Nanoimprint lithography: An old story in modern times? A review

Helmut Schift[a)]
Laboratory for Micro- and Nanotechnology, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

(Received 30 July 2007; accepted 13 February 2008; published 27 March 2008)

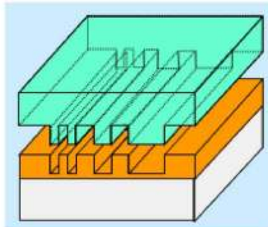
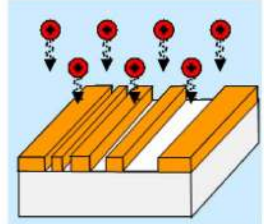
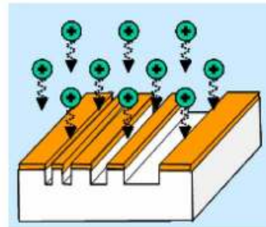
Nanoimprint lithography (NIL) is a high throughput, high-resolution parallel patterning method in which a surface pattern of a stamp is replicated into a material by mechanical contact and three dimensional material displacement. This can be done by shaping a liquid followed by a curing process for hardening, by variation of the thermomechanical properties of a film by heating and cooling, or by any other kind of shaping process using the difference in hardness of a mold and a moldable material. The local thickness contrast of the resulting thin molded film can be used as a means to pattern an underlying substrate on wafer level by standard pattern transfer methods, but also directly in applications where a bulk modified functional layer is needed. Therefore it is mainly aimed toward fields in which electron beam and high-end photolithography are costly and do not provide sufficient resolution at reasonable throughput. The aim of this review is to play between two poles: the need to establish standard processes and tools for research and industry, and the issues that make NIL a scientific endeavor. It is not the author's intention to duplicate the content of the reviews already published, but to look on the NIL process as a whole. The author will also address some issues, which are not covered by the other reviews, e.g., the origin of NIL and the misconceptions, which sometimes dominate the debate about problems of NIL, and guide the reader to issues, which are often forgotten or overlooked. [DOI: 10.1116/1.2890972]

I. INTRODUCTION

The state of the art in nanoimprint lithography (NIL) is currently well documented by a vast number of publications and conference contributions, ranging from the first publications from Chou *et al.* on thermal NIL[1–3] and Haisma *et al.* from Philips Research Laboratories on UV-NIL[4] to recent reviews from Cross on mechanical indentation[5] and Guo on material aspects in NIL.[6] A tendency can be seen toward an increasing number of process variations, which are mostly variants of the established thermal NIL and UV-NIL processes, particularly those using special methods of pattern transfer (e.g., reversal imprint) and hybrid processes (combinations of different processes) (see Table I). This is not only a sign of increased worldwide activity but also that a standard for NIL processing has not yet been established, which can be employed as it is common in standard optical or photolithography (PL). A standard process, however, cannot be defined as long as the many applications have different requirements in terms of resolution, design, resist, pattern transfer, and equipment used—which is more similar to the situation in microelectromechanical systems (MEMS) than in integrated circuit (IC) microchip manufacturing. This is because NIL has never been a process exclusively developed as the "next generation lithography" (NGL) used for semiconductor chip fabrication, but more and more for applications where "Moore's law" with all its requirements and implications on overlay of different lithographic steps does not play a significant role. Two developments can be seen. (1) NIL has now passed a barrier from a laboratory scale to industrial preproduction. Data storage and optical displays will most likely be the first industrial application fields where replication techniques will be able to replace standard methods of lithography. Apart from resolution requirements, this is simply because the cost of ownership (CoO), i.e., the total process cost associated with the manufacturing of a specific device, does not allow for using the more established lithographic methods. (2) Furthermore, much interest in NIL processes comes from a large community of sensor, biochip, and nano-optics manufacturers and institutes. They search for an available (low-cost) method where a number of identical devices, e.g., as a consumable for a research project, can be fabricated in a range of specific functional materials, e.g., for polymer light emitting diodes[7] (LED) and biocompatible templates for tissue engineering,[8,9] with resolutions currently not available by other methods. Apart from the high interest for NIL from the application side, the ability to create three dimensional (3D) structures with sub-10 nm resolution in confined geometries, i.e., in which the film thickness becomes similar to the structure size and height, is still a challenge for reliable manufacturing. It becomes a scientific endeavor to answer the unsolved questions of the inherent mechanical and chemical principles, and to learn how mechanics becomes a guiding principle of modern nanomanufacturing methods.

[a)]Electronic mail: helmut.schift@psi.ch

TABLE I. Nanoimprint lithography: patterning of a thin resist and pattern transfer.

Lithography	Pattern definition	Pattern transfer	
	Resist patterning	Residual layer etch	Substrate patterning
Nanoimprint lithography (NIL)			
Issues to be considered	3D rheology, inclusions, residual layer homogeneity, demolding, shrinkage, relaxation, distortion	Pattern fidelity and homogeneity, aspect ratio and contrast, surface contamination	Pattern fidelity, etch ratio, topological and chemical contrast (hard mask), resist removal

There are currently several reviews on NIL and related processes, including book chapters, with more to come. A comprehensive introduction into NIL, with emphasis on the more general thermal NIL, is given by Schift and Kristensen—which relates much to the work described here.[10] It contains a view on the recent developments and reflects on the most probable applications of NIL. First reviews on nanorheology are given in the thesis of Baraldi,[11] the articles of Heyderman *et al.*,[12–14] Scheer *et al.*,[15,16] and most general, in the book "Alternative Lithography," edited by Sotomayor-Torres, with its range of articles on NIL and related technologies.[17] Since the publication of this first general overview on NIL, further articles have appeared, by Schulz *et al.*,[18] on nanorheology and issues of viscosity, relaxation, and molecular weight, by Cross,[5] with a focus on the production of nanostructures by mechanical forming, and by Rowland *et al.*[19,20] on micro- and nanomanufacturing via molding. The review article of Guo[21] is the first compact overview about the state of the art of NIL, with many examples from applications, and was recently extended to a review on materials in NIL.[6] Since then, some review articles and chapters have evolved, and can be found in books on nanofabrication and biotechnology, e.g., from Park and Schift[22] and Hirai.[23] Several reviews on UV-NIL stem from the very broad activities of Willson and co-workers,[24,25] and the enterprises Molecular Imprints, Inc.[26,27] (MII) and AMO.[28–30] They are particularly focused on the industrial relevance of NIL processes and try to set up standard processes as needed by the chip industry.

I do not only refer to publications but also to the results presented at recent conferences such as EIPBN,[31] MNE,[32] MNC,[33] and NNT,[34] i.e., the abstract books and appropriate proceedings, which have become places of exchange and discussion between the NIL research community and industry. To enhance the readability of this article and find references, several tables summarize effects and references.

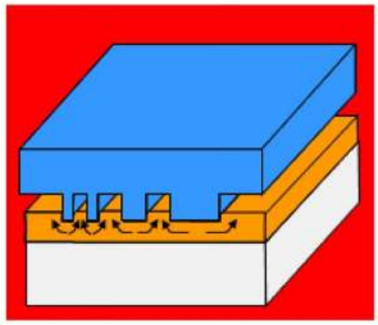
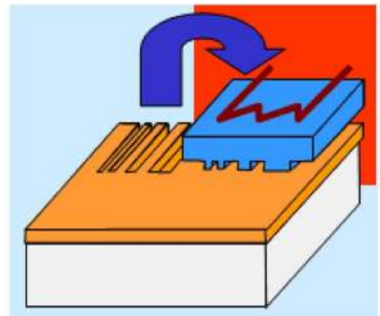
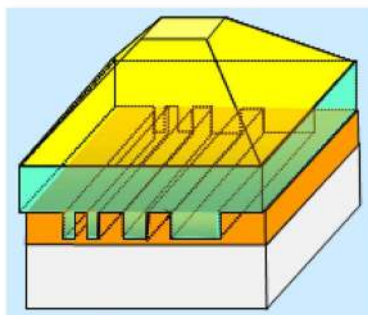
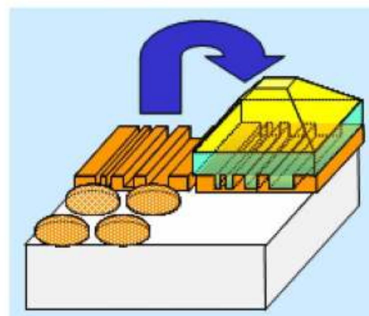
II. VARIANTS OF NANOIMPRINT LITHOGRAPHY

A. Nanoimprint lithography: A definition

Where does nanoimprint come from? After its first publication in 1995, NIL has been quickly recognized by researchers and industry as a potential low-cost, high throughput lithographic method for a range of applications. In 2003 NIL was accepted by ITRS as a next generation lithography candidate and found its way to the roadmap for the 32 nm node and beyond, scheduled for industrial manufacturing in 2013.[35] Interestingly, by showing a 10 nm metal dot array fabricated by thermal NIL in polymethylmethacrylate (PMMA) and lift-off, the first application Krauss and Chou were suggesting was patterned media (quantized magnetic disks), not complementary metal-oxide semiconductor (CMOS).[36] Thus this exciting field was opened to many researchers, and Chou continued by publishing pioneering papers on multilayer resist methods, large area imprint, roller NIL, lithographically induced self-assembled patterning, 5 nm resolution, real-time scatterometry, and finally, the patterning of silicon by laser assisted direct imprint,[37–43] along with a range of nanoapplications.

The name NIL is now widely accepted (for some time hot embossing lithography (HEL) was also used as a synonym for thermal NIL[44]), and variations of this name are growing everywhere. However, the genetic code of NIL shows traces of a range of other replication processes. These traces stem from different backgrounds and fields of research, such as record printing[45] and compact disc manufacturing by (compression) injection molding,[46] microreplication by LIGA technology (a German acronym for the process sequence LI: lithography of high aspect ratio microstructures, G: tooling by electroplating, and A: replication by molding),[47] roll embossing of holograms, or micro-optics and semiconductor manufacturing.[48–50] It also profits much from the impetus of microcontact printing, promoted by Xia and Whitesides,[51] who established simple laboratory-type micropatterning in biology and chemistry. In Ref. 52 it was demonstrated that this technique can be further extended to sub-100 nm resolution. From the view of LIGA technology, NIL is a downscaling of already well-established microtechniques.[53–55] For example, in Ref. 56, 100 μm high polymer microstructures were replicated by hot embossing on prepatterned silicon wafers. The fact that stamps can be made from standard silicon and fused silica wafers facilitated the step of NIL into the domain of IC fabrication and microtechnology.

TABLE II. Comparison of thermal NIL and UV-NIL.

Process	Patterning scheme	Step & repeat (S&R) variant
Thermal nanoimprint lithography (NIL, T-NIL) – also called **Hot embossing lithography (HEL)**	 **Process:** Compression of thin thermoplastic film between hard stamp and substrate and molding by squeeze flow	 **Step&stamp imprint lithography (SSIL):** Similar to standard stepping lithography using small stamps (dies): only local heating over T_g
UV-nanoimprint lithography (UV-NIL) (a) Hard stamp lithography (b) Soft (stamp) lithography (SL)	 **Process:** Low pressure filling of liquid resin at room temperature by capillary action and hardening by UV-exposure through the stamp; coating by dispensing or spin coating of precursor	 **Stamp&flash imprint lithography (SFIL/O):** SSIL using a negative resist: coating and UV-exposure only locally **SFIL/R (reverse tone SFIL):** Patterning of planarization layer + overcoating enables imprint over intrinsic substrate topology

The step and repeat (also known as stamp&stamp and step&flash) approaches currently developed for thermal and UV-NIL are very similar to the stepper approach in PL and are physically identical to full wafer parallel imprint (see Table II). They enable us to enlarge the imprinted area by repeated printing with a smaller stamp, as long as the following imprints do not affect adjacent patterned areas. Roll embossing is considered as a highly dynamic NIL process, since bending and delamination are concepts, which are also present in NIL.[50,57] A final word has to be said to the single probe approaches for serial nanopatterning. The "millipede" approach uses heated atomic force microscopy (AFM) tips as stamps, and massive parallelization is possible by integration of arrays of cantilevers using MEMS technology.[58] In a similar way, by using an indentation setup with a heated stage, microstamps with a flat or focused ion beam structured punch of 10 μm diameter are used for the measurement of load histories of imprint and demolding forces.[5,19] These approaches are not so different from the step&stamp approaches, as well as where the stamps are directly heated by resistance heating or by IR exposure.[59,60]

NIL is still so different from other lithographic methods, and it is important that nonexperts will recognize the technology base with its toolbox. Therefore, I define (see also abstract) *NIL as 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 includes all variants of reversal imprint, as long as a prepatterned film is transferred and bonded to another substrate.[61–65]

B. Characteristics of mechanical deformation

While high-end PL has always tried to avoid mechanical contact of mask and resist, by using proximity exposure or

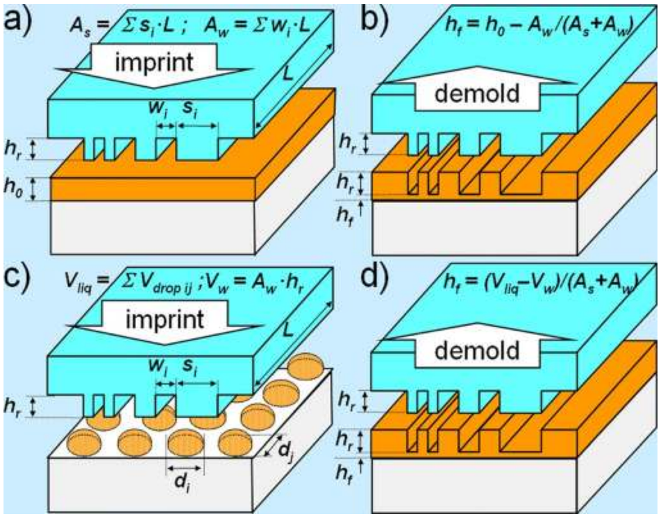


FIG. 1. Geometrical definitions used for the description of the flow process with volume conservation. (a) Before molding of a spin-coated resist, (b) after demolding, (c) before molding of a dispensed resist, and (d) after demolding.

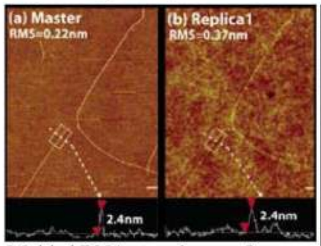
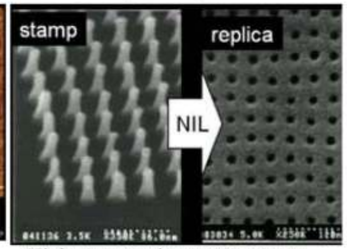
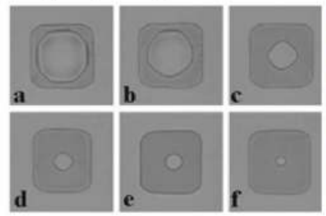
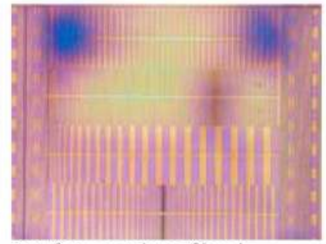
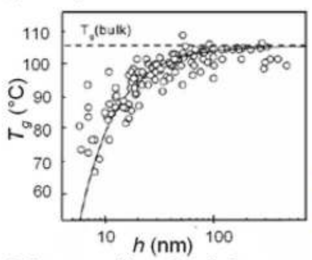
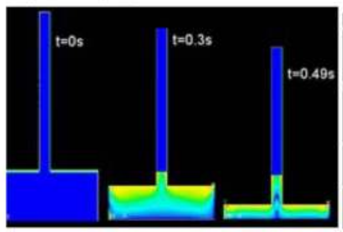
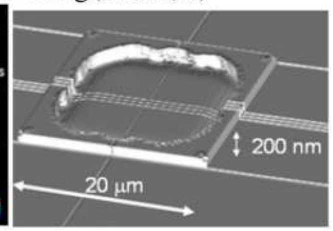
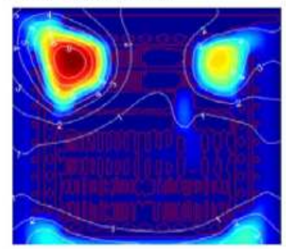
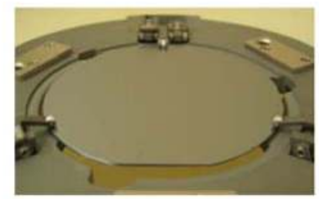
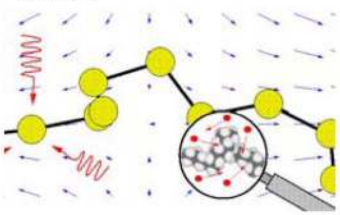
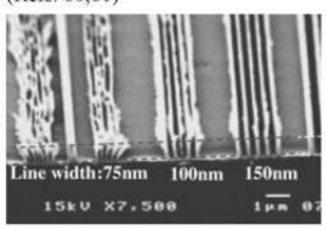
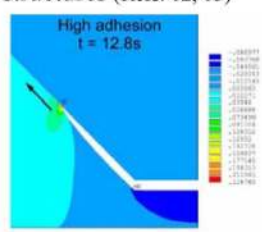
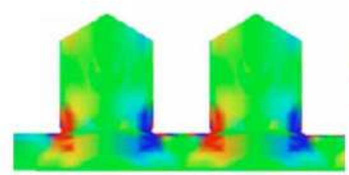
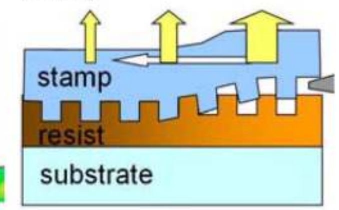
projection schemes with reticle reduction, NIL relies entirely on the concept of intimate contact between stamp and resist. Although different in terms of temperature and resists used, thermal NIL and UV-NIL deal with the same challenges imposed by the mechanical nature of the process. During imprint (also called molding, embossing, forming, or shaping), the resist is displaced by squeeze flow (pressure is the driving force to displace a viscous material) and capillary forces (surface energy controls the wetting and spreading of a viscous material), until it conforms to the surface relief of the stamp. During the demolding (also called detachment, separation, or de-embossing) high adhesion and friction forces are exerted on single stamp structures. The main difference between PL and NIL is that mechanical deformation of the whole surface rather than locally selective chemical modification is employed. It is three dimensional by definition, which in practice is a continuous polymer layer with a surface relief. The local selectivity (i.e., local substrate areas covered by resist) is generated by homogeneous thinning of the polymer by reactive ion etching (RIE), until windows are opened to the substrate (also called breakthrough etch), and the residual layer is removed while a thickness contrast of the remaining resist is preserved (see Table I). Both processes, relief forming and thinning, are global processes, and highly anisotropic RIE processes are available which preserve the pattern in the lateral direction while the resist height is reduced.[66]

Are there advantages of mechanical deformation over local chemical modification of a resist by exposure, when compared with PL? In molding of a viscous material, the advantage of mechanics is that deformation by displacement goes along with volume conservation (see Fig. 1), and complete filling can be achieved by pressure or wetting. Furthermore, for standard NIL the polymer is processed as a whole, and not locally, as it is in PL. This macroscopic redistribution of polymer and the evolution of the patterns can be made visible by optical means, through the stamp or substrate—even in real time! As a disadvantage, in contrast to PL, in both molding and demolding, mechanical damage of both stamp and molded structure can occur if forces exceed critical values.

C. Dimensional issues

Is NIL so different to molding of microstructures or simply a downscaling of known processes in a top-down approach? An overview of effects at different dimensional levels is presented in Table III, for different size ranges and processes. At the *nanoscopic level*, the resist thickness and the structure sizes become so small that confinement effects of single molecules have to be expected. If we can generate the replica of DNA strand with 2.4 nm height, as it was demonstrated for UV-NIL, it seems that the shaping mechanism is valid down to a molecular level. However, it is not clear whether macroscopic rules still apply in this shaping. A simple example is the thickness of the antiadhesive silane coating of around 1 nm. Can this be considered as negligible with respect to structure size, i.e., in the sub-20 nm regime? Is the coating thickness constant, and is the film hard or soft? Is there any wear and abrasion in the nanoregime, or does orientation of polymer chains take place during demolding? In thermal NIL, the size of polymer coils (defined by the radius of gyration) may play a role if structures below 10 nm have to be molded. This transition to smaller dimensions can be seamless, and it seems that the dependence of the glass transition temperature T_g from resist thickness and influence of the confinement of single polymer chains and coils may be negligible to dimensions much below 100 nm. However, even for larger dimensions interesting nanoscience can be found. In the *submicroscopic regime*, where most of the future applications of NIL will be found, effects from single molecules become less important, but displacement of whole entities in confined dimensions, e.g., plug flow in high aspect ratio cavities, and friction and strain causing deformation and cracking during demolding need to be considered. In addition, shape definition, tolerances, and roughness, by pushing the capabilities of state-of-the-art EBL and pattern transfer methods for stamp manufacturing, become important. In the *microscopic level*, squeeze flow, displacement of air, and capillary bridges have to be considered. In thermal NIL, extended cavities have to be filled and resist has to flow over large distances. In UV-NIL, the choice of the droplet size of dispensed resin is important for achieving a homogeneous filling without air inclusions. The *macroscopic level* is most important for process optimization. At high pressures, bending of stamps has to be taken into account, which compensates substrate unevenness. The quality of filling also depends on surface roughness, contamination control, etc. At the *tool and handling size level*, i.e., the stamp and substrate sizes used in production, we have to deal with manufacturing issues such as high throughput and fast speed, large areas, and tight tolerances, e.g., stitching precision in step and repeat processes and magnification effects,[67] furthermore controlled demolding by parallel separation or delamination. In

TABLE III. Levels of dimensions and dimensional effects in NIL (with concepts and examples from experiments and simulations). Numbers in brackets denote references.

Dimension	**Nanoscopic** 0.1 - 10 nm	**Submicroscopic** 10 - 1000 nm	**Microscopic** 1 - 100 μm	**Macroscopic** > 0.1 mm	**Handling size** 100 - 200 mm wafers
Level	**Molecular level**	**Single cavity / Pillar**	**Microcavity / Array**	**Stamp design area**	**Wafer level lithography**
NIL area and resolution	AFM micrograph of surface (Ref. 69)  Molded DNA strand on surface	SEM micrograph of structure (Ref. 36)  High aspect ratio nanostructures	Optical micrograph of arrays (Ref. 14)  States of molded microcavities	Large area opt. micrograph (Ref. 70)  Interference colors of local thickness variation of 2x2 mm^2	Photography of wafer (Ref. 71)  Homogeneity of resist heights on 200 mm (8 inch) wafer
Molding physics, rheology, simulation	T_g variation on thickness (Ref. 72)  Substrate and interface influence, chain dynamics, true molecular scale molding needed	Squeeze (plug) flow (Refs. 73,74)  Submicroscopic finite element analysis of single cavity plug flow (viscoelastic flow, wetting, strain)	Squeeze flow for mold filling (Refs. 75,76)  Microscopic finite element analysis of a large flat cavity	Pressure distribution / bending (Ref. 77)  Coarse grain (averaged density of cavities) simulation for the determination of the residual layer	Bond alignment fixture (Ref. 78)  Isothermal setup for fast heat transfer and pressure equilibration, balancing of thermal expansion at wafer level
Demolding experiments, concepts, simulation	Molecular orientation (Ref. 79)  Single chain elongation during flow and debonding, surface chemistry	Structure array demolding (Refs. 80,81)  Distortion and ripping of high aspect ratio nanostructures	Detachment of single structures (Refs. 82, 83)  Stress buildup, friction, resist adhesion and self-delamination	Multiple structure demolding (Ref. 68)  High local demolding forces (shrinkage, friction, strain)	Full wafer demolding setup (Ref. 84)  Parallel detachment and peeling, in a manual or automatical mode; measurement of demolding forces

thermal NIL, future heating schemes will confine the heat to the surface of a stamp or a substrate, e.g., by using heatable stamps and laser induced heating. From this overview, it becomes evident that in NIL the macroscopic rules often still apply in the wide range of dimensions. This is changing if processes have to be rapid and throughput has to achieve microchip production scales of several 10 or 100 s of imprints within 1 h, residual layers have to be small (and nearly zero) for better pattern transfer, and damage due to abrasion and deformation have to be eliminated in order to enhance the yield. For this optimization and pushing to the limits, the nanoscience behind all aspects of the NIL processes has to be clarified. It is even possible that nanoeffects, e.g., the variation of the T_g for small resist thickness and in confined dimensions, can be used for faster molding. Furthermore, demolding schemes may be found which make it possible to demold structures without exceeding critical strain values. This may be possible by adjusting the speed of processing, e.g., the cooling rate in thermal NIL and modification of stamp shapes and designs.[68] In the next section, we will look at the different process issues in more detail.

III. SPECIFIC QUESTIONS

In the main section of this review, several topics will be addressed. First, the basic processes will be presented, thermal NIL and UV-NIL, and the materials issues involved. Then an overview of different machine concepts for NIL is given (presented in Table IV), from machines with hard stampers for full wafer parallel NIL to hard and soft stamps in step and repeat (S&R) machines. Finally, several nonstandard processes are discussed (see Table V). Many process issues cannot yet been treated in a quantitative manner, because reliable experimental data are missing about speed of molding and demolding, local forces involved, or dynamical effects such as bending during demolding and stick-slip movement, or data are valid only for specific designs and setups.

Both thermal and UV-NIL have demonstrated a sub-10 nm resolution. The mechanism needed to achieve mold filling is a result of a complex interplay between different parameters. The difference in approach between low- and high-pressure moldings sometimes “obscures” the similarity of physical issues involved. While much understanding and improvement are still needed on specific issues, i.e., the optimization of single process steps, e.g., the residual layer homogeneity and reduction of demolding forces, most applications need to consider the full process chain for wafer scale substrates, and this includes the influence of materials and tools on the imprint process. An example is the fact that design issues play an essential role, and it is not surprising that this is in accordance with current high-end PL, where the mask design has to be adapted by optical enhancement techniques in order to achieve high feature resolution.[85] However, in contrast to phase mask design, in NIL the micro-rather than the nanodimensions play a role for process optimization. For example, in thermal NIL, the mold filling[12,14,70,86] depends on the structure size and density, and the polymer flow is governed by viscoelastic properties of the material, which are dependent on the temperature, and by the strain induced by the application of the force. Equally, in step&flash imprint lithography (SFIL), an UV-NIL variant, the local distribution, the density, and the size of the resin droplets, dispensed just before the stamp comes into contact with it, helps to determine the residual height of the resist and to eliminate air inclusions.[13] While many of these issues can be tackled easily in a research like environment, e.g., by taking sufficiently high imprint temperatures in thermal NIL or holding on in UV-NIL until the resin absorbs the air,[13,87] the need for extremely short process times in industry makes it necessary to push processes to its limits. Then it is possible that concepts of intentional partial cavity filling and shear thinning at low process temperatures will be used as a means to shorten process times.[18,88] Most probable, however, is the development of standard solutions with large process windows and adaptability to a specific application. One of the essential tasks is the possibility to simulate processes at die or wafer level, before the stamp pattern is designed, and to predict the behavior of the resist during the imprint. Then not only the residual layer thickness can be determined, depending on the design and the process parameters chosen, but also local hot spots can be identified where critical values are exceeded. Then recommendations can be given how the design can be optimized to keep tolerances, e.g., the homogeneity of the residual layer thickness. My aim is to pick out single issues from this process chain and point out where further understanding of the potential and true limitations of the NIL process is needed. Although some topics are related to thermal NIL or UV-NIL only, they may also be applied for the other process, too.

A. Thermal NIL processes

In thermal NIL, the high imprint pressure needed for the resist viscosities of 1000 Pa s and more enables us to compensate for the lack of flatness of substrate and stamp by conformal bending over large areas. Therefore, single polymer layers are often used. Then the thickness can be chosen from very thin layers for high pattern transfer fidelity (with a thickness less than the effective stamp protrusion sizes used), where cavities are only partially filled,[88,89] up to thick layers, which can be used for the integration of lenses and microfluidic channels.[90,21] Pressure equilibration is guaranteed by using a compliance layer at the back side of the stamp, or in the case of air-pressurized NIL systems, by a flexible (soft) membrane. A good choice of process parameters by rules of thumb is often sufficient to get a very good insight on how a polymer imprints—often already in the first test. These rules of thumb result from trade-offs between structure height, resist thickness, pressure, and temperature to be used.[14] Many polymers can be imprinted with high resolution, and even polymers without a known thermoplastic behavior can sometimes be patterned using pressure and/or heat.[7,91]

For many polymers the glass transition temperature T_g can be taken as the point of reference to determine both the imprint temperature T_{imprint} and the demolding temperature

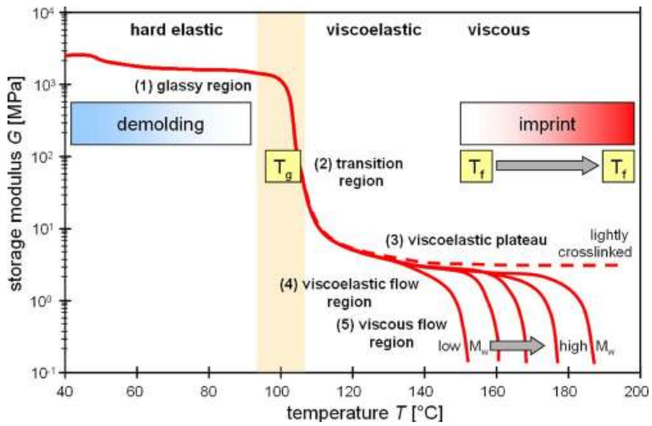


FIG. 2. Mechanical properties of polymers dependent on temperature, molecular weight, and cross-linking, after Ref. 95. Schematic for a polymer with a T_g around 100 °C for normal process conditions. Particularly important for thermal NIL are the large drops of G at two temperatures, T_g and T_f. At T_g the thermomechanical properties between stamp and polymer become sufficiently different for repeated molding. T_f characterizes a point at which viscosity drops to practical values molding needed for fast imprint.

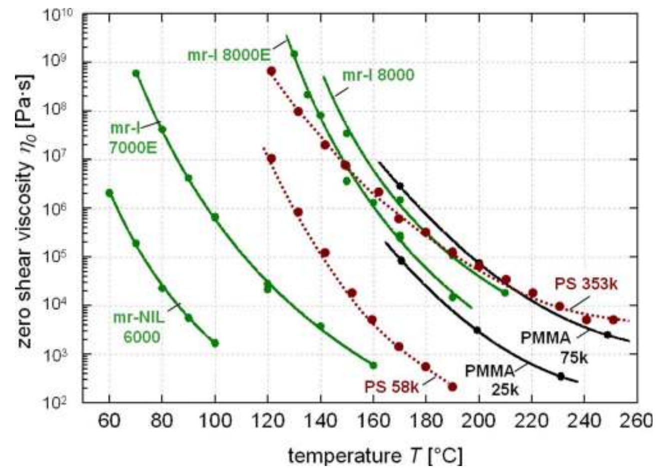


FIG. 3. Zero shear viscosity for some standard resists for thermal NIL for different polymers, taken from different sources: PMMA with M_w of 25 and 75 kg/mol,[14] PS with M_w of 58 and 353 kg/mol[18] (PS 58k and PS 353k), and the commercial resists mr-I 7000E, 8000, 8000E, and mr-NIL6000.[101] These curves are presented for the temperature range characterizes above the viscous T_g. A process window for imprint is limited by high viscosity where unwanted viscoelastic effects become dominant and molding slow. Lower viscosities than 10^3 Pa s are often not useful because it is often achieved with too low M_w or too high T_{imprint}.

T_{demold}.[14] For instance, in Ref. 78, for a range of thermoplastic polymers, T_{imprint} was choosen to be 50–70 °C higher and T_{demold} 20 °C lower than T_g, and similar results obtained. The reason that it is easy in thermal NIL to switch from one thermoplastic material to another is that simply by using a sufficiently high temperature above T_g, most polymers can be molded in the terminal flow regime. In a process window of 10^3–10^7 Pa s, the polymer viscosity is low enough for efficient squeeze flow at high pressure (see Fig. 2) and high enough that high pressure can be used which enables the equilibration of surface undulations. On the one hand, that profits from the fact that the process parameters such as pressure p, temperature T, and time t can be varied to a large extent, and trade-offs are possible between the parameters and, e.g., lower p can be compensated by a longer t. On the other hand, a wide range of materials with different molecular weight (or more correctly weight average molar mass) M_w is available, and process parameters can be chosen largely depending on the needs on molding temperature (see Figs. 2 and 3), dimensional stability in pattern transfer, and application. The key for optimization is Stefan's equation,[92] valid for purely viscous materials, where pressure and time determine the mold filling time in an equal way and the viscosity η_0 is a function of both the M_w (material property) and T_{imprint} (process). For line-shaped stamp protrusions and cavities, we find the following expression,[14] for the film thickness $h(t)$ when a constant imprint force F per length is applied to the stamp protrusion (h_0 the initial polymer height, η_0 the zero shear viscosity, and s the protrusion width):

$$\frac{1}{h^2(t)} = \frac{1}{{h_0}^2} + \frac{2p}{\eta_0 s^2}t. \quad (1)$$

It shows that the residual layer homogeneity depends largely on s. Gratings with small regular structures in the submicrometer range can be molded within a fraction of a second, while large unstructured areas can take minutes to fill. There are different ways to work toward a standard process, and one is to optimize stamp designs within the limitations given by the application, i.e., avoid large protrusion sizes and density variations over large areas, e.g., by backfilling "empty" stamp areas with dot and line arrays with small s. For thermal imprint the missing information in Stefan's equation is the dependence $\eta_0(T)$. As will be shown in the following, the full characterization of materials including dependence on shear rate over the whole temperature range would be beneficial for process optimization. Shear thinning may enhance the speed of mold filling, and is the result of a reduction of the viscosity due to a disentanglement (sliding) of the polymer chains. It is more pronounced in polymers with longer chain lengths. In Ref. 18 it was found that the maximum viscosity reduction is around 1.5 orders of magnitude for polystyrene (PS) with M_w 58 kg/mol and up to about four orders of magnitude for the higher M_w polymers.

1. Thermoplastic resist materials

Thermal NIL profits from the availability of polymers such as PMMA and PS with a range of molecular weights M_w, and with different polydispersities or molecular weight distribution characterized by M_w/M_n, weight average molecular weight/number average molecular weight. These resists can be easily prepared for a range of thicknesses in a spin-coating process. For molding processes, the glass transition temperature T_g, at which the thermomechanical properties of a polymer change significantly from glassy (below T_g) to rubbery (above T_g), is a good hint to determine the temperature range, at which molding by squeeze flow becomes possible. The transition is not sharp, nor is it thermodynamically defined. It is therefore different from melting, defined by T_m, which is an equilibrium transition only present in polymers with crystalline entities. Note that for very thin films (<100 nm) the T_g can be different from bulk values (see Table III).[51,72,93–95] A possible consequence of this is that not only thin films but also small high aspect ratio cavities can be molded much faster because the viscosity may be reduced by the confinement. This, however, has not yet been proven by experiment.

The resists provided by commercial suppliers (NanoNex, microresist technologies GmbH or Sumitomo Ltd.)[96–98] are alternatives with improved process properties such as enhanced etch resistance, lower T_g, lower viscosity, and enhanced mechanical strength. Interestingly, until recently, rheological characterization of thermoplastic materials was only available for a few commercially available materials, i.e., for PMMA and PS used by NIL groups. Now, as commercial resist manufacturers begin to provide measurements of $\eta_0(T)$, and methods using nanoindentation are developed to characterize the rheological properties of thin polymer films,[99,100] it is likely that these commercial resists will be used for testing the new simulation tools, e.g., for the effect of design on residual layer thickness. As can be seen in Fig. 3, the viscosities of PMMA with a M_w of 25 kg/mol (denoted as PMMA 25k) and mr-I 8000 E[101] match quite well within the process window for imprint, which means that they can be interchanged without varying the process parameters too much. However, other physical properties such as etch resistance, stiffness, refractive index, surface energy, and the ability to coat surfaces may determine which polymer is best suited for a specific application.

2. Implications of molecular weight and viscosity

Although it all seems to be a matter of viscosity, pressure, and time, one has to note that there is a difference between imprint in the viscoelastic or purely viscous state, which is reflected in experiments and simulations. For polymers such as PS and PMMA, imprinting in the viscous state almost means avoiding any effects of recovery in current setups. Scheer explains the role of stress relaxation by observing recovery in imprinted micropatterns in the viscoelastic state. When the temperature is too high, the probability of generating capillary bridges is increased. Therefore as a general rule, imprints should be done within a temperature range where the viscosity is low enough to achieve fast imprint, while imprint at too low viscosities enhances the danger of capillary bridges.[102–104] In the case of PMMA, a temperature window in the range of 160–190 °C is large enough for process optimization and enabling variants. This proved to be one strategy to overcome restrictions of Stefan's equation and thus to reduce imprint times, but it also needs much more optimization of the NIL process with respect to polymer rheology.

While the T_g is identical for polymers with different M_w (e.g., for the 25, 75, and 350 kg/mol PMMA 105, 98, and 95 °C were measured), the zero shear viscosity η_0 above T_g is dependent on M_w. This is described by $\eta_0 \propto M_w < M_c$ and $\eta_0 \propto {M_w}^{3.4} > M_c$. The M_c is the critical molecular weight, and imprint below M_c with the aim to reduce η_0 should be avoided, because this reduces entanglement and might lead to increased brittleness and thus to a reduced mechanical strength. For PMMA M_c is 3 kg/mol, which is low in contrast to the 25 kg/mol PMMA generally used. M_w and M_c are rarely given for commercial polymers, and comparisons with pure polymers may be difficult if other means (e.g., additives such as plasticizers) are used to reduce η_0. In order to compare such materials with known pure materials, in terms of mechanical properties, a structural fidelity for the whole process chain has to be demonstrated, i.e., also the pattern transfer of critical (e.g., high aspect ratio) nanostructures. A strategy to combine the advantages of low and high M_w materials is the use of bilayer resists with different M_w,[102] where for PMMA a low M_w of 10 kg/mol at the bottom ensures sufficient flow, while a high M_w of 95 kg/mol on the top ensures stability during demolding. A further example is curable polymers (thermocurable or UV curable). Then very low M_w can be applied for the precursors, which can be dispensed either as a liquid or spin coated to a solid film (e.g., a low M_w thermoplastic polymer) and which can be cross-linked to achieve a high mechanical strength during demolding. These considerations show that for the determination of process parameters the knowledge of the dependence of the zero shear viscosity η_0 on the temperature, i.e., $\eta_0(T)$, or at least a critical flow temperature T_f for a regime, above which a specific viscosity for fast molding with purely viscous flow is reached, is more appropriate for the determination of the imprint temperature as the T_g of a material. Therefore, another definition is more appropriate. In the $G(T)$ diagram in Fig. 2 a plateau can be seen for polymers with $M_w > M_c$, between the viscoelastic and flow states. For linear amorphous polymers the chain segments between entanglements can move. While G is nearly constant at this plateau, its drops again above a specific value, a second transition here named flow temperature T_f. M_w and M_c determine the width of this plateau. At temperatures higher than T_f, the terminal flow regime, imprints are possible at low viscosity and a reduced influence of relaxation and recovery. It only exists in the absence of cross-links, when entire chains can move in a coordinated fashion. This case is added in Fig. 2 as a dotted line.

The T_g keeps its significance mostly for the determination of the demolding temperature. For more complex situations, we even need to take into account the viscosity $\eta(T,\dot{\gamma})$, with its dependence from shear rate $\dot{\gamma}$ and with its characteristic time constants which determine stress relaxation and thus recovery. These time constants are contributions from several different scales of molecular motion, and result from relaxation processes due to reordering in the polymer material during processing.[18,103,104] A consequence of relaxation is either a reduced ability to transfer micropatterns or an unwanted modification in shape, e.g., in microprims.[83] If these values are small compared to the imprint times used, then stress-driven recovery leading to postimprint changes is avoided after the stamp is demolded. In Refs. 105 and 106 relaxation of molded structures during annealing was shown by x-ray diffraction.

Apart from these process-related parameters other properties such as the mechanical strength, Young's modulus, the thermal expansion, heat capacity, and heat conductivity play an important role, not only for pure materials but also for doped, nanoparticle loaded or porous materials.[107]

B. UV-NIL processes

UV-NIL processes are performed at room temperature, at which resist precursors are present as liquid films or droplets. The stamp either sinks down to the substrate or must be kept at constant distance to the substrate during both filling and exposure, due to the low resist viscosities. Patterning on nonflat substrates or over topography therefore requires a planarization strategy and often small stamps. A good strategy for this, as presented by Stewart *et al.*,[25] is that of a bilayer resist. Several types of UV-NIL systems have been realized for S&R and for large area (single wafer) NIL. The main difference from thermal NIL is the integration of an exposure system into one side of the mechanical setup, which has to be able to compensate for wedge errors in a low imprint pressure process. In terms of materials, two main process variants can be seen: (1) a moderate viscosity process (with $\eta_0 = 50$ mPa s and below) for providing liquid films by spin coating and (2) a low viscosity process (with $\eta_0 \leqslant 5$ mPa s), which uses local dispensing of defined quantities of a liquid resin prior to imprint.

1. Spin coating and multilayer films

The advantage of spin-on films is that large areas can be covered with films of high thickness homogeneity. Furthermore, they can be prepared in advance. In the imprint of thermoplastic thin films, solid spin-on films enable imprint in vacuum, allowing air inclusions and bubble defects to be avoided.[108,109] In a similar way, this method can be used with viscous resins, as long as the vapor pressure of the resin at room temperature is low.[110–115] Spin coating is also used for the patterning over topography, i.e., for the preparation of the thick solid planarization layer in bi- and multilayer resists. A resist stack used in SFIL typically consists of a Si containing NIL resist (called etch barrier or hard mask) on top of a functional layer (called transfer layer which acts as antireflective coating by absorbing light). By using this strategy, the thickness and aspect ratio of the top layer can be kept low. Furthermore the etch selectivity can be enhanced by this strategy.[116,117]

2. Coating by droplet dispensing

Particularly suitable for S&R processes is to form an array of droplets by dispensing low viscosity UV-curable monomer onto the substrate surface prior to imprint. This is applied both in the negative working SFIL (also called SFIL/O) and in reverse tone SFIL/R process. By contact of the stamp with the dense droplet array, a continuous film is formed by capillary action. Because of the difficulty of implementing a vacuum, and the inability to compress trapped air inclusions due to the low imprint pressure, inclusions have either to be dissolved or displaced. To handle pattern density variations, the drop-on-demand UV-imprint process at atmospheric environmental pressure has been developed.[116–119] Based on local volume requirements dictated by the design data for a stamp (template), a homogeneous residual layer thickness is achieved by locally varying the amount of liquid resin necessary to fill the cavities of the stamp. In Ref. 120 the multidroplet approach was found to have a significant advantage over other coating methods. By using a multinozzle inkjet technology droplets as small as 5 μm (i.e., less than 1 pl),[87] air bubbles are avoided because the air volume encapsulated during the forming of the film is small enough to be absorbed into the resin within a few seconds.[121] Solvent evaporation of single droplets during the coating of a die area limits the area of a single imprint, due to very low viscosity (<5 mPa s) of the liquids needed for high throughput. Significant improvements in throughput can also be achieved by a "contact geometry modulation," in which an inclined template descent creates a fluid wave front to sweep out air between contact of the stamp and the resin.[87,122–126] Thus, a continuous film is created from discrete drops without trapping voids between the discrete drops. This is particularly important when SFIL is extended toward full wafer NIL.[125] These strategies avoid long processing times until the air is absorbed and can be further enhanced if imprint is done in a He (small gaseous species) and CO_2 (dissolves well in polymer) atmosphere. For example, in Ref. 121, to lower the possibility of voids in the patterns, the space between the stamp and the substrate in the SFIL of the Imprio 100 was filled with helium. Another possibility is to use an auxiliary gas that has a very low vapor gas pressure but is able to condense under the high pressure of imprint.[126,127] In the case of pentafluoropropane, condensation starts when the gas pressure exceeds 0.15 MPa during NIL. These methods work well, if the environment allows for the integration of a sealed process chamber. However, until now investigations into the effect of dissolved gases on the curing have not been published.

Small droplets will evaporate more easily, but large droplets will bear the danger that air bubbles are pinned and difficult to displace. Therefore, the use of the very low viscosity resists in UV-NIL results in the need for a well-characterized geometries and setups and has to be compensated. This is clearly an advantage for a manufacturing environment, but difficult to introduce if the flexibility of a process is needed, e.g., as when functional resists have to be used. As will be explained in the following, the imprint material is subject to several constraints. In Ref. 120, several droplet-compression schemes have been evaluated theoretically and experimentally. A lubrification theory was applied to compare the force required to displace a single droplet to that of a spin-coated film, and the force to displace a fixed volume of fluid in a single drop to that of the same volume divided into n identical droplets (see Fig. 1). The compression of a fixed volume of a wetting fluid benefits from capillary force that augments the applied pressure and from a contact area that is initially quite small. This method also minimizes excess fluid expelled from underneath the template. The fixed force and fixed velocity cases are the most applicable to the current SFIL stepper design since the stepper can control velocity and monitor applied force. However, the single drop compression requires relatively large pressures in order to achieve a 100 nm base layer in 1 s. The throughput constraints of semiconductor manufacturing can be met by applying the multidroplet approach to the SFIL etch barrier delivery if alignment and separation time are neglected.

For the fluid dispensing process,[123] it was found that the characteristics of the droplet are functions of two key dimensionless numbers, i.e., the Weber number We (=inertia forces/surface-tension forces) and the capillary number Ca (=viscous forces / surface-tension forces). By conducting parametric studies, an optimal flow regime for the dispensing process was found in which a single, clearly defined drop forms (e.g., at We number of about 4.0 and Ca number of about 0.1). At low values of We and Ca numbers, the surface-tension force prevents the droplet from detaching and therefore the fluid follows the dispensing mechanism as it is retracted. At a high value of Ca number the droplet falls but remains attached to the dispenser by a viscous "strand" of fluid. Results from this parametric investigation will facilitate the selection of fluids that meet the SFIL design criteria.

3. UV-NIL materials

Different enterprises and institutes have made UV-curable materials. Nanonex, MII, AMO, and Obducat offer these materials adapted to their proprietary process and tool. For common users this is a difficult situation. Not only are the composition and properties of these materials not often disclosed but also materials are not available to other customers and therefore cannot be simply interchanged depending on the application. Toyo Gosei and microresist technology are now offering products for the moderate viscosity process. UV-curable NIL materials are composed of a mixture of monomers (or prepolymers) and a suitable photoinitiator, and often chemicals are added which decrease the effect of radical scavengers on photopolymerization.[6,111–119] Immediately during contact of the stamp with the liquid mixture, filling of the mold starts by capillary forces, which pulls the stamp toward the substrate. Therefore, the general strategy is as follows: Low viscosities are needed both for rapid dispensing and filling of mold cavities. Thin resin layers on top of a thicker transfer layer are used to achieve a homogeneous film thickness. Cross-linking and photopolymer conversion are adapted to achieve high curing speed and high etch resistance in the following breakthrough plasma etching process. Shrinkage and etching rate need to be controlled for optimum pattern transfer. Often trade-offs are needed to achieve a good balance between good physicochemical properties (wetting and curing kinetics) and the suitability for the NIL process.[120] For specific applications such as the dual damascene process for the structuring of interconnects on microchips, resists with adapted dielectric properties have been developed.[128,129]

4. Reverse tone NIL

The pattern imprinted onto the etch barrier is transferred into the bottom layer with a high fidelity pattern transfer process. Similar to this is the reverse tone SFIL (called SFIL/R) in which a silicon containing polymer film with high etch resistance is spun on top of an imprinted thick planarization layer, thus creating a thickness profile of a hard mask with inverse tone.[130] The advantage of SFIL/R is that it is more appropriate to printing over topography than the negative working SFIL/O process. The Si containing film does not need to be suitable for dispensing and printing, but needs to achieve good wetting of the planarization layer. If the imprinted film can be dissolved in specific solvents, lift-off becomes possible. It becomes obvious that in UV-NIL the mechanics of the stamp-resin-substrate stack prior to UV curing also needs to be taken into account. It is most important for the relationship between residual layer control, throughput, and defects in the presence of arbitrary pattern density variations. The current bottleneck is not so much at the physical mechanisms involved, but at the balancing between limited throughput and defectivity.

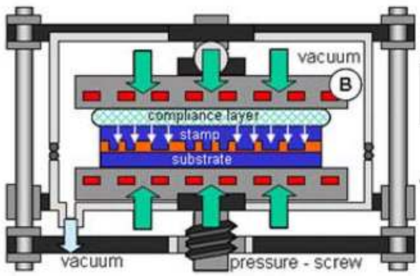
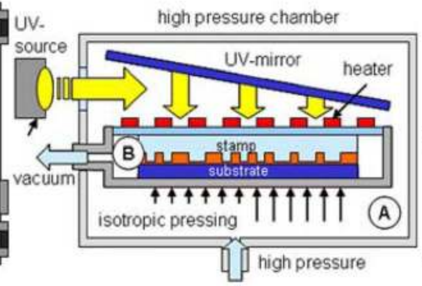
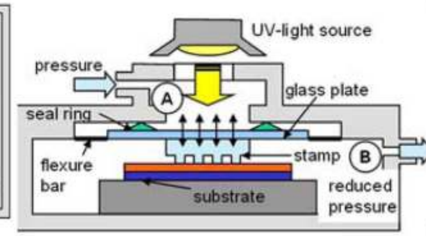
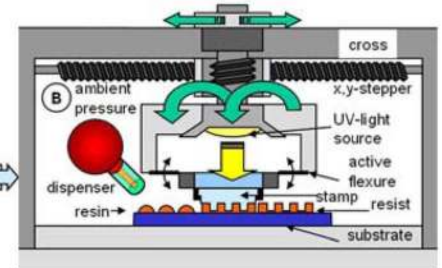
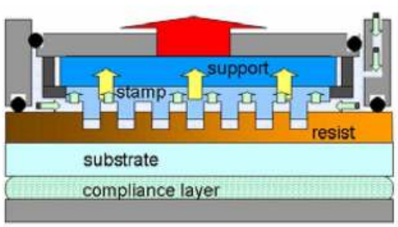
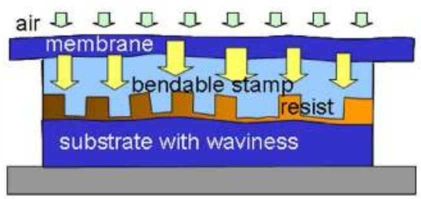
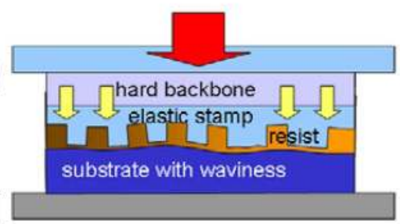
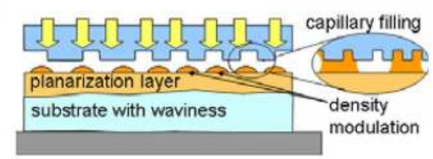
5. Thermoplastic UV-curable materials

In the case of thermoplastic UV-curable materials, which are solid at room temperature and imprinted in an isothermal process, several of the above-mentioned problems are elegantly solved. However, even more than with dispensable resist, the additional requirements imposed by the curing process will impose new restrictions on the choice of materials. Overall, this process, described in more detail in the following section on stamps, is nearer to the hot embossing approach. It does not only allow for the combined sequential thermoplastic nanoimprint and photolithography but also for simultaneous exposure of the imprinted structures through the stamp.[131–137]

C. Hard and soft tool concepts

NIL is a highly dynamic process where the vertical sinking movement of a stamp is transformed into a 3D flow with large lateral flow components. In thermal NIL the speed of the pressure buildup at the back side of substrate and stamp and equilibration of local homogeneities over a large surface can influence the mode of cavity filling. This determines how the stamp will bend during sinking. To cope with these inhomogeneities, different machine and tool concepts were developed which involve hard and soft elements (an overview is given in Table IV). They often stem from concepts already applied in semiconductor processing (mask aligners and anodic bonders) or by adapting the solid stamper imprint press from microembossing. Therefore trade-offs were often nec-

TABLE IV. Hard and soft tool concepts and setup for NIL. Numbers in brackets denote references.

Concepts	Hard stamper + compliant layer	Soft pressurized membrane	Soft (flexible) stamp	Hard stamper step and stamp
Modus	Pressure equilibration due to elastic compliance and bendable stamp	Elastic and inelastic pressure equilibration and bendable stamp	Conformal contact of elastic protrusions on bendable (hard) backbone	Hard stamp, active+passive gap equilibration + planarization strategy
Area	Full wafer (large area) parallel imprint		Segmented multiple imprint	
NIL	Thermal NIL (optional UV-NIL)	Thermal and UV, combined NIL	UV-NIL (wet embossing)	Thermal and UV-NIL
Schematic setup (example)				
Providers	EVG (Ref. 138), SÜSS (139), Jenoptik (140) (schematic), Obducat (141), AIST (142), Nat. Univ. Taiwan (143)	Obducat (Ref. 141) (see FIG. 4), NanoNex (96), Korea University (144) (schematic)	AMO (Ref. 145) (schematic from (25)), KIMM (146,147), NND (148)	MII (Ref. 149), AMO (150), EVG (138), SÜSS (151), AIST (152)
Solutions (established)	• High pressure, high temperature (10-100 bar @ 20 – 200°C), vacuum • Compensation of surface undulations • Micro- and nanostructure combination • Imprint on both sides possible • Isothermal processing • Opaque (Si) stamps (+ heatable stamps)	• High pressure, high temperature (10-100 bar @ 20 – 200°C), vacuum • Thermal NIL with metal membrane • Simultaneous thermal and UV-NIL with transparent hard stamp and polymer membrane (also on both sides)	• Hybrid transparent stamps (soft relief layer on hard (compliant) backbone) • Reduced environmental pressure • Low viscosity (η_0=50 mPa·s) • Demolding by pressurized air knife induced peeling for flat panel display	**UV-NIL (step&stamp and step&flash)** • Alignment through stamp (<10 nm) • Very low viscosity (η_0< 5 mPa·s) • Drop-on-demand coating process **Thermal NIL (step&stamp)** • High pressure, high temperature (10-100 bar @ 20 – 200°C), no vacuum
Example	 Air induced automated demolding	 Isotropic pressure by compliant membrane	 Conformal contact by elastic stamp	 Inkjet dispensing with density modulation

essary, and the question of which concept is most suitable is dependent on the application and therefore needs to be properly analyzed.

1. High-pressure tools in thermal NIL

While in a bonding machine two hard substrates are pressed together without any movement, in NIL the pressing mechanism has to compensate for the vertical movement of the stamp due to the squeeze flow, both globally and locally. Both the global movement of up to a few hundred nanometers and the compensation of local height variations of a few tens of nanometers are easy to implement with a compliance-type mechanism. In presses with a stiff mechanism based on hydraulic, air, and screw driven hard stampers, the buildup of the whole stack includes the use of an elastic compliance layer (e.g., flexible graphite, rubber, or Teflon), which is needed for the surface equilibration due to the lack of flatness of common substrates. Other concepts use an air-pressurized membrane as a soft cushion, which equilibrates local pressure variations during the sinking of the stamp in a more controlled way. For example, while a pressurized membrane (made from 50 to 100 μm thick Al or polymer foil) will equilibrate local pressure variations due to stamp sinking within a fraction of a second, an elastic element (e.g., a 1 mm thick rubber layer) will build up pressure with a short delay when compressed with a screw-driven press. In contrast to this, the constant speed for compression and demolding (in the Jenoptik HEX 0.2 mm/min, i.e., 3 μm/s) can be used for continuous molding of microstructures with several 100 μm of height when the rigid stamp is attached to one of the press stampers. It therefore has to have either a mechanism that applies a constant pressure over the whole movement or a constant vertical speed while the force is kept within certain limits during both molding and demolding and with no delay.[54–56] Because of this difference in ability to perform micro- and nanometer movements in a controlled way, not all presses are equally suitable for the molding of micro- and nanostructures, or microembossing and NIL, but can be adapted to do both cases reasonably well. In addition, the stamp hardness should be appropriate for the process to be used, as the stamp structures should not be altered by repeated and extended processing. In thermal NIL, the stamp surface should be as hard as possible to avoid any distortion due to the high stress induced during the vertical sinking of the stamp and the lateral viscous flow of the polymer. Until now, for the standard materials used in thermal NIL (Knoop microhardness is for Si 1150, fused silica 500, Si_3N_4 1450, and diamond 8000 kg mm^{-2}) there was no report of stamps wearing out after several 100 s of imprints due to the relatively high viscosities. The stamp as a whole, however, has to be flexible that it can accommodate surface undulations and the pressure inhomogeneities by structure density variations. New NIL concepts using heatable stamps,[59] heating of stamps by IR lasers,[60] or stamps composed of segments with compliant bridges are currently developed.[153] A particular setup using a stationary dynamical effect is that of an ultrasound aided molding.[154] Since the ultrasonic source provides a vibration with tens of kilohertz frequencies, the temperature of the polymer can increase rapidly. However, to date it is not evident whether these developments will have major advantages over more conventional approaches.

2. Low-pressure tools in UV-NIL

In UV-NIL, due to the lack of high imprint pressure, this equilibration needs to be either applied in the microregime with elastic stamps to compensate for small surface undulations[143,155–157] or to be completely avoided with small hard stamps (made from fused silica), e.g., in SFIL.[158] Then the fluid acts as a shock absorber, which slows down the stamp/substrate closing velocity by squeeze flow and reduces the risk of breaking fragile structures upon contact with the substrate. Furthermore force and image sensors on the head prevent the stamp from being damaged by gross particles.[159]

In contrast to thermal NIL, where thermal expansion has to be compensated for sub 50 nm alignment, alignment for UV-NIL has several advantages. Because of the transparent molds and the liquid resists, lateral alignment is done through the stamp, in proximity or in "lubricated" liquid contact while stamp and wafer are held at fixed vertical distance.[15] A self-leveling flexure aids the parallel alignment. The forces on the stamp protrusion are induced by capillary action rather than by squeeze flow and are therefore low. Therefore in UV-NIL, stamps made from elastomeric materials, e.g., polydimethylsiloxane (PDMS), an UV transparent rubber, can also be applied. The concept of layered stamps—a thin PDMS relief coated on a harder substrate—is particularly useful in full wafer concepts. It combines the complementary mechanical properties of a soft surface relief for the achievement of local conformal contact and a rigid, but bendable backbone, which can be used for mounting and alignment.[156,157,160] However, in the case of flexible molds, local deformations limit the resolution of soft UV-NIL principally. These deformations depend entirely on the imprint pressure applied, the elastic properties, and the aspect ratio of mold pattern transferred. So far, a resolution of 50 nm has been achieved on 100 mm wafers with a residual resist layer thickness of 140 nm at an imprint pressure of about 200 mbars.[156] However, not only the NIL process but also the mold fabrication is limited due to the high viscosity of the mold material precursor. Then the penetration of the material into cavities below 1 μm is inhibited. In Ref. 156 it was shown that by diluting the PDMS precursor (Sylgard 184 from Dow Corning) with toluene to reduce its viscosity, the filling of a 110 nm deep mold could be enhanced from 5 to 70 nm for 50 nm holes (with a 70% toluene content).

Different groups[161,162] performed alignment studies. In Ref. 161 a sub-150 nm lateral alignment was achieved over an area of 25×25 mm^2 and 250 nm over the entire area of a 100 mm wafer using simple low-resolution stages without temperature control or wafer-stamp mismatch compensation. With advanced Moiré fringe techniques a sub-20 nm alignment in NIL is possible.

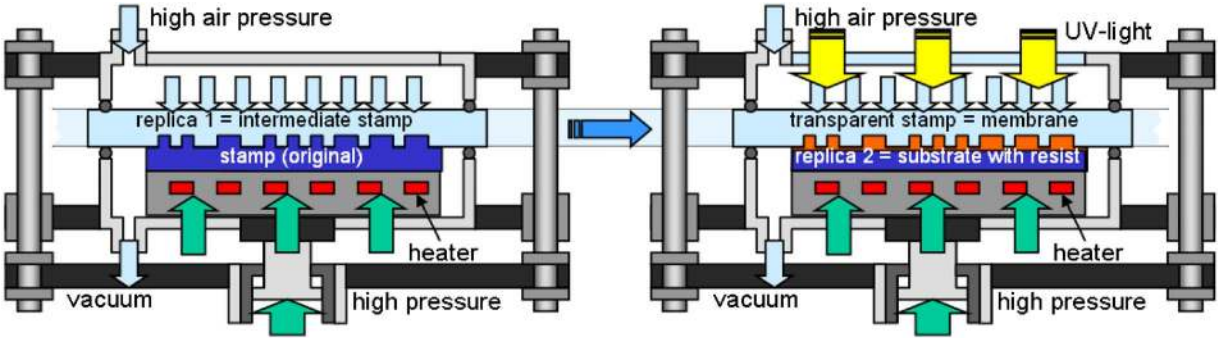


FIG. 4. Possible mass fabrication process for NIL (schematic) in a tandem setup with intermediate polymer stamp production by thermal NIL (left side) and simultaneous thermal and UV process for resist patterning (right side), both imprinted with a polymer foil acting as a soft pressurized membrane; Obducat has included a similar process in a manufacturing tool (Ref. 170).

3. Stamp copies and contamination control

Interestingly, an inherent advantage of the high-resolution replication capability of NIL is that stamp copies can be fabricated easily by using NIL.[163–165] The concept of mastering and fabrication of daughter stampers for mass fabrication—long used in compact disc molding[46]—is now also becoming state of the art in NIL fabrication in SFIL.[166] It is not only a means to enhance the lifetime of the original but also to reduce the effect of contamination and damage. By using advanced pattern transfer techniques, it does not only allow for the fabrication of identical daughters of one original,[82,167] but also to invert the tone of the surface relief, to modify depth and sidewall inclination, and to combine patterns.

In recent years, the quality of the templates used for SFIL has been continuously improved and defects stemming from different origins on the stamp and the imprints reduced.[159,168] This is essential in S&R processes because the same stamp has to be used for over 50 automated imprints per wafer without increase of defects. Therefore, strategies for self-cleaning are needed, i.e., particles stick to the substrate rather than to the stamp. Furthermore, appropriate cleaning procedures and an in-line control of contamination are necessary. For example, in thermal NIL polymer residues on stamps can be detected by using fluorescent thermoplastic resists,[169] which makes it possible to detect when cleaning or recoating of the stamp becomes necessary.

4. Intermediate stamps and combined thermal and UV-NIL

While in UV-imprint drastic improvements in the detection of contaminations have been made for the past few years, by improving substrate quality,[158] Obducat has solved the problem of contamination in a different way.[170] Instead of fabricating stamp copies in the same hard material as the original, intermediate polymer stamps are fabricated for every single imprint. This process, called intermediate polymer stamp (IPS), has similarities to the photopolymerization technology for high-density multilayer digital versatile disc (DVD) manufacturing,[171,172] and the spin-on-and-peel technique.[173] It is a two-step process, in which hot embossing onto a hydrophobic polymer foil, such as Zeonor or Topas,[174–177] transfers the surface relief of the silicon, nickel, or polycarbonate original. These foils are used as molds in a simultaneously combined thermal and UV nanoimprint (STU) process, allowing the complete imprint sequence into UV-curable thermoplastic prepolymers to be performed at a constant temperature (isothermal process conditions). The method allows the use of spin-coated UV-curable polymers with a homogeneous thickness distribution on wafer scale, crucial for critical dimension control and enabling pattern transfer to an underlying substrate. These resists, typically with properties similar to SU-8[178] or mr-I 6000 resists,[97] have already proven their suitability in mix-and-match applications.[131–133,136,137] This process has the advantage that fracture of hard material is avoided, because contamination, e.g., dust particles, if present between stamper and resist,[170] is completely enclosed by the intermediate stamp. Furthermore, the process is self-cleaning after separation: Because of the hydrophobic nature of the polymer stamp, no polymer residues adhere to the master, making intermediate cleaning procedures obsolete.[168] The IPS process was developed for the patterning of via holes in printed circuit boards. For a three-level structure with a minimum linewidth of 20 μm a residual layer thickness of 1.4 μm was measured in a STU resist. The process is not restricted to microstructures, and can be scaled down to structures with sub-100 nm resolution, where the standard residual layer thickness is below 20 nm with an accuracy of ± 5 nm across a 150 mm wafer.

The strength of Obducat's process lies in the combination of the two processes, STU for precise pattern transfer and IPS for yield improvement, with its Soft Press technology. Figure 4 shows a schematic of the possible realization of such a tool in a tandem approach. Here full area uniform imprint is achieved by using a polymer foil as a transparent membrane, which is pressed against the heated bottom layer by pressurized air. It is first patterned by the original and then used for patterning of the resist on the target substrate. It would be a further advantage if the residual layer within the moldable layer could be eliminated. By using a semitransparent stamp, where protrusions are coated with an opaque material, it is possible keep the resist beneath the protrusions unexposed, and prevent them from being cross-linked. Then it can be dissolved like an unexposed negative resist, resulting in chemical selective removal of the residual layer.[134,135] This concept needs stamps and resists with similar refractive indices. Otherwise, diffraction effects at stamp borders will restrict it to large patterns.[179] It also needs an additional step for mask making, and will most likely be implemented with stamps made from chromium coated fused silica templates.

D. Surfaces and interfaces

Since NIL is a process based on squeeze flow of a sandwiched viscous material between a stamp and a substrate, the interface between the two materials has to be considered throughout the entire process, both from topographical, chemical, and mechanical points of view. Often stamp and substrate are made from the same material, Si or SiO_2, but their surfaces need to exhibit opposite properties with respect to the resist, which can be created by different means. While the resist has to adhere well to the substrate, an extremely low adhesion to the stamp is a prerequisite of good demolding—therefore true antiadhesive properties are needed, either by modification of the stamp or the resist surface. In reverse NIL (see Table V), this has to be balanced in a way that the resist, when spin coated onto a prepatterned stamp, wets and replicates all the surface corrugations, while at the same time it has a low enough adhesion to detach. Then it can be transferred to a second substrate, and—after chemical or thermal bonding—released from the stamp. Using this process, the adhesion to the stamp should be so small that the demolding does not lead to local failures due to density variations on the stamp.

1. Antiadhesive coatings based on fluorinated silane chemistry

Different solutions have been proposed for stamp release: nonsticking stamp materials,[157,180,181] antiadhesive coatings,[182–189] nonsticking resist materials,[190,191] modifications of stamp and resist surfaces,[192–194] and one-way (polymer and dissolvable) stamps.[195] As long as silicon and silicon oxide can be used as stamp materials, the main strategy is to improve the antiadhesive properties of the stamp by coating with a fluorinated silane. These silanes are a proven solution by exhibiting strong covalent bonding and sufficient hydrophobicity.[186,189,196] Industrial solutions for molecular vapor deposition are available.[197,198] Fluorinated silanes are available with different carbon chain lengths and silane head groups; they are commonly used due to their low surface energy, high surface reactivity, and high resistance against excessive temperatures and pressures.[187,189] In thermal NIL they support multiple long embossing sequences with repeated temperature cycles higher than 200 °C. Currently it seems that as long as mechanical abrasion can be avoided, the silanes match the "normal use lifetime" of a Si stamp, which is a few thousand times, if automated S&R imprint processes or injection molding processes are used. However, some recent annealing tests indicate that imprint at high temperatures decreases the lifetime of this coating. In Ref. 199 it was shown for different coatings that the overall imprint time at a specific temperature might be a measure for the lifetime.

Therefore, further strategies are needed for coatings with extreme lifetimes and for structure sizes below 10 nm. Solutions have been proposed which are based on specific polymers and exhibit strong adhesion to the substrate but strong antisticking properties to the stamp. An example is the PS/PDMS diblock polymer,[190] or demixing,[192,193] by decoupling of surfaces, due to a nanoscopic alignment during spin coating (for planar substrates).

2. Template contamination in UV-NIL

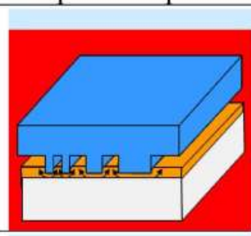
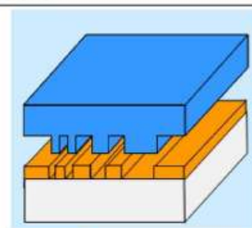
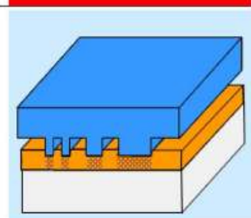
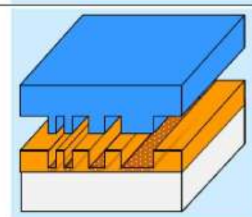
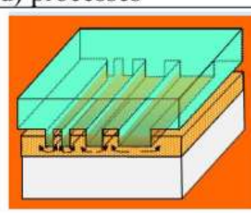
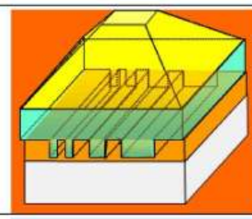
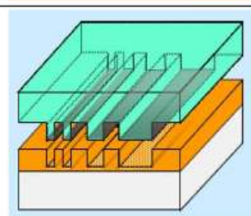
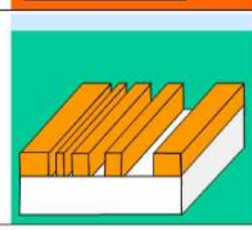
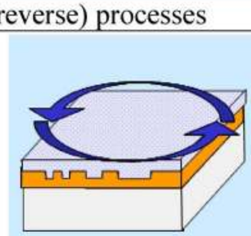
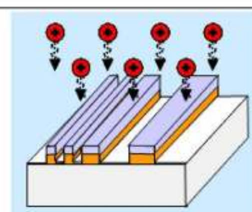
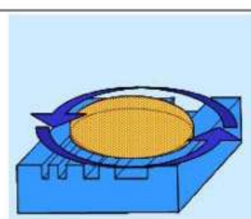
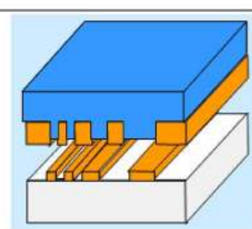
Cleaning of stamps becomes necessary if resist residues adhere and/or become lodged within the features of the stamp (called template fouling).[119] Once such a defect occurs, typically it continues at the same location in the succeeding imprint and continuously increases its size.[200] This is contrast to previous publications, where a self-cleaning effect was described, i.e., particles stick to the resist rather than to the stamp.

Preliminary research has shown that currently available surface treatments cannot exclusively prevent template fouling in UV-NIL. In SFIL, this is particularly critical,[119] since a chemical reaction between template and the resist cannot be excluded. Small feature sizes along with high silicon content and a large degree of cross-linking make any residual imprint polymer left on the mold almost impossible to remove from the template without damaging the expensive quartz template.

AIST reports about SFIL/R process tests with an Imprio 55 machine from MII[149] using a quartz mold with minimum patterns of 45 nm lines and spaces, which was coated with RelMat (MII) as a release layer.[200] The UV-curable resin MonoMat (MII) with a resulting residual layer of 100 nm was used on top of a 60-nm-thick DUV30J (Brewer Science) antireflective layer. More than 18 000 UV imprints (150 imprints per 100 mm wafer) were done. The maximum lifetime of a release coating was found to be about 2000 imprints, with an average of about 800, which means that about six wafers were imprinted before recoating was found to be necessary. This lifetime was shorter than expected. Furthermore, a difference in a pattern width of 6–8 nm between imprint Nos. 684 and 13122 was observed. It has to be clarified whether this can be attributed to structure erosion due to imprint or cleaning or simply to measurement errors. These preliminary results show that although a relatively good reproducibility is realized in UV-NIL during long-term use, there are questions to be solved if lifetimes of typical production scale have to be realized.

In Ref. 201 the underlying cause for release problems in UV-NIL was addressed. Double cantilever beam fracture specimens were fabricated from bar-shaped substrates by gluing two tabs on opposite sides of one end.[202] The specimens were repeatedly unloaded and reloaded using a micromechanical test system delaminator in order to obtain multiple compliance curves from which the crack length and the fracture energy G_c (J/m^2) could be determined. Measure-

TABLE V. Specific NIL processes for optimized pattern transfer, combined (hybrid) processes, and pattern transfer processes. Numbers in brackets denote references.

	Process	(1) Pattern generation	(2) Curing or transfer	Status
Process schemes for optimized pattern transfer				
T– NIL	**Partial mold filling and zero residual NIL**			**Process:** Self-limiting flow of a thin resist **Resolution:** (Refs. 88,89,225) lateral 200 nm, h_f nearly zero
RT– NIL	**Room temperature NIL (hard stamp)**			**Process:** Resist compaction by high pressure under protrusions **Resolution:** (Ref. 223) 80 nm line with 300 nm spacing (100 nm deep)
Combined (hybrid) processes				
T+UV– NIL	**Simultaneous thermoplastic and UV-NIL (e.g. STU)**			**Process:** Thermoplastic molding and UV curing **Resolution:** (Ref. 170) lateral <50 nm, h_f 20 nm
NIL+PL	**Combined NIL and photo-lithography (e.g. CNP)**			**Process:** Exposure through semitransparent stamp and removal of unexposed residual layer **Resolution:** (Ref. 134) lateral 350 nm
Pattern transfer (reverse) processes				
NIL / R	**Reverse tone NIL (e.g. SFIL / R) – Patterning over topography**			**Process:** Overcoating of Si-containing etch barrier on prepatterned organic transfer layer, etch back and dry developing (window opening) **Resolution:** (Ref. 166) lateral <100 nm
R-NIL (T or UV)	**Reversal NIL – With complete resist pattern transfer or "inking" mode** (partial transfer)			**Process:** Spincoating of resist onto stamp, complete or partial transfer to substrate by thermal bonding **Resolution:** (Refs. 61-65) lateral <100 nm, h_f nearly zero

ments of adhesion of bifunctional fluorinated silane during UV as a function of number of imprints using commercial resist and release formulations showed that initially low adhesion energy was not preserved with use. Instead, the fluorine disappeared, consistent with its conversion to volatile species that rapidly evaporate after removal of the template. This observation indicates that the silane layer degrades during use because of chemical attack by the abundant free radicals present. It was shown that a fluorosilane release layer applied to an UV-NIL template undergoes attack by acrylate, methacrylate, and vinyl ether UV-curable resist systems, pointing to its degradation being intrinsic to the chemistries involved. The low energy surface a fluorosilane layer presents is not unreactive, and it is rapidly and easily degraded during use. The successful use of diamondlike carbon (DLC) as a release layer for a methacrylate resist shows that a criterion of low reactivity rather than low energy is valid.[182,183,201]

A number of solutions have captured the interest of researchers for the improvement of this release-layer chemistry. Because surface treatments such as silanes are attractive solutions and thin in comparison to DLC coatings, many researchers have chosen to focus their efforts toward the possible use of degradable and reversible cross-linkers in resist in place of ethylene glycol diacrylate or its divinyl ether analog.

In my opinion, many of the above-mentioned problems are crucial for high throughout applications, but not so important if moderate numbers of imprints have to be done. They may be solved to a certain extent by using lower imprint temperatures in thermal NIL, or by using resists, which do not react with the release coating (no acid generator). Other suitable release coatings (such as DLC) having this property toward diverse resist chemistries have to be identified. Two major strategies have to be followed for the future development of NIL. (1) A recoating strategy, which either involves appropriate cleaning steps within the machine (e.g., inline for S&R) or outside (for full wafer parallel imprint). In SFIL, this means that strategies have to be developed which make resists soluble in specific solvents after cross-linking. (2) An auxiliary stamp manufacturing strategy by NIL (either for every single imprint or for a specific number of imprints), particularly significant stamp erosion, becomes evident. This is a different effect than the case described in Ref. 159, where fused silica templates were assumed resistant to damage from "stepping" on particles and from "wearout" by low viscosity liquids.

Probably a combination of several measures will be the best solution. The question to be solved is at which point the contamination with polymer residues sets in, or it becomes so high, that following imprints will accumulate more residues. Analytical tools have to be developed which make it possible to determine the onset of contamination and stamp erosion. This threshold is not only dependent on the technology used but also on the requirements on yield and error tolerance.

3. Assessment of the release-layer quality

A final word has to be said about the assessment of antisticking quality of a stamp or material. Often contact angle (CA) measurements or x-ray photoelectron spectroscopy analysis of freshly prepared samples are used to demonstrate the quality of antiadhesive coatings.[189,203] Since the common silane coating rarely results in a dense, well-oriented monolayer, a modification of this coating has to be anticipated

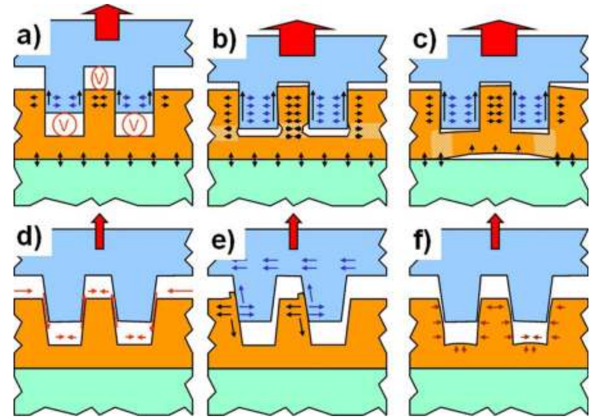


FIG. 5. Demolding issues: (a) generation of vacuum voids, (b) elongation and ripping of single structures, (c) ripping of resist from substrate, (d) penetration of air into voids (inclined sidewalls), (e) shrinkage and generation of rims, and (f) relaxation of frozen-in-strain.

during the first few imprints. Therefore, the measurement of a pristine coating is only a rough estimate of its quality for repeated imprints. Surface roughness, e.g., by excessively deposited material, i.e., cross-linked trichlorosilane only loosely bound to the surface, can contribute to enhancement of the CA (so-called superhydrophobic or Lotus effect[204,205]) and exaggerate the antiadhesive quality of the coating, but after a few imprints only the silanes chemically bound to the surface will remain. For instance, for the perfluorosilanes used as standard antiadhesive coating, a CA of more than 120° may be the result of contamination and enhanced surface roughness.[189] Therefore, measurements should involve the comparison of pristine and imprinted samples. A further problem is that CA measurements do not account for friction at the sidewalls of stamp structures during demolding. An assessment of surface quality not by measuring the surface quality but its effect on wetting with resist and demolding would enable the determination of the evolution of surface quality of an entire structured stamp as an average of global design and local hot spots.[206,207] An absolute measurement could be performed by measuring demolding forces of a specific stamp, deduced from the online load history in each imprint step.

E. Demolding

1. Parallel and peel demolding

During demolding the stamp is detached from the molded structure by a vertical movement of the stamp (see Fig. 5). If fully molded, the thickness profile in the resist exhibits the inverse tone of the relief of the stamp surface. The demolding process is normally performed in the "frozen" state, i.e., when both mold and molded material are considered solid. For thermoplastic materials, this happens at a temperature well below T_g, but high enough that frozen strain due to thermal contraction does not lead to damage during demolding. In cases in which the resist is cured, i.e., cross-linked by exposure or heat, demolding can take place at temperatures similar to the molding temperature.[208] As in molding, hard and soft concepts also play a role in demolding, and the ability to retrieve a stamp without damage, contamination and degradation have become major issues in NIL. For example, while in SFIL the 6.3 mm thick rigid quartz template is detached from the resist in a vertical movement, in thermal NIL the thin waferlike stamps use delamination by a peeling movement rather than parallel separation (see Table III). This concept is now also implemented in the large area UV-NIL by using thin transparent stamps.[124] A successful demolding process relies on a controlled balance of forces at the interfaces between stamp, substrate, and molded polymer film.

2. Adhesion, friction, and local geometry effects

Distortion or damaging of the molded structure during this movement can occur because of different effects such as adhesion at the surface, friction due to surface roughness, and trapping of the polymer due to negative slopes of cavity sidewalls (see Fig. 5). As a result, the polymer structures or parts of the wall profile are either ripped away or deformed during demolding. Structures with high aspect ratio may be more prone to ripping, and damage to structures often occurs at the structure base where residual strain is highest [Fig. 5(b)].[80,102] If many neighboring structures are pulled out, they exert a locally combined high force to the underlying substrate, and whole areas of resist may be detached from the substrate surface [Fig. 5(c)]. The forces present during the demolding processes are therefore a combination of adhesion and friction, but also, e.g., in the case of soft or flexible materials, in inelastic/elastic deformation. Apart from friction and adhesion forces, an additional force has to be overcome if a high aspect ratio stamp protrusion has to be pulled out of the solid materials. The atmospheric pressure of the surrounding areas tries to inhibit the creation of a void below the stamp protrusion [Fig. 5(a)]. With microstructures it has been shown that the demolding forces can be significantly smaller if sidewall inclinations of 5° are applied, which eliminates friction but also helps air to penetrate into the voids created by the pulling [Fig. 5(d)].

3. Lateral shrinkage and global geometry effects

The most critical point is that demolding forces greatly depend on the geometry of the mold, not only locally but also the overall design of a stamp structure has to be taken into account. Antiadhesion layers on the mold reduce friction forces, but do not have an effect on the strain induced by shrinkage, which result in local variation of lateral forces between stamp and polymer [Fig. 5(e)]. In hot embossing of thick polymer plates with stamps made from silicon or metal often defects can be seen, i.e., distortions and rims.[68,209] The asymmetric position of these defects indicates the influence of the shear force resulting from the difference of the thermal expansion coefficients of the polymer and the metallic mold insert. They are larger at the borders of the substrate because the difference in expansion coefficient α of the substrate and of the stamp adds up to several micrometers (e.g., in the range of 50 μm at the borders of a 100 mm wafer for $\alpha_{Si} = 2.6\times10^{-6}/K$, and $\alpha_{PMMA} = 50\times10^{-6}/K$, if demolding is done 20 K below T_g). In the case of very thin polymer layers coated onto a thick substrate, the global lateral expansion of the resist is determined by the substrate. Therefore, in thermal NIL the strategy to reduce and even eliminate this global expansion mismatch is to take the same material for stamp and substrate, and only thin functional layers as resists.

Therefore, the use of electroplated nickel stamps is limited for thermal NIL onto silicon substrates ($\alpha_{Ni} = 13.7\times10^{-6}/K$). It can be facilitated when extremely smalls stamp are used. In any case, effect of a local expansion mismatch (e.g., when thick resist layers or high aspect ratio structures are used) may be reduced by choosing a demolding temperature T_{demold} as near as possible to T_g, because the stress induced by thermal shrinkage should not exceed in critical areas where structures tend to break.[80,102] Both in thermal and UV-NIL local shrinkage is present, either due to thermal compression, process shrinkage due to reorientation of polymer chains, or cross-linking. In combination with strain relaxation and recovery it can lead to distortion of structures [Fig. 5(f)]. All other issues [Figs. 5(a)–5(d)] are valid for UV-NIL as well. It is an unsolved question how much the demolding can be optimized by choosing materials with adapted process shrinkage.

Interestingly, because damage, distortion, and ripping have to be avoided, there are a lot of scientific questions involved in the mechanical separation of mold and polymer, and even a controlled damage of structures is investigated to fabricate structures with new shapes and properties.[210,211] The elongation of pillars was employed to increase the aspect ratio or to create an undercut. In Ref. 212 the demolding of elastic structures with undercuts was investigated. Undercuts of up to 60% of the overall pattern width were successfully replicated. Finally it has to be mentioned that there is little understanding whether polymer chains can be locally oriented by molding, i.e., in semicrystalline polymers, to an extent that they can be used in applications.

F. Unwanted effects and unsolved questions

Capillary bridges, dewetting, air inclusions, and viscous fingering are signs of dynamic effects during mold filling.[213] They are good examples of how imprint is highly dependent on the process and the design of molds (structure density, size, and height).[214–217] Often a variation of process parameters or design, as well as small contaminations between stamp and substrate, enhances the probability that these effects may occur. They are unwanted effects, but in most cases can be avoided by simply enabling enough flow so that complete molding is achieved. In contrast to these unwanted effects, which are not treated in detail here, there are physical effects that are highly desired for improved processing such as zero residual layer molding and room temperature imprint (see Table V). It would be much better if these effects could be either eliminated completely or controlled in a way that they could be used for large process latitude, e.g., by choosing appropriate designs and process parameters, if low residual layers, low imprint temperatures, fast imprint times, or good pattern transfer were required. A possibility to observe the important parameters of molding, the evolution of the residual layer thickness, was described by Baraldi[12] by integrating a microscope into the imprint machine and by Yu *et al.*,[218] Jucius *et al.*,[219] and Lévéder *et al.*[220] for scatterometry. Apart from real-time measurements, visualization of mold filling can be done by freezing different states. In Ref. 76 this was done using a thermal NIL setup with fast cooling. In the next two paragraphs, examples of two effects are presented in more detail that would profit from these kinds of measurement techniques.

1. Zero residual layer imprint

Zero residual layer imprint means NIL with no noticeable residual layer left under the stamp protrusions and is probably mainly a consequence of Stefan's equation, and it is questionable, whether "zero" means a totally dewetted surface or simply an extremely thin residual layer. Therefore, in Refs. 148, 221, and 222 it is called "nearly zero." For example, according to Stefan's equation [Eq. (1)], a stamp full of 10 nm wide, 40 nm high ridges at 40 nm pitch can be imprinted into 40 nm high resist within less than 1 ms, resulting in a residual layer thickness of 10 nm (using $p = 100$ bars, $\eta_{0\mathrm{PMMA25k}}(180\ ^\circ\mathrm{C}) = 2\times10^4$ Pa s). In contrast to this, a stamp with 5 μm wide, 240 nm high line protrusions at a pitch of 10 μm can be imprinted in 1.5 s, when imprinted into a 300 nm resist ($h_f = 120$ nm). In contrast to this, with 130 nm initial thickness, it needs 250 s ($h_f = 10$ nm). The zero residual layer effect can be further explained by shear thinning, spinodal dewetting, and even chemical decomposition (i.e., chain scission due to overheating) of the polymer below the protrusions. Furthermore good imprints are sometimes achieved with extremely small stamps which do not need a compliance layer for the equilibration of unevenness.

In my opinion, good results are achieved because the actual local pressure is extremely high and that fast flow becomes possible. For example, from the overall force of 1 kN on a 10×10 mm^2, a stamp with a pillar array covering 10% of the surface results in an extremely high pressure of 1000 bars. Here for a good judgment we would need more information about the actual parameters used, the machine, and the stamp size and design. Then, at a given force for the overall stamp, we would be able to determine the pressure under each individual stamp protrusion at the beginning of the molding. As shown in Ref. 88, a partial cavity filling can be used to imprint with extremely small residual layer. In Ref. 10 a grating with 200/270 nm lines/spaces, 300 nm stamp height was imprinted into 150 nm thick PS (M_w350 kg/mol) at 160 °C, resulting in 150 nm high polymer structures with 150 nm space between resist ridge and mold cavity top. The process was self-limiting and resulted in a negligible residual layer. Although in Ref. 88 it was demonstrated that even metal lift-off was possible, it is questionable whether the process is reliable enough to be used for small structures down to a few nanometers without a short oxygen-etching ("descum") step.

2. Room temperature imprint

The feasibility of room temperature imprint (RT-NIL) of thermoplastic polymers with a T_{imprint} not much higher than ambient, as described in Ref. 223, is also a surprising development. It is used if high imprint temperatures have to be avoided, e.g., when optically active materials that are susceptible to temperature induced bleaching are used[7] or when nanostructures have to be printed on topography.[224–230] It is known that materials with no known thermoplastic behavior can be molded, i.e., cross-linked materials such a polyimide and polyaniline[7,91] and that metals can be molded well below their melting point.[231] If a material can be molded well below its T_g, both a compression of the material due to free volume contraction and plastic deformation of the resist layer under compressive stress can be responsible.[223] This is because in amorphous polymeric materials, a certain number of vacancies, called free volume, must always be present due to the absence of long-range order and chainlike character. Although the vacant volume is not completely available for thermal motion of the polymer chains, a compression, characterized by a compressibility factor, is possible by free volume compaction only. For example, in Ref. 223, a compression factor larger than 3 is reported (a 100 nm thick film was compressed to 30 nm and below) and identified as free volume contraction. This factor is extremely high, but may be explained by the additional occurrence of plastic deformation. Then the thickness can be further reduced if the applied stress exceeds the yield stress of the polymer. In order to achieve plastic deformation of the polymer only, the applied stress needs to be in the range between the yield stresses of polymer and of the inorganic mold and substrate material. Although this seems to be a sound method to generate surface topography, it is questionable whether the pattern transfer will benefit from the densification of the polymer layer below the protrusions. The etching time will be likely the same as for the noncompacted initial layer.

The concept of free volume can also be used to explain the decrease of the viscosity at temperatures near to but above T_g, because it is necessary in order for the molecular motion to occur (see Fig. 2).[223,232] It is associated with the space between molecules in a sample. Below T_g thermal expansion occurs with no change in free volume. That means that according to this simple model, the ability to dissolve air is enhanced when the free volume is increased, either by compressing the air or by using small gas species such as helium or other gases, which are easy to dissolve in organic materials such as CO_2.[122] It is also valid for the case for liquid resins as used in UV-NIL, where the take-up of air is dependent on the choice of gas and resin material.[120,233]

Finally, another method was developed to enable RT-NIL, so-called "solvent assisted NIL."[234,235] In an atmosphere of organic solvent vapor, imprints may be carried out at temperatures much below the T_g of the polymer. The solvent causes a plasticization effect. Consequently, the effective T_g of the system is lowered prior to imprint. Here the question is whether during the imprint process the solvent can be effectively removed from large area structures. For this purpose porous stamps made from PDMS are of advantage.

IV. CONCLUSION

A. Relevance

After more than ten years of NIL process development, a range of standard tools and materials is available from various industrial providers. Many engineers get impressive results with machines based on different concepts. However, not surprisingly, they often encounter difficulties[86,236,237] when they have to use stamps provided from other sources (e.g., when switching from a stamp with low-density protrusions to stamps with a few microcavities), vary their own process parameters (e.g., use a thinner resist thickness for enhancement of pattern transfer fidelity), or need to consider boundaries given by a specific application (large area and combined micro- and nanostructures). The need to improve speed, reliability, resolution, and tolerances will keep both researchers and engineers busy.

Where will NIL be in 10 years, or in 50 years?[238] NIL is still not yet established as a mass fabrication technique and in competition with other established and emerging lithographies. It is possible that other processes will be employed in target application areas first. Within the next ten years, we will probably see a range of products being fabricated with NIL. Whether NIL will be able to replace other NGL for CMOS fabrication for one of the next nodes is still an open question. Regarding the current activities, two first high-end NIL products can be seen: (1) subwavelength polarizers, optical components requiring fine-resolution patterning and three-dimensional features (e.g., high brightness LEDs and backlighting for flat panel displays) and (2) patterned media or discrete track recording hard disks. Both large area applications have high requirements on resolution but relatively simple geometries. Furthermore, they do not have the demanding requirements such as overlay of different levels as in microchip fabrication. Machines for production are currently developed, such as the "Sindre" high volume manufacturing by Obducat,[141,170] Imprio 250 and 1100 by MII,[149] or EVG 750 by EVGroup.[138] In order to achieve high throughput as it is possible with compact disc molding, imprint times of a few seconds will be needed, this is currently still difficult both for thermal and for UV imprint, because of the slow heating and cooling in thermal NIL and because of limitations of the curing and air dissolution speed in UV-NIL.[159] As an example, a CoO analysis of SFIL with the dual damascene process for back-end interconnection patterning was presented.[239–241] It takes into account not only the cost of equipment, masks, but also the number of lithography steps, effect of machine occupancy, yield, the need of redundancy, and backup solutions, e.g., additional numbers of masks because of contamination or necessary reserves. The consequence of this is that NIL is not automatically less expensive than PL, nor is it the process of choice for any kind of application. It may be the only solution in areas where the CoO of standard lithography is considered too high. For example, for the imprint of distributed feedback (DFB) gratings on a single wafer filled with hundreds of semiconductor lasers, a 5 min process time and even more would be acceptable. One process can look very different from another, and production facilities can range from simple processing tools to entire production lines. Therefore, one has to work strongly on real developments, innovative processes, and not simply on the replacement of PL by NIL. Then in long term, NIL will become an integral part of micro- and nanoprocessing.

B. Improving the NIL process

Although NIL machines are now widespread, most of them are still slow and not suitable for mass fabrication. In thermal NIL new problems such as homogeneous heat transfer, recovery due to material time constants, and reduction of defects due to limited air dissolution or mechanical abrasion will become more dominant after speed and resolution are increased. In a similar way, in UV-NIL questions due to the dynamics of the process have to be solved, i.e., fast curing speed, wetting, and nonreactive resists for lifetime enhancement of stamps.

To complete understanding, systematic empirical data are still needed. A way to do this is by benchmarking, i.e., by comparing imprints with different pieces of equipment to clarify the origins of dynamical effects and of material, process, and stamp design variations. Initial results achieved by the joint effort of research groups in the European Integrated Project NaPa[242] and published by Gourgon *et al.*[243] showed that although reliable processing can be achieved with a range of equipment, thermal NIL is governed by a lot of trade-offs. Similar results are expected from the benchmarking in the EU-project Fantastic,[244] which addresses the development and assessment of UV-NIL (SFIL) for high-resolution and high throughput microelectronic applications. The aim must be the full control of the process, which means that the full chain of processes has to be taken into account with all its optimization loops. In the future, the simulation tools must be able to predict the effect of design on pattern fidelity, including tolerances in the nanoregime. All these simulations need further knowledge about the materials used. In thermal NIL the manufacturers do often not give the M_w of common polymers and for detailed analysis, pure materials may be preferred but they are expensive and difficult to manufacture. In UV-NIL, future resist chemistries have to satisfy the criterion of low reactivity toward antiadhesive coatings and stamp materials.

A simple solution to compare mold filling and demolding capabilities would be the use of "fingerprint" stamps used as a standard by a larger community.[245,246] Then easy, low-cost procedures could be developed to derive imprint-relevant characteristic polymer data from simple imprint experiments.

Although drop-on demand techniques for resist dispensing have proven to be a good solution for SFIL, a large community will further prefer spin-coating techniques because they enable the use of a larger variety of materials. The development of innovative processes such as combined thermal and UV-NIL and reverse tone NIL (e.g., in SFIL/R resists with adapted dielectric properties), along with the possibility to imprint at reduced environmental pressure, will make these processes more flexible. Therefore in long term it is likely that for full wafer NIL, e.g., for photonics and patterned magnetic media, spin-coating will be preferred (NIL with or without UV curing), while processes for microchip applications will use liquid resins in S&R approaches.

"You ain't seen nothing yet," as Steve Chou pointed it out at the NNT conference 2005. I am sure we have seen quite a lot, but more has to come. The question is whether engineers and researchers will be able to enhance the understanding of the process issues to an extent that improvements are not only incremental but innovative imprint concepts compatible with production requirements are established in a wide community. Then NIL will not only be able to replace current processes where the CoO has become the major obstacle to improve resolution and throughput but become a standard process in future nanofabrication technology.

ACKNOWLEDGMENTS

The basis for writing this review was the development of thermal NIL over the past ten years in Paul Scherrer Institut (PSI). Already before, L. Baraldi developed a hot microembossing process for integrated optics.[11,49] This had already many of the "ingredients" of NIL, including low residual layer printing under vacuum and the buildup of a setup with real-time observation of polymer flow. Many thanks are due to all those researchers, engineers, technicians, and students, who contributed to the continuous development of the NIL technology in the Laboratory for Micro- and Nanotechnology (LMN) at PSI, particularly to K. Vogelsang, L. Heyderman, R. Jaszewski, and S. Park. Within NaPa,[242] special thanks go to the NaPaNIL committee consisting of C. Sotomayor-Torres, A. Kristensen, and M. Tormen; furthermore to J. Ahopelto, D. Mendels, S. Zaitsev, F. Reuther, I. Garcia Romero, and K. Seunarine, and to all contributors to the NaPa Library of Processes.[247] The author also profited much from exchanges with H.-C. Scheer, Y. Hirai, and F. Houle, and particularly indebted to S. Y. Chou who opened this exciting field and always pushed him toward new scientific challenges. This review was done within the framework of the INKA-Institut (Institute of Nanotechnological Applications in Polymers), co-founded by the University of Applied Sciences Nordwestschweiz and the PSI. The partial funding of the Swiss Federal Office for Science and Education in the framework of the EC-funded project NaPa (Contract No. NMP4-CT 2003-500120 and OFES No. 03.0424-4) is gratefully acknowledged.

[1] S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Appl. Phys. Lett. **67**, 3114 (1995).
[2] S. Y. Chou, P. R. Krauss, and P. J. Renstrom, Science **272**, 85 (1996).
[3] S. Y. Chou, P. R. Krauss, and P. J. Renstrom, J. Vac. Sci. Technol. B **14**, 4129 (1996).
[4] J. Haisma, M. Verheijen, K. van den Heuvel, and J. van den Berg, J. Vac. Sci. Technol. B **14**, 4124 (1996).
[5] G. L. W. Cross, J. Phys. D **39**, R363 (2006).
[6] L. J. Guo, Adv. Mater. (Weinheim, Ger.) **19**, 495 (2007).
[7] E. Mele, A. Camposeo, R. Stabile, P. Del Carro, F. Di Benedetto, L. Persano, R. Cingolani, and D. Pisignano, Appl. Phys. Lett. **89**, 131109 (2006).
[8] V. N. Truskett and M. P. C. Watts, Trends Biotechnol. **24**, 312 (2006).
[9] N. Gadegaard, S. Thoms, D. S. Macintyre, K. Mcghee, J. Gallagher, B. Casey, and C. D. W. Wilkinson, Microelectron. Eng. **67–68**, 162 (2003).
[10] H. Schift and A. Kristensen, in *Handbook of Nanotechnology* 2nd ed., edited by B. Bhushan (Springer, Berlin, 2007), Chap. A/8, pp. 239–278.
[11] L. G. Baraldi, Ph.D. thesis, ETH Zurich, 1994.
[12] L. J. Heyderman, H. Schift, C. David, J. Gobrecht, and T. Schweizer, Microelectron. Eng. **54**, 229 (2000).
[13] H. Schift, L. J. Heyderman, M. Auf der Maur, and J. Gobrecht, Nanotechnology **12**, 173 (2001).
[14] H. Schift and L. J. Heyderman, in *Alternative Lithography: Unleashing the Potential of Nanotechnology*, Book Series on Nanostructure Science and Technology, edited by D. J. Lockwood (Kluwer Academic, New York, 2003), Chap. 4, pp. 46–76.
[15] H.-C. Scheer, H. Schulz, T. Hoffmann, and C. M. Sotomayor Torres, in *Handbook of Thin Film Materials*, edited by H. S. Nalva (Academic, New York, 2002) Vol. 5, pp. 1–60.
[16] H.-C. Scheer and H. Schulz, Microelectron. Eng. **56**, 311 (2001).
[17] C. M. Sotomayor Torres, in *Nanostructure Science and Technology*, edited by D. J. Lockwood (Kluwer Academic, New York, 2003).
[18] H. Schulz, M. Wissen, N. Bogdanski, H.-C. Scheer, K. Mattes, and Ch. Friedrich, Microelectron. Eng. **83**, 259 (2006).
[19] H. D. Rowland, W. P. King, G. L. W. Cross, B. S. O'Connell, and J. B. Pethica, Abstract Book NNT Conference, San Francisco, CA, 17 November 2006 (unpublished).
[20] H. D. Rowland and W. P. King, in *BioNanoFluidic MEMS*, edited by P. J. Hesketh (Springer, Berlin, 2008).
[21] L. J. Guo, J. Phys. D **37**, R123 (2004).
[22] S. Park and H. Schift, in *BioMEMS and Biomedical Nanotechnology*, edited by R. Bashir, S. Wereley, and M. Ferrari (Springer, Berlin, 2006), Vol. 4, pp. 95–117.
[23] Y. Hirai, *Science and New Technology in Nanoimprint*, Frontier Publishing, Japan, 2006.
[24] M. Colburn *et al.*, Proc. SPIE **3676**, 379 (1999).
[25] M. D. Stewart, S. C. Johnson, S. V. Sreenivasan, D. J. Resnick, and C. G. Willson, J. Microlithogr., Microfabr., Microsyst. **4**, 011002 (2005).
[26] D. J. Resnick *et al.*, Proc. SPIE **5037**, 12 (2003).
[27] D. J. Resnick, S. V. Sreenivasan, and C. G. Willson, Mater. Today **8**, 34 (2005).
[28] M. Otto, M. Bender, B. Hadam, B. Spangenberg, and H. Kurz, Microelectron. Eng. **57–58**, 361 (2001).
[29] B. Vratzov, A. Fuchs, M. Lemme, W. Henschel, and H. Kurz, J. Vac. Sci. Technol. B **21**, 2760 (2003).
[30] U. Plachetka, M. Bender, A. Fuchs, B. Vratzov, T. Glinsner, F. Lindner, and H. Kurz, Microelectron. Eng. **73–74**, 167 (2004).
[31] EIPBN2007, Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication, 2007 (unpublished); URL: http://eipbn.org/
[32] MNE2007, Micro- and Nano-Engineering Conference, Europe, 2007 (unpublished); URL: http://www.mne07.org/
[33] MNC2007, International Microprocess and Nanotechnology Conference, Japan, 2007 (unpublished); URL: http://imnc.jp/
[34] NNT2007, Conference on Nanoimprint and Nanoprint Technology, 2007 (unpublished); URL: http://www.nntconf.org/
[35] ITRS International Technology Roadmap for Semiconductors, URL: http://public.itrs.net/
[36] P. R. Krauss and S. Y. Chou, Appl. Phys. Lett. **71**, 3174 (1997).
[37] S. Y. Chou, P. R. Krauss, W. Zhang, L. Guo, and L. Zhuang, J. Vac. Sci. Technol. B **15**, 2897 (1997).
[38] X. Sun, L. Zhuang, W. Zhang, and S. Y. Chou, J. Vac. Sci. Technol. B **16**, 3922 (1998).
[39] W. Zhang and S. Y. Chou, Appl. Phys. Lett. **79**, 845 (2001).
[40] H. Tan, A. Gilbertson, and S. Y. Chou, J. Vac. Sci. Technol. B **16**, 3926 (1998).
[41] S. Y. Chou and L. Zhuang, J. Vac. Sci. Technol. B **17**, 3197 (1999).
[42] M. D. Austin, H. Ge, W. Wu, M. Li, Z. Yu, D. Wasserman, S. A. Lyon, and S. Y. Chou, Appl. Phys. Lett. **84**, 5299 (2004).
[43] S. Y. Chou, C. Keimel, and J. Gu, Nature (London) **417**, 835 (2002).
[44] H. Schift, R. W. Jaszewski, C. David, and J. Gobrecht, Microelectron. Eng. **46**, 121 (1999).
[45] J. C. Ruda, J. Audio Eng. Soc. **25**, 702 (1977).

[46]K. C. Pohlmann, *Computer Music and Digital Audio Series*, 2nd ed. (A-R Editions, Madison, WI, 1992), Vol. 5.
[47]W. Menz, J. Mohr, and O. Paul, *Microsystem Technology* (Wiley-VCH, Berlin, 2001).
[48]M. T. Gale, in *Micro-Optics Elements, Systems and Applications*, edited by H. P. Herzig (Taylor & Francis, London, 1997).
[49]L. Baraldi, R. Kunz, and J. Meissner, Proc. SPIE **1992**, 21 (1993).
[50]H. Schift, in *Science and New Technology in Nanoimprint* (Frontier Publishing, Japan, 2006), Chap. 5, pp. 74–89.
[51]Y. Xia and G. M. Whitesides, Angew. Chem., Int. Ed. **37**, 550 (1998).
[52]B. Michel *et al.*, IBM J. Res. Dev. **45**, 697 (2001).
[53]A. Michel, R. Ruprecht, M. Harmening, and W. Bacher, Technical Report, KfK Bericht No. 5171 (1993).
[54]Y.-J. Juang, L. J. Lee, and K. W. Koelling, Polym. Eng. Sci. **42**, 539 (2002); **42**, 551 (2002).
[55]M. Heckele and W. K. Schomburg, J. Micromech. Microeng. **14**, R1 (2004).
[56]A. Both, W. Bacher, M. Heckele, and R. Ruprecht, Technical Report, KfK Bericht No. 5671 (1995).
[57]T. Ohta, M. Hennesey, D. Strand, D. Jablonsky, B. Walton, and B. Clark, IEEE Trans. Magn. **43**, 836 (2007).
[58]G. K. Binnig, G. Cherubini, M. Despont, U. T. Duerig, E. Eleftheriou, H. Pozidis, and P. Vettiger, in *Handbook of Nanotechnology*, 2nd ed. (Springer, Berlin, Chap. E/31, pp. 239–278.
[59]M. Tormen, R. Malureanu, A. Kristensen, and O. Hansen, *Abstract Book, MNE Conference*, Copenhagen, Denmark, 23–26 September 2007 [Microelectron. Eng. (to be published)].
[60]H. Yoon, K. M. Lee, D.-Y. Khang, H. H. Lee, and S.-J. Choi, Appl. Phys. Lett. **85**, 1793 (2004).
[61]T. Borzenko, M. Tormen, G. Schmidt, and L. W. Molenkamp, Appl. Phys. Lett. **79**, 2246 (2001).
[62]X. D. Huang, L.-R. Bao, X. Cheng, L. J. Guo, S. W. Pang, and A. F. Yee, J. Vac. Sci. Technol. B **20**, 2872 (2002).
[63]N. Kehagias *et al.*, Nanotechnology **18**, 175303 (2007).
[64]T. Yoshikawa, T. Konishi, M. Nakajima, H. Kikuta, H. Kawata, and Y. Hirai, J. Vac. Sci. Technol. B **23**, 2939 (2005).
[65]K. Sogo, M. Nakajima, H. Kawata, and Y. Hirai, Microelectron. Eng. **84**, 909 (2007).
[66]M. Li, L. Chen, W. Zhang, and S. Y. Chou, Nanotechnology **14**, 33 (2003).
[67]C. J. Martin, R. L. Engelstad, E. G. Lovell, D. J. Resnick, and E. J. Weisbrod, J. Vac. Sci. Technol. B **20**, 2891 (2002).
[68]M. Worgull, M. Heckele, J. F. Hétu, and K. K. Kabanemi, J. Microlithogr., Microfabr., Microsyst. **5**, 011005 (2006).
[69]F. Hua *et al.*, Nano Lett. **4**, 2467 (2004).
[70]V. Sirotkin, A. Svintsov, S. Zaitsev, and H. Schift, Microelectron. Eng. **83**, 880 (2006).
[71]C. Gourgon, C. Perret, J. Tallal, F. Lazzarino, S. Landis, O. Joubert, and R. Pelzer, J. Phys. D **38**, 70 (2005).
[72]J. A. Forrest and K. Dalnoki-Veress, Adv. Colloid Interface Sci. **94**, 167 (2001).
[73]H. D. Rowland, A. C. Sun, P. R. Schunk, and W. P. King, J. Micromech. Microeng. **15**, 2414 (2005).
[74]D. Mendels, Proc. SPIE **6151**, 615113 (2006).
[75]J.-H. Jeong, Y.-S. Choi, Y.-J. Shin, J.-J. Lee, K.-T. Park, E.-S. Lee, and S.-R. Lee, Fibers Polym. **3**, 113 (2002).
[76]H. Schift, S. Bellini, M. B. Mikkelsen, and J. Gobrecht, *Abstract Book, MNE Conference*, Copenhagen, Denmark, 23–26 September 2007 [J. Vac. Sci. Technol. B **25**, 2312 (2007)].
[77]V. Sirotkin, A. Svintsov, H. Schift, and S. Zaitsev, Microelectron. Eng. **84**, 868 (2007).
[78]H. Schift, S. Bellini, J. Gobrecht, F. Reuther, M. Kubenz, M. B. Mikkelsen, and K. Vogelsang, Microelectron. Eng. **84**, 932 (2007).
[79]E. A. J. F. Peters, Ph.D. thesis, Delft University, 2000.
[80]Y. Hirai, S. Yoshida, and N. Takagi, J. Vac. Sci. Technol. B **21**, 2765 (2003).
[81]D. A. Mendels, Abstract Book, NNT Conference, San Francisco, CA, 15–17 November 2006 (unpublished).
[82]H. Schift, S. Park, C.-G. Choi, C.-S. Kee, S.-P. Han, K.-B. Yoon, and J. Gobrecht, Nanotechnology **16**, S261 (2005).
[83]I. Fernandez-Cuesta, X. Borrisé, A. Retolaza, S. Merino, D.-A. Mendels, O. Hansen, A. Kristensen, and F. Pérez-Murano, Microelectron. Eng. (to be published).
[84]S. Merino, H. Schift, A. Retolaza, and T. Haatainen, Microelectron. Eng. **84**, 958 (2007).
[85]T. A. Brunner, J. Vac. Sci. Technol. B **21**, 2632 (2003).
[86]S. Landis, N. Chaix, C. Gourgon, C. Perret, and T. Leveder, Nanotechnology **17**, 2701 (2006).
[87]S. V. Sreenivasan, X. Lu, A. Cherala, P. Schumaker, J. Choi, and I. McMackin, Abstract Book, EIPBN Conference Denver, CO, 29 May–1 June 2007 (unpublished).
[88]N. Bogdanski, M. Wissen, S. Möllenbeck, and H.-C. Scheer, J. Vac. Sci. Technol. B **24**, 2998 (2006).
[89]N. Bogdanski, M. Wissen, A. Ziegler, and H.-C. Scheer, Microelectron. Eng. **78–79**, 598 (2005).
[90]V. Studer, A. Pépin, and Y. Chen, Appl. Phys. Lett. **80**, 3614 (2002).
[91]T. Mäkelä, T. Haatainen, P. Majander, and J. Ahopelto, *Nanotechnology in Northern Europe (NTNE)*, Helsinki, 26–28 April 2005 (Spinverse Consulting Oy, 2005), p. 64.
[92]M. J. Stefan, Akad. Wiss. Math.-Natur., Vienna, **2**, 713 (1874).
[93]C. B. Roth and J. R. Dutcher, in *Soft Materials: Structure and Dynamics*, edited by J. R. Dutcher and A. G. Maragnoni (Dekker, New York, 2004).
[94]J. N. D'Amour, U. Okoroanyanwu, and C. W. Frank, Microelectron. Eng. **73–74**, 209 (2004).
[95]A. Franck, *Kunststoff-Kompendium* (Vogel Buchverlag, Würzburg, 1996), Auflage 4, p. 255.
[96]Nanonex NIL solution; URL: http://www.nanonex.com/
[97]Micro Resist Technology GmbH, Germany; URL: http://www.microresist.de/
[98]Sumitomo Chemical Co., Ltd., Japan; URL: http://www.sumitomo-chem.co.jp/
[99]A. A. Svintsov, O. V. Trofimov, and S. I. Zaitsev, J. Vac. Sci. Technol. B **25**, 2435 (2007).
[100]H. D. Rowland, G. L. W. Cross, B. S. O'Connell, J. B. Pethica, and W. P. King, ACS Nano (to be published).
[101]I. Garcia Romero and F. Reuther, Micro Resist Technology GmbH, Berlin, Germany, unpublished results (2007).
[102]T. Konishi, H. Kikuta, H. Kawata, and Y. Hirai, Microelectron. Eng. **83**, 869 (2006).
[103]H.-C. Scheer, N. Bogdanski, M. Wissen, T. Konishi, and Y. Hirai, J. Vac. Sci. Technol. B **23**, 2963 (2005).
[104]Y. Hirai, T. Yoshikawa, N. Takagi, and S. Yoshida, J. Photopolym. Sci. Technol. **16**, 615 (2003).
[105]H. W. Ro *et al.*, J. Vac. Sci. Technol. B **24**, 2973 (2006).
[106]Y. Ding, H. W. Ro, J. F. Douglas, R. L. Jones, D. R. Hine, A. Karim, and C. L. Soles, Adv. Mater. (Weinheim, Ger.) **19**, 1377 (2007).
[107]H. W. Ro, H.-J. Lee, E. K. Lin, A. Karim, D. R. Hines, D. Y. Yoon, and C. L. Soles, Proc. SPIE **6517**, 651715 (2007).
[108]B. Heidari, I. Maximov, E.-L. Sarwe, and L. Montelius, J. Vac. Sci. Technol. B **17**, 2961 (1999).
[109]N. Roos, M. Wissen, T. Glinsner, and H.-C. Scheer, Proc. SPIE **5037**, 211 (2003).
[110]A. Fuchs, M. Bender, U. Plachetka, U. Hermanns, and H. Kurz, J. Vac. Sci. Technol. B **23**, 2925 (2005).
[111]M. Vogler, M. Bender, U. Plachetka, A. Fuchs, S. Wiedenberg, F. Reuther, G. Grützner, and H. Kurz, Proc. SPIE **6517**, 651727 (2007).
[112]M. Vogler, S. Wiedenberg, M. Mühlberger, I. Bergmair, T. Glinsner, H. Schmidt, E.-B. Kley, and G. Grützner, Microelectron. Eng. **84**, 984 (2007).
[113]P. Voisin, M. Zelsmann, R. Cluzel, E. Pargon, C. Gourgon, and J. Boussey, Microelectron. Eng. **84**, 967 (2007).
[114]H. Schmitt, L. Frey, H. Ryssel, M. Rommel, and C. Lehrer, J. Vac. Sci. Technol. B **25**, 785 (2007).
[115]W.-C. Liao and S. L.-C. Hsu, Nanotechnology **18**, 065303 (2007).
[116]J. Hao *et al.*, Proc. SPIE **6517**, 6517 (2007).
[117]S. Johnson *et al.*, J. Vac. Sci. Technol. B **23**, 2553 (2005).
[118]F. Xu *et al.*, Proc. SPIE **5374**, 232 (2004).
[119]B. K. Long, B. K. Keitz, and C. G. Willson, J. Mater. Chem. **17**, 3575 (2007).
[120]M. Colburn, B. J. Choi, S. V. Sreenivasan, R. T. Bonnecaze, and C. G. Willson, Microelectron. Eng. **75**, 321 (2004).
[121]X. Liang, H. Tan, Z. Fu, and S. Y. Chou, Nanotechnology **18**, 025303 (2007).
[122]K.-D. Kim, J.-H. Jeong, Y.-S. Sim, and E.-S. Lee, Microelectron. Eng. **83**, 847 (2006).
[123]A. Y. Abdo, L. Zheng, A. Wei, A. Mikkelson, G. Nellis, R. L. Engelstad,

and E. G. Lovell, Microelectron. Eng. **73–74**, 161 (2004).
[124]D. Lentz, G. Doyle, M. Miller, G. Schmidt, M. Ganapathisuramanian, X. Lu, D. Resnick, and D. D. L. LaBrake, Proc. SPIE **6517**, 65172F (2007).
[125]S. Reddy and R. T. Bonnecaze, Microelectron. Eng. **82**, 60 (2005).
[126]H. Hiroshima, M. Komuro, N. Kasahara, Y. Kurashima, and J. Taniguchi, Jpn. J. Appl. Phys., Part 1 **42**, 3849 (2003).
[127]H. Hiroshima and M. Komuro, *Abstract Book, EIPBN Conference*, Denver, CO, 29 May–1 June 2007 [J. Vac. Sci. Technol. B **25**, 2333 (2007)].
[128]G. M. Schmid *et al.*, J. Vac. Sci. Technol. B **24**, 1283 (2006).
[129]W. L. Jen *et al.*, Proc. SPIE **6517**, 6517 (2007).
[130]M. W. Lin *et al.*, Proc. SPIE **6151**, 688 (2006).
[131]F. Reuther, K. Pfeiffer, M. Fink, G. Gruetzner, H. Schulz, H.-C. Scheer, F. Gaboriau, and C. Cardinaud, Proc. SPIE **4343**, 802 (2001).
[132]K. Pfeiffer, M. Fink, G. Gruetzner, G. Bleidiessel, H. Schulz, and H.-C. Scheer, Microelectron. Eng. **57–58**, 381 (2001).
[133]K. Pfeiffer *et al.*, Microelectron. Eng. **67–68**, 266 (2003).
[134]X. Cheng and L. J. Guo, Microelectron. Eng. **71**, 277 (2004).
[135]X. Cheng and L. J. Guo, Microelectron. Eng. **71**, 288 (2004).
[136]M. B. Christiansen, M. Schøler, and A. Kristensen, Proc. SPIE **6462**, 64620 (2007).
[137]M. B. Christiansen, M. Schøler, and A. Kristensen, Opt. Express **15**, 3931 (2007).
[138]EV Group (EVG); URL: http://www.evgroup.com/
[139]SUSS MicroTec; URL: http://www.suss.com/applications/nil/
[140]Jenoptik Laser, Optik, Systeme GmbH; URL: http://www.jenoptik.com/, http://www.jo-mt.de/
[141]Obducat AB; URL: http://www.obducat.com/
[142]S.-W. Youn, H. Goto, M. Takahashi, S. Oyama, Y. Oshinomi, K. Matsutani, and R. Maeda, J. Micromech. Microeng. **17**, 1402 (2007).
[143]J.-H. Chang, F.-S. Cheng, C.-C. Chao, Y.-C. Weng, S.-Y. Yang, and L. A. Wang, J. Vac. Sci. Technol. A **23**, 1687 (2005).
[144]H. Lee and G. Y. Jung, Microelectron. Eng. **77**, 168 (2005).
[145]AMO Gesellschaft für Angewandte Mikro- und Optoelektronik MbH, Germany; URL: http http://www.amo.de/
[146]J. J. Lee, K. B. Choi, G. H. Kim, and S. W. Lee, Microelectron. Eng. **84**, 963 (2007).
[147]K.-D. Kim, J.-H. Jeong, D.-G. Choi, J. Choi, E.-S. Lee, H.-J. Kwon, H.-D. Rhee, and J.-Y. Choi, Abstract Book, EIPBN Conference, Denver, CO, 29 May–1 June 2007 (unpublished).
[148]H. Lee, J. Vac. Sci. Technol. B **23**, 1102 (2005).
[149]Molecular Imprints Inc.; URL: http://www.molecularimprints.com/
[150]M. Otto, M. Bender, F. Richter, B. Hadam, T. Kliem, R. Jede, B. Spangenberg, and H. Kurz, Microelectron. Eng. **73–74**, 152 (2004).
[151]T. Haatainen, J. Ahopelto, G. Grützner, M. Fink, and K. Pfeiffer, Proc. SPIE **3997**, 874 (2000).
[152]H. Hiroshima, M. Komuro, Y. Kurashima, S. H. Kim, and T. Muneishi, Jpn. J. Appl. Phys., Part 1 **43**, 4012 (2004).
[153]T. Nielsen, R. H. Pedersen, O. Hansen, T. Haatainen, A. Tollki, J. Ahopelto, and A. Kristensen, Proc. SPIE **5707**, 508 (2005).
[154]C.-H. Lin and R. Chen, J. Microlithogr., Microfabr., Microsyst. **5**, 011003 (2006).
[155]M. Bender, U. Plachetka, J. Ran, A. Fuchs, B. Vratzov, H. Kurz, T. Glinsner, and F. Lindner, J. Vac. Sci. Technol. B **22**, 3229 (2004).
[156]N. Koo, M. Bender, U. Plachetka, A. Fuchs, T. Wahlbrink, J. Bolten, and H. Kurz, Microelectron. Eng. **84**, 904 (2007).
[157]D. R. Barbero, M. S. M. Saifullah, P. Hoffmann, H. J. Mathieu, D. Anderson, G. A. C. Jones, M. E. Welland, and U. Steiner, Adv. Funct. Mater. **17**, 2419 (2007).
[158]G. M. Schmid, E. Thompson, N. Stacey, D. J. Resnick, D. L. Olynick, and E. H. Anderson, Microelectron. Eng. **84**, 853 (2007).
[159]M. Melliar-Smith, Proc. SPIE 6517 (2007).
[160]M. Otto, M. Bender, J. Zhang, A. Fuchs, T. Wahlbrink, J. Bolten, B. Spangenberg, and H. Kurz, Microelectron. Eng. **84**, 980 (2007).
[161]N. Li, W. Wu, and S. Y. Chou, Nano Lett. **6**, 2626 (2006).
[162]A. Fuchs, B. Vratzov, T. Wahlbrink, Y. Georgiev, and H. Kurz, J. Vac. Sci. Technol. B **22**, 3242 (2004).
[163]H. Schulz, D. Lyebyedyev, H.-C. Scheer, K. Pfeiffer, G. Bleidiessel, G. Grützner, and J. Ahopelto, J. Vac. Sci. Technol. B **18**, 3582 (2000).
[164]K. Pfeiffer *et al.*, Microelectron. Eng. **61–62**, 393 (2002).
[165]N. Roos, H. Schulz, L. Bendfeldt, M. Fink, K. Pfeiffer, and H.-C. Scheer, Microelectron. Eng. **61–62**, 399 (2002).
[166]M. Miller, G. Schmid, G. Doyle, E. Thompson, and D. J. Resnick, Microelectron. Eng. **84**, 885 (2007).
[167]H. Schift, S. Park, and J. Gobrecht, J. Photopolym. Sci. Technol. **16**, 435 (2003).
[168]W. J. Dauksher, N. V. Le, K. A. Gehoski, E. S. Ainley, K. J. Nordquist, and N. Joshi, Proc. SPIE **6517**, 651714 (2007).
[169]Ch. Finder, C. Mayer, H. Schulz, H.-C. Scheer, M. Fink, and K. Pfeiffer, Proc. SPIE **4764**, 218 (2002).
[170]M. Beck and B. Heidari, OnBoard Technology, 2006, pp. 52–55; URL: http://www.Onboard-Technology.com/
[171]New Medium Enterprises, Inc. (NME); URL: http://www.nmeinc.com/
[172]T. O'Kelly, White Paper of Memorix Company on 2P Process for DVD-9 Manufacturing; URL: http://www.memorex.com/
[173]A. H.-L. Martin, M. A. Jones, J. L. Hahnfeld, and G. D. Parsons, U.S. Patent No. 5,468,324 (30 November 2000); http://www.freepatentsonline.com/20010048991.html
[174]Zeonor® Cyclo Olefin Polymer (COP) by Zeon Chemicals L.P.; URL: http://www.zeonchemicals.com/
[175]Topas® Cyclo Olefin Co-Polymer (COC) by TOPAS Advanced Polymers; URL: http://www.topas.com/
[176]T. Nielsen, D. Nilsson, F. Bundgaard, P. Shi, P. Szabo, O. Geschke, and A. Kristensen, J. Vac. Sci. Technol. B **22**, 1770 (2004).
[177]B. Bilenberg *et al.*, J. Vac. Sci. Technol. B **23**, 2944 (2005).
[178]MicroChem Corp.; URL: http://http://www.microchem.com/
[179]M. Wissen, N. Bogdanski, H.-C. Scheer, A. Bitz, G. Ahrens, and G. Grützner, Microelectron. Eng. **78–79**, 659 (2005).
[180]Y. Hirai, S. Yoshida, N. Takagi, Y. Tanaka, H. Yabe, K. Sasaki, H. Sumitani, and K. Yamamoto, Jpn. J. Appl. Phys., Part 1 **42**, 3863 (2003).
[181]A. O. Altun, J. H. Jeong, J. J. Rha, D. G. Choi, K. D. Kim, and E. S. Lee, Nanotechnology **17**, 4659 (2006).
[182]S. Ramachandran *et al.*, J. Vac. Sci. Technol. B **24**, 2293 (2006).
[183]K.-I. Nakamatsu, N. Yamada, K. Kanda, Y. Haruyama, and S. Matsui, Jpn. J. Appl. Phys., Part 2 **45**, L954 (2006).
[184]N. Yamada, K.-I. Nakamatsu, K. Kanda, Y. Haruyama, and S. Matsui, Jpn. J. Appl. Phys., Part 1 **46**, 637 (2007).
[185]R. W. Jaszewski, H. Schift, B. Schnyder, A. Schneuwly, and P. Gröning, Appl. Surf. Sci. **143**, 301 (1999).
[186]C. U. Srinivasan, M. R. Houston, R. T. Howe, and R. Maboudian, J. Microelectromech. Syst. **7**, 252 (1998).
[187]M. Beck, M. Graczyk, I. Maximov, E.-L. Sarwe, T. G. I. Ling, M. Keil, and L. Montelius, Microelectron. Eng. **61–62**, 441 (2002).
[188]D. J. Resnick, D. P. Mancini, S. V. Sreenivasan, and C. G. Willson, Semicond. Int. (June 2002), p. 71.
[189]H. Schift, S. Saxer, S. Park, C. Padeste, U. Pieles, and J. Gobrecht, Nanotechnology **16**, S171 (2005).
[190]P. Choi, P.-F. Fu, and L. J. Guo, Adv. Funct. Mater. **17**, 65 (2007).
[191]Y. Kawaguchi, F. Nonaka, and Y. Sanada, Microelectron. Eng. **84**, 973 (2007).
[192]M. Bender, M. Otto, B. Hadam, B. Spangenberg, and H. Kurz, Microelectron. Eng. **61–62**, 407 (2002).
[193]K. Wu, X. Wang, E. K. Kim, C. G. Willson, and J. G. Ekerdt, Langmuir **23**, 1166 (2007).
[194]O. Arroyo, L. Bilbao, R. Muñoz, and I. Obieta, poster presented at NaPa Plenary Meeting, Berlin (2005) (unpublished); URL: http://www.phantomsnet.net/Docs/Inasmet_poster.pdf
[195]C. D. Schaper and A. Miahnahri, J. Vac. Sci. Technol. B **22**, 3323 (2002).
[196]Optool, Daikin, Inc.; URL: http://www.daikin.com/chm/
[197]Nanonex NIL Solution; URL: http://www.nanonex.com/
[198]Molecular Vapor Deposition (MVD), Applied MicroStructures Inc., San Jose, CA; URL: http://www.appliedmst.com/
[199]N. Yamada, K. Nakamatsu, K. Kanada, Y. Haruyama, and S. Matsui, Abstract Book NNT Conference, Paris, France, 11–12 October 2007 (unpublished).
[200]H. Hiroshima, M. Ogiwara, and A. Ueno, Abstract Book, NNT Conference, Paris, France, 11–12 October 2007 (unpublished).
[201]F. A. Houle, C. T. Rettner, D. C. Miller, and R. Sooriyakumaran, Appl. Phys. Lett. **90**, 213103 (2007).
[202]F. A. Houle, E. Guyer, D. C. Miller, and R. Dauskardt, J. Vac. Sci. Technol. B **25**, 1179 (2007).
[203]J. Tallal, M. Gordon, K. Berton, A. L. Charley, and D. Peyrade, Microelectron. Eng. **83**, 851 (2006).
[204]Z. Burton and B. Bhushan, Nano Lett. **5**, 1607 (2005).
[205]B. Bhushan, J. Vac. Sci. Technol. B **21**, 2262 (2003).
[206]V. Trabadelo, H. Schift, S. Merino, S. Bellini, and J. Gobrecht, *MNE*

Conference, Copenhagen, Denmark, 23–26 September 2007 [Microelectron. Eng. (to be published)].
[207]Y. Guo, G. Liu, X. Zhu, and Y. Tian, Microsyst. Technol. **13**, 411 (2007).
[208]T. Leveder, S. Landis, L. Davoust, and N. Chaix, Microelectron. Eng. **84**, 953 (2007).
[209]M. Worgull, M. Heckele, and W. K. Schomburg, Technical Report, FZKA Bericht No. 6922 (2003).
[210]K. Kuwabara, M. Ogino, S. Motowaki, and A. Miyauchi, Microelectron. Eng. **73–74**, 752 (2004).
[211]S. Nomura, H. Kojima, Y. Ohyabu, K. Kuwabara, A. Miyauchi, and T. Uemura, J. Artificial Organs **9**, 90 (2006).
[212]S. Möllenbeck, N. Bogdanski, M. Wissen, H.-C. Scheer, J. Zajadacz, and K. Zimmer, J. Vac. Sci. Technol. B **25**, 247 (2007).
[213]H. Schift, L. J. Heyderman, M. Auf der Maur, and J. Gobrecht, Nanotechnology **12**, 173 (2001).
[214]N. Chaix, S. Landis, D. Hermelin, T. Leveder, C. Perret, V. Delaye, and C. Gourgon, J. Vac. Sci. Technol. B **24**, 3011 (2006).
[215]N. Chaix, C. Gourgon, S. Landis, C. Perret, M. Fink, F. Reuther, and D. Mecerreyes, Nanotechnology **17**, 4082 (2006).
[216]L. Wu and S. Y. Chou, J. Non-Newtonian Fluid Mech. **125**, 91 (2005).
[217]K. Y. Suh and H. H. Lee, Phys. Rev. Lett. **87**, 135502 (2001).
[218]Z. Yu, H. Gao, and S. Y. Chou, Appl. Phys. Lett. **85**, 4166 (2004).
[219]D. Jucius, V. Grigaliunas, and A. Guobiene, Microelectron. Eng. **71**, 190 (2004).
[220]T. Lévéder, S. Landis, L. Davoust, S. Soulan, J.-H. Tortai, and N. Chaix, J. Vac. Sci. Technol. B **25**, 2365 (2007).
[221]H. Lee, and G.-Y. Jung, Microelectron. Eng. **77**, 42 (2005).
[222]K.-Y. Yang, J.-W. Kim, K.-J. Byeon, and H. Lee, Microelectron. Eng. **84**, 1552 (2007).
[223]D.-Y. Khang, H. Yoon, and H. H. Lee, Adv. Mater. (Weinheim, Ger.) **13**, 749 (2001).
[224]F. Zhang, and H. Y. Low, Nanotechnology **17**, 1884 (2006).
[225]Y. Lu, W. Hu, Y. Ma, L. Zhang, J. Sun, N. Lu, and J. Shen, Macromol. Rapid Commun. **27**, 505 (2006).
[226]J. L. Charest, M. T. Eliason, A. J. García, and W. P. King, J. Vac. Sci. Technol. B **23**, 3011 (2005).
[227]J. H. Song, H. Huh, S. H. Kim, and H. T. Hahn, Mater. Sci. Forum **505–507**, 85 (2006).
[228]X. Cheng, L. J. Guo, and P.-F. Fu, Adv. Mater. (Weinheim, Ger.) **17**, 1419 (2004).
[229]J. Tao, Y. Chen, X. Zhao, A. Malik, and Z. Cui, Microelectron. Eng. **78–79**, 665 (2005).
[230]D. Pisignano, L. Persano, M. F. Raganato, P. Visconti, R. Cingolani, G. Barbarella, L. Favaretto, and G. Gigli, Adv. Mater. (Weinheim, Ger.) **16**, 525 (2004).
[231]S. Buzzi, F. Robin, V. Callegari, and J. F. Löffler, Microelectron. Eng. **85**, 419 (2007).
[232]L. A. Utracki and R. Simha, J. Polym. Sci., Part B: Polym. Phys. **39**, 342 (2000).
[233]S. Y. Yang, F. S. Cheng, T. C. Huang, J. K. Chiu, and J. G. Loeser, Abstract Book, EIPBN Conference, Denver, CO, 29 May–1 June 2007 (unpublished).
[234]D. Y. Khang and H. H. Lee, Appl. Phys. Lett. **76**, 870 (2000).
[235]N. E. Voicu, S. Ludwigs, E. J. W. Crossland, P. Andrew, and U. Steiner, Nano Lett. **5**, 1915 (2005).
[236]H.-J. Lee, H. W. Ro, C. L. Soles, R. L. Jones, E. K. Lin, W.-L. Wu, and D. R. Hines, J. Vac. Sci. Technol. B **23**, 3023 (2005).
[237]F. Lazzarino, C. Gourgon, P. Schiavone, and C. Perret, J. Vac. Sci. Technol. B **22**, 3318 (2004).
[238]MIT Technology Review, 2003, pp. 33–44; URL: http://www.technologyreview.com/
[239]J. G. Maltabes, T. L. Perkinson, L. C. Litt, R. Hershey, and S. Murphy, Microelectron. Eng. **41–42**, 97 (1998).
[240]S. Murthy, M. Falcon, S. Sreenivasan, and D. Dance, Proc. SPIE **5751**, 1 (2005).
[241]W. Trybula, Microelectron. Eng. **83**, 614 (2006).
[242]Integrated Project in the framework of the Sixth European Research Program (NMP4-CT 2003-500120); URL: http://www.NAPAIP.org
[243]C. Gourgon *et al.*, J. Vac. Sci. Technol. B **25**, 2373 (2007).
[244]Project in the framework of the MEDEA+ Program (No. 2T305); URL: http://www.fantastic-project.org
[245]T. Leveder, S. Landis, L. Davoust, and N. Chaix, Microelectron. Eng. **84**, 928 (2007).
[246]H.-C. Scheer, N. Bogdanski, S. Möllenbeck, M. Wissen, K. Zimmer, and J. Zajadacz, Microelectron. Eng. **84**, 949 (2007).
[247]*NaPa Library of Processes*, 1st edition, edited by H. Schift (NaPa Consortium, 2008).