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Polymer to polymer to polymer pattern transfer: Multiple molding for 100 nm scale lithography

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We demonstrate a multiple molding procedure based on the combination of replica molding, *in situ* patterning of an ultraviolet curable epoxy resist, micromachining by elastomeric elements, and nanoimprinting lithography. The pattern, with features down to the 100 nm scale, is sequentially transferred to several different polymers, allowing one to realize high-resolution organic molds for imprinting compounds of lower glass-transition temperature. The intimate integration of soft and nanoimprinting lithographies enables a combined, multistep mechanical patterning, which can be very useful for a great range of applications for molecular lithography and devices. © 2006 American Vacuum Society. [DOI: 10.1116/1.2184327]

I. INTRODUCTION

Soft lithography includes a variety of nonphotolithographic techniques, in which an elastomeric stamp prepared by replica molding¹ (REM) is used to duplicate the pattern of a master and transfer it onto different substrates.² The low Young's modulus (3 MPa) of standard poly(dimethylsiloxane) (PDMS) makes it suitable for REM in the micrometer range, whereas it determines the collapse and deformation of the elastomeric features at higher resolution. A mold material, a vinyl and hydrosilane polymer, referred to as hard PDMS (*h*-PDMS),³ has been developed for sub-100 nm REM and phase-shifting lithography by virtue of its higher modulus (9 MPa).⁴ *h*-PDMS allows one to obtain extremely high resolution by the REM technique: the replication of 3 nm wide structures⁵ and of 0.5 nm vertical deflections⁶ has been demonstrated using this elastomer. Nevertheless, an open issue for high-resolution mechanical patterning has to date concerned the realization of high-resolution molds for nanoimprinting lithography (NIL),^{7,8} which has to be carried out by traditional, and expensive, lithographic techniques. The molds undergo particularly strong stresses under NIL, thus suffering from frequent distortions and breaks, hence the call for approaches able to realize them by alternative methods.

In our approach, elastomeric elements are used as the starting master to be replicated onto a photoresist that will act as a mold material for the subsequent NIL processes. Replication techniques, based on REM and microtransfer molding, have been proposed to produce masters using photochemically curable compounds^{9,10} and thermosetting polymers such as epoxy¹¹ and polyester¹² resins. In this work, we demonstrate multiple pattern transfer by the combination of complementary mechanical lithographies, generating templates by an epoxy-based photoresist, SU-8 2050 (molecular structure in Fig. 1) to be used as molds for NIL, allowing us

to reach a resolution as high as 100 nm. This method offers several advantages over traditional micro- and nanofabrication approaches, allowing one to carry out a single-step fabrication procedure without etching processes. In particular, while the fabrication of the starting master, which has to be made by sophisticated lithographic techniques (electron and focused ion beam writing, extreme, deep UV, and interferometric lithographies), remains expensive, with costs that can easily get into tens of thousands of dollars for large area stamps, the subsequent polymer replication is very cheap and the overall throughput increases. One is then able to replicate the master morphology in several copies, preserving the original one from possible damages. Moreover, the realization of polymeric masters from elastomeric templates extends the range of materials employable for the initial master structure to be used for subsequent mechanical patterning methods such as NIL. Among the range of materials to be used in the master realization, such as polycarbonate, polyethylene, polyolefin Zeonex, silicon, quartz, etc., we could include also more fragile materials, such as InP. The direct use of fragile templates is prevented in all the lithographic techniques that induce mechanical stress in the master structure by the application of pressure during the patterning process, such as nanoimprint lithography. Instead, by intermediate soft replication it is possible to create a faithful copy of the starting fragile master, without damaging the features, and to employ directly the replica in the following imprinting process. In addition, molding can be used in the replication of complex stamps that present surface relief with different aspect ratios difficult to achieve with other methods.^{13,14} Finally, we point out that the polymer to polymer pattern transfer is suitable for the realization of resist templates over a large area, since it is possible to realize elastomeric elements with an area up to 50 cm².¹⁵

II. EXPERIMENT

The multistep molding process is schematized in Fig. 1. First, we replicated our master geometry (Si and InP periodic

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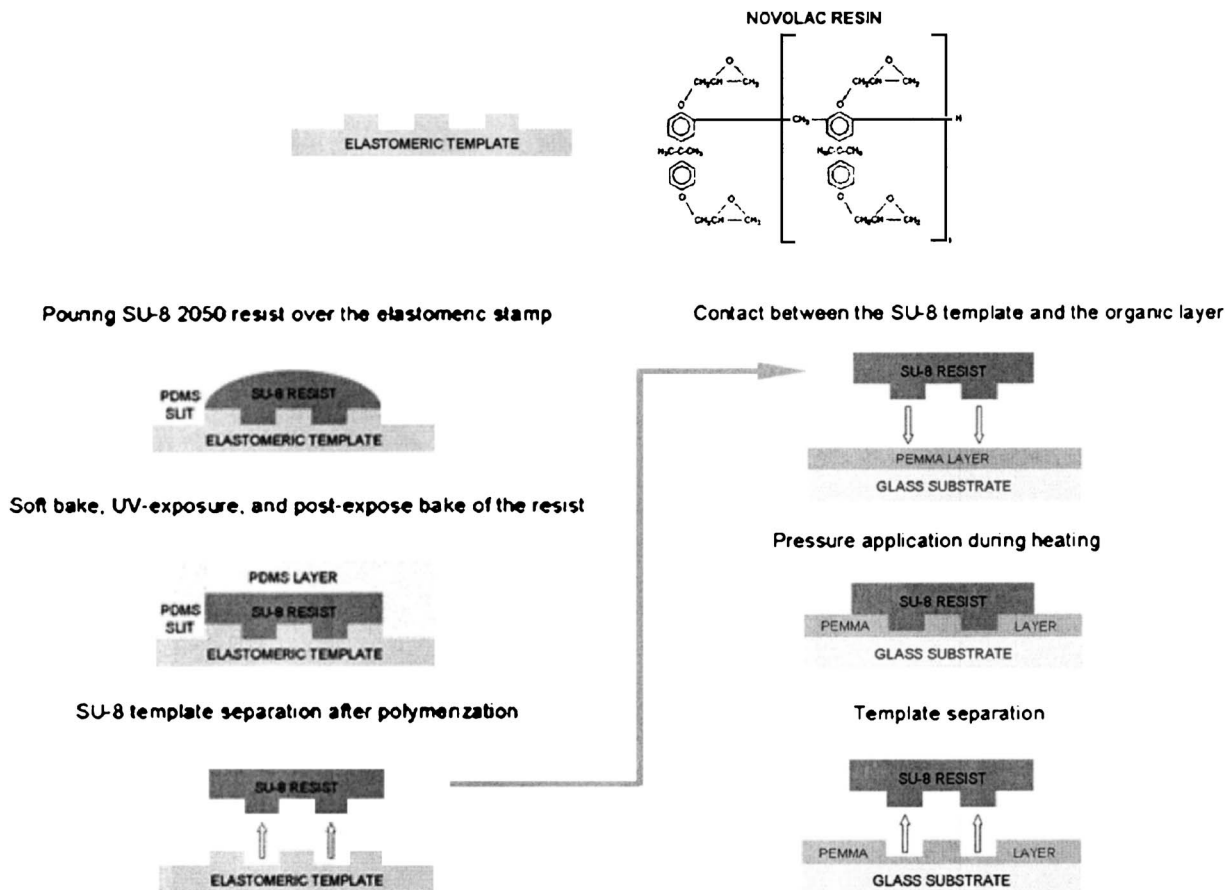


FIG. 1. Scheme of the multiple molding and the molecular structure of the mold resin.

gratings with features between 2 μm and 100 nm) by REM.² PDMS (Sylgard 184, Dow Corning, Midland, MI) and composite stamps (30–40 μm of *h*-PDMS bonded to a thick slab of PDMS)¹⁶ were realized for the micrometer scale and the 100 nm scale resolutions, respectively. The Sylgard 184 base (A) and curing agent (B) are mixed in a ratio of nine parts A and one part B, in weight. The silicone elastomer was cast on the master and polymerized *in situ* at 140 °C for 15 min. The *h*-PDMS solution was prepared by mixing 3.4 g of trimethylsiloxy-terminated vinylmethylsiloxane-dimethylsiloxane (VDT-731, ABCR, Karlsruhe, Germany), 18 μl of a Pt catalyst (platinum divinyltetramethylsiloxane, SIP6831.1, ABCR, Karlsruhe, Germany), and 5 μl of a modulator (2,4,6,8 tetramethyltetravinylcyclotetrasiloxane, Sigma Aldrich, St. Louis, MO). Afterwards the mixture was degassed for 1–2 min, 1 g of methylhydrosiloxane-dimethylsiloxane (HMS-301, ABCR, Karlsruhe, Germany) was added, and the *h*-PDMS solution was gently stirred. We then spin-coated (1500 rpm for 40 s) a thin *h*-PDMS layer onto the master surface and cured it at 60 °C for 30 min. After the polymerization, Sylgard 184 PDMS, in the form of liquid prepolymer, was poured onto the *h*-PDMS layer and cured at 60 °C for 1 h. Then, the composite stamp was carefully peeled off from the master surface.

The replica is then used as a starting master, and the soft features are reproduced into SU-8, which is poured onto the

elastomeric element and cured *in situ*. The resist is made up of a glycidyl-ether derivative of bisphenol-A Novolac as epoxy resin,¹⁷ cyclopentanone, and triarylium-sulfonium salt as photoinitiator. Under UV ($\lambda=350\text{--}400$ nm) exposure, the salt is converted into an acid, which reacts with the epoxy groups during the postexposure bake, thus providing a dense three-dimensional network of cross-links. After a soft bake process (100 °C for 10 min) to evaporate the solvent, the SU-8 is exposed to UV radiation, and it finally undergoes a postexposure bake (100 °C for 10 min). After the complete cross-linking, the freestanding epoxy template is easily peeled off from the replica. A great experimental accuracy is required during the separation of the resist template from the *h*-PDMS stamp in order to avoid the generation of cracks and tears in the high-resolution elastomeric features. We succeeded in producing crack-free patterns by slowly peeling off PDMS and SU-8, i.e., by separating the two materials in a range of 10–20 s (for ~ 1 cm² large replicas) and by avoiding too large bending of the elastomer, i.e., using radii of curvature of more than 0.5 cm during peeling. In our experiments, we used the same elastomeric element for producing more than ten resist NIL molds without observing features degradation.

Although the high viscosity value of SU-8 [17×10^3 cS (1 cS $\equiv 10^{-2}$ cm²/s)] ensures that the cast resist re-

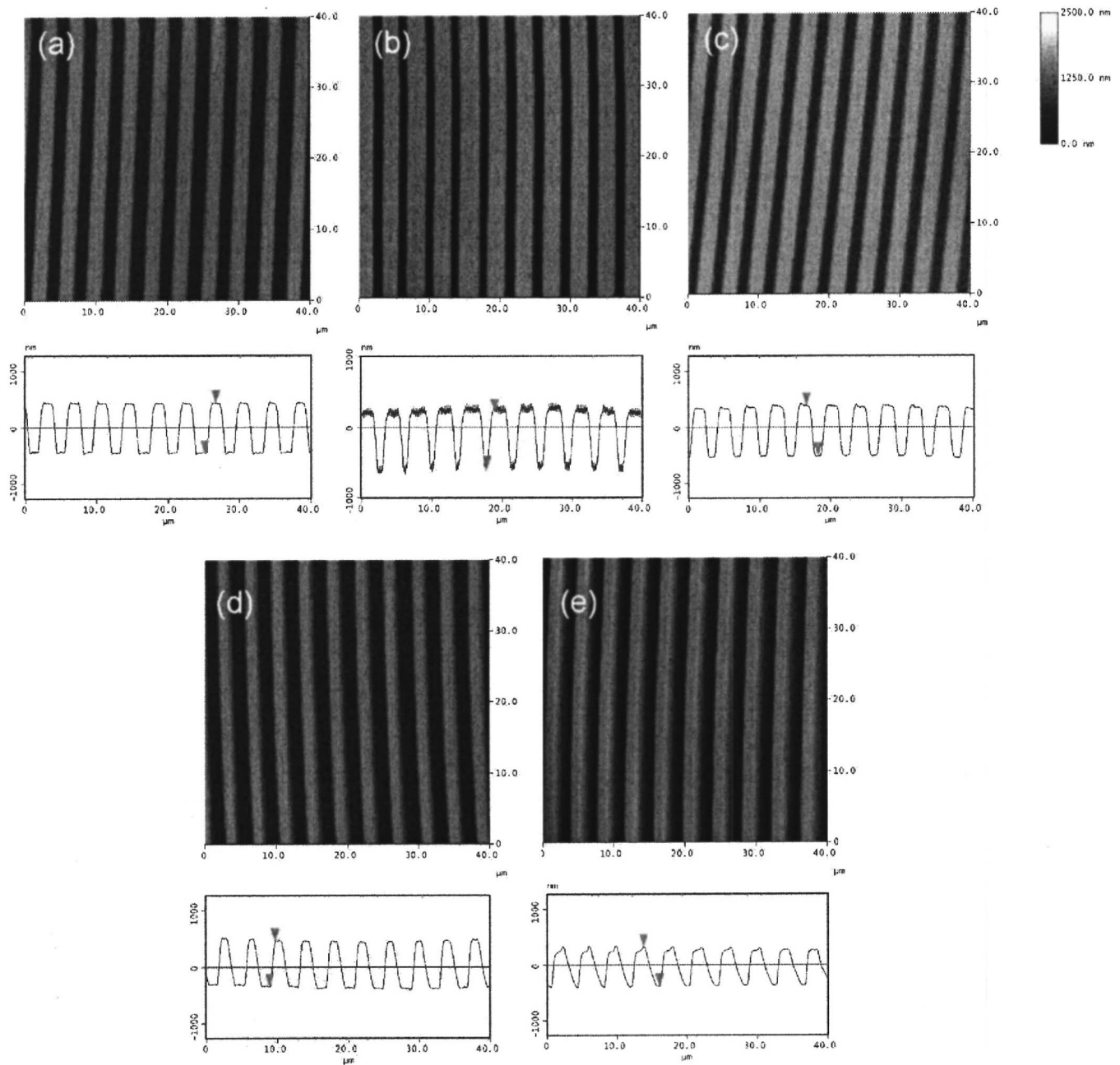


FIG. 2. (a) $4\ \mu\text{m}$ period Si master, (b) PDMS element, (c) PDMS element after thermal curing, (d) SU-8 2050 mold, and (e) PEMMA final imprinted grating. In (b), the duty cycle measured on PDMS by AFM is significantly overestimated, likely due to distortions of the elastomeric features.

mains on the patterned area of the elastomeric element, simple PDMS micromachining has been used to control the mold size and to achieve a uniform thickness of the template (essential for the subsequent NIL). A flat layer of PDMS has been placed over the replica, with a slit in the central region of the same width as the patterned area of the stamp. The conformal contact between the two PDMS elements avoids their relative shift and the penetration of the resist into the interface. In addition, the template height may be controlled straightforwardly by changing the thickness of the flat layer. A third PDMS sheet in conformal contact with the slit is also employed to level the top surface of the SU-8 mold.

The pattern transfer capability of the SU-8 mold has been evaluated by NIL. The template was mechanically pressed onto a substrate coated with a layer of a thermoplastic polymer. Afterwards, the system is heated above the glass-transition temperature (T_g) of the polymer, determining the strong decrease of the polymer viscosity according to the glass-transition phenomenology of the target compound and the conformation with the pattern up to 10 nm resolutions.¹⁸ We carried out the NIL process on the low- T_g compound poly(ethyl methacrylate-*co*-methyl acrylate) (PEMMA) as target material ($T_g=48\ ^\circ\text{C}$). After spin-casting (1500 rpm for

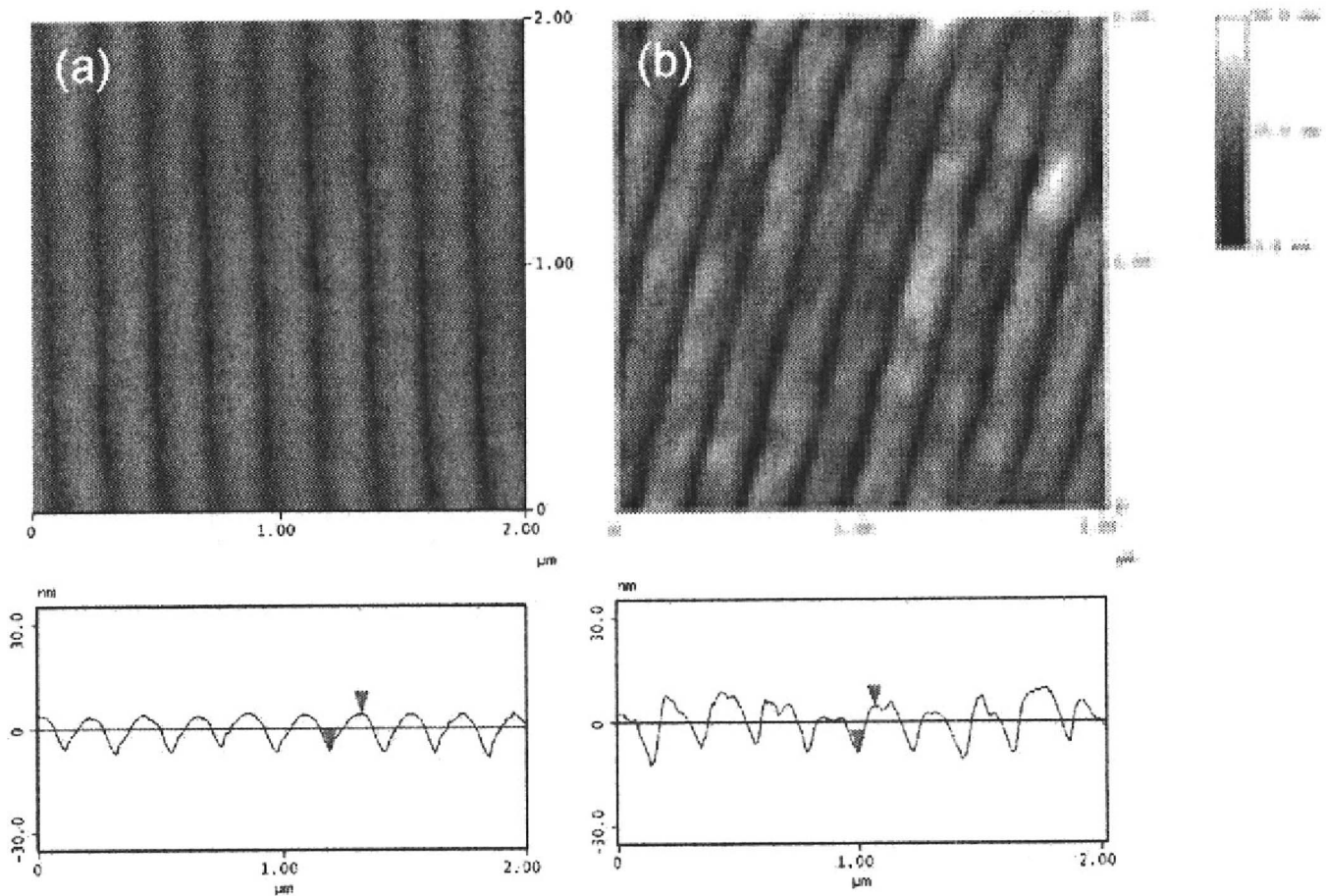


FIG. 3. (a) 200 nm period InP master and final grating imprinted in PEMMA by NIL using the SU-8 mold (b).

40 s) dichloromethane solution ($3 \times 10^{-3} M$) of the polymer onto a silicon substrate, the SU-8 2050 mold, without anti-sticking treatment, was manually positioned onto the polymeric film and directly employed as a stamp for NIL by a two-column precision manual press with an applied force of about 0.7 kN at 50 °C.

III. RESULTS AND DISCUSSION

We underline that, despite the use of photolithographic SU-8 masters for REM is quite common, the approach proposed here inverts the role played by the elastomeric material and by the epoxy resist, thus allowing us to fabricate rigid cross-linked molds for the subsequent 100 nm scale imprinting on other polymers. Indeed, different from previous reports,¹⁹ our molding method is based on the morphology replication of a soft template rather than a rigid one. The use of elastomeric replicas favors the realization of resist templates, suitable for NIL, that preserve the same shape (positive) of the starting master. In fact, the SU-8 mold reproduces the negative copy of the PDMS one and, consequently, the positive copy of the master. Such a multistep molding prolongs the life of the master (which is not used directly for the high-pressure NIL process), it enables positive-tone imprinting, and it reduces the overall cost of the lithography. We also point out that the elastomeric character of the mold

can be exploited to increase the resolution of the SU-8 master with respect to the starting one by imposing a mechanical compression to the soft element.² Hence, higher resolution molds for NIL can be obtained.

Hot embossing is challenging in several respects, strictly related to the polymer transport under the applied pressure: (i) micrometer features are often not molded as well as nanometer features, (ii) a range of sizes produced by NIL is sometimes challenging, and (iii) the embossed film may have a range of thicknesses, which prevent accurate etching processes in the subsequent fabrication steps. In NIL, the mechanical response of the amorphous polymers to the application of external pressure can be explained by their viscoelastic behavior. Upon increasing the temperature, the polymer reaches its rubber-elastic region, characterized by a plateau in the curve of the time-dependent shear compliance, $J(t)$.²⁰ At higher temperature, or for longer heating times, an irreversible flow of molten material occurs (the so-called terminal flow region). In this region, the deformation induced by the external force is irreversible and $J(t)$ exhibits a linear dependence on time. Thus, the heating time represents a fundamental parameter in the realization of patterns by hot embossing. In particular, the increment of the imprinting time allows the polymer to fill completely the recessed regions of the stamp and favors the realization of deeper features. Nev-

ertheless, during long imprinting processes the sticking between the master and the polymer to be structured can become important, with consequent damages both in the master and in the imprinted features. In order to avoid this problem, antisticking layers are commonly used. In our pattern transfer procedure by NIL, the employment of the SU-8 template reduces drastically the adhesion problems and the resist stamp (without antisticking layers) can be easily separated from the PEMMA film. Thus, the imprinting time can be increased and, consequently, the polymer transport over longer distances are more favored. Hence, features with a wide range of heights and lateral dimensions can be produced. In our experiments, we worked with aspect ratios between 0.1 and 1, and feature sizes between 0.1 and 100 μm , achieving faithful replication. In addition, the same resist mold could be used for at least ten times on PEMMA layers. Consequently, the original (semiconductor) master structure can produce more than 10^2 imprinted patterns.

A 4 μm period master grating, two first-generation replicas, the SU-8 mold, imaged by atomic force microscope (AFM), and the relative cross sections are shown in Figs. 2(a)–2(d), respectively. The realized resist mold presents the same period of the starting master and of the elastomeric stamp, and a feature height of 842 ± 2 nm, without a significant reduction in the aspect ratio with respect to that of the master, whose features present a height of 857 ± 2 nm. Concerning the feature size observed with the AFM investigation, by comparing Figs. 2(a) and 2(b) we note that the lateral dimensions of the recessed features of the Si master are different from the relief ones of the PDMS template. In particular, the value of the full width at half maximum (FWHM) of the Si voids and of the PDMS structures are 1.8 ± 0.2 and 2.7 ± 0.2 μm , respectively. This reproducibly observed increment of about 33% of the linewidth of the elastomeric elements can be due to elastic distortions suffered by the soft sample under the AFM investigation. In fact, as shown in Fig. 2(d), this deformation is not transferred to the SU-8 mold, which is on its turn obtained by the PDMS (first-generation) template. The SU-8 features regain the original dimensions of the starting master, the FWHM of the positive structures in the Si master and in the SU-8 mold being 1.9 ± 0.1 and 2.0 ± 0.1 μm , respectively. Performing further thermal polymerization (140 °C for 10 h) on the elastomeric elements, thus increasing Young's modulus of cured PDMS and achieving more rigid templates,²¹ allowed us to reduce the distortion effects observed under AFM investigation. As shown in Fig. 2(c), the elastomeric relief features after the thermal treatment present a FWHM of 2.1 ± 0.1 μm , matching the recessed ones of the starting master. By virtue of the very simple replication method, SU-8 replicas can be obtained by starting with elastomeric templates of whatever area; hence this method straightforwardly allows one to obtain high-resolution patterns of tens of cm^2 ,¹⁵ faithfully reproducing the lateral dimensions of the elastomeric features, which, by compounds of high Young modulus, can be as small as a few nanometers.⁵

The SU-8 2050 templates were employed in the patterning of a PEMMA layer by NIL. Figure 2(e) displays the AFM view of the obtained PEMMA grating. The transferred features are well defined and present a height of 700 ± 22 nm. Thus, the height of the imprinted grooves decreases with respect to that of the SU-8 master, showing a loss of aspect ratio of 12.5%. Deeper features can be obtained by increasing the heating times during the imprinting process, favoring the complete filling of the void spaces of the resist template, and the polymer conformation to the mold.

The resolution of the multiple pattern transfer by combined molding and imprinting on different polymers certainly depends on the starting master. The integrated use of SU-8 2050 as template material and of the elastomeric elements as replicated stamps offers the possibility to realize low-cost molds for NIL with a 100 nm scale (and possibly higher) resolution. In Figs. 3(a) and 3(b), we show the AFM images, and the relative cross sections, of an InP master with 100 nm lines spaced by 100 nm grooves and of the PEMMA grating obtained from the resist template by NIL, which exhibits the same aspect ratio as that of the starting master. Composite *h*-PDMS replicas were used to fabricate the SU-8 molds in this case. The reproducible resolution of the overall multistep process can certainly be further reduced, depending on the master features. Neither the InP nanostructure (that is too fragile) nor the elastomeric stamp (that is too flexible) would be usable directly for nanoimprinting: multiple molding, exploiting the different chemical-physical properties of polymers (and particularly the chemical inertia of elastomers and the very high glass-transition temperature of highly cross-linked resins), opens the way to the integration of different mechanical patterning methods. It starts from soft replication to obtain rigid molds for pressure-driven nanoimprinting.

IV. CONCLUSION

In summary, this paper describes a multiple molding procedure based on the combination of REM, *in situ* patterning of an UV-curable epoxy resist, PDMS micromachining, and NIL, that employs the realized molds. The pattern is sequentially transferred from the inorganic master to three different polymers, and resolutions up to 100 nm scale are demonstrated. Combined, multistep mechanical patterning can certainly be very useful for a great range of lithographic and surface-science applications.

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