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Soft nanoimprint mold with rigid relief features for improved pattern transfer

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Rigid nanoimprint molds offer the best possible pattern-transfer fidelity and resolution, but are also sensitive to surface contamination and defects. Alternatively, soft nanoimprint molds are insensitive to defects and can imprint nonplanar surfaces, but have limited resolution. Here, the author combined the advantages of the rigid and soft molds by producing a novel mold, in which rigid relief features are chemically attached to a soft substrate. The features were produced by electron-beam patterning of hydrogen silsesquioxane (HSQ) on a sacrificial substrate, and mechanically transferred to polydimethylsiloxane (PDMS). The attachment of the HSQ to PDMS is most likely due to Si–O–Si bonds formed on their interface. Using this molds, the authors obtained nanoimprinted pattern transfer with the fidelity typical for the hard molds. They found that a mold-release agent is essential to prevent the detachment of the rigid features from PDMS. To this end, the authors applied fluorinated silane onto the mold surface and showed that functionalized silane monolayers can effectively modify the surface properties of spin-on-glass materials like HSQ.
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I. INTRODUCTION

Since its invention a quarter-century ago,¹ nanoimprint lithography has become among the most popular and broadly used nanolithographic techniques. Nanoimprint can be done using rigid molds most commonly made of Si, quartz, or Ni.² These molds have very high pattern-transfer fidelity and offer both resolution and minimal feature size below 10 nm.³ However, rigid molds are very sensitive to surface defects and require high imprint pressure to overcome the local and global curvature of the imprinted substrates. Alternatively, soft elastomeric molds, which are most commonly produced from cast and cured polydimethylsiloxane (PDMS), conformally cover the imprinted substrate with the minimal applied pressure, and are much less sensitive to surface defects.⁴ Furthermore, they can imprint curved substrates.⁵ Yet their pattern-transfer fidelity and resolution are limited due to the deformation of the soft relief features during the imprint.

Pattern-transfer fidelity of soft molds can be improved by providing them with a hybrid structure consisting of (1) soft PDMS substrate and (2) hard imaging layer made of hardened polysiloxane⁶ or organic polymer.⁷ However, upon deflection the rigid layer is susceptible to cracking⁸ that, in turn, leads to defects over large areas of the transferred pattern. Li *et al.* achieved 15-nm resolution⁹ by using a hybrid mold with hardened polymeric imaging layer, whose elastic modulus was 2.16×10^6 Pa—more than 20-fold higher than that of PDMS. Yet, such imaging layer is still much softer than that of the materials used for rigid molds; e.g., Si, whose modulus is $\sim 1.5 \times 10^{11}$ Pa, or glass, whose modulus is $\sim 5 \times 10^{10}$ Pa. Notably, certain polymers have modulus of up to 2×10^{10} Pa.¹⁰ In theory, imaging layer made of such polymer could transfer the pattern with the fidelity close to that of rigid molds. However, it will likely crack upon the global mold deformation. Yet, can a nanoimprint mold have

both (1) pattern-transfer fidelity of rigid molds, and (2) the flexibility and crack resistance of soft molds?

In this work, we introduce a novel soft-substrate-rigid-features (SSRF) nanoimprint mold approach [Fig. 1(c)]. As opposed to the previously reported hybrid molds,^{6,8,9} here only the relief features are made of a rigid material, whereas the background area consists of a soft elastomer. Thus, such mold uniquely combines the advantages of the both soft and rigid molds and at the same time precludes their constrains.

It should be noted that the realization of the proposed hybrid structure of the SSRF mold is challenging, since PDMS—the materials of choice for the mold substrate—is incompatible with the standard nanofabrication. In other words, it cannot be used as a substrate for the lithographic fabrication of miniaturized rigid features. On the other hand, nanopatterned structures of Si and glass can be produced on a sacrificial substrate, and then transferred onto PDMS.¹¹ Such transfer is possible by exposing PDMS and Si or silica surfaces to oxygen plasma, which forms silanol (–OH) groups on both surfaces. Then, when the two surfaces are brought together, the silanol groups react with each other and form siloxane (Si–O–Si) bonds, causing irreversible adhesion of the two surfaces.¹²

In this work, we produced the relief features by electron-beam patterning of hydrogen silsesquioxane (HSQ). HSQ is a negative-tone electron-beam resist,¹³ which can be directly patterned to 3D inorganic relief structures on the Si mold surface, without the need for plasma etching.^{14,15} An additional reason for using HSQ is its high modulus that reaches values of up to 10^{10} Pa upon thermal annealing.¹⁶ Therefore, it is reasonable to assume that HSQ relief features will be rigid enough to transfer the pattern with the quality similar or close to that of Si or silica based rigid molds. Another advantage of direct HSQ patterning is that it allows precise control of the feature height through the thickness of the spin-coated HSQ film.¹⁷ As to the transfer of HSQ features

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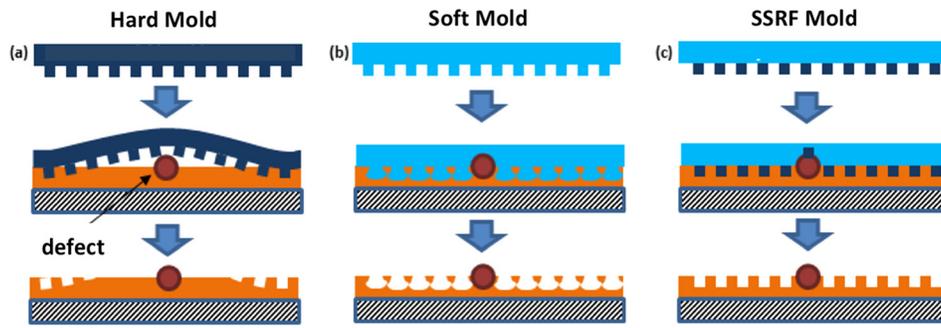


Fig. 1. (Color online) Schematic presentation of different molding approaches: (a) Hard mold offers high pattern-transfer fidelity, but is sensitive to defects. (b) Soft mold is insensitive to defects, but its relief features buckle during the imprint. (c) SSRF molds are insensitive to defect and at the same time offer high pattern-transfer fidelity.

to PDMS, we took into consideration that electron-beam exposure and plasma oxidation change HSQ to a material whose chemical composition is close to that of silica.¹⁸ This made us hypothesize that the electron-beam patterned and oxidized HSQ would chemically bond to PDMS similarly as it does in case of silica.

II. EXPERIMENT

To prepare SSRF molds, the PDMS substrate (~ 3 mm thick) was produced in advance by mixing the two parts (10:1) of Sylgard[®] elastomer kit, pouring the mixture onto a Si wafer in a petri dish, degassing, and curing it at 60°C overnight. A piece of PDMS with an appropriate size was then cut and peeled off the Si. The fabrication of SSRF mold is shown in Fig. 2. First, HSQ (XR-1541-006, Dow Corning, ~ 150 nm thickness) was applied by spin-coating onto the Si substrate covered with evaporated sacrificial Au film (30 nm). Electron beam lithography was done using Raith E-line writer. A typical pattern consisted of 2D arrays of $1\ \mu\text{m}$ squares spaced in the range from 1 to $2\ \mu\text{m}$. The exposed pattern was developed for 2 min (AZ760, Micro Chemicals), rinsed with DI water, and dried. Annealing at 350°C for 1 h was done to harden the obtained HSQ features.¹⁶ Then, the pattern was covered by spin-coated PMMA (Microchem, A8) and baked for 2 min at 150°C . Thermal tape (Revalpha, Nitto Denko) was mechanically applied on top of PMMA, and the Au-HSQ-PMMA-tape sandwich was peeled off the Si substrate. Notably, easy peeling-off is possible due to the pure adhesion of Au to Si. Then, the Au layer was stripped with the solution of $\text{KI}:\text{I}_2$:

H_2O (1:4:40 v/v) for 1 min, following rinsing with DI water, and drying. The purpose of this step was to expose the bottom side of HSQ features. Both PDMS and the flipped tape with the exposed HSQ features were plasma-oxidized (Harrick PDC-32G) for 1 min, and immediately pressed against each other. The entire assembly was thermally cured overnight in oven at 60°C . Finally, thermal tape was detached by heating to 110°C for a few seconds, and PPMA was stripped by acetone rinsing and drying. Notably, acetone may cause swelling of PDMS. To avoid the swelling completely, PMMA can be replaced by a water soluble polymer soluble in water, which can be then stripped by water.

III. RESULTS AND DISCUSSION

Figure 3(a) shows an SEM image of a HSQ pattern on Au film. Figure 3(b) shows an AFM image of a HSQ pattern transferred to PDMS. To the best of our knowledge, this is the first report of the transfer and chemical bonding of HSQ nanostructures onto PDMS. HSQ features were transferred to PDMS with 100% yield. Interestingly, the height of the features as measured by AFM was ~ 150 nm, which is equal to the thickness of the originally spin-coated HSQ film, confirming that HSQ shrinkage at 350°C is negligible.¹⁶ Thus, our process provides a facile and precise control of the feature height through the thickness of the spin-coated HSQ film.

To check the applicability of SSRF molds for nanoimprint, we used them to imprint of two UV-curable resists: (1) optical adhesive NOA-61 (Norland, Inc.) diluted in

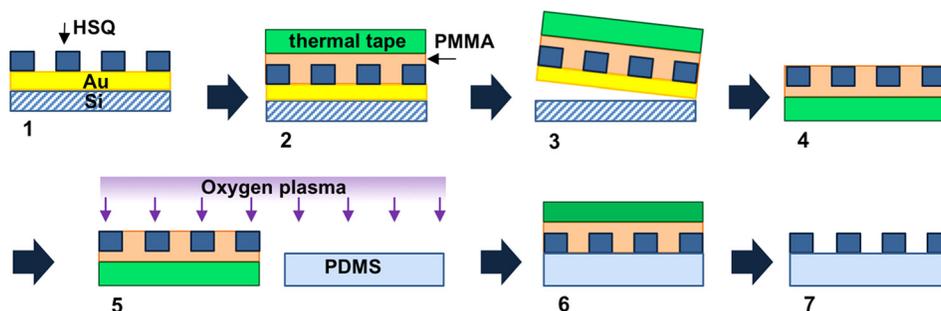


Fig. 2. (Color online) Fabrication of SSRF mold: (1) electron beam patterning of HSQ on Si/Au substrate and annealing; (2) application of PMMA protective layer and thermal tape; (3) detachment from the Si substrate; (4) Au stripping; (5) oxygen plasma treatment; (6) bonding to PDMS; and (7) removal of the thermal tape and PMMA.

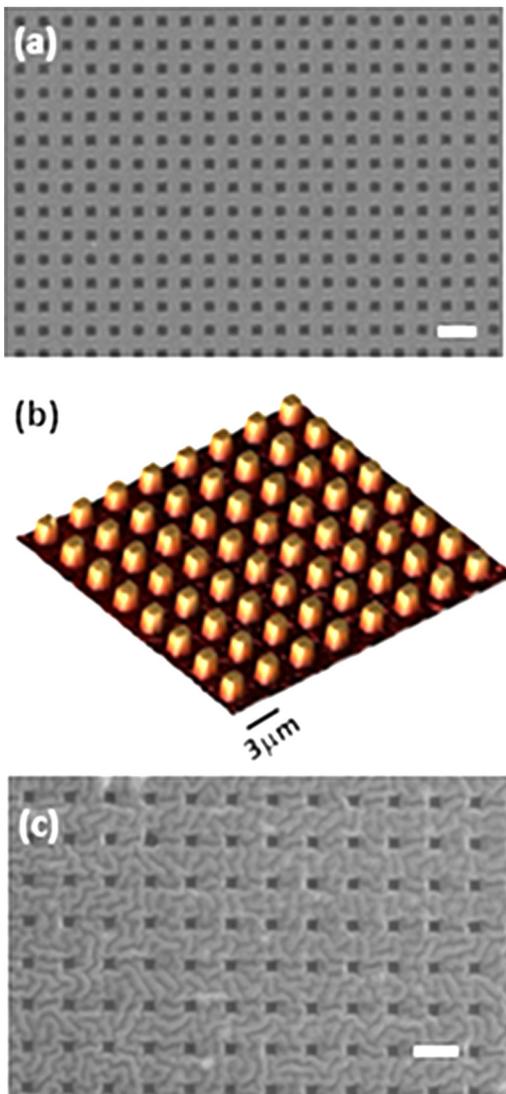


FIG. 3. (Color online) (a) SEM of the electron-beam, patterned HSQ on Si/Au substrate; (b) AFM of a SSRF mold; (c) NOA-61 UV adhesive imprinted with SSFR mold. Scale bar on (a) and (c): $3\ \mu\text{m}$. (a) SEM of the electron-beam, patterned HSQ on Si/Au substrate; (b) AFM of a SSRF mold; (c) NOA-61 UV adhesive imprinted with SSFR mold. Scale bar on (a) and (c): $3\ \mu\text{m}$.

propylene glycol monomethylether acetate,¹⁹ and mr-UVCur 21 (Nanonex). In both cases, we spin-coated the resist on Si substrate and brought it in contact with the mold, gently pressing it to evacuate air traps from the mold–substrate interface. Then, we exposed the resist through the mold with UV light for 5 min using MA-6 mask-aligner (Karl Suss MA-6, 365 nm) in the flood-exposure mode. Finally, the mold was mechanically peeled off. Figure 3(c) shows an SEM image of a typical pattern transferred from an SSRF mold to NOA-61. We speculate that the “wrinkles” in the resist are due to the shear forces caused by the resist shrinkage during UV curing. Another possible reason for the wrinkles is the effect of oxygen plasma on the PDMS surface.²⁰ However, plain PDMS surfaces treated in the same plasma process showed no change in their surface morphology; thus, our plasma treatment is unlikely the reason for the wrinkles. Nevertheless, the imprinted features look sharp and with no

visible buckling often typical for PDMS molds.⁸ Notably, these features are 1 micron in size. Future downscaling of the imprinted features to submicron regime will require addressing the wrinkles issue, presumably by finding a resist that will not change its surface morphology during the UV imprint.

It should be noted that in some cases, we observed missing features on SSRF molds after several cycles of imprint [Fig. 4(a)]. AFM imaging of the imprinted patterns revealed trapped relief features that had been ruptured from PDMS during the demolding [Fig. 4(b)]. The rupturing was most probably caused by sticking of the HSQ features to the resist. Therefore, to prevent the rupturing, SSRF relief features should be treated with a mold-release agent. The most commonly used mold-release agents for Si- or silica-based molds are fluorocarbon-terminated silane molecules that bind to the mold surface via silane groups, and form densely packed self-assembled monolayer (SAM). In particular, fluoro-silane SAMs are effective mold-release agents for silicon molds with HSQ relief features.^{14,17} At the same time, it is unclear whether the silanized SAMs applied onto Si-HSQ

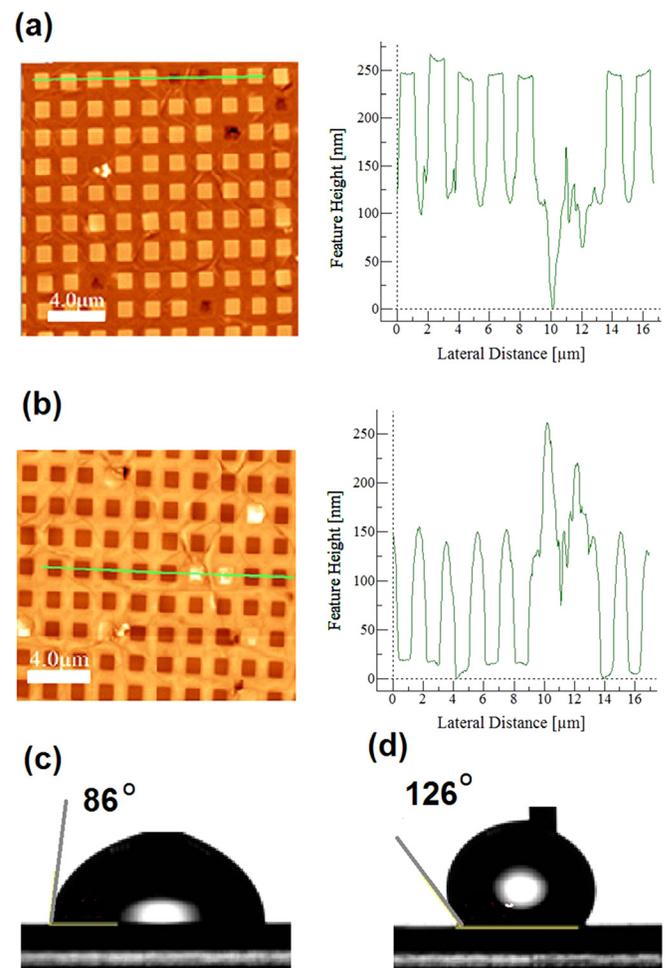


FIG. 4. (Color online) (a) AFM of a SSRF mold with detached relief features; (b) AFM of an imprinted resist with trapped relief features detached from the mold; and (c) water contact angle on bare HSQ; (d) water contact angle on HSQ treated with the mold-release agent. Scale bar on (a) and (b): $4\ \mu\text{m}$.

molds cover only Si surface or also HSQ features. In general, the applicability of silane SAM onto the HSQ surface has not been studied up today, to the best of our knowledge. Here, we again hypothesized that since silica and oxidized HSQ are chemically similar,²¹ fluorinated silane molecules would chemisorb on the HSQ surface as they do on silica. As the result, the surface energy of HSQ would be reduced, and HSQ adhesion to the imprint resist would be prevented.

To explore the possible formation of the fluorinated silane SAM, we applied a mold-release agent onto plain HSQ and characterized its wettability. For this, we first applied the HSQ film (~ 150 nm) onto the Si substrate by spin-coating, and cured it at 450°C for 1 h in N_2 atmosphere. The purpose of the curing was to obtain a network-structured HSQ, which is similar to that produced by electron-beam irradiation.²² The surface was treated with oxygen plasma, and immediately immersed into the solution of a commercial mold-release agent [NXT-110A, diluted in NXT-110B 1:50 v/v (Nanonex)] for 2 min inside a glovebox, following acetone rinsing. Advancing contact angles of water were measured on bare HSQ, as well as on HSQ treated with the mold-release agent, and found to be 86° and 126° , respectively. The latter angle is similar to those typically obtained for silicon molds coated with fluorinated mold release agents,²³ confirming that silane molecules chemisorb on HSQ surface. This finding paves a way to a new approach for the surface modification of spin-on-glass thin films, such as HSQ, via their surface silanization.

After we verified the formation of mold-release monolayer on the HSQ surface, we applied it to SSRF molds. The application procedure was kept the same as for the plane HSQ films. No visible damage or change in the PDMS surface was observed upon its immersion to the mold-release agent. The treated molds were used for the nanoimprint with high quality pattern transfer (Fig. 5).

In summary, we demonstrated a novel mold approach for soft lithography. Its soft substrate enables flexibility similar to those of standard soft molds, whereas its rigid relief

features enable pattern-transfer fidelity similar to those of rigid molds. Here, the direct electron-beam patterning of HSQ enables facile mold fabrication with precise control of the feature shape and geometry. As the part of the SSRF mold fabrication, we demonstrated for the first time the transfer of HSQ structured onto PDMS through silane bonding. We found that the surface of HSQ features must be functionalized with a mold-release agent to prevent their detachment from PDMS. For this purpose, we demonstrated for the first time that silane SAMs, commonly used for Si or silica surfaces, can effectively modify surface properties of HSQ as well. In this paper, we showed the pattern transfer of the features of micron size, aiming at demonstrating the general concept of SSRF mold. Yet, the resolution limits of this molding approach are still to be explored. Notably, HSQ is the electron-beam resist with the best possible resolution and minimal feature size below 10 nm.²⁴ We believe that in the future our approach will pave the way to soft flexible nanoimprint molds with sub-10 nm resolution impossible today. Such molds can be used in the future for the realization of novel nanosized devices and structures on nonplanar surfaces, with endless possible applications, including but not limited to plasmonics,²⁵ photovoltaics,²⁶ nanophotonics,²⁷ and nanomedicine.²⁸

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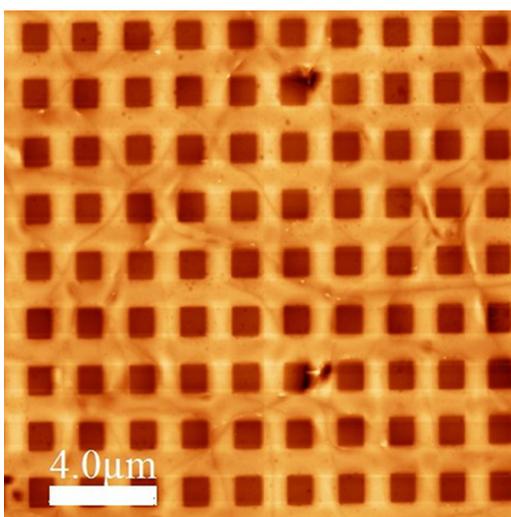


Fig. 5. (Color online) Resist film imprinted with SSRF mold treated in the mold-release agent. Scale bar: $4\ \mu\text{m}$.

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