High-Throughput and Etch-Selective Nanoimprinting and Stamping Based on Fast-Thermal-Curing Poly(dimethylsiloxane)s**

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Nanoimprint lithography (NIL) is a patterning technique that has emerged as one of the most promising technologies for high-throughput nanoscale replication.[1,2] Several applications in electronics, photonics, magnetic devices, and the biological field have been developed using this simple, low-cost, and high-resolution technique. In the biological field, DNA,[3] proteins,[4–6] and guides for molecular motors have been patterned;[7] nanowire arrays have been fabricated for electronic applications;[8] new magnetic devices, such as patterned magnetic media[9,10] and high density quantized magnetic discs,[11] have been engineered; and wire grid polarizers,[12,13] light-emitting diodes,[14,15] and diffractive optical elements[16] have been developed for photonics.

The success of NIL as a next generation lithographic technique strongly depends on the research for new materials that are better suited as the nanoimprint resist. Because imprint lithography makes a conformal replica of surface relief patterns by mechanical embossing, the resist materials used in imprinting should be deformed easily under an applied pressure. The most commonly used materials in the original NIL scheme are thermal plastic polymers, which become viscous fluids when heated above their glass transition temperatures (T_g). However the viscosity of the heated polymers is typically high and thus the imprinting process requires significant pressure. In addition, these thermal plastic resists normally have a high tendency to stick to the mold because of non-optimized chemistry and orientation of the polymer backbone structures, which seriously affects the fidelity and quality of the pattern definition. Furthermore they do not offer the necessary etch resistance. Therefore, a nanoimprint resist system with combined mold-release and etch-resistance properties that allows fast and precise nanopatterning is highly desirable.

Thermally curable monomers are very attractive materials for nanoimprint applications because they present in the liquid state, making it possible for them to be imprinted in a short period of time under low pressure and temperature, in sharp contrast to thermal plastic polymers. As one of these materials, poly(dimethylsiloxane) (PDMS) has previously been used by several research groups for micropatterning, mainly in the context of soft lithography,[17–21] and has found numerous applications in fields as diverse as microelectro-chemical systems (MEMS), biotechnology, photonics, and nanoelectronics. In addition to its well known transparency to UV and visible light along with its good biocompatibility, it has a low surface energy (18–21 mN m^{-1})[22] that allows easy mold release without causing any structural damage to the imprinted structures; moreover, it posses a high resistance to oxygen plasma because of a higher silicon content. However, the PDMS material made from commercial Sylgard 184 as precursor is not suitable for nanoimprint applications because of two significant drawbacks. Firstly, its curing typically requires hours, which is impractical as a resist material for NIL. Secondly, the cured material has a low modulus of ca. 2 MPa, which not only makes the imprinted pattern prone to lateral collapsing when replicating submicrometer patterns, but more importantly, it makes it impossible to replicate features less than hundreds of nanometers. The latter point can be understood by considering the radius of curvature of a cured PDMS with a modulus E and surface energy (γ), which is $r = \gamma/E$.[23] Well-defined and sharp-corner structures required for nanometer scale lithography can not be satisfied with a large radius of curvature. As an illustration, an attempt was made to replicate a grating pattern with a 350 nm line width and spacing by using the Sylgard 184 formulation. As shown in the atomic force microscopy (AFM) images (Figure 1), not only are all the lines rounded at the top, but massive collapsing can be seen everywhere in the sample. As an improvement, a higher modulus (ca. 8 MPa) poly(dimethylsiloxane) (hard-PDMS) was developed by Schmid and Michel[24] to achieve the patterning of 80 nm diameter posts with an aspect ratio 1.25 (depth/width) for soft lithography. Unfortunately, the imprinting cycle (heating–cooling time) for this hard-PDMS remained very long (about 2 h). Following the same strategy,

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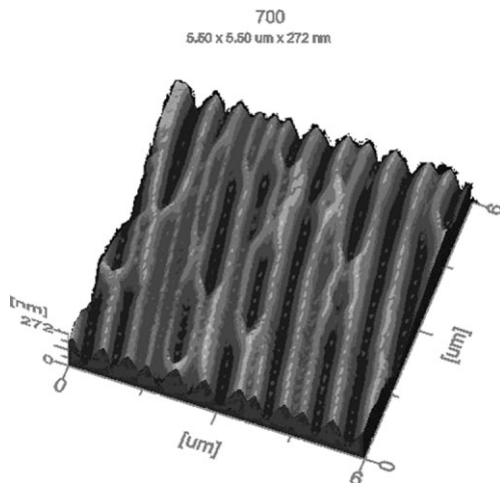E-mail: pengfei.fu@dowcorning.com

700
5.50 x 5.50 um x 272 nm

Figure 1. AFM image of an imprinted 350 nm line-width and spacing grating replicated using Sylgard 184 PDMS. Corner rounding and line collapsing are clearly visible.

Vieu and co-workers[25,26] used Sylgard 184 as well as a reformulated PDMS as a thermally curable resist for nanoimprinting. However, the improvement was rather limited. The crosslinking time is still too long (5–15 min) and the substrate surface requires tedious treatments,[27,28] both of which seriously prevent it from being practically useful for nanoimprinting. Furthermore, feature sizes below 200 nm and structures with an aspect ratio larger than 1 could not be obtained. Recently, Lee and co-workers[18] were able to obtain 50 nm line-width patterns with an aspect ratio of 1.3 by modifying the wetting properties of hard-PDMS as well as reducing its viscosity for improving the penetration of the fluid prepolymer into the cavities of the master template. This was achieved by mixing the prepolymer with an adequate solvent and delaying the cross linking reaction by adding an excessive amount of modulator. The imprinting time lasted about 1.5 h.

Consequently, it is critical to develop a PDMS-based nanoimprinting system offering high throughput and excellent etch selectivity, so that the nanoimprint technology can be realized in actual industrial applications. In this context, we have recently investigated a number of PDMS-based polymer and copolymer systems to simultaneously address the sticking and dry etching issues.[29,30] In this Communication, we report a novel thermally curable PDMS-based nanoimprinting resist that allows successful replication of 70 nm line-width structures within a few seconds, a 20-fold reduction compared to previously reported PDMS-based materials and typical thermoplastic nanoimprint resists. Moreover, the crosslinked PDMS has sufficient mechanical strength and integrity to be used as a mold for nanoimprinting or as a stamp for many soft-lithography applications.

The thermally curable resist formulation consists of four components: vinyl-terminated PDMS, a methylhydrosiloxane copolymer which acts as a crosslinker, a Pt catalyst, and an inhibitor. The inhibitor is an unsaturated organic ester that coordinates to the Pt catalyst and keeps it inactive at ambient

temperature so that the liquid resist can have an extended shelf life, which is required for normal nanoimprint processing. When heated at a higher temperature, such as 80–120 °C, the inhibitor undergoes either hydrosilylation or fast disassociation from the Pt center, releasing the catalyst in its active form.[31] The active species then catalyze the addition of the silyl hydride (SiH) of the methylhydrosiloxane across the double bond of the vinyl-terminated PDMS, forming a crosslinked network (Scheme 1). The network provides the mechanical integrity needed for subsequent pattern transfer steps, as well as for the clean separation of the mold after the imprint. Vinyl-terminated prepolymers with several different
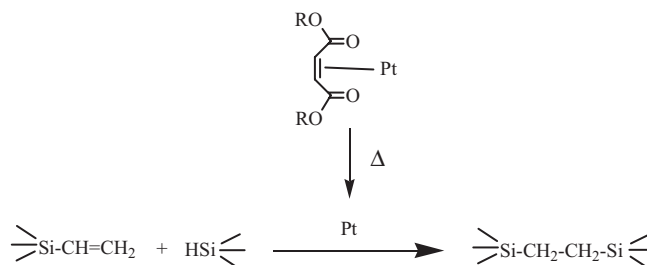
Scheme 1. Chemistry of the crosslinking reaction of poly(dimethylsiloxane).

degree of polymerization (DP = 7, 10, 25, 65), and two crosslinkers with a SiH weight percent of 1.05 wt % and 1.56 wt % were employed in this study. In total, eight different formulations were obtained by combining the four prepolymers and the two crosslinkers.

In nanoimprint experiments, a vinyl prepolymer, a SiH crosslinker, Pt catalyst, and inhibitor were mixed together according to calculated ratios. Once the monomeric liquid precursor was prepared, its concentration was adjusted with low-viscosity silicone fluids, such as octamethylcyclotetrasiloxane (D_4) and pentamethylcyclopentasiloxane (D_5) to achieve the desired film thickness after spin coating. The precursor solution was then spun on a silicon substrate and a mold treated with a fluorosurfactant was placed on top of it. The imprinting was performed at 80–115 °C in less than 10 min with a hydraulic hot press and a Nanonex 2000 nanoimprinter. It is highly recommended that the imprinting is carried out immediately after spin coating the polymer solution so as to avoid the dewetting of the polysiloxane thin film.

The low viscosity of the precursor liquid allows very quick filling of trench structures on the mold.[32] A pressure of 20–100 psi (1 psi ≈ 6895 Pa) is sufficient for the imprinting process, which is carried out at room temperature. Moreover, the improved formulation utilized in this work allows an extremely fast curing (10 s) at moderate temperature (80–120 °C). The rise time of the heating process is ca. 2 s by using an IR lamp in an Nanonex imprinter. These mild conditions help to greatly increase the process throughput over that permitted by most thermoplastics. The liquid resist precursor applied by spin-coating ensures its suitability for high-throughput nanoli-

thography processes, in sharp contrast with the liquid droplet dispensing method used in step and flash-imprint lithography (SFIL).[33,34] Importantly, the application of low-viscosity silicone fluids, such as D_4 or D_5, as the diluents for the PDMS-based resist, completely eliminates the tedious substrate-surface-treatment step. Typically, shrinkage occurs when materials crosslink upon curing. The shrinkage for our system is about 3–5 % (close to epoxy), which is also lower than the acrylate-based systems used in SFIL. Lower shrinkage allows faithful pattern replication during the NIL process.

The modulus of a crosslinked material is a critical factor for nanoimprint lithography. Ideal imprinting requires a careful balance between the ease of mold separation and the mechanical integrity of the imprinted structures, especially those with high aspect ratios. A resist with a high modulus allows tall structures to be replicated without lateral collapsing due to capillary force, but they are typically brittle and may crack and break during mold separation. A resist with a low modulus allows for a clean mold separation, but the replicated structures may suffer from collapsing (an example is shown in Fig. 1). In general the modulus of a cured polymer material depends on the crosslinking density. In our material formulation, the modulus of the cured PDMS can be adjusted by tuning the molecular mass as well as the SiH concentration of the crosslinker (Fig. 2). As presented in Figure 2 (data obtained by dynamical mechanical analysis, DMA), we show that a high modulus material can be achieved by either employing a lower DP prepolymer (e.g. DP 10 vs. 25) or a crosslinker with a higher amount of SiH functional groups (e.g. 1.56 % vs. 1.05 %). Both strategies will increase the crosslinking density per unit volume of cured material.
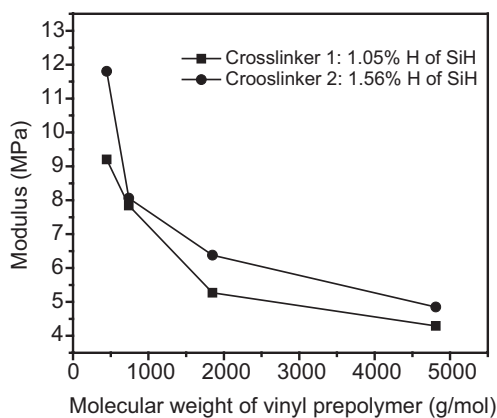

Figure 2. Modulus of the cured material as a function of molecular weight of vinyl-terminated PDMS polymers.

Isothermal differential scanning calorimetry (DSC) scans were performed to obtain the time required to cure the resist formulation at different temperatures. For these experiments, a prepolymer with a DP of 25 and a crosslinker with 1.56 wt % of SiH groups were utilized. Three different catalyst concentrations (Pt % by weight) in the formulated resists

were tested: 120 ppm, 230 ppm, and 340 ppm. At a temperature higher than 120 °C, the resists cure almost instantly, even before reaching the set temperature for the isothermal scan, because of the relatively slow rise time of the instrument. For this reason, the data reported here corresponds to the total time required from the start to the end of the curing process below 120 °C. It should be pointed out that fast curing at elevated temperature is a desirable property for high throughput applications, while the imprinting step itself is carried out at ambient or relatively low temperature. Fast heat rising time is also necessary for high-throughput imprinting, which can be provided by high-power IR lamp heating (as in Nanonex tool) or other suitable mechanisms. Figure 3 shows the time to complete the curing as a function of temperature. The results indicate that the curing kinetics is strongly temperature dependent. For example, when the curing temperature for the
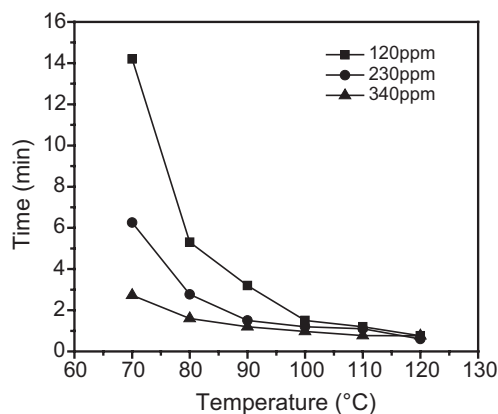

Figure 3. Curing time versus temperature for different catalyst concentrations.

PDMS resist with 120 ppm of catalyst is increased from 70 to 90 °C, the crosslinking is completed in less than 4 min instead of 14 min. This is due to more efficient deactivation of the inhibitors at higher temperatures that releases the catalyst faster. As expected, increasing the amount of catalyst also significantly reduces the curing time, especially at low temperatures. A threefold increase in the amount of catalyst reduces the curing time from 14 min to 2.7 min at 70 °C. This effect is less evident at temperatures above 110 °C since the curing time becomes extremely short (less than 1 min) and difficult to measure with the current instrument. In actual nanoimprint experiments, a 700 nm period grating was replicated at 115 °C in less than 10 s (see below), a curing speed that is over two orders of magnitude faster than that of the previously reported PDMS materials.

Next we present results that correlate the dimension of the replicated PDMS resist structures with the modulus of the cured materials. Figure 4 shows the replicated microscale structures by using a low modulus resist formulated with a prepolymer with a DP of 65. As the structures were of a relatively large size, a modulus of 4.3 MPa was sufficient. In this case, the silicon oxide mold was employed without any fluoro-
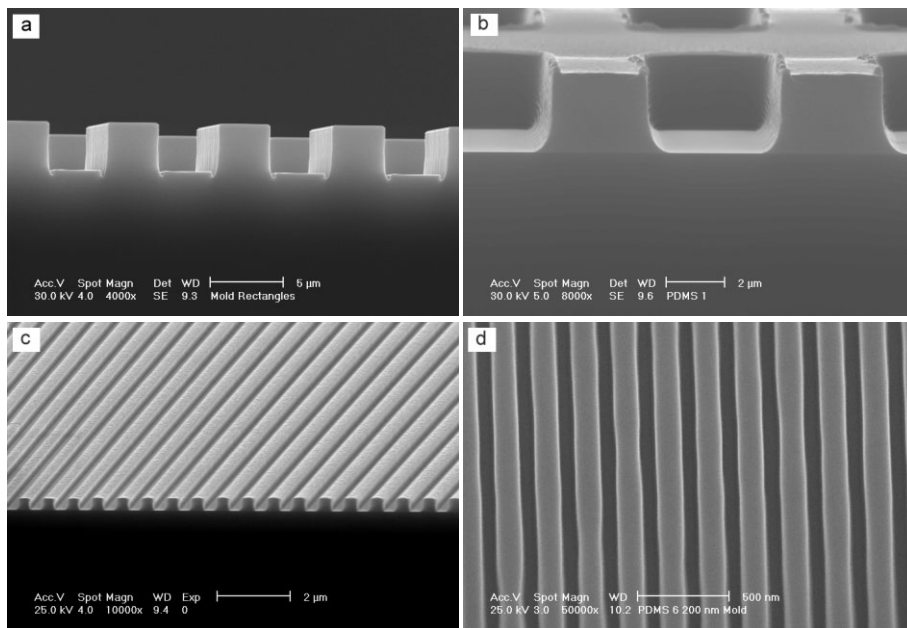
Figure 4. Scanning electron microscopy (SEM) images of thermally curable polysiloxane resist formulations: a) Imprinted microstructures (DP 65), and b) its corresponding silicon oxide mold; c) patterns with a 350 nm line width and spacing, using a resist with DP 25, d) 120 nm line-width patterns, using a resist with DP 10.

surfactant monolayer coatings that are normally used to prevent the adhesion of the imprinted pattern to the mold. The 1.56 % SiH crosslinker was used to ensure fast curing for the thick resist used in this experiment.

For patterning structures in the sub-micrometer regime, a higher modulus elastomer was required. For that purpose, a prepolymer with a lower DP as well as the crosslinker with 1.56 wt % of SiH groups was used. As can be seen in Figure 4c, the vinyl poly(dimethylsiloxane) with a DP of 25 presented good properties for generating 350 nm line-width patterns after curing for 5 min at 80 °C. By increasing the amount of catalyst from 120 to 340 ppm and the temperature up to 115° C, we were able to replicate the same sub-micrometer features within only 10 seconds. In comparison with hard-PDMS (viscosity of 362 cP (1 P = 0.1 Pa s)) reported previously, the present resist shows a very low viscosity (22 cP), which facilitates the flow of the liquid into the mold holes. This value is even lower than the viscosity reported by Lee and co-workers[18] (50 cP) after mixing PDMS with a compatible solvent to increase wettability. As a consequence, for the sub-micrometer and nanoscale replication reported here, resist flow is not a concern.

When small-dimension gratings are replicated, the capillary forces between the structures significantly increase. As a consequence, the resist requires increased stiffness to prevent the structures from collapsing after mold release. To satisfy this requirement, a DP 10 prepolymer along with the higher SiH crosslinker was used, providing the structural integrity required to imprint sub-200 nm dense line gratings (Fig. 4d). The higher crosslink density achieved with this formulation

resulted in a resist with a modulus of 8 MPa.

For sub-100 nm scale features, we found that 70 nm line width structures could be patterned using the same DP 10 prepolymer along with the higher SiH crosslinker. However, as the grating replicated was not completely uniform (collapsing can be observed through several areas), a DP 7 prepolymer was utilized instead (the crosslinker remained the same) to achieve the desired results (Fig. 5a). The higher modulus of this formulation provided sufficient structural integrity to withstand the high capillary forces acting at the nanometer level.

In addition to fast curing and easy mold releasing due to the low surface energy presented by the PDMS material, the high silicon content of the polymer also makes it highly resistant to reactive-ion etching (RIE). The oxygen plasma etch rate of this crosslinked PDMS resist is 1 nm min^{-1}, which is two orders of magnitude lower than that of commonly used thermal plastic imprinting resist poly(methyl methacrylate) (PMMA; etch rate of 100 nm min^{-1}), making the former material an excellent etch mask for pattern transfer. A 70 nm line-width pattern (Fig. 5a) was etched using CHF$_3$ plasma to remove the residual layer. As can be seen in the scanning electron microscopy (SEM) image (Fig. 5b), after the residual layer was removed by RIE, the PDMS structures present no apparent roughness from the plasma etching, in contrast to the results obtained previously with PDMS copolymers.[30] Finally, the patterned PDMS was used as an etch mask to transfer the pattern into a SiO$_2$ layer by RIE using the combined gases of CF$_4$, Ar, and O$_2$. As presented in Figure 5c and d, the SiO$_2$ pattern remained smooth. This illustrates the excellent capability of the imprinted PDMS for direct pattern transfer without the use of any additional hard-etching mask.

PDMS elastomers have found a wide range of applications in the context of soft-lithography and microstamping,[17–21] however as noted earlier, commercial PDMS materials are not suitable to produce sub-500 nm scale features due to their low modulus. Since the material formulation presented in this paper works very effectively as a nanoimprint resist, capable of sub-100 nm resolutions, we anticipate that it will find a range of applications if a thick-layer of imprinted PDMS is used directly as an elastomeric stamp. As a demonstration, we were able to use the replicated 700 nm period grating sample (structures similar to that shown in Fig. 4c) as a stamp to print submicrometer-scale conductive polymer (poly(3,4-ethylene-dioxythiophene) (PEDOT)) patterns using a polymer inking
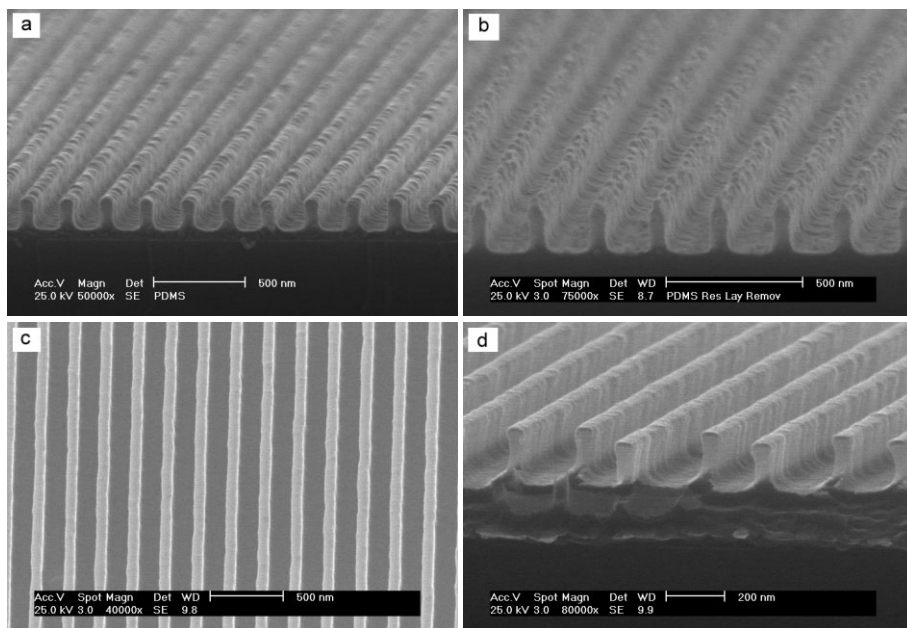
Figure 5. SEM images of a) a 70 nm line-width, thermal-curable PDMS grating pattern; b) a PDMS grating after residual layer removal using CHF_3 RIE; c, d) structures etched in SiO_2 obtained by $CF_4/Ar/O_2$ RIE using the patterned PDMS mask.

and stamping technique (Fig. 6).[35] In addition, the imprinted 350 nm line-width grating structures have recently been used to successfully replicate agarose stamps for reactive wet stamping[36] on various substrates to produce deep submicrometer features.[37]

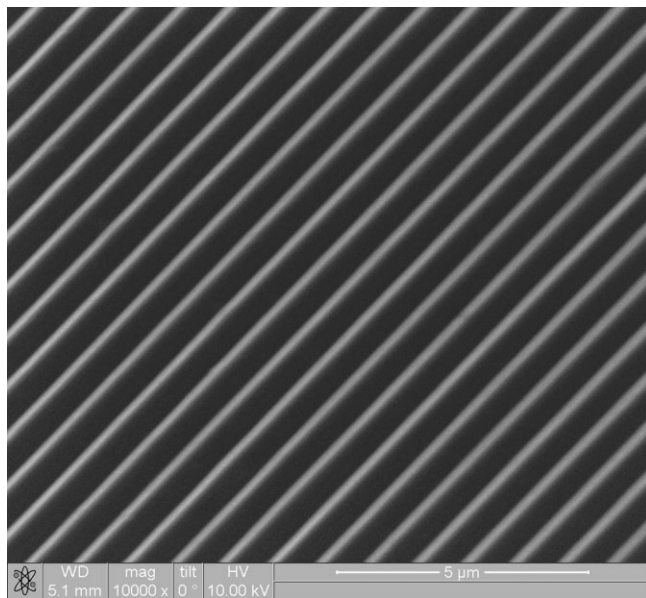In summary, a low pressure and fast thermally curable system based on the hydrosilylation chemistry of siloxane polymers was developed. A thermal curing time of less than 10 s was obtained, in strong contrast to earlier PDMS-based resists, which require tens of minutes to hours to be fully cured. The fast crosslinking time ensures the high throughput needed in nanoimprint lithography. The application of low-viscosity silicone fluids, such as D_4 or D_5, as the diluent for the poly(dimethylsiloxane)-based resist, completely eliminates the tedious substrate-surface-treatment step, and further increases the efficiency of the nanoimprinting process. The ability to tune the modulus imparts flexibility to the resist in meeting different process conditions. This property allowed the replication of nanometer-scale structures with satisfactory results. The PDMS-based resists exhibit a low surface energy, which eases mold releasing, and a high etching resistance because of the high silicon content. The replicated PDMS material can also be used as a stamp in many soft-lithography and microstamping applications to produce deep sub-micrometer structures.

Experimental

Mechanical tests at room temperature were performed with a dynamical mechanical analyzer Perkin–Elmer 7e. An isothermal scan mode was run for 1 min with the frequency set at 10 Hz. The three point bending probe with rectangular geometry was used. The samples were prepared by pouring the liquid precursor in a metallic mold and then heating at 100 °C for 5 min.

The thermal curing of the resist was characterized by using a heat flux differential scanning calorimeter. Isothermal experiments were carried out between 70 °C and 120 °C in 10 °C intervals. The samples were encapsulated using aluminum pans. The mass of the samples was kept at ca. 10 mg. The sample was heated from 30 °C to the curing temperature by using a heating rate of 50 °C min^{-1}.

In stamp fabrication, a SiO_2 film was thermally grown on a Si wafer, and then Cr of 10 nm thickness was deposited on the SiO_2 layer by using a radiofrequency (RF) sputter. The Cr layer was used for the improvement of adhesion properties between the photoresist and the SiO_2 layer as well as for an etch mask for the SiO_2 layer [38]. Photoresist was spin-coated on the Cr layer, and laser interference lithography (LIL) was performed to form a grating pattern [39,40]. The Cr layer was etched with Cl_2 and O_2 RIE, and then the SiO_2 layer with CHF_3 RIE. After etching the SiO_2, the Cr mask was removed by a Cr wet etchant. The He–Cd laser used has a wavelength of 325 nm and a power of 50 mW. The patterns were obtained through the laser interference between the direct beam and the reflected beam from the mirror.

Nanoimprint was also used to fabricate the replicated stamp from the original one produced by LIL. For the replication, a substrate with a SiO_2 film on Si was used. Before imprinting, the fabricated stamp was pretreated by an antisticking layer (1*H*,1*H*,2*H*,2*H*-perfluorodecyl

Figure 6. Patterned 700 nm period grating structures in a conductive polymer PEDOT with a cured PDMS stamp by using the polymer inking and stamping technique [35].

trichlorosilane) to prevent the stamp from adhering to the imprint pattern for the demolding step. A thin 10 nm film of Cr was also used as a mask layer and was deposited in an electron beam evaporation system. The nanoimprint resist was spin-coated, baked on a hotplate to remove residual solvent, and imprinted using a Nanonex 2000 nanoimprinter. RIE was used to first remove the residual polymer layer and then pattern the Cr masking layer. The nanoimprint resist was then dissolved in acetone and the sample was rinsed using methanol and isopropyl alcohol and dried in N_2. The SiO_2 was reactive-ion etched to its full depth and then the Cr was removed using a wet etchant.

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