DOI: 10.1002/adma.200601599

Solvent-Vapor-Assisted Imprint Lithography**

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Nanoimprint lithography (NIL) or hot embossing is one of the most promising techniques for low-cost, high-throughput patterning of polymeric materials. Since its discovery by Chou et al.,[1–3] it has developed into a highly active field in nanoscience and nanotechnology.[4] Both sub-10 nm pattern replication[5] and pattern-transfer fidelity on large areas[6] have been demonstrated, suggesting potential applications in the fields of nanoelectronics,[7,8] optics,[9] and high-density storage media.[10] Particularly interesting is the use of NIL for polymer light-emitting diodes.[11] One advantage of NIL compared to conventional optical lithography is that its resolution is not limited by factors such as wave diffraction, scattering, and interference in the resist, or backscattering from the substrate.

The imprinting process consists of mechanically embossing a master mold, typically made of silicon or silicon oxide, into a resist material that is, in most cases, a thermoplastic elastomer. The process is typically carried out at high temperatures (50–100 °C above the glass-transition temperature (T_g) of the polymer) and high pressures (ca. 40 bar; 1 bar = 100 000 Pa). The mold is released after lowering the temperature below T_g, revealing the replicated mold pattern in the polymer film.

Although NIL is a successful and widely used lithographic method, there are a number of problems inherently associated with NIL that have to be carefully avoided: 1) The high pressures that have to be applied during the imprinting process can cause the molds to break. 2) The molds are usually modified with antiadhesive layers, such as self-assembled monolayers, in order to facilitate mold release: the NIL thermal cycle degrades this protection layer so that the multiple use of masters is often limited. 3) The large difference in thermal expansion coefficients of the rigid mold and the polymer resist can lead to the distortion of imprinted mold features. 4) For thermosensitive polymers, resist degradation is a problem and the imprinting process has to be performed in vacuum.[12] 5) NIL often requires an additional processing step: a thin residual resist layer is left in the compressed area which has to be removed by reactive ion etching (RIE).

Addressing these issues, several groups have in recent years further developed the NIL technique. Low-pressure imprint lithography was for example reported by Khang et al.[13] Instead of rigid masters, they used flexible molds made from a fluoropolymer material that were pressed into polymer resists at 2–3 bar. Mold fracture was however a problem because the fluoropolymer masks were very thin. Using a similar principle Barbero et al.[14] used thick fluoropolymer molds, which were resistant to high temperatures and high pressures, demonstrating reliable large-area replication of mold features down to 12 nm.

So-called room-temperature imprint lithography (RTIL) was proposed by Khang et al.[15] who used the fact that polymers can be deformed and pressed into shape under compressive stress. Pisignano et al. showed that this principle also works for nonthermoplastic organic films,[16] which are difficult to structure by using conventional NIL. Sub-100 nm organic light-emitting diode (OLEDs) were fabricated using RTIL.[17]

A temperature-annealing protocol is generally needed to induce mobility in the polymer to provide sufficient flow. However, the narrow window between the glass-transition and the thermal-degradation temperature of most polymers limits the viscosity range at which NIL can operate. Many semiconducting polymers, for example, chemically decompose at high temperatures. The high viscosities of high-molecular-weight polymers in the accessible temperature window are the reason why high NIL pressures are typically required. Polymers with very high molecular weights can therefore not be patterned by using NIL.

An alternative to temperature annealing is swelling the polymer by exposing it to a solvent vapor. Solvent vapor very effectively lowers the glass-transition temperature and thereby the viscosity of the polymer. For example, a toluene uptake of 12 % by weight lowers the glass transition of polystyrene (PS) to room temperature[18] and thereby lowers its viscosity by many orders of magnitude.[19] NIL using this approach was

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[**] We acknowledge financial support from the Dutch "Stichting voor Fundamenteel Onderzoek der Materie" (FOM) for N.E.V, and the European Network "Polyfilm" under RTN-6 for S.L. and U.S.

demonstrated by Khang et al.[20] who used trichloroethylene (TCE) vapor to lower both the viscosity and the glass-transition temperature of polymer films. The films were prepared by spin-coating followed by exposure to TCE vapor (58 mm Hg at 20 °C) at an elevated temperature to facilitate the solvent absorption by the polymer film. The swollen films were then removed from the solvent atmosphere and loaded into a conventional hydraulic press for the NIL process. No further heating was required and imprinting could be performed at room temperature. Although this is an improvement over conventional NIL, this procedure is not well controlled and cannot be extended to highly volatile solvents, many of which are good solvents for polymers. In addition, the solvent partially evaporates from the film in an uncontrolled way during the transfer to the hydraulic press, giving rise to partial drying and concentration gradients in the film, which may have a negative impact on NIL.

Here we demonstrate NIL in a controlled solvent-vapor atmosphere, which extends NIL to low-pressure, room-temperature replication of structured molds into polymer films in a reliable fashion. Similar to conventional NIL, a structured silicon mold was pressed into a thin resist layer on a rigid substrate. Prior to and during the imprinting process the resist was swollen in a controlled solvent-vapor atmosphere to enhance the mobility of the polymer.

The experimental approach is summarized in Figure 1. Polymer films were swollen in a N_2 stream of a well-defined partial vapor pressure p/p_{sat} of a solvent (Fig. 1b). The mold was brought into contact with the film and imprinting took place in the absence of an externally applied pressure (Fig. 1c). The sample was then quenched in dry N_2 and the mold was released (Fig. 1d).

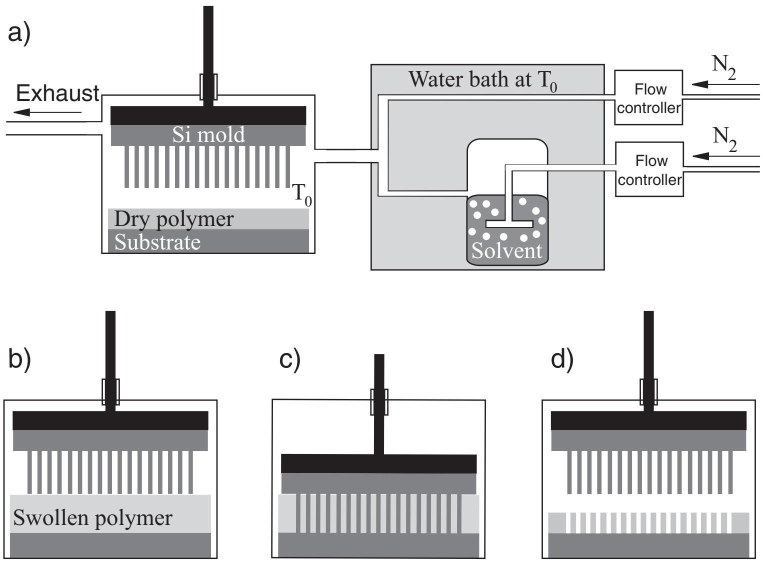

Figure 1. a) Schematic diagram of the experimental setup. The sample chamber contained the polymer film supported on a substrate and a silicon mold mounted on a copper block that could be brought into contact with the polymer film. The chamber could be filled with solvent vapor with a well-defined partial pressure. The partial vapor pressure in the gas stream was achieved by mixing two controlled flows of N_2, one of which was passed through a solvent bath. b) Initial phase of the experiment, in which the polymer film was swollen close to its equilibrium film thickness for a given vapor pressure. c) Subsequently the mold was pressed into the swollen film. d) Removal of the mold after quenching the polymer film by a flow of dry N_2. The dry polymer film had the replicated pattern of the mold.

The structures imprinted into PS films consisted of arrays of lines and holes. Figure 2a shows an atomic force microscopy (AFM) height image of 1 μm wide and 430 nm high lines imprinted into PS70 (70 kg mol^{-1} PS). Both the line width and the 2 μm periodicity of the replica match the groove dimensions of the mold. The protocol was as follows: a 215 nm thick PS film was exposed to chloroform vapor with $p/p_{\mathrm{sat}} = 0.7$ until an equilibrium film thickness of ca. 1.5 times the initial film thickness[21,22] was reached after 20 min. The mold was lowered onto the sample for 5 min, followed by quenching the film in dry N_2 for 35 min.

The complete nature of the replication process is shown in the AFM phase-contrast image in Figure 2b, which comes from the same sample that is shown in Figure 2a. In the lower left part of the figure, the replicated polymer was scratched off, revealing the substrate. The pattern that is visible there consists of bare substrate areas and residual polymer. Note that this pattern is not visible in the corresponding topography image, clearly demonstrating the high material contrast of the phase signal of the AFM tapping mode. This pattern provides a reference for the upper part of the image. Although the embossed lines have the same gray value as the residual polymer of the bottom part of the image, there is no contrast between the bare substrate and the grooves separating the lines. This is a clear indication that no residual polymer was left in the spaces that delimit the imprinted polymer structure. This is in contrast to conventional NIL, which usually leaves a residual layer in the compressed areas, which has to be removed by a subsequent step such as reactive ion etching. Our method does not need any additional processing steps.

The method presented here has therefore several advantages over standard NIL: the swelling of the polymer film in a solvent vapor makes the films much more mobile compared to thermal annealing, leading to a much-increased in-plane flow of the material. This results in the complete removal of the resist from the compressed areas, which is presumably aided by the dewetting process: because of the low surface energy of the master, the polymer solution does not wet the slit pore consisting of the mold and the substrate. In addition, the much-increased film compliance results in a lowered requirement for imprinting pressures, thereby significantly reducing the risk of mask damage.

A further feature of solvent-assisted NIL is shown in Figure 2c and d. These patterns were imprinted in PS532 (532 kg mol^{-1} PS). With conventional NIL, such high-molecular-weight polymers are very difficult to imprint, because their viscosity

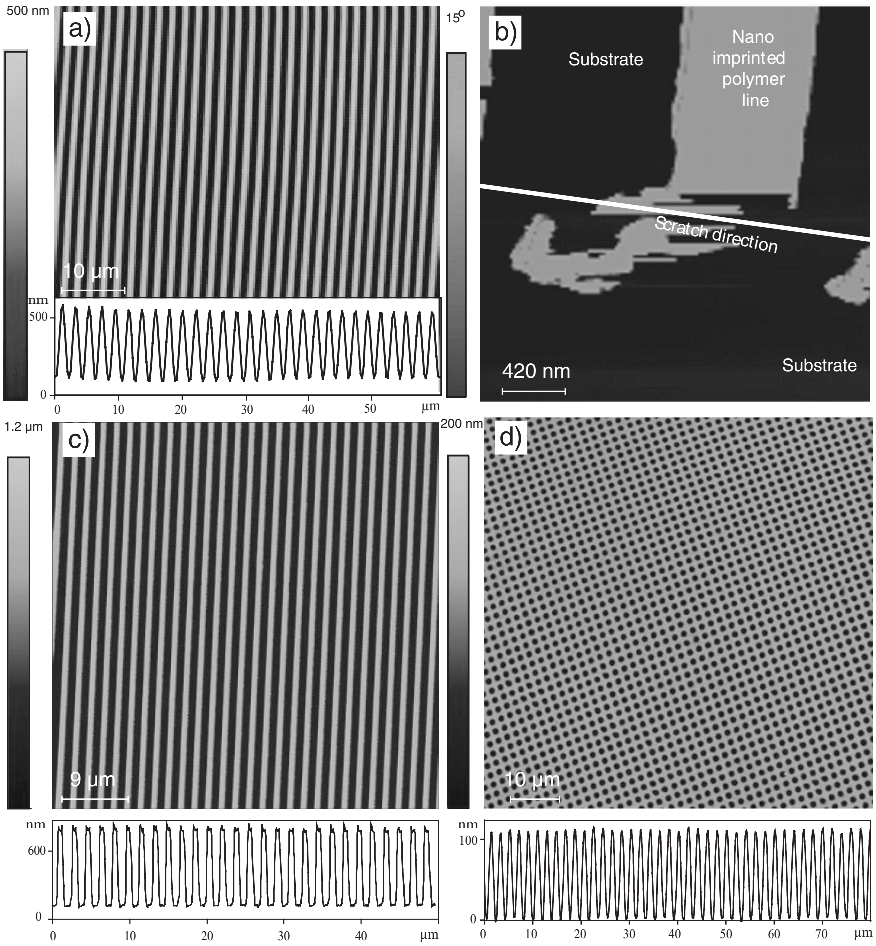

Figure 2. Atomic force microscopy (AFM) images of PS films made by solvent-assisted NIL. a) AFM height image of 1 µm wide PS70 lines with a periodicity of 2 µm, directly mirroring the imprinted silicon master. The 215 nm thick PS film was swollen for 20 min at $p/p_{sat} = 0.7$ in chloroform vapor, imprinted for 5 min, and then dried in N_2 for 35 min. b) Higher magnification AFM phase image of a single line of (a), revealing the material contrast between the polymer and the substrate (see main text). c) 700 nm wide NIL lines in a PS532 film that was swollen in a $p/p_{sat} = 0.95$ toluene partial pressure for 1 h, imprinted for 48 min and dried for 12 min. (c). d) 1 µm wide holes in PS532 that resulted from swelling in $p/p_{sat} = 0.95$ $CHCl_3$ for 16 min, imprinting for 50 min, and drying for 20 min. The periodicities are 1.8 and 2 µm, and the feature heights are 650 and 120 nm for (c) and (d), respectively.

cannot be sufficiently reduced by thermal annealing to provide the flow required by NIL. Because the melt viscosity of polymers scales with the 3.4th power of the molecular weight, NIL of high-molecular-weight polymers requires very high temperatures and pressures, which is harmful for molds, resists, and substrates.

In contrast, the samples in Figure 2c and d were imprinted at room temperature with millibar pressures. Figure 2c was prepared by swelling the film in toluene vapor at $p/p_{sat} = 0.95$ for 60 min, followed by a 48 min imprinting process and quenching for 12 min. The resulting polymer pattern showed 600 nm wide lines with a periodicity of 1.8 µm and a height of 650 nm. In this case the line width matches the width of the 1.5 µm deep mold grooves. Again, the features extended down to the substrate, and no material was left between the lines. Figure 2d was imprinted in chloroform vapor at $p/p_{sat} = 0.95$ for 50 min. Prior to imprinting, the films were swollen for 16 min, followed by drying for 20 min. The diameter of the holes was 1 µm and the periodicity was 2 µm.

None of the samples showed a measurable degree of lateral shrinkage. The volume contraction during drying therefore took place only in the vertical direction. The absence of lateral shrinkage, which is presumably caused by the pinning of the polymer to the side walls and corners formed by the substrate and mold, is an essential feature of the replication process—it is unlikely that laterally contracted lines would faithfully replicate the mold. As the swollen polymer did not fully fill the mold grooves, pinning of the polymer to the recessed parts of the mold did not take place.

Finally, we demonstrate the extension of the approach to submicrometer pattern sizes. Figure 3a shows scanning electron microscopy (SEM) and AFM images of PS70 line patterns, which were prepared in the same way as described above. The film was swollen for 6 min in chloroform at $p/p_{sat} = 0.7$, imprinted for 10 min, and quenched for 10 min in dry N_2. The line width was 200 nm and the periodicity was 380 nm. Figure 3b shows an AFM height image of the same mold in PS532. The film was swollen for 7 min in chloroform at $p/p_{sat} = 0.95$, imprinted for 12 min, and dried for 8 min. The height of the structures was ca. 30 nm. Despite the high molecular weight, the 200 nm lines were a perfect replica of the mold.

In summary, we have demonstrated a new NIL technique consisting of embossing polymer films in controlled solvent-vapor atmospheres. Solvent, rather than temperature annealing, enables NIL at room temperature and millibar pressures. This makes NIL suitable for thermosensitive polymers and greatly reduces the risk of damaging the mold, substrate, or resist. Room-temperature NIL also leaves the antiadhesive layer on the mold intact, which can therefore be used many times without retreatment during repeated NIL. A further advantage of viscosity reduction by solvent annealing is that pattern replication is complete, leaving no polymer between the imprinted resist structures, and that polymers with very high molecular weights can be used as resists yielding identical performance to low-molecular-weight polymers. As the smallest replicated feature size was limited by the mold availability, it is likely that solvent-assisted NIL can

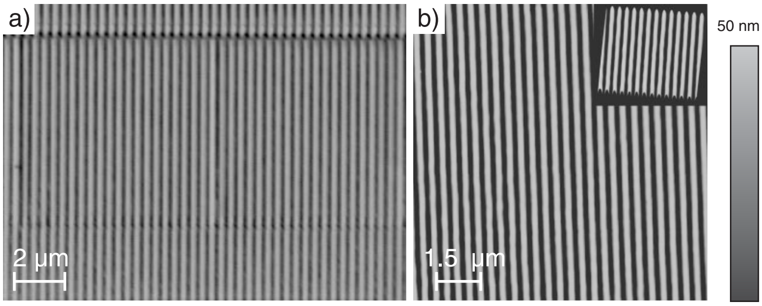

Figure 3. a) Scanning electron microscopy (SEM) image of 200 nm wide PS70 lines with a periodicity of 380 nm. The film was swollen for 6 min in $CHCl_3$ vapor at $p/p_{sat} = 0.7$, imprinted for 10 min, and dried for 10 min in N_2. b) AFM height image of the same mold pattern in PS532. The film was swollen for 7 min in $p/p_{sat} = 0.95$ in chloroform vapor, imprinted for 12 min, and dried for 8 min. The inset shows a three dimensional view of the imprinted lines (image size: 5 µm × 5 µm).

be extended to replicate sub-100 nm feature sizes. We expect this technique to find applications for the patterning of semiconducting organic materials, which often can be liquefied only at high temperatures where thermal oxidation (and degradation of electroluminescence behavior) is a serious issue. Solvent-assisted NIL may therefore be useful for the manufacture of polymer-based light-emitting diodes (PLEDs) and plastic electronic circuits.

Experimental

As resists we used thin PS films that were spin-cast from toluene solutions onto polished silicon wafers. The silicon wafers were subjected to snow-jet cleaning prior to use. Solution concentrations ranging from 1 wt % to 3 wt % polymer in combination with spinning speeds ranging from 2000 rpm to 10 000 rpm were used to obtain well-defined film thicknesses from 20 nm to 160 nm. Two different PS molecular weights were studied, 70 kg mol^{-1} (PS70) and 532 kg mol^{-} (PS532) (Polymer Standards Service GmbH, Mainz, Germany). The silicon molds fabricated by using e-beam lithography (eXtreme Lithography) were rendered hydrophobic by deposition of a 1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane (Fluorochem, 97 %) self-assembled monolayer. This results in a reduction of the surface energy of the mold and significantly reduces the adhesion of the polymer to the mold.

The polymer-film-coated sample was loaded into the chamber (Fig. 1a) and the silicon mold was fixed to a copper block using silver paste, the structured surface facing the sample. The copper support could be vertically translated, allowing the mold to impinge on the resist. Prior to bringing the mold and resist into contact, the polymer film was exposed to a controlled partial vapor pressure of a solvent for the polymer, which resulted in a swelling of the film, forming a highly concentrated solution. For PS films we used chloroform and toluene, both of which are known as good solvents for the polymer. The solvent vapor pressure in the chamber was adjusted using a home-made apparatus [21,22]. Mass-flow controllers (MKS Instruments Model 1179A with a PR4000F readout) regulated the flux of the carrier gas, N_2, through two lines. In one line, the N_2 was bubbled through a solvent-filled bottle resulting in a solvent-saturated gas stream. Both streams were mixed and passed through the sample chamber. The flow volumes per time were individually regulated to values between 1 and 20 $\text{cm}^3\,\text{min}^{-1}$. The vapor pressure in the mixing chamber can be estimated by the ratio of the saturated (p_{sat}) to dry gas (p) flow as determined by the flow-meter readout. All tubes and connectors were made from solvent-resistant materials (glass and Teflon). To prevent solvent condensation inside the setup, the experiments were carried out at 20 °C (room temperature, T_0). The chamber and a regulated water bath containing the solvent bottle and the mixing chamber were held at the same temperature. For the low-(PS70) and high- (PS532) molecular-weight polystyrene films typical values for the vapor pressures were $p/p_{sat} = 0.7$ and $p/p_{sat} = 0.95$, respectively.

The films were allowed to swell in the controlled solvent atmosphere until an equilibrium film thickness was reached (Fig. 1b). This condition was determined by experiments using a sample chamber lid with a window, providing optical access to the chamber. Using a light microscope in reflection mode the change in film thickness as function of time was qualitatively monitored. The polymer concentration in the equilibrated film at a set vapor pressure is given by $\phi_b = d_0/d$, with d_0 and d the dry and swollen film thicknesses, respectively (assuming additivity of the partial volumes of polymer and solvent). For PS films swollen in vapors at $p/p_{sat} = 0.7$, the polymer concentration was $\phi_b = 0.69$ for toluene and $\phi_b = 0.56$ for chloroform, as previously determined by Elbs et al. and Knoll et al. using a spectroscopic ellipsometer connected to a similar setup [21,22]. For PS films swollen at $p/p_{sat} = 0.95$, polymer concentrations of $\phi_b = 0.5$ and $\phi_b = 0.4$ were determined for toluene and chloroform, respectively.

Once there was no further detectable change in film swelling, the silicon mold was brought into contact with the polymer film. No additional force was applied to the support of the mold. The pressure exerted on the swollen film was determined by the weight of the mold support (60 g) and the mold surface area (9 cm^2). The corresponding pressure of 6.5 mbar is 4 orders of magnitude smaller than typical NIL pressures. The swollen film thickness was in all cases small enough to be entirely accommodated in the recessed volume per unit area of the mold. The mold was kept in contact with the swollen film for several minutes followed by the removal of the solvent by passing dry N_2 through the sample chamber. Although the evaporation of solvent from the confined film is greatly reduced, our experiments indicated that the polymer was solidified in a time span between several seconds and a few minutes. After drying the film the mold could easily be removed (Fig. 1d). After the quenching process the initial amount of polymer per unit area was recovered, revealing the mold pattern in the polymer film.

Additional experiments were performed to determine the maximum rate with which NIL can be performed. The maximum swelling rate was determined in an earlier experiment [23]. For a nearly saturated toluene atmosphere, an equilibration time of several minutes (depending on the film thickness and polymer molecular weight) was found. In our setup, swelling rates were lower, limited by the flow rate of the mass-flow controllers. In a second control experiment, a 100 nm thick layer was first equilibrated in chloroform ($p/p_{sat} = 0.95$), confined by a 1 cm^2 glass slide, and then quenched in a N_2 flow. The deswelling of the PS was complete after ca. 3 min, determined by the change in interference colors of the sandwich. As the embossing time itself is short in comparison, an overall minimum process time of ca. 5–10 min, is achievable. Larger imprint areas require a mold design that facilitates the evaporation of the solvent.

Contact-angle measurements of water drops on the mold (CAM 200, KSV Instruments Ltd, Helsinki) before and after the imprinting process showed no significant change in the surface energy. Freshly silanized molds had typical water contact angles of 102° ± 2°, and 100° ± 6° was measured after the mold was used to imprint 10 samples.

The imprinted polymer films were analyzed using tapping-mode AFM (Veeco Dimension D3100) and field-emission scanning electron microscopy (FESEM, LEO 1530). For some AFM measurements, the film was scratched with a needle to facilitate height measurements and as a phase-contrast reference.

Received: July 18, 2006
Revised: October 18, 2006

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