot\text{s}$</td>
<td>$10^3-10^4 \text{ Pa}\cdot\text{s}$</td>
</tr>
<tr>
<td>stamp material</td>
<td>Si, SiO$_2$, OrmoStamp$^\oplus$ opaque</td>
<td>glass, SiO$_2$, OrmoStamp$^\oplus$ transparent</td>
</tr>
<tr>
<td>stamp area</td>
<td>full wafer, $\leq$ 300 mm diameter</td>
<td>25x25 cm$^2$, limited by control of gap</td>
</tr>
<tr>
<td>stamp contact</td>
<td>facilitated by bending</td>
<td>planarization layer</td>
</tr>
<tr>
<td>embossing time</td>
<td>from sec to minutes</td>
<td>$&lt; 1 \text{ min (per exposure)}$</td>
</tr>
<tr>
<td>Advantage</td>
<td>low-cost, large area equipment and stamps</td>
<td>room temperature, low pressure, alignment through stamp</td>
</tr>
<tr>
<td>Challenge</td>
<td>process time, thermal expansion due to thermal cycle</td>
<td>step and repeat needed for large areas</td>
</tr>
<tr>
<td>development needed</td>
<td>alignment, residual layer homogeneity</td>
<td>material variety and resist stripping</td>
</tr>
<tr>
<td>Hybrid approaches</td>
<td>thermost set resists: embossing and curing before demolding</td>
<td>thermoplastic resists: hot molding and UV-curing before demolding</td>
</tr>
<tr>
<td>Advantage (hyb. app.)</td>
<td>low temperature variation cycle: demolding at high temperature possible</td>
<td>solid resist: full wafer single imprint possible</td>
</tr>
</tbody>
</table>
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:**


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

Main application
- Step & Flash Imprint Lithography (SFIL) process.

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

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

References:
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:
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:**

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

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

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

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

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

References:
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:


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 lithography.

References:
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 Tg) and reflow temperature (around the Tg of the original resist), the imprinted structures and nonexposed areas are not affected by reflow.

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

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

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

References:
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.](image)

**Process description: Step and Stamp Nanoimprint Lithography**
Sequential imprint method, in which stamp heating and cooling are repeated in each pressure applying cycle.

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

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

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

**References:**


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

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

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

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

Company: ThunderNIL by NaPANIL partner Dr. Massimo Tormen from IOM-CNR.
- Pulsed NIL and nanopatterning of thermoplastic polymer films within ~100 µs.
- Design and manufacturing of ultrafast thermal machines

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

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.

**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.

<table>
<thead>
<tr>
<th>Nanoimprint Process</th>
<th>Thermal NIL</th>
<th>UV-NIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaPANIL partner</td>
<td>VTT (ICN)</td>
<td>AMO</td>
</tr>
<tr>
<td>Tool</td>
<td>NPS300</td>
<td>EVG 770</td>
</tr>
<tr>
<td>Manufacturer</td>
<td>SET S.A.</td>
<td>EV Group</td>
</tr>
<tr>
<td>Stamp holder</td>
<td>50x50mm²</td>
<td>25x25mm²</td>
</tr>
<tr>
<td>Typical stamp size</td>
<td>&lt; 10x10mm² (4x4 mm²)</td>
<td>25x25mm²</td>
</tr>
<tr>
<td>Substrate size</td>
<td>20-200 mm (round or square)</td>
<td>Circular 150 or 200 mm</td>
</tr>
<tr>
<td>Max. imprint force (N)</td>
<td>150 (4000 optional)</td>
<td></td>
</tr>
<tr>
<td>Temperature range (°C)</td>
<td>Room temperature to 450 °C</td>
<td>Room temperature</td>
</tr>
<tr>
<td>Cycle time (s)</td>
<td>&gt; 30 s</td>
<td></td>
</tr>
<tr>
<td>Rotated imprint</td>
<td>±180° (with head rotation)</td>
<td></td>
</tr>
<tr>
<td>Stitching distance (nm)</td>
<td>&lt; 100 nm</td>
<td>N/A</td>
</tr>
<tr>
<td>Conditions</td>
<td>Low pressure environment</td>
<td></td>
</tr>
</tbody>
</table>
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.

Reference:

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.

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**Process description: Micro-Injection Molding (µIM)**

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

**Stamp and materials**

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

**Process parameters**

- Typically thermoplastic polymers are used which change their thermomechanical properties from solid to viscous. The mold is kept below or near to the 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.

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**References:**


**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:

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:

\[ \rho = \frac{r_2}{r_2} = \tan(\Psi) \exp(\Delta) \]

with \( \Psi = \arctan \left( \frac{r_2}{r_2} \right) \) and \( \Delta = \delta_p - \delta_s \), called scatterometric angles, linked to two intensities, \( I_s \) and \( I_c \):

\[ I_s = \sin(2\Psi) \cdot \sin(\Delta) \]
\[ I_c = \sin(2\Psi) \cdot \cos(\Delta) \]

\( \Psi \) and \( \Delta \) 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.

Optical signature

Inverse problem resolution

Depends on:
- Experimental conditions
- Optical properties
- Geometry

Experimental setup
- Ellipsometry
- Reflectometry
- …

Parametric optimization
- Levenberg-Marquardt algorithm
- Library method
- Neural Network

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

Scatterometry exhibits high accuracy and high speed for lines on silicon wafers. It can be used to measure line width, imprinted depth and residual thickness, with some limitations: the grating period has to be smaller than 2 µm, and the patterns have to be uniform. In these cases, it is also possible to introduce other parameters such as top rounding or slope of the pattern sidewalls.
Circular imprinted pillars have been characterized by scatterometry. Patterns need a specific complex model to take into account the circular section. Scatterometry can be used to measure such structures, but computing time is main limitation. The accuracy of measurement is also more dependent on pattern uniformity, as compared to the case of lines.

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

### 5.14.2 Measurements of lines and 3-D structures: Example

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

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

An introduction into nanoimprint for engineers and scientists:


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


Review article with emphasis on nanorheology and material deformation:


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

Figure 5.57: Nanoimprint Lithography in the Springer Handbook on Nanotechnology.
PART II: APPENDIX - PROCESS LIBRARY

Content

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

1. Tools and Machines

Contributions to this section of the library are from

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

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

PTMTEC OY / Finland
Dr. Tapio Mäkelä

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

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

NILT - Denmark
Theodor Nielsen
1.1 Compact NIL-2-GO tool from NILT

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

Process: thermal nanoimprint lithography

Figure: The frontside of the CNI Tool.

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

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

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

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

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

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

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

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

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

Major challenges: Flatness, compliance.

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

References:

Contact information:
Theodor Nielsen, CEO
NIL Technology ApS
Diplomvej 381
2800 Kongens Lyngby, Denmark
Direct: +45 3171 9036
E-mail: tkn@nilt.com
Web: www.nilt.com

LoP2012_NIL001_CNI-Tool
## Compact NIL-2-GO Nanoimprint tool

**Process:** thermal nanoimprint lithography

<table>
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<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
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<td><strong>1.0</strong></td>
<td><strong>Process 1: Wafer preparation</strong></td>
<td><strong>Silicon wafer format</strong></td>
</tr>
<tr>
<td>1.1</td>
<td>wafer selection and preparation</td>
<td>What it should work</td>
</tr>
<tr>
<td></td>
<td></td>
<td>critical issues</td>
</tr>
<tr>
<td>1.2</td>
<td>System principle with flexible stamp</td>
<td>how it should work</td>
</tr>
</tbody>
</table>

**1.2 System principle with flexible stamp**

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**

**2.1 Proof-of concept on a hotplate**

**System**

The imprint process in the compact-system. The total size of the system (excluding hotplate and pressure connections) is 128 mm diameter and 3 cm thickness. (a) The bottom chuck (PTFE sealing layer not shown).

### 2.2 Proof-of concept on a hotplate

**Stamp/substrate mounting**

The stamp is mounted on the bottom chuck and a substrate is placed on top.

### 2.3 Proof-of concept on a hotplate

**Imprint**

Imprint in progress. The entire system is placed on a hotplate.

Typical parameter values employed for imprints.

\[
T_{\text{Imprint}} = 190 \, ^{\circ}\text{C} \\
T_{\text{Separation}} = 23 \, ^{\circ}\text{C}
\]
<table>
<thead>
<tr>
<th>2.4 Proof-of concept on a hotplate</th>
<th>De-mounting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imprint is complete. Due to the integrated demolding capability, the substrate is easily removed by hand.</td>
<td></td>
</tr>
</tbody>
</table>

End of Process 2

3.0 Process 3: 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 atmospheric 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 micrometer-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.
Thermal nanoimprint with NIL-2-GO tool: Process description

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

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

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

Restrictions – and how to deal with them
- Pressure regime may be modified (contact pressure during heating instead of full pressure)
- No evacuation before imprint, automated demolding only with segmented flexible stamp
1.2 Step&repeat thermal NIL process with NPS300

Step&repeat thermal NIL for master enlargement with NPS300

Process: thermal nanoimprint lithography

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

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

Application: Optical grating for light directing elements

Keywords: Thermal nanoimprint, Step&repeat, surface enlargement

Partner: VTT Technical Research Centre of Finland, VTT
Address: Helsinki, FI
Web-Address: http://www.vtt.fi
Process: Step & Repeat thermal NIL
Responsible: Tomi Haatainen
E-mail: tomi.haatainen@vtt.fi

Partner: S.E.T. SAS (Smart Equipment Technology)
Address: 74490 Saint Jeoire, France
Process: NPS300 Step&stamp Tool
Responsible: Gilbert Lecarpentier
E-mail: glecarpentier@set-sas.fr

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

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

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

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

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

References:
### Step&repeat thermal NIL for master enlargement with NPS300

#### Process: Thermal nanoimprint lithography

<table>
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<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
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</thead>
<tbody>
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<td><strong>1.0 Process 1: Primary silicon master</strong></td>
<td>EBL and dry etching</td>
<td><strong>how it should work</strong> <strong>critical issues</strong></td>
</tr>
<tr>
<td><strong>1.1 Substrate preparation</strong></td>
<td>Silicon wafer 4” &lt;100&gt;</td>
<td><strong>what</strong> <strong>how it should work</strong> <strong>critical issues</strong></td>
</tr>
<tr>
<td><strong>1.2 Resist coating</strong></td>
<td>Spin-coating EBL resist. Prebake</td>
<td><strong>what</strong> <strong>how it should work</strong> <strong>critical issues</strong></td>
</tr>
<tr>
<td><strong>1.3 Pattern definition</strong></td>
<td>Electron beam lithography</td>
<td><strong>what</strong> <strong>how it should work</strong> <strong>critical issues</strong></td>
</tr>
<tr>
<td><strong>1.4 Pattern transfer into Si</strong></td>
<td>Dry etching</td>
<td><strong>what</strong> <strong>how it should work</strong> <strong>critical issues</strong></td>
</tr>
</tbody>
</table>

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 mm² | **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 thermoplastic 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 4x4mm², micrometer features with sizes of down to 2 µm and height of ~ 200nm. Stamp Temperature: 140 °C, substrate temperature 70 °C, cycle time ~ 3 minutes (without collimation and arm movements).
Nanoimprint Machine from SET: NPS 300

**KEY FEATURES**

- Aligned Hot & Cold Embossing
- Step & Repeat mode
- Sub-20 nm embossing capability
- Sub micron (250 nm) stamp-to-wafer alignment
- Rotation head: ±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

<table>
<thead>
<tr>
<th>Project leader:</th>
<th>PTMTEC</th>
<th>Process:</th>
<th>R2R UV-NIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address:</td>
<td>Jousimiehentie 4 I 00740 Helsinki, Finland</td>
<td>Responsible:</td>
<td>Tapio Mäkelä</td>
</tr>
<tr>
<td>Web-Address:</td>
<td><a href="http://www.ptmtec.com">http://www.ptmtec.com</a></td>
<td>E-mail:</td>
<td><a href="mailto:tapio.makela@ptmtec.com">tapio.makela@ptmtec.com</a></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Partner:</th>
<th>VTT Technical Research Centre of Finland, VTT</th>
<th>Process:</th>
<th>Step &amp; Repeat thermal NIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address:</td>
<td>Helsinki, FI</td>
<td>Responsible:</td>
<td>Tapio Mäkelä</td>
</tr>
<tr>
<td>Web-Address:</td>
<td><a href="http://www.vtt.fi">http://www.vtt.fi</a></td>
<td>E-mail:</td>
<td><a href="mailto:tapio.makela@vtt.fi">tapio.makela@vtt.fi</a></td>
</tr>
</tbody>
</table>

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:


Contact information:

Dr. Tapio Mäkelä
PTMTEC OY
Jousimiehentie 4 I 123
00740 Helsinki
Finland

LoP2012_NIL003_UV-R2R-Tool
## Continuous roll-to-roll UV-NIL process

### Process: UV-nanoimprint lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td><strong>Process 1: Substrate, Ink and Mold</strong></td>
<td><strong>how it should work</strong></td>
</tr>
<tr>
<td>1.1</td>
<td><strong>Substrate selection</strong></td>
<td>Flexible ca. 100 micrometre thick PET film with good adhesion properties</td>
</tr>
<tr>
<td>1.2</td>
<td><strong>Ink modification</strong></td>
<td>Viscosity should be in the range of 1000 cP. No pre-treatment needed if wetting and adhesion good</td>
</tr>
<tr>
<td>1.3</td>
<td><strong>Flexible mold</strong></td>
<td>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.</td>
</tr>
</tbody>
</table>

End of Process 1

| 2.0 | **Process 2: Polymer coating for UV lithography** | **for UV lithography** |
| 2.1 | **Reverse gravure coating of UV-polymer** | 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 microscopy/camera**

inline meteorology can be inserted into tool

---

**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 vario-thermal injection molding tool

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

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

Keywords: thermal nanoimprint, variothermal processing, injection molding

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

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

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

Process: Thermal Nanoimprint
Responsible: Helmut 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 50x50mm².

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

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

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

References:

Contact information:
Prof. Dr. Per Magnus Kristiansen
University of Applied Sciences and Arts FHNW
Institute of Polymer Nanotechnology
Klosterzelgstrasse 2
CH-5210 Windisch, Switzerland

LoP2012_NIL004_variothermIM-Tool
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. 50x50mm²) arrays of functional micro- and nanostructures. Rapid variotherm temperature control was realized by a thermally de-coupled mounting stage with fluidic channels optimized for heat transfer. A two-chamber water heating/cooling system (HB Therm) is used. For in-situ process monitoring, the variothermal molding tool is equipped with multiple pressure and temperature sensors which enable exact determination of process and rheological parameters in-situ during the injection molding process. Data acquisition is accomplished by a dedicated software tool developed by Priamus System Technologies GmbH.

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

**Thermal injection molding with variothermal injection molding tool: Process description**

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

**Advantages of variothermal injection molding**

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

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

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

**Restrictions – and how to deal with them**

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

Contributions to this section of the library are from

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

ICN, Barcelona, Spain
Dr. Vincent Reboud / Dr. Nikolaos Kehagias / Prof. Dr. Clivia Sotomayor-Torres

AMO GmbH, Aachen, Germany
Dr. Ulrich Plachetka

CRF Fiat - Orbassano/Italy
Dr. Vito Lambertini

CEA-LETI MINATEC- Grenoble/France
Dr. Stéfan Landis

LTM-CNRS - Grenoble/France
Dr. Cécile Gourgon

DTU - Lyngby/Denmark
Prof. Dr. Anders Kristensen

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

IOM CNR - Trieste/Italy
Dr. Massimo Tormen

University of Glasgow - Glasgow/ United Kingdom
Dr. Nikolaj Gadegaard / Dr. Mathis Riehle / Dr. Kris Seunarine / Prof. Dr. Christopher Wilkinson
2.1 Stamps for Nanoimprint Lithography

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

Process: nanoimprint lithography

<table>
<thead>
<tr>
<th>Figure:</th>
<th>Process:</th>
<th>Application:</th>
</tr>
</thead>
<tbody>
<tr>
<td>SEM micrograph of a Grating with 100 nm period etched in Si using dry etching process (ICP) and PMMA resist as an etch mask.</td>
<td>Electron beam lithography on positive or negative resists and plasma etching</td>
<td>NIL stamps for optical, photonic, electronic or micro/nano-fluidics.</td>
</tr>
</tbody>
</table>

**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):


**Contact information:**
Dr. Massimo Tormen
CNR-Istituto Nazionale per la Fisica della Materia
Laboratorio Nazionale TASC
Area Science Park - Basovizza
S.S.14 - km163,5
I-34012 Basovizza - Trieste (TS), Italy

**LoP2007_NIL001_Stamps for NIL**
## Stamps for Nanoimprint Lithography

### Process: nanoimprint lithography

<table>
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<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>What</strong></td>
<td>how it should work</td>
<td>critical issues</td>
</tr>
<tr>
<td>1.0 Process 1: Wafer preparation</td>
<td>Silicon wafer format</td>
<td></td>
</tr>
<tr>
<td>1.1 wafer selection and preparation</td>
<td>standard Si substrate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Si substrate, 4&quot;, &lt;100&gt;, thickness d=400-600 µm one side polished</td>
<td></td>
</tr>
<tr>
<td>1.2 substrate preparation</td>
<td>pretreatment</td>
<td></td>
</tr>
<tr>
<td></td>
<td>no pre-treatment needed (if wafer is clean an hydrophilic)</td>
<td></td>
</tr>
<tr>
<td><strong>End of Process 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 Process 2: Resist coating</td>
<td>for electron lithography</td>
<td></td>
</tr>
<tr>
<td>2.1 dispensing of resist</td>
<td>resist</td>
<td></td>
</tr>
<tr>
<td></td>
<td>no priming, PMMA 4 % in ethyllactate (safer solvent) (EL) (600k), process lab (clean room)</td>
<td></td>
</tr>
<tr>
<td>2.2 coating resist (homogeneous layer)</td>
<td>spincoating of PMMA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>speed: 3000rpm, acceleration: 3000rpm/sec, time: 45 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-&gt; ~200 nm thickness</td>
<td></td>
</tr>
<tr>
<td>2.3 post bake</td>
<td>solvent evaporation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>bake 1 min @ 170°C (hot plate)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alternative: convection oven at 180°C, for 30 min</td>
<td></td>
</tr>
<tr>
<td><strong>End of Process 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0 Process 3: Lithography</td>
<td>Electron beam lithography</td>
<td></td>
</tr>
</tbody>
</table>
### 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/cm²

**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. C₄F₈ 45sccm / O₂ 3 sccm /SF₆ 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$_2$O$_2$:H$_2$SO$_4$ (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 anymore 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

<table>
<thead>
<tr>
<th>Partner</th>
<th>AMO GmbH</th>
<th>Process: LIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>52074 Aachen, Germany</td>
<td>Responsible: M. Möller</td>
</tr>
<tr>
<td>Web-Address</td>
<td><a href="http://www.amo.de">http://www.amo.de</a></td>
<td>E-mail: <a href="mailto:moeller@amo.de">moeller@amo.de</a></td>
</tr>
</tbody>
</table>

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:

Contact information:
M. Moeller
Otto-Blumenthal-Strasse 25
52074 Aachen
Germany

LoP2012_NIL005_LIL-Stamps
# Laser Interference Lithography

**Process:** LTIL

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Substrate preparation</strong></td>
<td>how it should work</td>
<td>critical issues</td>
</tr>
<tr>
<td>1.1 Preparation of BARC layer</td>
<td>Spin coating of BARC (DUV5214) 45sec.@1800rpm -hardbake on hotplate 60sec@200°C</td>
<td>BARC= bottom antireflection coating</td>
</tr>
<tr>
<td>1.2 Preparation of DUV resist</td>
<td>Spin coating of standard DUV pos. resist for 248nm 30sec.@3000rpm -bake 60sec.@130°C</td>
<td></td>
</tr>
<tr>
<td>1.3 Exposure for 1D-Gratings</td>
<td>1st exposure -exposure dosis 40mJ/cm² -α=15.24° → 500nm period ( p_1 = \frac{\lambda}{2 \sin(\alpha)} )</td>
<td></td>
</tr>
<tr>
<td>1.4 Second exposure for Moiré double patterning</td>
<td>2nd exposure under rotated substrate angle ( \beta=2.86° ) → 10µm period ( p_2 = p_1/(2\sin(\beta)) )</td>
<td></td>
</tr>
<tr>
<td>1.5 Development of double patterned grating</td>
<td>development of resist in MF26@30sec.</td>
<td></td>
</tr>
<tr>
<td>1.6 Process result</td>
<td>After LIL process and standard etching into Silicon a double grating with two distinct periods of 500nm and 10µm is visible</td>
<td></td>
</tr>
<tr>
<td>1.7 Process result close-up</td>
<td>Close-up of etched LIL double grating in Silicon with two distinct periods of 500nm and 10µm</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Figure:</th>
<th>Scheme of fabrication of a nickel master tool with a few-period sawtooth grating. The released nickel shim is used for hot emboss the structure defined on its edge.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Main technologies required:</td>
<td>Electron beam lithography, Soft and Deep X-ray lithography, electroplating and assembly (modified LIGA)</td>
</tr>
<tr>
<td>Ancillary processes used:</td>
<td>Optical lithography, wet etching, sputtering.</td>
</tr>
<tr>
<td>Application:</td>
<td>Stamp for Step and stamp NIL for large area optical sheets for backlighting of flat panel displays.</td>
</tr>
<tr>
<td>Keywords:</td>
<td>deep X-ray lithography, electron beam lithography, LIGA, electroplating, blazed gratings, sawtooth gratings, high aspect ratio structures, nickel master stamps, edge embossing</td>
</tr>
</tbody>
</table>

| Project leader: | TASC Laboratory |
| Address: | 34012 Basovizza-Trieste, Italy |
| Web-Address: | http://www.tasc-infm.it |
| Process: | XR-lithography, electroplat. |
| Responsible: | Massimo Tormen |
| E-mail: | tormen@tasc.infm.it |

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

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

| Partner: | VTT Technical Research Centre of Finland, VTT |
| Address: | Helsinki, FI |
| Web-Address: | http://www.vtt.fi |
| Process: | Step & Repeat thermal NIL |
| Responsible: | Tomi Haatainen |
| E-mail: | tomi.haatainen@vtt.fi |

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

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

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

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


Contact information:
Dr. Massimo Tormen
CNR-Istituto Nazionale per la Fisica della Materia
Laboratorio Nazionale TASC
Area Science Park - Basovizza
S.S.14 - km163,5
I-34012 Basovizza - Trieste (TS), Italy

LoP2012_NIL006_Sawtooth-Stamps
## Saw-tooth stamps

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

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0 Process 1: Primary X-ray Mask fabrication (for soft X-rays)</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 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%), 2.1 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/cm² 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 |
methacryloxypropyltrimethoxy 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/cm³ were absorbed by PMMA at the bottom of the deposited layer. A 104 µm thick graphite filter was interposed in the optical path as a cut-off for the low energy end of the beam spectrum, resulting in a higher dose uniformity as a function of the depth in the PMMA layer.

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-aminoethanol-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 titanium oxide in a 5 M KOH solution at 75 °C overnight.

End of Process 3
<table>
<thead>
<tr>
<th>4.0</th>
<th>Process 4: Pattern enlargement</th>
</tr>
</thead>
</table>
| 4.1 | **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 (∅ 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 mi-
|     | croscopy 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

**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. micro-nano-fluidics).

**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:** 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. cm²) can be accomplished by step & repeat replication approaches.

**References:**


**Contact information:**
Dr. Helmut Schift
Paul Scherrer Institut
Laboratory for Micro and Nanotechnology
5232 Villigen PSI
Switzerland
e-mail: helmut.schift@psi.ch
URL: http://www.psi.ch

**LoP2012_NIL007_3D-Stamps for NIL**
### Three-dimensional surface topographies

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

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td><strong>Process 1: substrate preparation</strong></td>
<td><strong>PMMA coated silicon wafer</strong></td>
</tr>
</tbody>
</table>
| 1.1     | **Substrate preparation** | Pretreatment  
Dehydration  
**Surface activation** *(if needed)*  
Oxygen plasma surface activation |
| 1.2     | **Dispensing, spin-coating and pre-baking of PMMA resist** | Polymethyl (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)* |
|         | 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)* |
<p>|         |                      | Dose modulation not only according to desired dose-depth variations, but also have to take the areal proximity effect into account. |</p>
<table>
<thead>
<tr>
<th>Section</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2a</td>
<td>Development of PMMA exposed to different doses leads to variations in the etching rates, thus stepped contours</td>
<td>It is recommended to temperature control the developer bath to optimize the reproducibility.</td>
</tr>
<tr>
<td></td>
<td>Developer: Methyl isobutyl ketone (MIBK)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rinse: IPA and DI water</td>
<td></td>
</tr>
<tr>
<td>2.1b</td>
<td>Topography origination by 3D thermal NIL</td>
<td>Alternative way to generate stepped topographies is to replicate stepped stamps into PMMA by thermal NIL.</td>
</tr>
<tr>
<td></td>
<td>Stamp: silicon or nickel</td>
<td>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.</td>
</tr>
<tr>
<td></td>
<td>PMMA molecular weight: ≤ 120 kg/mol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Standard imprint parameter using Jenoptik HEX 03 press: 180 °C / 5 MPa / 15 min</td>
<td></td>
</tr>
<tr>
<td>2.2b</td>
<td>Residual layer etching</td>
<td>Oxygen plasma might harm the stepped contours and thus lead to an unwanted pattern deviation.</td>
</tr>
<tr>
<td></td>
<td>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.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Exemplary etch recipe: Power: 20 W Pressure: 20 mtorr Oxygen: 20 sccm</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Resulting etch rate: 30 nm/sec</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>Process 3: flood exposure</td>
<td>Adjusting thermo-mechanical properties</td>
</tr>
</tbody>
</table>
### 4.0 Process 4: topography equilibration

Controlled transformation of steps into slopes

**4.1 Selective contour transformation**

Thermal treatment (e.g. on hot plate) allows to selectively transform stepped contours into continuous slopes.

Heating temperature: e.g. 110 °C for 120 min.

Instant cooling by removing sample from hotplate.

*Heating temperature according to modulation of thermal properties by previous flood exposure: For PMMA with reduced $T_g$ below 90 °C (i.e. exposed to 400 uC/cm²), a reflow at 110 °C ideal since the original $T_g$ of 120k PMMA is at 120 °C.*

---

**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)](image)

[*] experimental sample provided by micro resist technology GmbH
2.5 Proportional RIE of 3-D resist structures

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

Process: Proportional reactive ion etching of 3D resist structures

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

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

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

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

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

Partner: TASC Laboratory
Address: 34012 Basovizza-Trieste, Italy
Web-Address: http://www.tasc-infm.it
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:

Contact information:
Dr. Helmut Schift
Paul Scherrer Institut
Laboratory for Micro and Nanotechnology
5232 Villigen PSI
Switzerland
e-mail: helmut.schift@psi.ch
URL: http://www.psi.ch

LoP2012_NIL008_3D RIE-Stamps
# 3-D stamps with proportional reactive ion etching

**Process:** Proportional reactive ion etching of 3D resist structures

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0 Process 1: Wafer preparation</strong></td>
<td>Silicon Wafer format</td>
<td>Critical issues</td>
</tr>
<tr>
<td><strong>1.1 Wafer selection and preparation</strong></td>
<td>Standard Si substrate&lt;br&gt;Si substrate, 4&quot;, &lt;100&gt;, thickness d=400-600 µm&lt;br&gt;one side polished</td>
<td></td>
</tr>
<tr>
<td><strong>1.2 Substrate preparation</strong></td>
<td>Pretreatment&lt;br&gt;no pretreatment needed (if wafer is clean and hydrophilic)</td>
<td></td>
</tr>
</tbody>
</table>

End of Process 1

| **2.0 Process 2: Resist coating** | For electron beam lithography |  |
| **2.1 Dispensing of the resist** | Resist<br>mr-I PMMA120k*<br>* experimental PMMA sample provided by micro resist technology GmbH |  |
| **2.2 Coating resist** | Spincoating of mr-I<br>PMMA<br>speed: 3000rpm,<br>acceleration: 3000rpm/sec,<br>time: 30 s<br>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 performed according to the **contrast curve** (i.e. etch depth vs. exposure dose)

#### 3.2 Development of PMMA

- Exposed to different doses leads to variations in the etching rates, thus stepped contours
- Developer: Methyl isobutyl ketone (MiBK)
- It is recommended to temperature control the developer 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 contamination during dry etching process, i.e. nucleation of polymer components during plasma step.

---

**End of Process 3**
### 4.0 Process 4: Pattern transfer

**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. \((C_2F_8\) 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
- **Temperature:** 0°C

The use of a RIE system with an 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.

<table>
<thead>
<tr>
<th>4.2 End of Process 4</th>
</tr>
</thead>
</table>

### 5.0 Process 5: Anti-adhesive coating

**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**

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 anymore 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.

### General remarks:

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

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

---

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

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

**Process:** Deep ultra violet photo lithography

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

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

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

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

**Project leader:** CEA-LETI-Minatec

**Address:** 17 rue des martyrs 38054 Cedex 9

**Web-Address:** http://www-leti.cea.fr/

**Process:** DUV 193 nm-Lithography

**Responsible:** Stefan Landis

**E-mail:** slandis@cea.fr

**Partner:** Paul Scherrer Institut (PSI)

**Address:** 5232 Villigen PSI, Switzerland

**Web-Address:** http://www.psi.ch

**Process:** Thermal Nanoimprint

**Responsible:** Helmut Schift

**E-mail:** helmut.schift@psi.ch

**Partner:** TASC Laboratory

**Address:** S.S.14km 163,5; 34012 Basovizza (Trieste, Italy)

**Web-Address:** www.tasc-infm.it

**Process:** Isotropic wet etching / NIL

**Responsible:** Massimo Tormen

**E-mail:** tormen@tasc.infm.it

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

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

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

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

**Contact information:**

Stéfan LANDIS PhD
Senior Scientist
NanoImprint Lithography
CEA-Leti MINATEC Campus, 17 rue des Martyrs
38054 GRENOBLE Cedex 9
slandis@cea.fr
Tél. : + 33 (0)4 38 78 44 03 – Fax : + 33 (0)4 38 78 50 46

**LoP2012_NIL009_Multilevel DUV-Stamps**
# Multilevel stamps

## Process: DUV 193 nm photolithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>What</td>
<td>how it should work</td>
<td>critical issues</td>
</tr>
<tr>
<td>1.0</td>
<td>Process 1: Wafer preparation</td>
<td>Silicon wafer format</td>
</tr>
<tr>
<td>1.1 wafer selection and preparation</td>
<td>standard Si substrate, 12&quot;, &lt;100&gt;, thickness d=700-800 µm two side polished</td>
<td></td>
</tr>
<tr>
<td>1.2 substrate preparation</td>
<td>no pretreatment needed (if wafer is clean an hydrophilic)</td>
<td></td>
</tr>
<tr>
<td>End of Process 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>Process 2: Resist coating</td>
<td>for DUV 193 nm optical lithography</td>
</tr>
<tr>
<td>2.1 dispensing of resist after spin coating a (BARC) bottom anti reflective coating (requested for optical lithography)</td>
<td>Commercial DUV193 nm resist and BARC, no priming, positive tone resist for optical lithography, process lab (clean room)</td>
<td>These commercial resists use safe solvents.</td>
</tr>
<tr>
<td>2.2 coating resist (homogeneous layer)</td>
<td>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)</td>
<td>Automatic coating track or procedure is requested to obtain a thin uniform film over 12&quot; wafer.</td>
</tr>
<tr>
<td>2.3 post bake</td>
<td>solvent evaporation, see resist supplier specifications</td>
<td></td>
</tr>
<tr>
<td>End of Process 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>Process 3: Lithography</td>
<td>DUV 193 nm photolithography</td>
</tr>
<tr>
<td>3.1 Design and file generation</td>
<td>Functional structures</td>
<td>The exposure strategy often depends on the preference for positive or negative resists and the pattern transfer process to be used.</td>
</tr>
<tr>
<td></td>
<td>Draw patterns with Cadence, Layout Editor softwares (for example). Create a GDS file with one layer for one level that will be manufactured in your 3D stamp. Add some alignment marks compatible with the alignment strategy of your optical stepper or scanner.</td>
<td></td>
</tr>
<tr>
<td>3.2 Optical Mask manufacturing</td>
<td>Transfer complete GDS file to a maskshop to manufacture your exposure mask.</td>
<td>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 design on the same mask. However, the exposed surface will be smaller.</td>
</tr>
<tr>
<td>3.3 Mask alignment, resist exposure and development</td>
<td>wet development of the exposed resist, see resist supplier specifications</td>
<td></td>
</tr>
</tbody>
</table>
### Process 4: Pattern transfer dry etching of silicon

<table>
<thead>
<tr>
<th>Substrate patterning</th>
<th>Dry etching of silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>A typical process uses combination of gases (e.g. C₄F₈/O₂/Cl₂/HBr/SF₆). The etching parameters are usually strongly dependent on the tool and the resist chemistry.</td>
<td>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.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Resist removal (stripping)</th>
<th>RIE or ICP resist ashing</th>
</tr>
</thead>
<tbody>
<tr>
<td>A low bias oxygen plasma for few seconds allows to remove the resist without damage of the patterned silicon surface. Then a final clean in wet chemistry may be used to remove fluoropolymer created during plasma treatments.</td>
<td>destructive (cleaving, metal coating) in SEM profilometry</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Process control</th>
<th>optical and electron microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-destructively</td>
<td>destructive (cleaving, metal coating) in SEM profilometry</td>
</tr>
</tbody>
</table>

### Process 5: Anti-adhesive coating

<table>
<thead>
<tr>
<th>Preparation of stamp surface</th>
<th>cleaning and activation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Typically, RIE treatment with O₂ plasma removes organic contaminants and activates the surface (generation of free reactive silanol bonds for silane binding).</td>
<td></td>
</tr>
</tbody>
</table>

| Solution preparation | Prepare a solution 1/1000 of optool DSX in perfluorohexane solvent. |

| Dip of the stamp | The stamp is inserted in the silane solution for 1 minute. |

| Activate the ASL layer | Put the stamp in a hot (typically 70°C) vapor contant environment for 1 hour. |

| Rinse the stamp | Dip of stamp in perfluoro-hexane solvent for 5 minutes to remove the excess amount of anti sticking mole- |
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 repeated. Two processes flow may be used depending on the number of levels and control of the final exact shape. These two approaches are described below. In the second process flow, a planarization layer is used between each optical lithography exposure, in order to achieve better process window and protect already etched patterns from next steps.

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

Standard fabrication process for OrmoStamp working stamps

Process 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:


Contact information:
Dr. Helmut Schift
Paul Scherrer Institut
Laboratory for Micro and Nanotechnology
5232 Villigen PSI
Switzerland
e-mail: helmut.schift@psi.ch
URL: http://www.psi.ch
### Standard fabrication process for OrmoStamp working stamps

**Process:** nanoimprint lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>What</td>
<td>How it should work</td>
<td>Critical issues</td>
</tr>
<tr>
<td>1.0 Process 1: Wafer preparation</td>
<td>Borofloat® Wafer</td>
<td></td>
</tr>
<tr>
<td>1.1 Wafer selection and preparation</td>
<td>Borofloat® substrate Glass substrate, 4”, thickness d = 700 µm</td>
<td></td>
</tr>
<tr>
<td>1.2 Substrate preparation</td>
<td>Pretreatment&lt;br&gt;- Acetone rinse to remove organic residues&lt;br&gt;- Isopropanol to rinse away acetone&lt;br&gt;- Nitrogen blow drying&lt;br&gt;- DI-water rinse to remove solvent residues (this is very important for the following etch step)&lt;br&gt;&lt;br&gt;Piranha etch bath&lt;br&gt;- H₂O₂:H₂SO₄ (1:2) at 90°C for 10 min. <strong>Attention:</strong> exothermal reaction bath heating up to 150°C. Danger of explosion, if stamp surface contain solvent residues!&lt;br&gt;- DI-water rinse&lt;br&gt;- Dehydration on a hot-plate 10 min. @ 200°C&lt;br&gt;&lt;br&gt;Surface activation&lt;br&gt;- Oxygen plasma surface activation</td>
<td>Wear safety glasses, gloves and clothes! &lt;br&gt;The etch bath will grow a thin SiO₂ layer on top of your substrate</td>
</tr>
</tbody>
</table>

End of Process 1

| 2.0 Process 2: Primer coating | To improve the adhesion | |
| 2.1 Dispensing of the primer | Primer<br>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.: O2/CHF3). 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 removes possible air inclusions and improves the uniformity of the Ormocer layer after the coating process. The prebake is necessary when hybrid polymer diluted by a solvent is processed. Please note: Hybrid polymer does not harden during the prebake step and is still viscous thereafter! Alternative: convection oven at 180°C, for 30 min

End of Process 2

3.0 Process 3: Lithography

3.1 Dispensing of OrmoStamp

Dispense some droplets OrmoStamp with a pipette on the stamp surface, not on the BOROFLOAT! Try to continuously dispense the material to avoid air bubbles. The necessary amount to cover the whole surface will differ depending of the stamp size and cavity structures.

Alternatively, it is also possible to spin-coat the OrmoStamp onto substrate or stamp. For details, we refer to the data sheet by micro resist technology GmbH.

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.
- Bring the OrmoStamp droplet into contact with the glass substrate. Then, slowly lower the substrate.
- Slowly lower the substrate, while the OrmoStamp spreads in the closing gap.

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 molding.
### 3.3 UV exposure

<table>
<thead>
<tr>
<th>Jenoptik HEX03 UV-Module</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intensity: 2.8 mW/cm²</td>
</tr>
<tr>
<td>Wavelength: 365 nm</td>
</tr>
<tr>
<td>Dose: 1000 mJ/cm²</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Preparation of stamp surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cleaning and activation</td>
</tr>
<tr>
<td>Typically, RIE treatment</td>
</tr>
<tr>
<td>with O₂ plasma removes</td>
</tr>
<tr>
<td>organic contaminants and</td>
</tr>
<tr>
<td>activates the surface</td>
</tr>
<tr>
<td>(generation of free reactive</td>
</tr>
<tr>
<td>silanol bonds for silane</td>
</tr>
<tr>
<td>binding)</td>
</tr>
<tr>
<td>Oxford Plasmalab RIE80+</td>
</tr>
<tr>
<td>Power: 20 W</td>
</tr>
<tr>
<td>Time: 20 sec.</td>
</tr>
<tr>
<td>Oxygen: 20 sccm</td>
</tr>
</tbody>
</table>

Attention!!!

Use a very short and gentle oxygen process otherwise porous silicon dioxide will be formed.
4.2 Solution preparation

Prepare a solution 1-10 mM of perfluorotr dichlorosilane 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.

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 formation of a bulky deposit of molecules instead of a monolayer, washing of the stamp in acetone has to be performed in dry atmosphere.

4.4 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 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 features and the possibility to use standard lithography processing 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 substrate surface with a thin film. Fixing the stack in step 3.3 (e.g. by small PDMS pieces placed at the sides) avoids drift movement of the substrate with respect to the mold during the phase of material spreading.

OrmoStamp is a material for permanent applications; hence for removal of the material from the substrate extreme conditions are necessary. A PGMEA solution at increased temperature (~ 60° C) assisted by ultrasonification for several hours or hot piranha etch will usually (especially on glass) result in pealing off of OrmoStamp. Alternatively O₂ /CHF₃ plasma can be used. Do NOT use pure oxygen plasma! Porous SiO₂ will be formed.

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

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

Structure description: Nanopillars fabricated on a silicon mesh

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

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

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

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

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

Process 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.

Contact information:
Dr. Massimo Tormen
CNR-Istituto Nazionale per la Fisica della Materia
Laboratorio Nazionale TASC
Area Science Park - Basovizza
S.S.14 - km163,5
I-34149 Basovizza - Trieste (TS), Italy

LoP2012_NIL011_Two-level Stamps
Iterative fabrication process for self-aligned nanopillars on silicon mesh for NIL applications

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Process 1: Preparation of stamp</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Stamp</td>
<td>characteristics: silicon substrate, 2x2cm², &lt;100&gt;, 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.</td>
<td></td>
</tr>
<tr>
<td>1.2 Preparation of stamp surface</td>
<td>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.</td>
<td></td>
</tr>
</tbody>
</table>

End of Process 1

<table>
<thead>
<tr>
<th>Process 2: Wafer preparation</th>
<th>Silicon wafer format</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 wafer selection and preparation</td>
<td>standard Si substrate: Si substrate, 4&quot;, &lt;100&gt;, thickness d=400-600 µm, one side polished</td>
</tr>
<tr>
<td>2.2 substrate preparation</td>
<td>pretreatment: no pretreatment needed (if wafer is clean and hydrophilic)</td>
</tr>
</tbody>
</table>

End of Process 2

<table>
<thead>
<tr>
<th>Process 3: Resist coating</th>
<th>for nanoimprint lithography</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 dispensing of resist</td>
<td>resist: no priming resist mr-I 7010E process lab (clean room)</td>
</tr>
<tr>
<td></td>
<td>mr-I 7000E is a high resolution thermoplastic polymer resist (“E” series was replied by “R”, i.e. mr-I 7000R, see Page 34/35)</td>
</tr>
</tbody>
</table>
### 3.2 first coating resist (homogeneous layer)

**spincoating of mr-l 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 released at 50°C.

#### 4.2 structures definition

**shrinking of resist structures**  
The residual layer after NIL is removed in an ICP reactor by oxygen plasma; this step is also used to obtain a controlled lateral shrinking of the lines.  
*The etching parameters are usually strongly dependent on the equipment, thus dimensional shrinkage can be minimized under optimal etching conditions.*
### 4.3 Pattern Transfer

**silicon etching**
The pattern is transferred into the silicon substrate by plasma etching in an ICP reactor. A fluorine based plasma allows the anisotropic silicon etching. A typical recipe is composed by SF₆ 30 sccm/ C₄F₈ 60 sccm/ Ar 10 sccm, pressure of 8 mTorr, RF power 400 W (ICP RF source), 20 W (Platen RF source).

### 4.4 Resist Stripping

**ICP resist ashing**
Resist is removed by an isotropic oxygen plasma with low bias in the ICP tool.

### 5.0 Process 5: Resist Coating for Nanoimprint Lithography

#### 5.1 Dispensing of Resist

- no priming
- resist mr-I 7020E
- process lab (clean room)

#### 5.2 Second Coating Resist

- spincoating of mr-I 7020E
- speed: 2000 rpm, acceleration: 1000 rpm/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.*

---

*The etching parameters are usually strong dependent on the tool.*
| 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

Project leader: TASC Laboratory
Address: 34012 Basovizza-Trieste, Italy
Web-Address: http://www.tasc-infm.it
Process: NIL, evaporation, dry etching
Responsible: Massimo Tormen
E-mail: tormen@tasc.infm.it

Partner: C.R.F. Societa Consortile per Azioni, CRF
Address: Torino, Italy
Web-Address: http://www.crf.it
Process: EBL
Responsible: Vito Lamberti
E-mail: vitoguido.lamberti@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:

Contact information
Dr. Massimo Tormen
CNR-IOM
Laboratorio Nazionale TASC
Area Science Park - Basovizza
S.S.14 - km163,5
34149 Basowizza - Trieste (TS), Italy

LoP2012_NIL012_Microhollow-Stamps
# Half hemi-cylindrical lenses for day lighting applications

## Process: Isotropically wet etched micro-hollows in quartz plate

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 Process 1: Preparation of Substrate</td>
<td>10x10 cm wide quartz plate</td>
<td>critical issues</td>
</tr>
<tr>
<td>1.1 Substrate preparation</td>
<td>Sputter coating quartz glass with 100 nm chromium film.</td>
<td>Quality of the deposited chromium film, that should be exempt from pin-holes</td>
</tr>
</tbody>
</table>

### End of Process 1

<table>
<thead>
<tr>
<th>Process 2: Layout preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Layout</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>2.2 Substrate preparation</td>
</tr>
<tr>
<td></td>
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</tbody>
</table>

### End of Process 2

<table>
<thead>
<tr>
<th>Process 3: Resist coating for nanoimprint lithography</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1 Dispensing of resist</td>
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<tr>
<td></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>3.2 First coating resist</td>
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</table>

### End of Process 3

<table>
<thead>
<tr>
<th>Process 4: Mask preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Pattern definition</td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>Process</td>
</tr>
<tr>
<td>---------</td>
</tr>
</tbody>
</table>
| 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 |
| 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. |
| 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. |
| 7.0     | Process 7: Mask stripping Cr wet etching  
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 Total Process
3. Processes

Contributions to this section of the library are from

**VTT Information - Technology/Finland**
Dr. Tapio Mäkelä / Tomi Haatainen / Päivi Majander / Prof. Dr. Jouni Ahopelto

**ICN - Barcelona/Spain**
Dr. Vincent Reboud / Dr. Nikolaos Kehagias / Prof. Dr. Clivia Sotomayor-Torres

**AMO GmbH - Aachen/Germany**
Dr. Ulrich Plachetka

**CRF Fiat - Orbassano/Italy**
Dr. Vito Lambertini

**LTM-CNRS - Grenoble/France**
Dr. Cécile Gourgon

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

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

**INFM TASC - Trieste/Italy**
Dr. Massimo Tormen

**University of Glasgow - Glasgow/United Kingdom**
Dr. Nikolaj Gadegaard / Dr. Mathis Riehle / Dr. Kris Seunarine / Johnny Stormonth-Darling / Prof. Dr. Christopher Wilkinson /

**micro resist technology – Berlin/Germany**
Dr. Arne Schleunitz / Dr. Manuel Thesen / Dr. Marko Vogler
3.1 Thermal NIL Process (thermoplastic resist)

Thermal NIL using thermoplastic polymers

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

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

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

Keywords: thermal nanoimprint, thermoplastic resist, release properties

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

Process description: Thermoplastic polymers with strongly improved release properties.

Purpose: The mr-I 8000R is a thermoplastic polymer system designed for nanoimprint lithography. Upon heating above the glass transition temperature (T\text{g}), the viscosity of the resist is sufficiently reduced enabling the filling of the stamp cavities when pressure is applied during imprint step (the resist’s T\text{g} is 105 °C). The resist has excellent release properties and exhibits high plasma etch resistance. mr-I 8000R polymers are provided as ready-to-use solutions for various film thicknesses.

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

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

References:

Contact information:
Dr. Marko Vogler
micro resist technology GmbH
12555 Berlin
Germany
e-mail: m.vogler@microresist.de
URL: http://www.microresist.com

LoP2014_SP01_Thermal-NIL_Thermoplastic
## Thermal NIL using thermoplastic polymers

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

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
</table>
| 1.0 Process 1: substrate preparation | | Best patterning results are obtained at 20 – 25 °C and a rel. humidity of 40 – 46 %.
| 1.1 Substrate preparation | Dehydration: baked at 200 °C for 30 min and cooled to room temperature immediately before coating. Surface activation (if needed): oxygen plasma surface activation | Substrates have to be free of impurities and moisture (dewetting of the polymer layer may be induced by surface impurities).
| 1.2 Dispensing, spin-coating and pre-baking of mr-I 8000R | Standard spin-coating should be performed with 3000 rpm for 30 sec (acceleration 1000 rpm/s). Pre-bake at 100 °C on hot plate (or oven) for one minute. | Film thickness can be varied by using different standard resist formulation, i.e. mr-I 8010R (100 nm), mr-I 8020R (200 nm) and mr-I 8030R (300 nm) Further adaptations are accomplished by using appropriate resist spin-curves. The pre-bake step is necessary to evaporate residual solvent.

### End of Process 1

<table>
<thead>
<tr>
<th>2.0 Process 2: Thermal Imprint</th>
<th>Pattern replication</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1a Alignment of Stamp</td>
<td>Stamp (e.g. made of Silicon, quartz, Nickel or OrmoStamp®) is positioned on and aligned to the coated substrate. Stack is heated to 150 – 180 °C to lower resist’s viscosity (see Part 1 – 5.6).</td>
</tr>
<tr>
<td>2.2a Pattern replication</td>
<td>Typically the polymers are heated to 150 – 180 °C (i.e. 50 – 80 K above Tg ~ 105 °C) and the stamp with nanometer-scale patterns is pressed into the films with a pressure of e.g. 2 – 4 MPa to transfer the pattern. Time at maximum temperature 60 – 240 sec (pattern dependent).</td>
</tr>
</tbody>
</table>

**End of Process 2**
3.0 Process 3: Demolding

3.1 Separation of stamp and resist
After having cooled to a temperature not higher than the T\(_g\) of the polymer, the stamp is released. Release temperature 85 – 105 °C.
Examples shows replication of 12 nm wide lines pattern.

For optimized demolding step, please see comments below.
In case mr-I 7000R is used (lower T\(_g\) ~ 50 °C), the release temperature is 35 - 50 °C.

4.0 Process 4: Residual Layer Removal

4.1 Remove of Residual Layer
Residual layer remaining in the recessed areas of the polymer film after the imprint is removed by oxygen reactive ion etching (RIE) in order to open the window to the substrate.

After the whole process residue-free removal of mr-I 7000R is preferably achieved using common organic solvents such as acetone or 1-methoxy-2-propyl acetate (PGMEA). The polymer may also be removed by applying oxygen plasma.

General remarks:
mr-I 8000R is a thermoplastic polymer system designed for nanoimprint lithography, which has excellent release properties and exhibits high plasma etch resistance. It has a glass transition temperature (T\(_g\)) of 105 °C. mr-I 8000R characteristics can be summarized as follows:
- Tailor-made for thermal nanoimprint lithography due to excellent properties
  - Short cycle times due to fast polymer flow
  - Low imprint pressure
  - Sub-20 nm resolution
  - Low residual layer thickness
  - Low release forces (easy demoulding, efficient release force reduction)
- Longer life-time of anti-sticking layers on the mould
- High uniformity of the residual layer thickness
- High plasma etch resistance comparable to novolak-based photoresists

For industrial use and fast processes it is recommended to treat the mould with a release agent like F13-OTCS or other fluorinated silanes before use. F13-OTCS (trichloro-(1H,1H,2H,2H-perfluorooctyl)-silane, CAS number [78560-45-9]) is commercially available from many suppliers of laboratory chemicals. The anti-sticking character of the mr-I 8000R polymer system prolongs the lifetime of the release coating on the mould. Using moulds without any anti-sticking layer may work in certain cases, but this has not been fully investigated so far. A process with such a mould would require very diligent substrate pretreatment.
Figure 1: Example of a process cycle with mr-l 8030R. Imprint temperature 165°C, time at max. temperature 3 min and demoulding at 90 °C (air cooling).
3.2 Thermal NIL Process (thermoset resist)

Thermal NIL using thermosetting polymers

**Process:** Standard mr-I 9000M

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

**Application:** Etch mask for pattern transfer processes, dry and wet etching, single and multilayer systems.

**Keywords:** thermal nanoimprint, thermoset resist, isothermal processing

**Partner:** micro resist technology GmbH
**Address:** Koepenicker Str. 325, 12555 Berlin, Germany
**Web-Address:** http://www.microresist.com
**Process:** polymer materials
**Responsible:** Marko Vogler
**E-mail:** m.vogler@microresist.de

**Process description:** Advanced thermoset for pattern transfer

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

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

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

**Contact information:**
Dr. Marko Vogler
* micro resist technology GmbH
  12555 Berlin
  Germany
  e-mail: m.vogler@microresist.de
  URL: http://www.microresist.com

LoP2014_SP02_ Thermal-NIL-Thermoset
# Thermal NIL Process using Thermosetting Polymers

## Process: Standard mr-I 9000M

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>What How it should work</td>
<td>Critical issues</td>
<td></td>
</tr>
</tbody>
</table>
| 1.0 Process 1: substrate preparation | Best patterning results are obtained at 20 – 25 °C and a rel. humidity of 40 – 46 %.

### 1.1 Substrate preparation

- **Dehydration**: baked at 200 °C for 30 min and cooled to room temperature immediately before coating. Surface activation (if needed): oxygen plasma surface activation
- **Substrates**: have to be free of impurities and moisture

### 1.2 Dispensing, spin-coating and pre-baking of mr-I 9000M

- **Standard spin-coating**: should be performed with 3000 rpm for 30 sec
- **Pre-bake**: at 100 °C on hot plate (or oven) for 2 min.
- **Film thickness**: can be varied by using different standard resist formulation, i.e. mr-I 9010M (100 nm), mr-I 9020M (200 nm), mr-I 9030M (300 nm), mr-I 9050M (500 nm) and mr-I 9100M (1 µm). Further adaptations are accomplished by using appropriate resist spin curves. The pre-bake step is necessary to evaporate residual solvent.

---

## End of Process 1

### 2.0 Process 2: Thermal Imprint Pattern replication

#### 2.1a Alignment of stamp

- **Stamp**: (e.g. made of Silicon, quartz, Nickel, polymer mold or OrmoStamp®) is positioned on and aligned to the coated substrate.
- **Stack**: is heated to 90–120 °C to lower resist's viscosity.
- **The mr-I 9000M series can be imprinted in any tool suitable for doing thermal nanoimprint lithography. Commercial nanoimprinters as provided e.g. by EV Group (Austria) or Obducat (Sweden) may be used.**
2.2a Pattern replication

Substrate coated with mr-I 9000M ($T_g = 35 \, ^\circ\text{C}$; before curing) is heated to 120 °C in the imprint machine and the stamp is pressed into the resist film with a pressure of ~10 - 40 bar to transfer the pattern, flow time is 1 – 5 min (pattern depended).

Optional: two-step imprint process for improved pattern stability (see descriptions below).

End of Process 2

3.0 Process 3: Demolding

3.1 Separation of stamp and resist

Isothermal imprint processes are possible, since the $T_g$ of the thermosetting mr-I 9000M polymer is increased during the imprint and can reach values higher than the imprint temperature itself.

Recommendations for suitable imprint conditions:
- For micron size patterns an imprint temperature of 90 °C may be sufficient.
- Nanometre size patterns require at least 100 °C imprint temperature. ($T_{im} = T_r = 90 - 140 \, ^\circ\text{C}$).

Examples shows replication of 200 nm pillars.

End of Process 3

4.0 Process 4: Residual Layer Removal

4.1 Remove of Residual Layer

The residual layer remaining in the recessed areas of the polymer film after the imprint is removed by oxygen reactive ion etching (RIE) in order to open the window to the substrate.

Since mr-I 9000M does not contain any inorganic components like silicon, there are no residuals left on the substrate after plasma treatment with pure oxygen. As the mr-I 9000M polymer forms three-dimensional polymer networks during thermal curing, drastic conditions for wet-chemical removal are necessary. The solvent PGMEA or NMP-based solvents in an ultrasonic bath at higher temperature (40–60 °C) for several hours will
usually result in a peel off. Hot piranha etch is also suitable.

End of Process 4

End of Total Process

General remarks:
expected polymer system (thermally curing) designed for thermal nanoimprint lithography. The mr-I 9000M series is provided as ready-to-use solutions for various film thickness ranges. The cured polymer has high thermal and mechanical stability after the imprint process. This particularly enables imprinting and etching of dense nanostructure designs in the sub 100 nm range. Besides being applied as etch mask for pattern transfer mr-I 9000M can also be used for permanent applications. The unique features can be summarized as follows:
- Thermosetting polymer for outstanding pattern stability and for demanding imprint designs
- No reflow in subsequent process steps with thermal load
- Mold release at imprint temperature possible (no cooling step), i.e. nearly isothermal imprint process:
  - Imprint temperature 120 °C
  - Mould release at 100 °C
- Very low residual layer thickness down to 5 nm
- Excellent pattern transfer fidelity
- High plasma etch resistance comparable to Novolak-based resists
- Attainable smallest feature size at least 50 nm (depending on mould resolution)
- Ready-to-use solutions
- Safe solvents

Hard stamps: For defect-free imprints and low release forces with hard moulds it is highly recommended to treat the stamp before use with a release agent. The most common release agent for silicon or silicon dioxide is F13-TCS (trichloro-(1H,1H,2H,2H-perfluorooctyl)-silane, CAS number [78560-45-9]), commercially available from many suppliers of specialty chemicals. Polymer stamps: As polymeric working stamps various materials can be applied. One common commercially available product is OrmoStamp® which is fully compatible with the mr-I 9000M series. Other options are PFPE-based polymer systems.

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

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

UV-NIL using UV-curable polymers

**Process:** Standard mr-UVCur21

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

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

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

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

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

**Process description:** UV-based NIL process

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

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

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

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

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**Contact information:**
Dr. Marko Vogler
**micro resist technology GmbH**
12555 Berlin
Germany
e-mail: m.vogler@microresist.de
**URL:** http://www.microresist.com
### UV-NIL using UV-curable Polymers

**Process: Standard mr-UVCur21**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0</strong> Process 1: substrate preparation</td>
<td></td>
<td>Best patterning results are obtained at 20 – 25 °C and a rel. humidity of 40 – 46 %.</td>
</tr>
<tr>
<td><strong>1.1</strong> Substrate preparation</td>
<td>Dehydration: baked at 200 °C for 30 min and cooled to room temperature immediately before coating. Surface activation (if needed): oxygen plasma surface activation. For improving the polymer film adhesion to Si or SiO₂ substrates it is advisable to apply an adhesion promoter. Using mr-APS1 () is recommended. HMDS (hexamethyldisilazane) is not suitable.</td>
<td>Substrates have to be free of impurities and moisture.</td>
</tr>
<tr>
<td>1.2 Dispensing, spin-coating and soft-baking of mr-UVCur21</td>
<td>Standard spin-coating should be performed with 3000 rpm for 60 sec (). Soft-back at 80 °C for 60 s on hot plate (or oven). The soft-bake step is necessary to evaporate residual solvent. Film thickness can be varied by using different standard resist formulation, i.e. mr-UVCur21-100nm, mr-UVCur21-200nm, and mr-UVCur21-300nm. Further adaptations are accomplished by using appropriate resist spin-curves. A spin time of 60 s is recommended, since lower film thicknesses and a higher film quality can be achieved compared to 30 s.</td>
<td></td>
</tr>
</tbody>
</table>

End of Process 1

**2.0** Process 2: Thermal Imprint

**2.1a** Alignment of transparent stamp

Transparent stamp (e.g. made of Quartz, polymer (i.e. IPS – intermediate polymer stamp) or OrmoStamp) is positioned on and aligned to the coated substrate. mr-UVCur21 can be imprinted in any tool suitable for doing thermal nanoimprint lithography, in tools combining thermal imprinting and UV exposure. Commercial nanoimprinters as provided e.g. by Obducat (Sweden), EVG (Austria) and Suss MicroTec (Germany) may be used.
### 2.2a Pattern replication

Substrate coated with mr-UVCur21 is imprinted at room temperature. The UV-transparent stamp is pressed into the resist film with a low imprint pressure of > 100 mbar to transfer the pattern. Imprint in vacuum or under atmospheric pressure. UV exposure: broad band or i-line, curing time few seconds.

The imprint pressure and time necessary to get complete filling of the mould cavities depends on the pattern density and pattern width. Since mr-UVCur21 has a very low viscosity, the time necessary to build up the imprint pressure is sufficient to completely fill the patterns. Main factors determining the imprint conditions are the viscosity of the polymer system, the mould layout (feature size, density of the patterns etc.), the residual layer thickness to be attained and the imprinting tool.

### 3.0 Process 3: Crosslinking Resist Pattern curing

#### 3.1 UV-exposure through transparent stamp while imprinting

Exposure dose ~700 mJ/cm² using broadband UV light (320 – 420 nm), intensity measured at $\lambda = 365$ nm

Options:
- UV broadband,
- Monocromatic (365-395 nm),
- LED up to 395 nm
  - curing in vacuum

Applying higher doses or broader UV wavelength ranges do not affect the imprint quality or the properties of the cured polymer. Exposure applying a smaller UV range of e.g. 350 - 400 nm or applying the 365 nm line works as well, but will require higher doses. The degree of shrinkage of mr-UVCur21 during the UV exposure is approximately 3 – 4 % (linear shrinkage). Reproducible exposure conditions will lead to reproducible shrinkage values.

### 4.0 Process 4: Demolding

#### 4.1 Separation of stamp and resist

Release at room temperature
Examples shows replication of mould patterns with demanding filling factors, i.e. 100x100 μm² squares.

<table>
<thead>
<tr>
<th>End of Process 4</th>
</tr>
</thead>
</table>

5.0 Process 5: Residual Layer Removal

5.1 Remove of Residual Layer

The residual layer remaining in the recessed areas of the polymer film after the imprint is removed by oxygen reactive ion etching (RIE) in order to open the window to the substrate.

After the whole process residue-free removal of mr-UVCur21 is preferably achieved applying oxygen plasma. Since mr-UVCur21 does not contain any inorganic components like silicon, no residues are left on the substrate after plasma treatment with pure oxygen.

<table>
<thead>
<tr>
<th>End of Process 5</th>
</tr>
</thead>
</table>

End of Total Process

General remarks:

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

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

Figure 1: Example for a typical process cycle of mr-UVCur21 demonstrating the isothermal process with UV exposure step finalizing the imprint step.
3.4 Combined Thermal and UV-NIL Process

Combined T- and UV-NIL using photochemically curing resist

**Process:** Standard mr-NIL 6000E

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

**Application:**
Etch mask for pattern transfer processes, dry and wet etching, single and multilayer systems.

**Keywords:** combined nanoimprint and photolithography, STU

**Partner:** micro resist technology GmbH
**Address:** Koenenicker Str. 325, 12555 Berlin, Germany
**Web-Address:** http://www.microresist.com
**E-mail:** m.vogler@microresist.de

**Process description:** High performance resist with decreased imprint temperature

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

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

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

**References:**

**Contact information:**
Dr. Marko Vogler
micro resist technology GmbH
12555 Berlin
Germany
e-mail: m.vogler@microresist.de
URL: http://www.microresist.com
## Combined T- and UV-NIL using photochemically curing resist

**Process:** Standard mr-NIL 6000E

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>What</td>
<td>How it should work</td>
</tr>
<tr>
<td>1.1</td>
<td>Substrate preparation</td>
<td>Dehydration: baked at 200 °C for 30 min and cooled to room temperature immediately before coating. Surface activation (if needed): oxygen plasma surface activation. Substrates have to be free of impurities and moisture.</td>
</tr>
<tr>
<td>1.2</td>
<td>Dispensing, spin-coating and pre-baking of mr-NIL 6000E</td>
<td>Standard spin-coating should be performed with 3000 rpm for 30 sec. Pre-bake at 90 °C on hot plate (or oven) for one minute. Film thickness can be varied by using different standard resist formulation, i.e. mr-NIL 6000.1E (100 nm), mr-NIL 6000.2E (200 nm) and mr-NIL 6000.3E (300 nm). Further adaptations are accomplished by using appropriate resist spin-curves. The pre-bake step is necessary to evaporate residual solvent.</td>
</tr>
</tbody>
</table>

### End of Process 1

<table>
<thead>
<tr>
<th>2.0</th>
<th>Process 2: Thermal Imprint</th>
<th>Pattern replication</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1a</td>
<td>Alignment of transparent stamp</td>
<td>Transparent stamp (e.g. made of quartz, polymer (i.e. IPS – intermediate polymer stamp) or OrmoStamp®) is positioned on and aligned to the coated substrate. Stack is heated to 65 – 70 °C to lower resist’s viscosity. Mr-NIL 6000E can be imprinted in any tool suitable for doing thermal nanoimprint lithography, in tools combining thermal imprinting and UV exposure. Commercial nanoimprinters as provided e.g. by Obducat (Sweden), EVG (Austria) and Suss MicroTec (Germany) may be used.</td>
</tr>
<tr>
<td>2.2a</td>
<td>Pattern replication</td>
<td>Substrate coated with mr-NIL 6000E is heated to 65 – 70 °C in the imprint machine and the UV-transparent stamp is pressed into the resist film with a pressure of ~30 bar to transfer the pattern, flow time is 20 – 100 sec (pattern depended). Main factors determining the imprint conditions are the rheological behaviour of the resist, the mould layout (feature size, density of the patterns etc.), the degree of cavity filling, the residual layer thickness to be attained and the imprinting tool.</td>
</tr>
</tbody>
</table>
### Process 3: Crosslinking Resist Pattern curing

**3.0 Process 3: Crosslinking Resist Pattern curing**

**3.1 UV-exposure through transparent stamp while imprinting**

End of Process 2

<table>
<thead>
<tr>
<th>Process</th>
<th>UV-exposure through transparent stamp while imprinting</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Exposure dose ( \text{[mJ/cm}^2 ) \sim 350 ]</td>
</tr>
</tbody>
</table>

Options:

- UV broadband, i-line (365 nm), Monochromatic (365-395nm)

After the time required to allow the resist flowing and conforming to the mould (flow time depending on the mould layout) the resist is UV flood exposed (under pressure at the imprint temperature in the imprinter). The dose to be applied depends on the imprint temperature and the desired thermal pattern stability: Lower imprint temperatures require a somewhat higher exposure dose. Also if a very high thermal pattern stability is necessary for the subsequent processing a higher exposure dose is recommended. Alternatively, an even higher imprint temperature of up to 100 °C can be applied if a very high thermal pattern stability is decisive.

End of Process 3

**4.0 Process 4: Demolding**

**4.1 Separation of stamp and resist**

End of Process 3

<table>
<thead>
<tr>
<th>Process</th>
<th>Demolding</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Stamp release</td>
</tr>
<tr>
<td></td>
<td>Release temperature 65-70 °C (= imprint temperature)</td>
</tr>
</tbody>
</table>

Additional annealing after the exposure – which would correspond to the post exposure bake (PEB) in radiation based lithography – is not necessary. The stamp is released at the imprint temperature. This isothermal process is possible, since \( T_g \) of the resist has increased to roughly the imprint temperature due to the curing reaction initiated by the exposure.

End of Process 4

**5.0 Process 5: Residual Layer Removal**

**5.1 Remove of Residual Layer**

End of Process 4

<table>
<thead>
<tr>
<th>Process</th>
<th>Residual Layer Removal</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Opening Resist Windows</td>
</tr>
<tr>
<td></td>
<td>The residual layer remaining in the recessed areas of the polymer film after the imprint is removed by oxygen reactive ion etching (RIE) in order</td>
</tr>
</tbody>
</table>

After the whole process residue-free removal of mr-NIL 6000E is achieved applying oxygen plasma. Also the
End of Process 5
End of Total Process

General remarks:
The mr-NIL 6000E is a photochemically curing resist for thermal nanoimprint lithography. It forms a solid resist film after spin coating. mr-NIL 6000E is well suited for pattern transfer processes as well as for permanent structures e.g. in microfluidics and microoptics. The resist can be patterned under isothermal conditions applying lower imprint temperatures compared to other nanoimprint materials. The main resist characteristics can be summarized as follows:
- Solid resist film after spin coating
- Short imprint cycle times due to isothermal NIL process (no cooling step)
- Excellent film quality on various substrate materials e.g. Si, SiO₂, Al, Al₂O₃
- Designed for combined thermal and UV nanoimprint lithography
- $T_g \approx 1 \degree$C before curing
- Imprinting, UV curing during imprinting, and mould release at the same temperature
- Low imprint temperature (65–70 °C), low thermal load
- High uniformity of the residual layer thickness
- Very low residual layer thickness < 10 nm
- Excellent pattern transfer fidelity
- High plasma etch resistance comparable to conventional novolak-based photoresists
- Ready-to-use solutions
- Safe solvents

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

![Figure 1: Example for a typical process cycle of mr-NIL 6000E demonstrating the isothermal process with UV exposure step finalizing the imprint step.](image-url)
3.5 Nanoimprint Lithography of 3D structures

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

Process: nanoimprint lithography

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

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

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

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

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:

Contact information:
Dr. Helmut Schift
Paul Scherrer Institut
Laboratory for Micro and Nanotechnology
5232 Villigen PSI
Switzerland
e-mail: helmut.schift@psi.ch
URL: http://www.psi.ch

LoP2012_NIL013_3D NIL molding process
Thermal nanoimprint lithography of 3D structures and contact angle based filling of cavities with sloped sidewalls

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process 1: Wafer preparation</td>
<td>Silicon wafer format</td>
<td></td>
</tr>
<tr>
<td>1.1 wafer selection and preparation</td>
<td>standard Si substrate, 4&quot;, &lt;100&gt;, thickness d=400-600 µm one side polished</td>
<td>Alternatively, 0.7 mm thick Borofloat glass has proven to be a good substrate (if transparency is needed)</td>
</tr>
<tr>
<td>1.2 substrate preparation</td>
<td>pretreatment no pretreatment needed (if wafer is clean and hydrophilic)</td>
<td></td>
</tr>
<tr>
<td>End of Process 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process 2: Resist coating</td>
<td>for nanoimprint lithography</td>
<td></td>
</tr>
<tr>
<td>2.1 dispensing of resist</td>
<td>resist no priming PMMA 25 kg/mol in ethyl-lactate (safer solvent)</td>
<td>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 available resists from micro resist technology GmbH, e.g. mr-I 8000E (see Page 34)</td>
</tr>
<tr>
<td>2.2 coating resist (homogeneous layer)</td>
<td>spincoating of thermoplastic resist PMMA -&gt; ~990 nm thickness</td>
<td>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</td>
</tr>
<tr>
<td>2.3 post bake</td>
<td>solvent evaporation bake 1 min @ 170°C (hot plate)</td>
<td>Alternative: convection oven at 180°C, for 30 min</td>
</tr>
<tr>
<td>End of Process 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process 3: Thermal imprint</td>
<td>dry etching of silicon</td>
<td></td>
</tr>
<tr>
<td>3.1 Stamp with 3D surface topography</td>
<td>Stamp preparation A 3D stamp with microcavities with sloped (30°) and Asymmetric structure</td>
<td></td>
</tr>
</tbody>
</table>
vertical sidewalls was prepared using grayscale electron beam lithography and the TASTE process. With a fixed height of 1 μm and a varying footprint of 3 – 5 μm

<table>
<thead>
<tr>
<th>3.2</th>
<th>Resist removal (stripping)</th>
<th>TASTE (thermally assisted selective topography equilibration) – see Page 100.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2</td>
<td>Resist removal (stripping)</td>
<td>Thermal imprint</td>
</tr>
<tr>
<td></td>
<td></td>
<td>A typical imprint process consists of a contact phase in which polymer is able to assume a surface of minimum energy due to the wetting of the sidewalls</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3.3a</th>
<th>process control</th>
<th>Incomplete molding</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stamp and resist show partially identical (opposite polarity) profiles but large areas where the surface profile of the resist is determined by a meniscus</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Capillary action completed and squeeze flow not yet completed</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3.3b</th>
<th>process control</th>
<th>Complete molding</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Stamp and resist show identical (opposite polarity) profiles</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3.4</th>
<th>process control</th>
<th>electron microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>asymmetric structures resist: PMMA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>destructive (cleaving, metal coating) in SEM</td>
</tr>
<tr>
<td></td>
<td></td>
<td>The three micrographs show different pre-fill states for different cavity lengths, all of them in equilibrium (volume conservation)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>While different meniscus depths are generated, the</td>
</tr>
<tr>
<td></td>
<td></td>
<td>non-destructive process control would be possible using profilometry</td>
</tr>
<tr>
<td>Contact angle</td>
<td>PMMA 34kg/mol: 90°</td>
<td>mr-I 8000E: 85°</td>
</tr>
<tr>
<td>---------------</td>
<td>---------------------</td>
<td>------------------</td>
</tr>
</tbody>
</table>

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

Figure 1: During imprint of extended arrays of microcavities (which are not too extended for the stamp to bend), transport of material for the filling of cavities is done by squeeze flow from the borders of the array. Due to the lack of material flow in the center, pre-fill states are generated in which capillary action dominates.
Figure 2: In case of (almost) vertical sidewalls, the filling is abrupt, i.e. the structures are filled by spontaneous wetting of sidewall surfaces (particularly at corners) and “jumps” up to the cavity top. In case of inclined sidewalls, a contact angle forms and results in the generation of a resist surface with the form of a meniscus, being the result of volume conservation and formation of a surface of minimum energy. These states are also forming in absence of pressure. They are stable, as long as squeeze flow does not interfere with the formation of an equilibrium. Different resists types result in different contact angles, which in case of PMMA 9k is about 98° and in case of mr-I 8000E (here: experimental sample mr-I 8150E XP provided by micro resist technology GmbH) is about 85°.

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

### Fabrication of suspended polymer membranes on LOR resist

| Process: nanoimprint lithography | Figure: SEM micrograph of a pore array in 1 µm thick polystyrene supported by 2 µm high pillars with 3 µm hole diameter and 5 µm period (cleaved sample) | Process: Thermal nanoimprint of a thermoplastic polymer on top of a sacrificial polymer. Pattern transfer using RIE and underetch. |
|----------------------------------|------------------------------------------------------------------------------------------|----------------------------------------------------------------|-----|
| **Keywords:** thermal nanoimprint, double resist, sacrificial layer, perforated membrane |

**Project leader:** 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 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:**


**Contact information:**
Dr. Helmut Schift  
Paul Scherrer Institut  
Laboratory for Micro and Nanotechnology  
5232 Villigen PSI  
Switzerland  
e-mail: helmut.schift@psi.ch  
URL: http://www.psi.ch

LoP2007_NIL002_suspended polymer membranes
### Suspended polymer membranes

**Process**: nanoimprint lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0 Process 1: Wafer preparation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 wafer selection and preparation</td>
<td>standard Si substrate Si substrate, 4&quot;, &lt;100&gt;, thickness d=465 µm one side polished</td>
<td></td>
</tr>
<tr>
<td>1.2 substrate preparation</td>
<td>no pretreatment</td>
<td></td>
</tr>
<tr>
<td><strong>End of Process 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2.0 Process 2: Stamp preparation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 layout</td>
<td>Functional structures the stamp consist of large arrays of pillars (about 1mm² 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</td>
<td></td>
</tr>
<tr>
<td>2.2 antiadhesive coating</td>
<td>silane CVD evaporation standard process silane coating from gas phase is beneficial for sidewall coating</td>
<td></td>
</tr>
<tr>
<td><strong>End of Process 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3.0 Process 3: Lithography</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 coating of layer 1 (sacrificial layer)</td>
<td>double-spincoating of LOR no priming LOR 10B from MicroChem Corp. 3000rpm, 60 s -&gt; ~1000nm bake 3 min @ 190°C (hot plate) 3000rpm, 60 s -&gt; ~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 Tg and a low etching rate almost independent from further heat treatment</td>
<td></td>
</tr>
<tr>
<td>3.2 coating of layer 2 (functional NIL layer)</td>
<td>spincoating of PS no priming of LOR Polystyrene 125kg/kmol, Polyscience GmbH, dissolved in dissolved in tolu- Resist with inherent anti-</td>
<td></td>
</tr>
</tbody>
</table>
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

3.5 Process Control

- Optical Microscopy
  - Non-destructively
- Profilometry
  - 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 O₂: 20 sccm
- Gas pressure: 20 mtorr
- Power: 20 W
- Temperature: 300 K

- Etching 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\textsubscript{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.

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.

<table>
<thead>
<tr>
<th>4.4</th>
<th>process control</th>
<th>optical microscope</th>
<th>100 x</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Connected cavities with supporting columns (PS 1 µm / LOR 1 µm, view size 30 x 30 µm²). 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.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>online, without breaking substrate pores and undercuts with &lt;0.4µm can be resolved, not suitable for nanopores (&lt; 200nm)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4.5</th>
<th>process control</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>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)</td>
<td></td>
</tr>
</tbody>
</table>

General remarks: Further information on alternative resists (including those with inherent antiadhesive properties) are described in 5.6 Resists, substrates and tools.
3.7 Polymer multilayers by reverse UV-NIL

**Fabrication of multi layered woodpiles by reverse UV-NIL**

**Process:** nanoimprint lithography

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

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

**Application:** Microfluidic devices, Photonic crystals

**Keywords:** reverse nanoimprint lithography, three-dimensional nanofabrication

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

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

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

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

**References:**


**Contact information (2012):**
Prof. Dr. Clivia M. Sotomayor Torres
ICREA Research Professor
Phononic and Photonic Nanostructures Group
Catalan Institute of Nanotechnology (CIN2-CSIC)
Campus Bellaterra - Edifici CM3
08193 Bellaterra (Barcelona), SPAIN

**LoP2007_NIL003_RUVNIL woodpile**
# Polymer multilayeres by reverse UV-NIL

**Process:** nanoimprint lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>wafer selection and preparation</td>
<td>Standard Si substrate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Si substrate, &lt;100&gt;, thickness d=500 µm one side polished Standard glass or Pyrex substrate</td>
</tr>
<tr>
<td>1.2</td>
<td>substrate preparation</td>
<td>no pre-treatment for the first layer</td>
</tr>
<tr>
<td></td>
<td>End of Process 1</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>Process 2: Stamp preparation</td>
<td>Standard glass or Pyrex substrate with metal protusion</td>
</tr>
<tr>
<td>2.1</td>
<td>layout</td>
<td>Functional structures</td>
</tr>
<tr>
<td></td>
<td></td>
<td>the stamp consist of gratings (about 5 mm² area) with a pitch variation from 200 nm to 10 µm between lines, all over the wafer.</td>
</tr>
<tr>
<td>2.2</td>
<td>Spin coat sacrificial polymer layer</td>
<td>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 planarization layer and to protect the stamp from contamination by the photocuring resist.</td>
</tr>
<tr>
<td>2.3</td>
<td>Spin coat UV crosslinkable polymer</td>
<td>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</td>
</tr>
<tr>
<td></td>
<td>End of Process 2</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>Process 3: Lithography</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Reverse imprint</td>
<td>The polymer bilayer is reverse imprinted onto a Si substrate. Stamp and substrate are then heated to a temperature above the T&lt;sub&gt;g&lt;/sub&gt; of mr-NIL 6000 and exposed to UV radiation. Optimized imprint parameters on a non-flat substrate</td>
</tr>
</tbody>
</table>
Schematic of RUVNIL process showing the time at which point of UV light exposure occurs and the time of post exposure baking.

### 43.2 Separation and development.

**Demolding**

Demolding in a developer bath. Unexposed polymer areas as well as the LOR layer are removed with acetone and/or remover 1165 (Shipley) leaving behind the negative features of the original stamp. No residual layer in final structure.

**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

<table>
<thead>
<tr>
<th>Optical microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>non-destructively</td>
</tr>
<tr>
<td>SEM</td>
</tr>
<tr>
<td>destructive (cleaving, metal coating)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>End of Process 4</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>End of Total Process</th>
</tr>
</thead>
</table>

**Other references:**

3.8 Combined Nanoimprint and Photolithography

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

Process: Combined Nanoimprint and Photolithography (CNP)

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

Process: Combined nanoimprint and photolithography using a hybrid stamp/UV mask

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

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

Process description: A process is described for wafer-scale definition of nm to mm sized optical structures by combining nanoimprint lithography with UV lithography. A hybrid stamp/UV mask 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 straightforward.

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

References:

Project leader: DTU - Department of Micro- and Nanotechnology
Address: DTU building 345E, 2800 Lyngby, Denmark
Web-Address: www.nanotech.dtu.dk

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

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**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td><strong>Process 1: Wafer preparation</strong></td>
<td></td>
</tr>
<tr>
<td>1.1</td>
<td>wafer selection and preparation</td>
<td>Si substrate, 10 cm,</td>
</tr>
<tr>
<td>1.2</td>
<td>substrate preparation</td>
<td>oxidation, thermal oxide, approximately 3 µm</td>
</tr>
</tbody>
</table>

End of Process 1

| 2.0     | **Process 1: Stamp preparation** | |
| 2.1     | layout | Functional structures, the stamp is made of fused silica, with an integrated Cr shadow mask. In the mask windows, which are 1 mm by 250 microns, 100 nm tall glass lines with a width of approx. 100 nm and a period of approx. 200 nm are protruding. |
| 2.2     | antiadhesive coating | FDTS coating, Standard recipe in MVD 100 molecular vapour deposition tool from Applied Microstructures Inc. |

End of Process 2

<p>| 3.0     | <strong>Process 3: Combined nanoimprint and UV lithography (CNP)</strong> | |
| 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 mmol Rh6G dye per g solid. Spun at 7000 RPM, 3000 RPM/s, 60s. Pre-baked @ 90°C for 1 min |
| 3.2     | thermal imprint | EVG 520HE imprinter, stack preassembled before heating and pressing (order from top to bottom): Al foil, graphite (standard) 0.5 mm, stamp substrate with resist, graphite, Al foil temperature..(heat)......100°C pressure.....................(10 kN) |</p>
<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>hold time</td>
<td>(100°C)……10 min</td>
</tr>
<tr>
<td>overall time</td>
<td>.................45 min</td>
</tr>
<tr>
<td>temperature</td>
<td>(release)....40°C</td>
</tr>
<tr>
<td>residual polymer thickness</td>
<td>in grooves 150 nm on purpose. We just want a surface corrugation</td>
</tr>
</tbody>
</table>

### 3.3 UV exposure

- SUSS 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 definition

#### 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
- SUSS 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
3.9 Fast isothermal imprint

Fast isothermal imprint for full wafers

Process: nanoimprint lithography

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

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

Application: Large scale imprint applications

Keywords: thermal nanoimprint, throughput

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:

Contact information:
Cécile Gourgon
Laboratoire des Technologies de la Microélectronique LTM
17 Rue des Martyrs (c/o CEA Grenoble)
F- 38 054 Grenoble Cedex 9
cecile.gourgon@cea.fr

LoP2007_NIL010_Fast isothermal imprint
# Fast isothermal imprint

**Process:** nanoimprint lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0 Process 1: chamber and wafers preparation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>1.1 Pre-heating of the equipment</strong></td>
<td>EVG® 520HE heating up to ( T_{\text{imprint}} ) 5 min waiting time to stabilize the temperature</td>
<td>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.</td>
</tr>
<tr>
<td><strong>1.2 Mold/wafer assembly</strong></td>
<td>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</td>
<td>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).</td>
</tr>
<tr>
<td><strong>2.0 Process 2: imprint process</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2.1 Pumping and temperature uniformization</strong></td>
<td>Pressure down to 100 mbars in 30 seconds</td>
<td>Limited by the pumping speed</td>
</tr>
<tr>
<td><strong>2.2 imprint</strong></td>
<td>Applied force: 40 kN During 1 minute</td>
<td></td>
</tr>
<tr>
<td><strong>2.3 decrease of the force and chamber venting</strong></td>
<td>( T = T_{\text{imprint}} )</td>
<td></td>
</tr>
<tr>
<td><strong>3.0 Process 3: demolding</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3.1 Unloading of the stack</strong></td>
<td>The mold/wafer stack is put on a plate cold with water to fasten the cooling Waiting time: 2 minutes</td>
<td></td>
</tr>
<tr>
<td><strong>3.2 Demolding</strong></td>
<td>Manual demolding with a razor blade</td>
<td></td>
</tr>
<tr>
<td><strong>3.3 process control</strong></td>
<td>SEM 250 nm dense lines covering the 200 mm wafer</td>
<td></td>
</tr>
</tbody>
</table>

End of Process 1

End of Process 2

End of Process 3

End of Total Process
3.10 Pattern transfer optimization

Pattern transfer optimization for full wafer NIL

<table>
<thead>
<tr>
<th>Process: development of anisotropic transfer processes</th>
<th>Figure: Photograph of a 200 mm wafer imprinted and etched using an anisotropic process</th>
<th>Process: Plasma etching processes are optimized to anisotropic pattern transfer, allowing the transfer of various densities of structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Application: Si devices with various patterns size and densities</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Keywords: plasma etching, critical dimension, residual layer

Project leader: LTM
Address: 17 R. Martyrs, 38 054 Grenoble, France
Web-Address: http://www.ltm-cnrs.fr/

Process description: Large surfaces require a high imprint uniformity, which is easier to achieve with residual layers in the 50-100 nm range. An 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 an O₂/Cl₂/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:


Contact information:
Cécile Gourgon
Laboratoire des Technologies de la Microélectronique LTM
17 Rue des Martyrs (c/o CEA Grenoble)
F- 38 054 Grenoble Cedex 9
cecile.gourgon@cea.fr

LoP2007 NIL011 Pattern Transfer Optimization
### Pattern transfer optimization

**Process: nanoimprint lithography**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>What</strong>&lt;br&gt;how it should work</td>
<td><strong>Remarks</strong>&lt;br&gt;critical issues</td>
<td></td>
</tr>
<tr>
<td>1.0 <strong>Process 1: imprint</strong>&lt;br&gt;<strong>1.1 Wafers preparation</strong>&lt;br&gt;200 mm Si wafers&lt;br&gt;Thin film of resist spin-coated on the Si substrate&lt;br&gt;Mold coated with a standard anti-sticking layer&lt;br&gt;Teflon sheet to improve the printing uniformity</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.2 <strong>Imprint process</strong>&lt;br&gt;<strong>EVG® 520HE</strong>&lt;br&gt;40 kN, 120°C, 5 minutes</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>End of Process 1</strong>&lt;br&gt;**2.0 <strong>Process 2: residual thickness (hr) measurement</strong>&lt;br&gt;<strong>2.1 Ellipsometry for scatterometry</strong>&lt;br&gt;Spectroscopic ellipsometer 300 – 800 nm&lt;br&gt;Spot size 40 µm&lt;br&gt;Mapping on the 8” surface</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.2 <strong>Fit of the ellipsometry spectra</strong>&lt;br&gt;Calculation time determined by the pattern geometries: few seconds for 200 nm dense lines, but few hours for 3D structures</td>
<td><strong>Remarks</strong>&lt;br&gt;A high accuracy measurement of n( ) and k( ) has to be performed before.&lt;br&gt;Limitation: homogeneous pattern gratings with standard geometries</td>
<td></td>
</tr>
<tr>
<td>2.3 <strong>SEM characterization</strong>&lt;br&gt;Top-down SEM for pattern quality and homogeneity control, or cross-section SEM</td>
<td><strong>Test wafer needed if cross-section measurement</strong>&lt;br&gt;Line width: 209 nm</td>
<td></td>
</tr>
<tr>
<td><strong>End of Process 2</strong>&lt;br&gt;**3.0 <strong>Process 3: hr etching</strong>&lt;br&gt;<strong>3.1 Loading of the imprinted wafer</strong>&lt;br&gt;Plateform 5200 from applied Materials, DPS ICP reactor</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3.2 Etching process</strong>&lt;br&gt;O2/Cl2/Ar plasma&lt;br&gt;O2: 30 sccm, Cl2: 40sccm, Ar:30sccm&lt;br&gt;Pressure 10 mTorr&lt;br&gt;Source power: 500 W&lt;br&gt;Bias power: 60 W for NEB22 resist</td>
<td><strong>Remarks</strong>&lt;br&gt;The anisotropy is mostly dependent on the bias power. Some resists, which are less resistant, require lower bias, and this limits the anisotropy control.</td>
<td></td>
</tr>
</tbody>
</table>
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
3.11 Liquid Transfer Imprint Lithography (LTIL)

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

Process: resist coating and UV-imprint

**Figure:** Plastic foils with resist grating.

**Application:** Imprint over massive topography especially on all kinds of substrates (like plastic foil) where resist cannot be spin coated or dispensed upon.

**Keywords:** UV-NIL, surface coating, conformal imprinting on topography

**Partner:** AMO GmbH
**Address:** 52074 Aachen, Germany
**Web-Address:** http://www.amo.de

**Process:** LTIL
**Responsible:** J.W. Kim
**E-mail:** kim@amo.de

**Process description:** This process is used to imprint over massive topography especially on all kinds of substrates (like plastic foil) where resist cannot be spin coated or dispensed upon. The stamp is coated using an inking wafer that can be coated using standard processes as spin coating or dispensing. During a contact step with a soft stamp (PDMS/PFPE, etc.) resist fills up the pattern on the stamp. Then the stamp is peeled off from the inking substrate thereby splitting the liquid resist layer in half. The coated stamp can then be set down on the target substrate that may have massive roughness (like mc-Si-wafers) or structures (like lens arrays or blazed gratings) on its surface. The soft imprint stamp conformal envelopes the structures and sets down the patterned resist layer that is cured by UV-light after conformal contact between substrate and stamp is achieved.

**Purpose:** Imprint process for very rough and uneven surfaces, especially where spin-coating or dispensing are not suited. The process also improves pattern filling and residual resist uniformity.

**Major challenges:** The stamp material must be adapted in modulus to conformal contact different topographies.

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

**References:**
## Liquid Transfer Imprint Lithography (LTIL)

**Process:** resist coating and UV-imprint

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>LTIL-process</td>
<td>how it should work</td>
<td>critical issues</td>
</tr>
</tbody>
</table>

### 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
### General remarks:
The process is used to imprint onto substrates that cannot be used for spin coating or dispensing due to substrate mechanical instability (thin plastic foils) or nonflat surfaces with massive topography (like lens arrays, blazed gratings, mc-Si-wafers, etc.).
3.12 Nanoimprinting of hydrogels

UV and Thermal imprinting of hydrogels

Process: Thermal and UV-nanoimprint lithography

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

Process: UV and Thermal Nanoimprint
Application: Biosensing, reconfigurable surfaces, lenses.

Keywords: thermal and UV nanoimprint, hydrogel

Project leader: TECNALIA
Address: Pº Mikeletegi 2, 20009 San Sebastian, Spain
Web-Address: www.tecnalia.com

Process: UV-NIL
 Responsible: Isabel Obieta
 E-mail: isabel.obieta@tecnalia.com

Partner: Catalan Institute of Nanotechnology
Address: 08193 Bellaterra (Barcelona), Spain
Web-Address: http://www.icn.cat

Process: Step and Repeat NIL
 Responsible: Achille Francone
 E-mail: achille.francone@icn.cat

Process description: Fabrication of 3D nanopatterns on hydrogels

Purpose: The aim of this process is to obtain 3D nanopatterns in different hydrogels

Major challenges: The material does not easily fill in the cavities

Application and state-of-the-art: Currently patterns below 50nm have been demonstrated and 3D nanostructures have been obtained

References (mainly on antiadhesive coatings):

Contact information
Dr. Isabel Obieta
Tecnalia Research & Innovation
Pº Mikeletegi 2
20009 San Sebastian, SPAIN

LoP2012_NIL015_Hydrogel imprint-process
# Nanoimprinting of hydrogels

**Process: UV and thermal nanoimprint lithography**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 Process 1: Wafer preparation</td>
<td>Silicon wafer format</td>
<td>how it should work</td>
</tr>
<tr>
<td>1.1 wafer selection and preparation</td>
<td>standard SiO$_2$ substrate</td>
<td>critical issues</td>
</tr>
<tr>
<td>1.2 substrate preparation</td>
<td>pretreatment</td>
<td>In samples without TPM treatment, hydrogel layer peels off the substrate when it swells</td>
</tr>
<tr>
<td></td>
<td>TPM (3-trichlorosilyl propyl methacrylate) coating</td>
<td></td>
</tr>
<tr>
<td>End of Process 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 Process 2: Resist coating for UV - NIL</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Hydrogel concentration</td>
<td>Hydrogel dilution in order to get thin homogeneous layers</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Depending on the hydrogel formulation.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Less concentration than P30 (30%w) does not get uniform layers.</td>
<td></td>
</tr>
<tr>
<td>2.2 dispensing of resist</td>
<td>DROP DISPENSING or SPINNER</td>
<td></td>
</tr>
<tr>
<td>2.3 post bake</td>
<td>solvent evaporation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Not necessary</td>
<td></td>
</tr>
<tr>
<td>End of Process 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0 Process 3: Lithography</td>
<td>UV-NIL</td>
<td></td>
</tr>
<tr>
<td>3.1 Stamp</td>
<td>Stamp characteristics</td>
<td></td>
</tr>
<tr>
<td></td>
<td>It works with soft and hard stamps</td>
<td></td>
</tr>
</tbody>
</table>
### 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/cm²)

### 3.3 Resist development

**Residual layer etch.**
The residual layer is etched by RIE, using a combination of gases: Ar (1sccm) – O₂ (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 octadecyltrichlorosilane molecules in hexane. The preparation of the solution and the surface treatment have to be performed in an atmosphere with low content of humidity.

*Other SAMs work worse than OTS.*

### 4.3 Dip of the stamp

The stamp is dipped into the silane solution for 5-8 minutes. After 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 Lamberti

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

**IOM-CNR - 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 describes for the double side patterning is UV nanoimprinting.

Purpose: The aim of this process is demonstrate the increasing of efficiency more than 50% introducing low cost nanostructured surfaces enhancing the light extraction.

Major challenges: Anti-sticking treatments and deposition of ITO on plastic materials.

Application and state-of-the-art: the structuring of OLED device has been proposed in several work mainly based on microstructuring. Only in the last 2 years the introduction of sub-wavelength patterns has been proposed.

References:
[1] Improvement of the external extraction efficiency of OLED by using a pyramid array, Stanley Electric Co., Ltd. (Japan)

Contact information:
Vito Lambertini
CENTRO RICERCHE FIAT
Micro and Nanotechnologies department
Strada Torino 50,
Orbassano (TO), Italy
Email: vitoguido.lambertini@crf.it
URL: www.crf.it

LoP2007_NIL005_Double_side_OLED
## Double side patterned OLED

Process: nanoimprint lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0 Process 1: Substrate preparation</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| **1.1 wafer selection and preparation** | transparent substrate  
Glass substrate 35x45 mm  
Thickness 1 mm | | |
| **1.2 substrate preparation** | Cleaning  
washing in Micro90 solution diluted (2%);  
ultrasonic baths cycles (5 min) in water and ethanol | | |
| **1.3 adhesive coating** | treatment  
spin coating of MICROPOSIT or AP300 followed by 80°C for 2 min. | | |
| **End of Process 1** | | |
| **2.0 Process 2: Flexible stamp preparation** | | |
| **2.1 Layout** | Functional structures  
the stamp consist of:  
nickel mould  
squared pattern  
height 300 nm  
period 1 μm  
wafer selection  
100 μm sheet PET | | |
| **2.2 stamp preparation** | Hot embossing  
JRP recombiner machine:  
Nickel shim thickness 50 μm;  
Shim dimensions 30x40 mm;  
Heating time 0.5 s  
Cooling time 10 s  
DC current 80 A  
Pressure 1.4 tons | | |
<table>
<thead>
<tr>
<th>2.3</th>
<th>Process control</th>
<th>SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Flexible stamp image" /></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2.4</th>
<th>antiadhesive coating</th>
<th>silane saturation chamber</th>
</tr>
</thead>
<tbody>
<tr>
<td>End of Process 2</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3.0</th>
<th>Process 3: Double UV imprinting</th>
</tr>
</thead>
</table>

| 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). |
| ![Flexible stamp image](image2.png) |

| 3.2 | UV curing | EVG620 mask aligner |
| stack pre-assembled before UV exposition outside the machine. Exposition time 10 s. |
| ![Glass substrate and UV polymer image](image3.png) |

| 3.3 | Demolding | Manual demolding HEX03 (PSI) |
| demolding manually by peeling the flexible stamps. |
| ![Flexible stamp image](image4.png) |
### 3.4 Replication

<table>
<thead>
<tr>
<th>Glass substrate</th>
<th>Repeat processes form 2.1 to 2.3 to get the second side patterned.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replica</td>
<td>The process can be done in a single UV exposition using a stack composed by 2 flexible stamps.</td>
</tr>
</tbody>
</table>

**End of Process 3**

### 4.0 Process 4: OLED fabrication

#### 4.1 Anode deposition

<table>
<thead>
<tr>
<th>ITO</th>
<th>DC/RF sputtering system</th>
<th>Rotating sample holder to increase homogeneity; Alternating on/off of plasma to avoid overheating of the polymer layer.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Target:</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Indium-tin oxide 10-90 (Lesker)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Vacuum 5x10^-3 mbarr</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Current 300 mA</td>
<td></td>
</tr>
<tr>
<td>Rotate sample</td>
<td>holder to increase</td>
<td></td>
</tr>
<tr>
<td>holder</td>
<td>homogeneity; Alternating on/off</td>
<td></td>
</tr>
<tr>
<td>holder</td>
<td>of plasma to avoid</td>
<td></td>
</tr>
<tr>
<td>holder</td>
<td>overheating of the</td>
<td></td>
</tr>
<tr>
<td>holder</td>
<td>polymer layer.</td>
<td></td>
</tr>
</tbody>
</table>

#### 4.1 Process control

<table>
<thead>
<tr>
<th>Profilometer</th>
<th>Thickness 250 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV/Vis spectra</td>
<td>Transmittance 75%</td>
</tr>
<tr>
<td>Multimeter</td>
<td>Resistance 100 W/</td>
</tr>
</tbody>
</table>

#### 4.2 Active layers deposition

<table>
<thead>
<tr>
<th>PEDOT</th>
<th>Spin coating SÜSS RC8 spin coater</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPV</td>
<td>Double layer: PEDOT/PSS suspension (Bayer)</td>
</tr>
<tr>
<td></td>
<td>no vacuum</td>
</tr>
<tr>
<td></td>
<td>2500 rpm</td>
</tr>
<tr>
<td></td>
<td>5000 rpm/s</td>
</tr>
<tr>
<td></td>
<td>20-40 nm</td>
</tr>
<tr>
<td>PEDOT/PSS</td>
<td>PPVs (yellow/orange from Merck)</td>
</tr>
<tr>
<td>suspension</td>
<td>no vacuum</td>
</tr>
<tr>
<td>(Bayer)</td>
<td>2000-2500 rpm</td>
</tr>
<tr>
<td>PEDOT/PSS</td>
<td>5000 rpm/s</td>
</tr>
<tr>
<td>suspension</td>
<td>75-90 nm</td>
</tr>
</tbody>
</table>

#### 4.3 Cathode deposition

<table>
<thead>
<tr>
<th>Ca/Al</th>
<th>Thermal vacuum evaporation</th>
</tr>
</thead>
<tbody>
<tr>
<td>AUTO306 coater</td>
<td>Double layer: Ca</td>
</tr>
<tr>
<td></td>
<td>Vacuum 9x10^-6 mbarr</td>
</tr>
<tr>
<td></td>
<td>20-40 nm</td>
</tr>
<tr>
<td></td>
<td>Al (capping layer)</td>
</tr>
<tr>
<td></td>
<td>Vacuum 9x10^-6 mbarr</td>
</tr>
<tr>
<td></td>
<td>20-40 nm</td>
</tr>
</tbody>
</table>

### 3.4 Packaging

<table>
<thead>
<tr>
<th>Epoxy resin casting</th>
<th>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</th>
</tr>
</thead>
<tbody>
<tr>
<td>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.</td>
<td>The curing is made:</td>
</tr>
</tbody>
</table>
### NaPANIL_Library of Processes

**4.5 Measurement**

<table>
<thead>
<tr>
<th>Electro-optical analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>I/V curves</td>
</tr>
<tr>
<td>Efficiency curves (Lm/W)</td>
</tr>
<tr>
<td>Software CLEM (CRF):</td>
</tr>
<tr>
<td>power supply HP3432A</td>
</tr>
<tr>
<td>multimeter HP34401</td>
</tr>
<tr>
<td>photodiode/integrated sphere IL1700</td>
</tr>
</tbody>
</table>

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

**Address:** FI-02044 VTT, Finland

**Web-Address:** http://www.vtt.fi

**Process:** Step&stamp NIL

**Responsible:** Tomi Haatainen

**E-mail:** tomi.haatainen@vtt.fi

**Partner:** S.E.T. SAS (Smart Equipment Technology)

**Address:** 74490 Saint Jeoire, France

**Web-Address:** http://www.set-sas.fr

**Process:** NPS300 Step&stamp Tool

**Responsible:** Gilbert Lecarpentier

**E-mail:** glecarpentier@set-sas.fr

**Process description:** This document contains a description of a general thermal imprint process for fabrication of periodical structures using sequential imprinting to pattern large areas. The parameters are valid for small stamps (< 5x5 mm²) and submicron scale features.

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

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

**Application and state-of-the-art:** Anti-reflection gratings etc.

**References:**


---

**Contact information:**

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

LoP2007 NIL007 Step and Stamp NIL for optical gratings
## Optical grating by step&stamp NIL

**Process: nanoimprint lithography**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>What</strong></td>
<td>how it should work</td>
<td>critical issues</td>
</tr>
<tr>
<td><strong>1.0</strong></td>
<td><strong>Process 1: Wafer preparation</strong></td>
<td></td>
</tr>
</tbody>
</table>
| **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 °C (hotplate)  
The thermoplastic polymer 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 SUSS 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

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
<th>Details</th>
<th>Equipment</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>O₂ RIE:</td>
<td>O₂.............40 sccm gas pressure 125 mtorr power 150 W time 5 sec temperature 300 K</td>
<td>Plasmalab 80Plus RIE</td>
</tr>
</tbody>
</table>

#### 3.2 Process Control

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>AFM</td>
<td>Before substrate etching residual removal confirmed by AFM</td>
</tr>
</tbody>
</table>

#### 3.3 Substrate Etching

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>CF₄+Ar RIE</td>
<td>CF₄.............20 sccm Ar.............5 sccm gas pressure....20 mTorr power........100 W time............temperature.....300K</td>
</tr>
</tbody>
</table>

#### 3.4 Process Control

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>Optical microscope 100 x</td>
<td></td>
</tr>
</tbody>
</table>

#### 3.5 Process Control

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>Ellipsometer</td>
<td>Resist thickness check</td>
</tr>
</tbody>
</table>

#### 3.6 Measurement

<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>AFM, SEM</td>
<td></td>
</tr>
<tr>
<td>-</td>
<td>SEM LION video prints No.</td>
<td></td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Project leader:</th>
<th>Tyndall National Institute</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address:</td>
<td>Lee Maltings, Prospect Row, Cork, Ireland</td>
</tr>
<tr>
<td>Web-Address:</td>
<td><a href="http://www.tyndall.ie">http://www.tyndall.ie</a></td>
</tr>
<tr>
<td>Process:</td>
<td>Thermal nanoimprint</td>
</tr>
<tr>
<td>Responsible:</td>
<td>C.M. Sotomayor Torres</td>
</tr>
<tr>
<td>E-mail:</td>
<td></td>
</tr>
</tbody>
</table>

**Process description:** A process is described for two-dimensional nanoimprinted polymer photonic crystal coupled to surface plasmons. A stamp with different lattice constant PhCs was fabricated in a silicon wafer by using electron-beam lithography and dry etching. A thermal NIL process is used to replicate these 2D periodic patterns in a dye-doped polymer.

**Purpose:** The aim of this process is to provide a method to enhance the photoluminescence of dye chromophores-loaded by coupling the emission to surface plasmons in nanoimprinted photonic crystals.

**Major challenges:** The major challenge in this process is to control clusters formation on the metallic film to allow the matching of the surface plasmon resonance wavelength with the emission wavelength of the dyes.

**Application and state-of-the-art:** The combination of surface plasmons and nanoimprinted structures in an active layer can lead to a new class of cost effective and high efficiency OLEDs. Furthermore, the metallic surface could be used as an electrical contact.

**References:**


**Contact information (2012):**

Prof. Dr. Clivia M. Sotomayor Torres  
ICREA Research Professor  
Phononic and Photonic Nanostructures Group  
Catalan Institute of Nanotechnology (CIN2-CSIC)  
Campus Bellaterra - Edifici CM3  
08193 Bellaterra (Barcelona), SPAIN

**LoP2007_NIL008_photonic crystals**
## Photonic crystals for enhanced light extraction

### Process: nanoimprint lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>What</strong></td>
<td><strong>how it should work</strong></td>
<td><strong>critical issues</strong></td>
</tr>
<tr>
<td><strong>1.0</strong> Process 1: Wafer preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>1.1</strong> wafer selection and preparation</td>
<td>Standard glass or Pyrex substrate</td>
<td></td>
</tr>
<tr>
<td><strong>1.2</strong> substrate preparation</td>
<td>no pre-treatment of the substrate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dye-doped polymer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Metal (Al, Ag, Au or none)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Glass substrate</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>1.3</strong> Process control</td>
<td>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 μm²) 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.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The dye-doped polymer is composed of rhodamine 6G (from Sigma Aldrich) directly dissolved in an imitable resist mr-NIL 6000 from micro resist technology GmbH (see description below).</td>
<td></td>
</tr>
<tr>
<td></td>
<td>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.</td>
<td></td>
</tr>
</tbody>
</table>

End of Process 1

### 2.0 Process 1: Stamp preparation

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>2.1</strong> layout</td>
<td>Functional structures</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The stamp consists of 10 arrays of pillars (350 nm height) on an area of 100x100 mm² with a 100 mm pitch between arrays. The size of the Si is 2x2 cm².</td>
<td></td>
</tr>
<tr>
<td><strong>2.2</strong> stamp preparation</td>
<td>wafer selection</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The stamp was fabricated in a silicon wafer by using electron-beam lithography and dry etching (for details, see introduction of this process).</td>
<td></td>
</tr>
<tr>
<td>Section</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>2.3</td>
<td>Anti-adhesive coating</td>
<td>The silicon stamp is treated with a self-assembled anti-adhesive monolayer (tridecafluoro-1, 1, 2, 2-tetrahydrooctyl trichlorosilane deposited in vapour phase).</td>
</tr>
<tr>
<td>3.0</td>
<td>Process 3: Nanoimprint Lithography</td>
<td></td>
</tr>
<tr>
<td>3.1</td>
<td>Process control: SEM top-view of the nanoimprinted photonic crystals</td>
<td>The stamp and the coated substrates are pressed together in a 2.5 inch Obducat nanoimprinter at 60 bar for 5 min at 90 °C. The pressure is sustained during the cooling phase until the temperature fell below 35 °C.</td>
</tr>
<tr>
<td>2.2</td>
<td>Measurement: Optical characterization</td>
<td>Figure: a/ Photoluminescence spectra of a nanoimprinted unpatterned dye-doped polymer film on a quartz substrate (black line), of a 2D photonic crystal with a 380 nm lattice constant (blue line), with a 500 nm lattice (green line) and with a 700 nm lattice (red line), b/ photoluminescence spectra of a flat surface imprinted on a quartz substrate (black line), of a 2D photonic crystal with a 700 nm lattice constant imprinted on a 50 nm Ag quartz substrate (blue line), of a 2D photonic crystal with a 700 nm lattice constant imprinted on a quartz substrate (red line), of a nanoimprinted unpatterned dye-doped polymer film on a 50 nm Ag quartz substrate (green line).</td>
</tr>
</tbody>
</table>

End of Process 2

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/cm² 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 °C for 10 min before the NIL process. The stamp and the coated substrates are pressed together in a 2.5 inch Obducat nanoimprinter at 60 bar for 5 min at 90 °C. The pressure is sustained during the cooling phase until the temperature fell below 35 °C. The metal films were deposited using NFC 2000 Temescal 6 kW electron beam guns with a deposition rate of 10 Angstroms per second. The control of the deposition rate allows the tuning of the surface plasmon frequency of the film throughout the visible.

**Purpose:** The aim of this process is to provide a method to enhance the photoluminescence of dye chromophores-loaded by coupling the emission to surface plasmons in nanoimprinted photonic crystals. Two critical research issues in organic optoelectronics are to reduce the cost of organic LEDs and to improve their external efficiency. One approach to improve the extraction efficiency is to use two-dimensional (2D) photonic crystals (PhCs). A PhC structure enhances the light emitted from the active layer by slowing the propagation speed of the photons, thus increasing the coupling to the out-of-plane radiative modes. Another approach is to increase the spontaneous recombination rate of the emitters. This can be based on the energy transfer between light emitters and surface plasmons (SPs).

**Major challenges:** The major challenge in this process is to control clusters formation on the metallic film to allow the matching of the surface plasmon resonance wavelength with the emission wavelength of the dyes.

**Application and state-of-the-art:** The two approaches mentioned above have been combined to enhance the light-emission efficiency of organic thin films. An active polymer film deposited on a metal surface is patterned by NIL and the SP energy is matched to that of the emitter in the PhC, reaching up to a x 27 enhancement. Our results indicate that nanoimprint lithography is a well suited process to fabricate these challenging photonic structures and that the combination of surface plasmons and nanoimprinted structures in an active layer can lead to a new class of cost effective and high efficiency OLEDs. Furthermore, the metallic surface could be used as an electrical contact.
### 4.4 Refractive microlenses

#### Fabrication of microlenses and complex refractive surfaces

<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Figure:</strong> 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.</td>
<td><strong>Application:</strong> Spherical or cylindrical microlens arrays with full control on radii of curvature and diameter</td>
</tr>
</tbody>
</table>

**Keywords:** Isotropic wet etching, glass template, hot embossing, polymer casting

<table>
<thead>
<tr>
<th><strong>Project leader:</strong> TASC Laboratory</th>
<th><strong>Process:</strong> Isotropic etching / NIL</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Address:</strong> S.S.14km 163,5; 34012 Basovizza (Trieste, Italy)</td>
<td><strong>Responsible:</strong> Massimo Tormen</td>
</tr>
<tr>
<td><strong>Web-Address:</strong> <a href="http://www.tasc-infm.it">www.tasc-infm.it</a></td>
<td><strong>E-mail:</strong> <a href="mailto:tormen@iom.cnr.it">tormen@iom.cnr.it</a></td>
</tr>
</tbody>
</table>

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


**Contact information:**

Dr. Massimo Tormen
Beamline scientist
CNR - Istituto Nazionale per la Fisica della Materia
Laboratorio Nazionale TASC
Area Science Park - Basovizza
S.S.14 - km163,5
34012 Bassowizza - Italy

**LoP2007_NIL009_Microlenses with spherical molds**
## Refractive microlenses

**Process: nanoimprint lithography**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0a</strong></td>
<td><strong>Process 1: Stamp preparation</strong> First option (a)</td>
<td></td>
</tr>
<tr>
<td><strong>1.1a</strong></td>
<td>Stamp substrate preparation</td>
<td>Sputter coating soda-lime glass with 100 nm chromium film.</td>
</tr>
<tr>
<td><strong>1.2a</strong></td>
<td>Layout</td>
<td>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.</td>
</tr>
<tr>
<td><strong>1.3a</strong></td>
<td>Pattern definition by lithography</td>
<td>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/cm² 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</td>
</tr>
<tr>
<td><strong>1.4a</strong></td>
<td>Chromium etching</td>
<td>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)</td>
</tr>
<tr>
<td><strong>1.5a</strong></td>
<td>Wet etching of glass</td>
<td>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.</td>
</tr>
<tr>
<td><strong>1.6a</strong></td>
<td>Chromium stripping</td>
<td>Stripping the chromium film by etching in aqueous solution of ammonium cerium (IV)</td>
</tr>
<tr>
<td>1.7a</td>
<td><strong>Second step of wet etching of glass</strong></td>
<td>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.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0b</td>
<td><strong>Process 1: Stamp preparation</strong>&lt;br&gt;Second option (b)</td>
<td></td>
</tr>
<tr>
<td>1.1b</td>
<td><strong>Process 1: Stamp substrate preparation</strong></td>
<td>Clean soda-lime glass surface is required as initial substrate.</td>
</tr>
<tr>
<td>1.2b</td>
<td><strong>Focused ion beam</strong></td>
<td>Holes are milled at different depths in a quartz substrate by focused ion (Ga+) beam at 30 KeV. Centers of curvature can be located at different coordinates (x,y,z), below the glass surface.</td>
</tr>
<tr>
<td>1.3b</td>
<td><strong>Wet etching of glass</strong></td>
<td>Different diameter (same radius of curvature) are obtained as a function of the height of the milled holes.</td>
</tr>
<tr>
<td>1.8a and 1.4b</td>
<td><strong>Process control: SEM, AFM</strong></td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td><strong>Process 2: Coating for anti-adhesion</strong></td>
<td></td>
</tr>
<tr>
<td>2.1</td>
<td><strong>Coating with a hydrophobic monolayer of dodecyltrichlorosilane</strong></td>
<td>The glass stamp is immersed for 10 min in freshly prepared solution of $H_2O_2:H_2SO_4$ (1:4). Dodecyltrichlorosilane 1-5 mM in toluene is prepared in glovebox under nitrogen atmosphere. 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.</td>
</tr>
</tbody>
</table>
| 3.0 | Process 3: Embossing or polymer casting

3.1 Different option for producing plastic microlenses.  
- nanoimprinting  
- hot embossing  
- polymer casting  

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

<table>
<thead>
<tr>
<th>Process: Nanoimprint, hot embossing</th>
<th>Figure: Photograph of a 200 mm wafer imprinted and etched using an anisotropic process</th>
<th>Process: Plasma etching processes are optimized to anisotropic pattern transfer, allowing the transfer of various densities of structures</th>
</tr>
</thead>
<tbody>
<tr>
<td>Keywords: thermal nanoimprint, PDMS, rolling</td>
<td>Application: Si devices with various patterns size and densities</td>
<td></td>
</tr>
</tbody>
</table>

Process description: Large surfaces require a high imprint uniformity, which is easier to achieve with residual layers in the 50-100 nm range. An 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 O₂/Cl₂/Ar plasma chemistry in an 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:

Contact information:
Dr. Mathis Riehle
Centre for Cell Engineering
University of Glasgow
Glasgow G12 8QQ - UK
### Biodegradable polymer scaffold

**Process**: nanoimprint lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0 Process 1: Micro master fabrication</strong>&lt;br&gt;Micrograting: 6 µm pitch, 6 µm deep</td>
<td><strong>1.1 Wafer selection</strong>&lt;br&gt;standard Si substrate&lt;br&gt;Si substrate, 4&quot;. &lt;100&gt;, d=525 µm, one side polished</td>
<td><strong>1.2 Resist coating</strong>&lt;br&gt;spin coat resist&lt;br&gt;Primer at 5 krpm for 5 s&lt;br&gt;S1818 @ 4 krpm for 60 s&lt;br&gt;Bake 10 minutes @ 90°C (hot plate)</td>
</tr>
<tr>
<td><strong>1.3 Photolithography</strong>&lt;br&gt;SÜSS Mask Aligner MA6&lt;br&gt;Expose (i-line) for 5 s&lt;br&gt;Develop in 1:1 Microposit concentrate:RO water for 70 s&lt;br&gt;Dry in N₂ stream</td>
<td><strong>1.4 Dry etch - micro grooves</strong>&lt;br&gt;C₄F₈, SF₆&lt;br&gt;50 sccm, 40 sccm&lt;br&gt;Coil power&lt;br&gt;600 W&lt;br&gt;Platen power&lt;br&gt;10 W&lt;br&gt;Pressure&lt;br&gt;10 mT&lt;br&gt;Etc rate&lt;br&gt;825 nm/min&lt;br&gt;6 µm deep</td>
<td><strong>1.5 Spacers</strong>&lt;br&gt;SU8 2050 @ 3 krpm (75 µm)&lt;br&gt;30 min at 95°C&lt;br&gt;MA6, 20 seconds&lt;br&gt;PEB 95°C for 7 minutes&lt;br&gt;Develop in EC solvent for 7-10 minutes&lt;br&gt;Rinse in IPA and dry in N₂ stream</td>
</tr>
</tbody>
</table>

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*Note: The table contains technical parameters and remarks for each step of the nanoimprint lithography process.*
<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.7 PDMS micro stamp</td>
<td>Cast 4:1 (pre-polymer:curing agent) Sylgard 184 to make inverse replica of stamp</td>
</tr>
<tr>
<td>2.0 Process 2: Nano master fabrication</td>
<td></td>
</tr>
</tbody>
</table>
| 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/cm² exposure dose for an array of 10⁹ spots/cm²  
Develop O-xylene 60 s  
Rinse in IPA and dry in N₂ stream |
| 2.4 Dry etch | C₄F₈, SF₆  
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
<table>
<thead>
<tr>
<th>2.6</th>
<th>PDMS nano stamp</th>
<th>silane ((\text{C}_8\text{H}_4\text{Cl}<em>3\text{F}</em>{13}\text{Si})) from Gelest for 5-10 minutes. Rinse in heptane and dry in (\text{N}_2) stream</th>
<th>is a highly oxidizing solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.6</td>
<td>PDMS nano stamp</td>
<td>Cast 4:1 (pre-polymer:curing agent) Sylgard 184 to make inverse replica of stamp</td>
<td>See also 5.3.2 Soft and hybrid layered stamps.</td>
</tr>
</tbody>
</table>

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 sandwiched between the PDMS micro and nano-stamps. Melt embossed (80°C) at a low pressure and allowed to cool. |  |

End of Process 3
<table>
<thead>
<tr>
<th>4.0</th>
<th>Process 4: Rolling</th>
</tr>
</thead>
</table>
| **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 cellulose acetate 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

**Address:** FI-02044 VTT, Finland

**Web-Address:** http://www.vtt.fi

**Process:** Roll-to-roll NIL

**Responsible:** Tapio Mäkelä

**E-mail:** Tapio.Makela@vtt.fi

**Process description:** A process is based on continuous roll to roll manufacturing of fluidistic channels by using custom made manufacturing tool. Printing instrument consist two sequential units: thermal imprint lamination. In continuous manufacturing process; fluidics channels were imprinted on cellulose acetate web and sealed with an laminate foil during the same printing cycle. In roll to roll NIL process a softening temperature of web is higher than in a laminate film.

**Purpose:** The aim of this process is to demonstrate a high volume continuous roll to roll nanoimprinting process. In this process we show possibility to manufacture fluidics channels with continuous process. A specific requirements of sequential process were shown.

**Major challenges:** In this novel process a many challenges can be listed: Manufacturing methods for imprint master (on a roll) and optimal parameters for pressure, temperature and time. Suitable plastic materials on web is needed,since in roll to roll manufacturing typical imprint time is 1 s or shorter. This process is developed by optimizing parameters suitable for cellulose acetate but PMMA, TOPAS, PS and other materials where softening or glass transition 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:**


**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

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>What</strong></td>
<td><strong>how it should work</strong></td>
<td><strong>critical issues</strong></td>
</tr>
<tr>
<td><strong>1.0 Process 1: Master fabrication</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>1.1 Metallic cylinder</strong></td>
<td>Metal roll and engraved channel structure on roll</td>
<td></td>
</tr>
<tr>
<td></td>
<td>roll size 66 x 60 mm (diameter x width)</td>
<td></td>
</tr>
<tr>
<td><strong>1.2 Substrate preparation</strong></td>
<td><strong>Substrates</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Plastic roll: 50 mm width, 95 um cellulose acetate, no pre-treatment</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Laminate roll: 50 mm width, 90 um thick laminate with meltable glue</td>
<td></td>
</tr>
<tr>
<td><strong>End of Process 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2.0 Process 2: Stamp preparation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2.1 layout</strong></td>
<td><strong>Functional structures</strong></td>
<td>engraved grooves are relatively good but edges not clean</td>
</tr>
<tr>
<td></td>
<td>Engraving of roll</td>
<td></td>
</tr>
<tr>
<td></td>
<td>The stamp consist of 150 μm width and 500 μm depth grooves.</td>
<td></td>
</tr>
<tr>
<td><strong>2.2 process control</strong></td>
<td><strong>optical microscope 100 x</strong></td>
<td></td>
</tr>
<tr>
<td><strong>End of Process 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3.0 Process 2: Roll to roll nanomprinting</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>3.1 Roll to roll imprint</strong></td>
<td><strong>Thermal roll to roll imprint</strong></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pressure 8 MPa</td>
<td>T_g of cellulose acetate 120 C</td>
</tr>
<tr>
<td></td>
<td>Temperature 105 C</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Speed 0.2 – 8 meter/minute</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 mm contact area between printing and backing rolls</td>
<td></td>
</tr>
</tbody>
</table>
### 3.2 Cooling/demolding

- **Cooling**
  - at room atmosphere (no blow)
  - 30 cm distance between units

### 3.3 process control

- **Optical microscope**

#### End of Process 3

### 4.0 Process 3: Cover

#### 4.1 Laminated cover for fluidics

- **Thermal roll to roll laminating**
  - Pressure < 0.1 MPa
  - Temperature 80°C
  - Speed 0.2 – 8 meter/minute
  - 1 mm contact area between printing and backing rolls

#### 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/](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](http://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:**

**Contact information:**
Anders Kristensen
Department of Micro- and Nanotechnology
Technical University of Denmark
DTU Nanotech, Building 345 East
2800 Kongens Lyngby
Denmark
Email: Anders.Kristensen@nanotech.dtu.dk

**LoP2007_NIL014_V-Groove Waveguides**
# V-grooves for plasmon confinement

**Process**: nanoimprint lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0 Process 1: Stamp fabrication</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 <strong>wafer selection</strong></td>
<td>standard Si (100) substrate 4&quot;, d=500 µm double side polished</td>
<td></td>
</tr>
<tr>
<td>1.2 <strong>substrate preparation</strong></td>
<td>Wet oxidation at 1100ºC (oxide thickness ~200nm)</td>
<td></td>
</tr>
<tr>
<td>1.3 <strong>Photolithography 1</strong></td>
<td>Spin coating of UV resist (1.5µm of AZ5214B), UV exposure, and development.</td>
<td></td>
</tr>
<tr>
<td>1.4 <strong>RIE</strong></td>
<td>RIE of 200 nm of SiO2. Stripping of the photoresist (acetone)</td>
<td></td>
</tr>
<tr>
<td>1.5 <strong>KOH to define V</strong></td>
<td>Anisotropic wet etching in KOH (wt 30%), at 80ºC, during 1h.</td>
<td></td>
</tr>
<tr>
<td>1.6 <strong>Oxide removing</strong></td>
<td>HF 50%, 1 minute.</td>
<td></td>
</tr>
<tr>
<td>1.7 <strong>Photolithography 2</strong></td>
<td>Spin coating of UV resist (1.5µm of AZ5214B), UV exposure, and development.</td>
<td></td>
</tr>
<tr>
<td>1.8 <strong>D-RIE to define the channels</strong></td>
<td>Deep RIE of silicon, to define the channels (300 µm deep). <strong>Vertical and smooth side-walls should be obtained, otherwise demolding would be difficult.</strong></td>
<td></td>
</tr>
<tr>
<td>1.9 <strong>Resist stripping</strong></td>
<td>Acetone and ultrasounds, to remove the resist.</td>
<td></td>
</tr>
<tr>
<td>1.9 b <strong>Process control</strong></td>
<td>SEM</td>
<td></td>
</tr>
<tr>
<td>1.10 <strong>Optional: improvement of the sharpness of the V.</strong></td>
<td>Wet oxidation, 6h at 1150ºC. <strong>For each size of the grooves, the oxidation time can be optimized (by simulations), to achieve the sharpest angle in the bottom.</strong></td>
<td></td>
</tr>
</tbody>
</table>
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-perfluorodecytri-chlorosilane) using a MVD system (Applied Microstructures Inc.)

End of Process 1

2.0 Process 2: NIL

2.1 Substrate preparation
PMMA sheet, 5mm thick. Dehydrated in an oven, at 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, otherwise, 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 available UV-curable hybrid polymers especially suited for the fabrication of micro-optical components. Further information on sol-gel materials and hybrid polymers can be found in on Page 37.
4.8 Hydrogel waveguide optical sensor structure

Fabrication of UV curable hydrogel waveguides with outcoupler

**Process:** Nanoimprint lithography

**Figure:** SEM image of waveguide with crossed grating outcouple imprinted in hydrogel

**Keywords:** optical sensor, waveguide, outcoupler, UV nanoimprint, hydrogel

**Process:** UV Nanoimprint

**Application:** Environmental and chemical sensor, humidity, pH

**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):**


**Contact information:**

Prof. Clivia Sotomayor Torres
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

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td><strong>Process 1: Stamp preparation</strong></td>
<td>E-beam lithography</td>
</tr>
<tr>
<td>1.1</td>
<td><strong>Wafer selection and preparation</strong></td>
<td>Standard Si substrate 100mm &lt;100&gt; Thickness 525 µm</td>
</tr>
<tr>
<td>1.2</td>
<td><strong>Stamp layout</strong></td>
<td>The pattern consists of 10 – 20 ridge waveguides of width 1 – 5 µm, length 20 mm and height 1 µm, and separated by 1 mm. Overlaid on this in the perpendicular direction is a grating pattern of period 750nm, line width 450 nm, and height 100 nm, covering an area of 10mm x 1mm.</td>
</tr>
<tr>
<td>1.3</td>
<td><strong>Pattern first level of structure</strong></td>
<td>E-beam lithography of ridge waveguides Reactive Ion Etch to depth of 600 nm</td>
</tr>
<tr>
<td>1.4</td>
<td><strong>Pattern second level of structure</strong></td>
<td>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.</td>
</tr>
<tr>
<td>1.5</td>
<td><strong>Anti-adhesion coating</strong></td>
<td>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</td>
</tr>
<tr>
<td>1.6</td>
<td><strong>Process control</strong></td>
<td>Optical microscopy SEM</td>
</tr>
</tbody>
</table>

End of Process 1
2.0 Process 2: Stamp Replication

2.1 Substrate selection and preparation

- **Quartz substrate**
  - Area: 20mm x 20 mm, 0.5mm thick
  - Oxygen plasma treatment to improve adhesion.

  *OrmoStamp 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 3 bars (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 (Octadecyltri-chlorosilane)**
  - 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
### 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/cm$^2$ at 365 nm)
- Imprinting was performed on a home-made imprinting module.

#### 3.4 Process Control
- Optical microscopy, SEM, AFM

---

**General remarks:**
The generation of pattern copies in terms of working stamps can be advantageous for a wide range of reasons (see Page 30). Hybrid polymers like OrmoStamp used for working stamps are low-cost alternative to electroplated stamps (see Page 37) and thus are accessible for a wide range of engineers and researchers.
4.9 All-silica micro and nanofluidic device

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

**Process:** Sol-gel imprint with silicon stamp

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

**Process:** Imprint of micro- and nanochannels in sol-gel silica with hard stamp and fusion bonding to glass lid.

**Application:** Micro- and nanofluidic lab-on-a-chip devices.

**Keywords:** sol-gel silica, nanoimprint, nanofluidics, lab-on-a-chip, fusion bonding

**Project leader:** Technical University of Denmark (DTU)
**Address:** Build. 345 B, DK-2800 Kgs. Lyngby, Denmark
**Web-Address:** http://www.nanotech.dtu.dk
**Process:** Sol-gel NIL with hard stamp
**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
**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:**

**Contact information:**
Prof. Anders Kristensen
DTU Nanotech
Technical University of Denmark
Build. 345 B
DK-2800 Kgs. Lyngby
Denmark

**LoP2012_NIL017_SVI hybrid materials**
## All-silica micro and nanofluidic device

### Process: Thermal imprint

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0 Process 1: Material preparation</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Mix sol-gel material</td>
<td>Sol preparation</td>
<td>Methytriethoxysilane (MTES) is mixed with HCl (pH 2.0) at a molar mixing ratio MTES:H₂O of 1:14.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Process described in Mikkelsen et al. Lab Chip 12, 262-267 (2012) [1].</td>
</tr>
<tr>
<td>1.2 Aging of sol</td>
<td>Aging</td>
<td>The two-phased solution is vigorously stirred to obtain a single-phased sol, which is aged for 3.5 hours. Reaction kinetics and gel properties are highly sensitive to the pH of the solution.</td>
</tr>
</tbody>
</table>

**End of Process 1**

<table>
<thead>
<tr>
<th><strong>2.0 Process 2: Spin-coating</strong></th>
<th>Gel formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1 Dispensing of sol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Dispensing of sol</td>
</tr>
<tr>
<td>2.2 Spin-coating</td>
<td>Spin-coating to produce gel film</td>
</tr>
<tr>
<td></td>
<td>Sensitive to humidity during spin-coating. A relative humidity of 45% is used. If the relative humidity drops to 25%, the gel is hard after coating and the storage and pre-curing steps must be changed.</td>
</tr>
<tr>
<td>2.3 Storage</td>
<td>Storage and drying</td>
</tr>
<tr>
<td></td>
<td>Reduction of water content before imprint</td>
</tr>
</tbody>
</table>

**End of Process 2**

<table>
<thead>
<tr>
<th><strong>3.0 Process 3: Imprint</strong></th>
<th>Imprint</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### 3.1 Stamp

**Hybrid stamp**
A hybrid stamp with nanostructures defined in SiO$_2$ and microstructures defined in OrmoComp on a silicon substrate is used for imprint. Perfluorodecyltrichlorosilane (FDTS) is used as anti-sticking coating.

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 temperature profile. Imprint: 5 min at 10 kN, heating: to 120°C at 7°C/min, stay at 120°C for 20 min to fully cure the gel, cooling to 60°C and pressure release.

Slow condensation at 60°C and reduced viscosity assures good filling 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 dimension. For imprinted pattern with large density of free surfaces the deformation 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 described 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 increased when the bonded substrates are annealed at 550°C for 12 hours.

End of Process 5

End of Total Process
4.10 Roll-to-roll NIL for backlight devices

**Roll-to-roll pilot nanoimprinting process for backlight devices**

<table>
<thead>
<tr>
<th>Process: Thermal nanoimprint lithography</th>
<th>Main technologies required: Roll to Roll NIL lithography, Flexible Ni-mold and assembly</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure: A pilot scale Roll to Roll manufacturing process for backlight devices on Poly(methylmethacrylate) (PMMA) film.</td>
<td>Application: Roll to roll NIL in high volume applications and continuous processing. R2R NIL for backlighting of flat panel displays</td>
</tr>
</tbody>
</table>

**Keywords:** Roll to roll nanoimprinting, thermal NIL, flexible Ni-mold, Roll to roll tools

<table>
<thead>
<tr>
<th>Project leader: VTT Technical Research Centre of Finland</th>
<th>Process: Roll to Roll thermal NIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address: Helsinki, FI</td>
<td>Responsible: Tapio Mäkelä</td>
</tr>
<tr>
<td>Web-Address: <a href="http://www.vtt.fi">http://www.vtt.fi</a></td>
<td>E-mail: <a href="mailto:tapio.makela@vtt.fi">tapio.makela@vtt.fi</a></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Partner: Senidomia Oy</th>
<th>Process: Design, application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address: Helsinki, FI</td>
<td>Responsible: Leo Hatjasalo</td>
</tr>
<tr>
<td>Web-Address: <a href="http://www.senidomia.com">http://www.senidomia.com</a></td>
<td>E-mail: <a href="mailto:leo.hatjasalo@senidomia.com">leo.hatjasalo@senidomia.com</a></td>
</tr>
</tbody>
</table>

**Process description:** Light illumination device is imprinted on PMMA web using a laboratory scale Roll to Roll imprinting machine. Backlight device (28 x 28) mm² consist more than 78 000 binary elements with different orientation. Each element has 40 trenches with 5 micron width and 1.3 micron thick, totally 3.1 million trenches in one device. Parameters were optimized in continuous roll-to-roll imprinting. More than 1000 device printed to demonstrate pilot production.

**Purpose:** The aim of this process is to demonstrate a pilot processing of display illumination device.

**Major challenges:** Printing quality of optical elements in Roll to Roll process and wearing of the mold.

**Application and state-of-the-art:** Partially standard process, but continuous high quality manufacturing not yet shown.

**References:**

# Roll-to-roll pilot nanoimprinting process for backlight devices

Process: Thermal nanoimprint lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0</strong> Process 1: Designing of backlight elements and materials</td>
<td>Designing</td>
<td>how it should work: critical issues</td>
</tr>
<tr>
<td>1.1 Design of backlight device</td>
<td>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.</td>
<td></td>
</tr>
<tr>
<td>1.3 Light element</td>
<td>Backlight device (28 x 28) mm² consist more than 78 000 binary elements with different orientation. Each element has 40 trenches with 5 micron width and 1.3 micron thick, totally 3.1 million trenches in one device.</td>
<td></td>
</tr>
<tr>
<td>1.4 Device material</td>
<td>375 micron thick PMMA with good optical parameters is be used to achieve optimum performance. optical transparency is 92% refractive index 1.49 softening temperature 100°C</td>
<td>PMMA quality critical</td>
</tr>
</tbody>
</table>

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.

---

3.0 **Process 3: Pilot Roll to Roll production of 1000 device**

**Pilot process**

3.1 **Unwinder**

PMMA substrate (50 mm wide) is located in unwinder.

3.2 **Thermal Roll to roll NIL**

The mold is wrapped on metallic cylinder (width 60 mm) and heated to operation temperature 115 °C. The printing speed 0.6 meter/minute and pressure 8 MPa. Printing parameters are critical

3.5 **Rewinder**

Printed devices were wrapped on rewinder roll. Web tension accurately tuned

3.7 **1000 printed device on roll**

The wearing of the mold does not effect to the quality of the printed binary element at least in a volumes up to 1000 pcs

**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 2

End of Process 3
### 4.0 Process 4: LED connection and characterization of device

<table>
<thead>
<tr>
<th>4.1 Illumination element</th>
<th>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.</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2 Depth variation</td>
<td>Depths of printed grooves are typically within 1.2-1.4 µm. 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.</td>
</tr>
<tr>
<td>4.3 Backlight device</td>
<td>LED attachment and luminance measurement Three LED connected to the device. Average luminance value was 120 cd/m². The standard deviation for the measured luminescence values for all devices was within 17 %.</td>
</tr>
</tbody>
</table>

| End of Process 4         | |
| End of Total Process     | |
4.11 Replication by Injection Molding

Conventional injection molding with 100 mm full wafer tool

**Process:** Thermal injection molding

**Figure:** Photograph of an injection molded specimen of an array (44x44mm²) of pillars with 200nm diameter and 600 nm period, replicated directly from a 100mm silicon wafer using a dedicated molding tool for wafer injection molding. This example was replicated in transparent polyamide

**Process:** Conventional (isothermal) injection molding for micro- and nanostructure replication from silicon wafers

**Application:** Microfluidics, DOEs, photonics, security features.

**Keywords:** thermal nanoimprint, PHABLE, plasma etching, surface coating

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

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

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

**Process:** Thermal Nanoimprint
**Responsible:** Helmut 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 produce high volume micro/nanostructured parts made out of bulk polymers, displaying a surface structure that adds functionality.

**Major challenges:** The durability of the silicon mold insert depends very much on the tool integration method as well as on the structures to be replicated and the quality of the antisticking coating. Filling of nanostructured cavities is challenging as the polymer melt freezes rapidly (within milliseconds) upon contact with the mold, usually held close to the T_g of the polymer.

**Application and state-of-the-art:** This dedicated tool is mainly used for preliminary studies on the replication behavior of nanostructures created by lithographic methods and transferred into silicon

**References (mainly on antiadhesive coatings):**


**Contact information:**

Prof. Dr. Per Magnus Kristiansen
University of Applied Sciences and Arts FHNW
Institute of Polymer Nanotechnology
Klosterzelgstrasse 2
CH-5210 Windisch, Switzerland

**LoP2012_NIL019_full wafer injection molding**
## Conventional injection molding with 100 mm full wafer tool

**Process**: wafer injection molding

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>What how it should work</td>
<td>critical issues</td>
<td></td>
</tr>
</tbody>
</table>

### 1.0 Process 1: Master generation

<table>
<thead>
<tr>
<th>What</th>
<th>Critical Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon wafer format</td>
<td></td>
</tr>
</tbody>
</table>

#### 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

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

#### 2.1 Tooling preparation

<table>
<thead>
<tr>
<th>Tooling and materials</th>
<th>Tooling and materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clamping Ring</td>
<td>Metal Support</td>
</tr>
<tr>
<td>4” silicon wafer</td>
<td>PI-film: 25µm</td>
</tr>
</tbody>
</table>

- Dedicated molding tool integration of silicon wafer into tool insert by clamping

Polyimide (Kapton) films are used as spacers to compensate for surface roughness of the metal support and to minimize the danger for.

#### 2.2 Material preparation

<table>
<thead>
<tr>
<th>Tooling and materials</th>
<th>Tooling and materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drying of polymer</td>
<td>Respective drying conditions can be found in respective product brochures</td>
</tr>
</tbody>
</table>

Many thermoplastic materials need drying before processing.

#### 2.3 Tool mounting and alignment

<table>
<thead>
<tr>
<th>Tooling and materials</th>
<th>Tooling and materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mounting of tool</td>
<td>And proper alignment of molding tools</td>
</tr>
</tbody>
</table>

#### 2.3 Connection of periphery

<table>
<thead>
<tr>
<th>Tooling and materials</th>
<th>Tooling and materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suitable periphery includes</td>
<td>The process protocol needs to be adjusted to account for all necessary process steps. This is particularly important for the robot handling system</td>
</tr>
</tbody>
</table>

Mold temperature control, Pressure- and temperature sensors, robot handling system for part removal.

### End of Process 2
3.0 Process 3: Injection molding

<table>
<thead>
<tr>
<th>3.1 System setup and equilibration with starting parameters</th>
<th>Process definition</th>
<th>This is typically straightforward to those skilled in the art of injection molding.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Process definition</td>
<td>Involves programming the entire process cycle and corresponding periphery addressing (venting, mold temperature variation, handling system, …)</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3.2 Filling study to determine optimum injection volume</th>
<th>Particularly important for unknown materials</th>
<th>This approach offers additional insight into the filling behavior of investigated nanostructures, in comparison to NIL filling studies.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particularly important for unknown materials</td>
<td>This step can be avoided when optimum process conditions have been established previously.</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3.3 Injection molding</th>
<th>Replication</th>
<th>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</th>
</tr>
</thead>
<tbody>
<tr>
<td>Replication</td>
<td>mold temperature close to ( T_m ) melt temperature: flexible pressure: depends on structure filling velocity: flexible</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>3.4 Online process control</th>
<th>The integration of pressure and temperature sensors</th>
<th>Allows online monitoring of the injection molding process, including flow adjustment</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>3.5 Inspection of replicated specimen</th>
<th>Many methods are suitable</th>
<th>SEM: requires metallization AFM: quite work-intensive Laserscanning confocal microscopy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Many methods are suitable</td>
<td>SEM: requires metallization AFM: quite work-intensive Laserscanning confocal microscopy</td>
<td></td>
</tr>
</tbody>
</table>

End of Process 2

End of Total Process

Further references:


4.12 Polymeric microcantilevers

Polymeric microcantilevers for bioanalytics applications

Process: Thermal thin-wall injection molding

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

Process: Conventional injection molding for micro- and nanostructure replication from silicon wafers

Application: Biosensing and cell force measurements

Keywords: thermal nanoimprint, polymer inserts, injection molding, microcantilevers

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

Process: Polymeric microcantilevers
Responsible: Per Magnus Kristiansen
E-mail: magnus.kristiansen@fhnw.ch

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

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

Partner: University of Basel, Biomaterials Science Center
Address: 4031 Basel, Switzerland
Web-Address: http://www.bmc.unibas.ch

Process: Biosensing
Responsible: Bert Müller
E-mail: bert.mueller@unibas.ch

Process description: Injection molding of microcantilevers with microstructured surfaces for bioanalytics and cell force measurements.

Purpose: The aim of this process is to produce high volume micro/nanostructured parts made out of bulk polymers, displaying a surface structure that adds functionality.

Major challenges: Manufacturing of the microcantilever mold with sufficient surface finish requires picosecond pulsed laser ablation. In view of the small dimensions of the molded cantilevers (thickness ~35 µm, length 500 µm and width 100 µm), large draft angles have to be used to allow for demolding without plastic deformation of the polymeric microcantilevers. Filling of the cavities is challenging as the dimensions are in the range of venting channels in classical injection molding.

Application and state-of-the-art: This dedicated tool is used for preparation of polymeric microcantilevers for biosensing – a joint research effort between PSI, FHNW and the University of Basel.

References:

Contact information:
Prof. Dr. Per Magnus Kristiansen
University of Applied Sciences and Arts FHNW
Institute of Polymer Nanotechnology
Klosterzelgstrasse 2
CH-5210 Windisch, Switzerland

LoP2012_polymer micro cantilevers
### Polymeric microcantilevers for bioanalytics applications

**Process: wafer injection molding**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0 Process 1: Polymer master inserts</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Preparation of silicon master</td>
<td>Structure generation</td>
<td>Alternative materials such as quartz wafers may also be used with the present setup</td>
</tr>
<tr>
<td>1.2 Application of antisticking coating</td>
<td>Mandatory for allowing defect-free de-molding</td>
<td></td>
</tr>
<tr>
<td>1.3 Thermal nanoimprint</td>
<td>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)</td>
<td></td>
</tr>
<tr>
<td><strong>End of Process 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2.0 Process 2: Tool manufacturing</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Mold manufacturing</td>
<td>State of the art machining is used to manufacture the injection molding tool</td>
<td></td>
</tr>
<tr>
<td>2.2 Cantilever tool manufacturing</td>
<td>Pulsed laser ablation</td>
<td>Very fine venting channels are needed at the tip of the microcantilevers to avoid diesel effect caused by compressed air</td>
</tr>
<tr>
<td><strong>End of Process 2</strong></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## 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

---

## 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
<table>
<thead>
<tr>
<th>Process</th>
<th>Description</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.4 Thiol adsorption</td>
<td>Standard procedures</td>
<td>Immersion in respective thiol solution to add functionality for detection of specific moieties</td>
</tr>
<tr>
<td>4.5 DNA hybridization</td>
<td>Detect complementary DNA strands in test solution</td>
<td>Detection by differential signal between sensing MCs (Thiol-Sf162) and reference MCs (Thiol-NI4-3); sample DNA: 100µl of 1µM complementary Sf162</td>
</tr>
<tr>
<td>4.6 Cell force measurements</td>
<td>Cantilever deflection</td>
<td>Is anticipated by the action of cell forces exhibited by cells aligned along line patterns of the cantilever</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Project leader</th>
<th>University of Glasgow</th>
<th>Process</th>
<th>Roll to Roll thermal NIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Address</td>
<td>Oakfield Avenue, Glasgow, Scotland</td>
<td>Responsible</td>
<td>Nikolaj Gadegaard</td>
</tr>
<tr>
<td>Web-Address</td>
<td><a href="http://www.glasgow.ac.uk">http://www.glasgow.ac.uk</a></td>
<td>E-mail</td>
<td><a href="mailto:nikolaj.gadegaard@glasgow.ac.uk">nikolaj.gadegaard@glasgow.ac.uk</a></td>
</tr>
</tbody>
</table>

**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:**


**Contact information:**

Dr. Nikolaj Gadegaard  
School of Engineering  
Rankine Building  
University of Glasgow  
Glasgow  
G12 8LT  
United Kingdom

LoP2012_NIL020_inlay IM-process
Standard injection moulding process with polymer inlays

Process: Thermal injection moulding

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td><strong>Process 1: Stamp preparation</strong></td>
<td>Quartz wafer format</td>
</tr>
<tr>
<td>1.1</td>
<td><strong>substrate selection and preparation</strong></td>
<td>standard quartz substrate 25 x 25 mm, 1 mm thick, polished on both sides</td>
</tr>
<tr>
<td>1.2</td>
<td><strong>stamp fabrication</strong></td>
<td>Stamps fabricated by photolithography and RIE as described in NaPa Library of Processes section 3.15 (process 1) and [1-2].</td>
</tr>
</tbody>
</table>

End of Process 1

<table>
<thead>
<tr>
<th>2.0</th>
<th><strong>Process 2: Substrate preparation</strong></th>
<th>Polyimide (PI) film</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td><strong>sample selection</strong></td>
<td>Standard PI substrate Sample is cut or machined from 740µm thick Cirlex® sheet to the appropriate size for the injection moulder tool.</td>
</tr>
<tr>
<td>2.2</td>
<td><strong>sample cleaning</strong></td>
<td>Prior to application of resist, sample must be cleaned in acetone, methanol and IPA with ultrasonic agitation for 5 minutes each. Nitrogen blow dry.</td>
</tr>
</tbody>
</table>

End of Process 2

<table>
<thead>
<tr>
<th>3.0</th>
<th><strong>Process 3: Resist coating</strong></th>
<th>For UV-NIL</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td><strong>surface activation</strong></td>
<td>Plasma treatment To enhance resist adhesion perform oxygen plasma treatment at 150-200 W for 15-20 s.</td>
</tr>
<tr>
<td>3.2</td>
<td><strong>coating resist</strong></td>
<td>Resist No primer, SU-8 3000 series, apply with pipette evenly over surface</td>
</tr>
<tr>
<td>3.3</td>
<td><strong>coating resist (homogeneous layer)</strong></td>
<td>Spin coating of SU-8 Thickness: 20-50 µm, spin speed depends on resist grade/dilution.</td>
</tr>
</tbody>
</table>

End of Process 3
<table>
<thead>
<tr>
<th>Section</th>
<th>Process</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>Process 4: Imprinting</td>
<td>UV nanoimprint lithography</td>
</tr>
<tr>
<td>4.1</td>
<td>prepare assembly</td>
<td>Assemble samples Place stamp above light source, bring substrate into contact with stamp and apply weak pressure (~1 bar). Leave for 2 minutes.</td>
</tr>
<tr>
<td>4.2</td>
<td>UV exposure</td>
<td>Expose SU-8 Turn on UV source (ideally 356 nm wavelength) for 4 minutes</td>
</tr>
<tr>
<td>4.3</td>
<td>demoulding</td>
<td>Separate samples Turn off UV source, release pressure and carefully separate stamp from substrate</td>
</tr>
<tr>
<td>4.4</td>
<td>curing</td>
<td>Soft bake Hotplate, 65°C for 1 minute and 95°C for 5 minutes</td>
</tr>
<tr>
<td>4.5</td>
<td>resist hardening</td>
<td>Hard bake oven, 180-300°C, 1-3 hours</td>
</tr>
<tr>
<td>4.6</td>
<td>process control</td>
<td>Optical, electron and atomic force microscopy non-destructively</td>
</tr>
<tr>
<td>5.0</td>
<td>Process 5: Injection moulding</td>
<td>Replicate structures</td>
</tr>
<tr>
<td>5.1</td>
<td>preparation</td>
<td>Set up as normal prepare polymer (drying etc) and set up machine to your standard processing conditions</td>
</tr>
<tr>
<td></td>
<td></td>
<td>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.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>If such changes are not made you are likely to observe stretching of raised features (e.g. pillars). This effect can be tuned by</td>
</tr>
<tr>
<td>Process 5 Details</td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| **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

**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

**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:**


**Contact information:**

Dr. Nikolaj Gadegaard  
School of Engineering  
Rankine Building  
University of Glasgow  
Glasgow  
G12 8LT  
United Kingdom

**LoP2012_NIL021_non-flat IM-process**
## Non-flat nanostructured surfaces by injection moulding

**Process: Thermal injection moulding**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1.0 Process 1: Top layer preparation</strong></td>
<td>Thin polyimide (PI) film</td>
<td></td>
</tr>
<tr>
<td>1.1 sample selection</td>
<td>Thin PI substrate</td>
<td>Choice of film thickness will depend on the planned feature size of the bottom layer (subtopography).</td>
</tr>
<tr>
<td></td>
<td>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.</td>
<td></td>
</tr>
<tr>
<td>1.2 preparation and patterning</td>
<td>Standard inlay process</td>
<td>Very thin films (less than 50 µm) can be very difficult to spin resist on to and pattern by NIL.</td>
</tr>
<tr>
<td></td>
<td>fabricate nonpatterned stamp by the process described in Section X.X</td>
<td></td>
</tr>
<tr>
<td><strong>End of Process 1</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2.0 Process 2: Bottom layer preparation (photolithography example)</strong></td>
<td>Polyimide (PI) film or any inlay material</td>
<td></td>
</tr>
<tr>
<td>2.1 sample selection</td>
<td>Standard PI substrate</td>
<td>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).</td>
</tr>
<tr>
<td></td>
<td>Sample is cut or machined from 740µm thick Cirlex® sheet to the appropriate size for the injection moulder tool.</td>
<td></td>
</tr>
<tr>
<td>2.2 sample cleaning</td>
<td>Prior to application of resist, sample must be cleaned in acetone, methanol and IPA with ultrasonic agitation for 5 minutes each. Nitrogen blow dry.</td>
<td></td>
</tr>
<tr>
<td>2.3 resist coating</td>
<td>Spin coating of resist</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Apply SU-8 resist as described in Section X.3.</td>
<td></td>
</tr>
<tr>
<td>2.4 soft bake</td>
<td>Solvent evaporation</td>
<td>Bake time may be extended for very thick layers</td>
</tr>
<tr>
<td></td>
<td>hot plate, 95°C, 30 minutes</td>
<td></td>
</tr>
<tr>
<td>2.5 Photolithography</td>
<td>Mask aligner</td>
<td>The minimum feature size should be greater than the film thickness.</td>
</tr>
<tr>
<td></td>
<td>expose (i-line); time depends on feature size and resist thickness</td>
<td></td>
</tr>
<tr>
<td>2.6 post exposure bake</td>
<td>Curing</td>
<td>Bake time may be extended for very thick layers</td>
</tr>
<tr>
<td></td>
<td>hot plate, 65°C, 1 minute 95°C 5 minutes</td>
<td></td>
</tr>
<tr>
<td>2.7 pattern development</td>
<td>Developer</td>
<td></td>
</tr>
<tr>
<td></td>
<td>EC Solvent, 5 minutes.</td>
<td></td>
</tr>
<tr>
<td>2.8</td>
<td>resist hardening</td>
<td>Hard bake oven, 180-300°C, 1-3 hours</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td><strong>End of Process 2</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>Process 3: Injection moulding</td>
<td>Replicate structures</td>
</tr>
<tr>
<td>3.1</td>
<td>preparation</td>
<td>Set up as normal prepare polymer (drying etc) and set up machine to your standard processing conditions</td>
</tr>
<tr>
<td>3.2</td>
<td>tool assembly</td>
<td>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.</td>
</tr>
</tbody>
</table>

Rinse in IPA and blow dry with nitrogen
### 3.3 Injection Moulding

<table>
<thead>
<tr>
<th>Description</th>
<th>Instructions</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Injection Moulding</strong></td>
<td><strong>Perform injection moulding as normal</strong>&lt;br&gt;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.</td>
</tr>
<tr>
<td><strong>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.</strong></td>
<td></td>
</tr>
</tbody>
</table>

| **Process Control**             | **Optical, electron and atomic force microscopy**<br>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
Address: CH-8803 Rueschlikon / Switzerland
Web-Address: http://www.zurich.ibm.com/

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:

Contact address:
IBM Research Laboratory
Saueumerstrasse 4
CH-8803 Rueschlikon / Switzerland
http://www.zurich.ibm.com/

LoP2007_mCP001_microcontact printing alkaethiols
## Alkanethiol printing

**Process:** microcontact printing lithography

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1. Stamp</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 <strong>Master fabrication</strong></td>
<td>Fabricate patterned silicon master by photo- or E-beam lithography</td>
<td>ideal with smooth bottom surfaces and smooth vertical sidewalls</td>
</tr>
<tr>
<td>1.2 <strong>Master preparation</strong></td>
<td>Coat master with fluorinated separation layer</td>
<td>hydro-phobic surface treatment to facilitate stamp separation</td>
</tr>
<tr>
<td>1.3 <strong>Mixing of PDMS</strong></td>
<td>Mix precursor SYLGARD 184 elastomer base with curing agent 10:1</td>
<td>good mixing required for catalytic reaction,</td>
</tr>
<tr>
<td>1.4 <strong>Degasing</strong></td>
<td>Degas mixture to avoid air bubbles in stamp</td>
<td>premixed aliquots can be stored at -20 °C for 1-3 months</td>
</tr>
<tr>
<td>1.5 <strong>Stamp curing</strong></td>
<td>Pour liquid prepolymer onto master inside of petri dish and cure at 60 °C for 12-24 hours.</td>
<td></td>
</tr>
<tr>
<td>1.6 <strong>Stamp work-up</strong></td>
<td>Cut and peel stamp off master. Rinse stamp three times with EtOH and dry under a flow of N₂ for 30 s.</td>
<td></td>
</tr>
<tr>
<td><strong>2. Ink [1]</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 <strong>Alkanethiols as ink</strong></td>
<td>Chose an alkanethiol, e.g. decanethiol (DDT), hexadecanethiol (HDT) octadecanethiol (ODT) or eicosanethiol (ECT)</td>
<td>higher molecular weight thiols decrease ink diffusion, but increase disorder of monolayer and tend to crystallize at the stamp surface</td>
</tr>
<tr>
<td>2.2 <strong>Purification (optional)</strong></td>
<td>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 &lt;100 mTorr for 24 h.</td>
<td>purification removes low-molecular-weight thiols</td>
</tr>
<tr>
<td>2.3 <strong>Ink solution</strong></td>
<td>Prepare diluted thiol solution in ethanol, e.g. 0.1 mM</td>
<td>changing the concentration allows to control the amount of ink transferred to the stamp</td>
</tr>
<tr>
<td>2.4 <strong>Storage</strong></td>
<td>Store purified ink solution at 4 °C in the dark for up to one week.</td>
<td></td>
</tr>
<tr>
<td><strong>3. Substrate [1]</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.1 <strong>Surface preparation</strong></td>
<td>Evaporate ~1 nm Ti onto a Si/SiO₂ wafer, e.g. with an e-beam evaporator at ~2x10⁻⁷ Torr and a rate of ~0.5 nm s⁻¹.</td>
<td></td>
</tr>
<tr>
<td>3.2 <strong>Au deposition</strong></td>
<td>Immediately following, evaporate rate 15 nm gold (same evaporation parameters)</td>
<td></td>
</tr>
<tr>
<td><strong>4. Inking</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4a <strong>Immersion inking [2]</strong></td>
<td>Inking by placing a drop of ink solution onto the stamp.</td>
<td>only the average amount of ink transferred can be controlled.</td>
</tr>
<tr>
<td>4a.1 <strong>Inking</strong></td>
<td>Place two drops (~0.2 mL) of the freshly prepared (&lt;1 h) ink solution on top of the stamp.</td>
<td>make sure there’s enough liquid to cover the surface.</td>
</tr>
<tr>
<td><strong>4a.2</strong></td>
<td><strong>Drying</strong></td>
<td>After 30 s remove liquid quickly (&lt;0.5 s) under a stream of N₂.</td>
</tr>
<tr>
<td>----------</td>
<td>------------</td>
<td>---------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>4b</strong></td>
<td><strong>Contact inking [1]</strong></td>
<td>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.</td>
</tr>
<tr>
<td><strong>4b.1</strong></td>
<td><strong>Ink pad fabrication</strong></td>
<td>Prepare small blocks (~2 cm² and 4 mm thick) of cured PDMS as ink pads.</td>
</tr>
<tr>
<td><strong>4b.2</strong></td>
<td><strong>Impregnation</strong></td>
<td>Immerse the ink pad in the thiol solution for at least 12 h.</td>
</tr>
<tr>
<td><strong>4b.3</strong></td>
<td><strong>Drying and storage</strong></td>
<td>Withdraw from the solution, dry in a stream of N₂ for 10 s and store in a small glass flask.</td>
</tr>
<tr>
<td><strong>4b.4</strong></td>
<td><strong>Inking</strong></td>
<td>Place the patterned stamp on the ink pad without applying pressure for 40 s. conformal contact allows transfer of thiols. Inking times control amount of thiols transferred.</td>
</tr>
<tr>
<td><strong>5</strong></td>
<td><strong>Printing</strong></td>
<td></td>
</tr>
<tr>
<td><strong>5.1</strong></td>
<td><strong>Making Contact</strong></td>
<td>Place stamp onto gold substrate, monitor formation of conformal contact optically. conformal contact is made by the stamps own weight.</td>
</tr>
<tr>
<td><strong>5.2</strong></td>
<td><strong>Detaching</strong></td>
<td>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.</td>
</tr>
<tr>
<td><strong>6</strong></td>
<td><strong>Etching [3]</strong></td>
<td></td>
</tr>
<tr>
<td><strong>6.1</strong></td>
<td><strong>Preparation of etch bath</strong></td>
<td>Prepare a ferric nitrate etch bath (20 mM Fe(NO₃)₃•9H₂O 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</td>
</tr>
<tr>
<td><strong>6.2</strong></td>
<td><strong>Etching</strong></td>
<td>The bath should be operated at 23-25 °C 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).</td>
</tr>
</tbody>
</table>
5.2 Optical resonators

Fabrication of optical resonators by soft UV-NIL

**Process:** soft lithography

**Keywords:** soft UV-NIL, PDMS stamps

**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

**Process description:** An imprint template is fabricated via cast moulding of 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 modulus.

**Application and state-of-the-art:** Products and prototypes that rely on large area nano-patterning at high resolutions at cheap costs. In this library it is used to fabricate photonic structures in silicon waveguide technology.

**References:**


**Contact information:**

AMO GmbH
Otto-Blumenthal-Str. 25
52074 Aachen, Germany

U. Plachetka
+49-(0)241-8867202

LoP2007_SoftNIL001_Resonators by SoftNIL
## Optical resonators

**Process: soft lithography**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>What</strong></td>
<td><strong>how it should work</strong></td>
<td><strong>critical issues</strong></td>
</tr>
<tr>
<td>1.0a  Process 1: Master preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Master fabrication:</td>
<td>Si substrate, 6&quot;, &lt;100&gt;, one side polished, standard ebeam, followed by RIE (other substrates may also be used, i.e. metals, resist, etc.)</td>
<td></td>
</tr>
<tr>
<td>1.2 Deposition of anti-adhesion layer:</td>
<td>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)</td>
<td></td>
</tr>
</tbody>
</table>

End of Process 1

1.0b Process 2: Stamp preparation

| 1.1 Elastomeric template material: | A 10:1 (base:curing agent) mixture of Sylgard 184 (Dow Corning) is prepared and degassed in a vacuum | |
| 1.1 Cast moulding of imprint template: | The mixture is poured onto the master, degassed in a vacuum and afterwards cured on a hotplate (110°C@30min) | |
| 1.2 Detachment | The template is then cut and detached from the silicon master. | |

2.0 Process 3: Lithography

| 2.1 Spin-coating | spincoating of UV-curable resist onto an SOI-substrate (depending on the application other substrates may be used freely) imprint resist: AMONIL MMS4 (3000rpm@30sec) | |
| 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 polymerized imprint resist; the moulded flexible imprint template can be used for other imprints.

---

### 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 Etching

**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

**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

**Keywords:** soft UV nanoimprint lithography

**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.

**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

**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:**


**Contact information:**

Yong Chen  
Department of Chemistry  
Ecole Normale Supérieure  
24 rue Lhomond  
75231 Paris, France  
Phone : +33 1 4432 2421  
Fax : +33 1 4432 2402

LoP2007_SoftNIL002_NIL Mix&Match
<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 Process 1: Master fabrication</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.1 Pattern definition of by electron beam lithography</td>
<td>Standard EBL</td>
<td>Including only nanostructures and alignment markers</td>
</tr>
<tr>
<td></td>
<td>Silicon substrate</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PMMA resist</td>
<td></td>
</tr>
<tr>
<td>1.2 Pattern transfer</td>
<td>40nm Nickel evaporation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lift off</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reactive ion etch with SF$_6$ gas</td>
<td></td>
</tr>
<tr>
<td>1.3 Surface treatment</td>
<td>Evaporation of anti-sticking reagent</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In TMCS vapour during 1 min</td>
<td></td>
</tr>
<tr>
<td>End of Process 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0 Process 2: Soft stamp preparation</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.1 Thin layer PDMS deposition</td>
<td>Spin coating</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Approximately 10µm thickness</td>
<td></td>
</tr>
<tr>
<td>2.2 Soft PDMS layer deposition</td>
<td>Casting and curing</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5-10mm thick and baked at 80°C for 30min</td>
<td></td>
</tr>
<tr>
<td>2.3 PDMS stamp separation</td>
<td>Manual</td>
<td></td>
</tr>
<tr>
<td>2.4 Surface treatment</td>
<td>Evaporation of anti-sticking reagent</td>
<td></td>
</tr>
<tr>
<td></td>
<td>In TMCS vapour during 1 min</td>
<td></td>
</tr>
<tr>
<td>End of process 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0 Process 3: Photolithography mask</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mask design and fabrication</td>
<td>Standard photolithography</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Including all large size features and alignment markers</td>
</tr>
<tr>
<td>4.0 Soft UV nanoimprint</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.1 Spin coating of layer 1 (sacrificial layer)</td>
<td>Spin-coating of PMMA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300 nm thickness</td>
<td>A thin quartz plate can be used for facilitating optical imaging of DNA migration.</td>
</tr>
<tr>
<td>4.2 Spin coating of layer 2 (UV-NIL layer)</td>
<td>Spin coating of AMONIL</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 nm thickness</td>
<td></td>
</tr>
<tr>
<td>4.3 Soft UV Nanoimprint</td>
<td>Imprint at low pressure</td>
<td></td>
</tr>
<tr>
<td></td>
<td>UV expose (1 min)</td>
<td>Nanostructures alone can be easily replicated with large process latitude.</td>
</tr>
<tr>
<td>4.4</td>
<td>De-moulding</td>
<td></td>
</tr>
<tr>
<td>4.5 Residual Layer (Break-through) Etching</td>
<td>Reactive ion etch</td>
<td></td>
</tr>
<tr>
<td></td>
<td>O$_2$ plasma</td>
<td></td>
</tr>
<tr>
<td>End of Process 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5.0 Process 5: First lift-off</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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
Reactive ion etch

8.1 Etch of micro and nanostructure into the substrate
Reactive ion etch
SF6 plasma
Both micro and nanostructures are etched simultaneously.

8.2 Nickel mask removal
Chemical etch
HNO3 for 1min
End of Process 8

9.0 Process 9: Device assembling

9.1 Preparation of PDMS cover slide
PDMS coating (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 nanodevices 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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**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 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):**
3. http://www.exploratorium.edu/cooking/cooks/article_5-03.html
5. Swiss waffle recipe with high content of eggs – private source

---

**Contact information:**
Dr. Helmut Schift
Head INKA-PSI Group
Laboratory for Micro- and Nanotechnology
Paul Scherrer Institut
5232 Villigen PSI
Switzerland
Phone: +41 56 310 2839

**LoP2012_NIL022_baking of waffles**
## Fabrication process for waffles made with a waffle iron

**Process: thermal nanoimprint lithography**

<table>
<thead>
<tr>
<th>Process</th>
<th>Technical Parameters</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>What</td>
<td>how it should work</td>
<td>critical issues</td>
</tr>
<tr>
<td>1.0</td>
<td>Process 1: Preparation</td>
<td>Silicon wafer format</td>
</tr>
<tr>
<td>1.1</td>
<td>Preparation of tools</td>
<td>Waffle iron</td>
</tr>
<tr>
<td></td>
<td>Waffle irons typically consist of two thick metal (cast iron) plates that are flat at one and structured on the other side. Both structures are designed to yield structures with constant thickness (also disc and rims) and allow space for 2-5 mm. For alignment and handling purposes they are connected with a hinge.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Prepare large and smaller bowl, electric hand beater and ladle</td>
</tr>
<tr>
<td></td>
<td>Waffles are different from so-called “Bretzel”, which are thinner and often more ornamented (not to confuse with the pretzels made from sour dough)</td>
<td></td>
</tr>
<tr>
<td>1.2</td>
<td>Preparation of batter (dough)</td>
<td>Ingredients (for 4 persons)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>butter: 250 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>granulated sugar: 100 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>eggs (separated): 6</td>
</tr>
<tr>
<td></td>
<td></td>
<td>whole milk (3.5 %): ¼ liter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>all-purpose flour: 300 g</td>
</tr>
<tr>
<td></td>
<td></td>
<td>lemon zest: 1 tea spoon</td>
</tr>
<tr>
<td></td>
<td></td>
<td>salt: 1 pinch (dash)</td>
</tr>
<tr>
<td></td>
<td>Directions</td>
<td>1. Separate eggs into yolk and whites, set whites aside in a small mixing bowl.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2. Put butter, sugar and yolks into a large mixing bowl, whisk them together with hand beater until fluffy.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3. Add flour, milk, and finally the lemon zest to the ingredient mixture, and mix gently until combined. Don’t overmix!</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4. Beat whites until moderately stiff.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5. Fold stiff egg whites into mixture.</td>
</tr>
<tr>
<td>2.0</td>
<td>Process 2: Fabrication of waffles</td>
<td>Baking of waffles</td>
</tr>
<tr>
<td>2.1</td>
<td>Coating and pre-heating of iron</td>
<td>Coat the waffle irons generously with fat or vegetable oil (using a brush) should be repeated every time – or every second time</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pre-heat your waffle iron to its hottest setting.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Butter of vegetable fat is normally used to guarantee the release of the baked waffle without damage</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alternative: Spray both surfaces with cooking spray. State-of-the-art</td>
</tr>
</tbody>
</table>
Fatal damage due to adhesion.

### 2.1 Baking

**Baking**

Ladle 120 to 180 g (1/2 to 3/4 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 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 thickness of the waffles (the "residual layer") – can be controlled by the amount of batter.

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**End of Process 2**

**3.0 Process 3: Serving**

### 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, blueberries and meat.

Cross-section of a thick (Belgium) waffle.

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**End of Process 3**

**End of Total Process**

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**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 soufflés. Even in batters containing baking powder, beaten egg whites are an additional source of leavening.

Starch, a carbohydrate that makes up about 70% of flour by weight, also plays an important role. Starch reinforces gluten and absorbs water during baking, helping the gluten to contain the pockets of gas, e.g. produced by the yeast or present due to the egg foam. During baking, the gas in the batter continues to expand. As the temperature of the cooking dough rises, the gluten hardens, and the dough solidifies.

Ref.: http://www.exploratorium.edu/cooking/icooks/article_5-03.html
Figure 2: A typical presentation of aspects of molding which are helpful to understand the optimization of the thermal nanoimprint process.

Figure 3: The Swiss traditional enterprise Kambly specializes in fabrication of Swiss Bretzeli (Bricelets), which are thin waffles without soft “interior”. The photograph (left) shows a machine in the Kambly museum in Trubschachen in Emmental, Switzerland. However, in contrast to waffles, the dough is not liquid and applied as soft balls. A range of old-fashioned wooden molds can also be found in Einsiedeln, Switzerland, in the Lebkuchen museum. Since Einsiedeln was one of the most important Benedictine monasteries from medieval ages up to today, the ginger bread making was well connected with the technique to pattern bread for holy mass. The photograph shows flat wooden stampers and roll molds.
NaPANIL – Library of Processes
Nanopatterning, Production and Applications based on Nanoimprint Lithography


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Please reference the NaPANIL LoP as: