Microelectronic Engineering 88 (2011) 2192–2195

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

# Fabrication of flexible mold for hybrid nanoimprint-soft lithography

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ARTICLE INFO

*Article history:*
Available online 14 January 2011

*Keywords:*
Sacrificial mold
Hybrid nanoimprint-soft lithography
PMGI
Electron beam lithography

ABSTRACT

We fabricated molds consisting of features in rigid UV-cured resist on an elastic poly(dimethylsiloxane) (PDMS) support for hybrid nanoimprint-soft lithography. The molds were duplicated through coating and curing a UV-curable resist onto a poly(dimethyl glutarimide) (PMGI) sacrificial mold that was subsequently dissolved using an aqueous basic solution that did not swell the PDMS support. Three methods are developed to fabricate the PMGI sacrificial mold: direct imprint into it at >200 °C, imprint into another polymer layer at sub-100 °C and then RIE transfer the pattern into PMGI, and direct writing by e-beam lithography. Using the hybrid nanoimprint-soft lithography process, we demonstrated pattern replication with sub-10 nm features size.



## 1. Introduction

Nanoimprint lithography (NIL) is a high throughput and high resolution molding process [1,2]. In typical thermal NIL, a hard mold containing nanoscale surface-relief features is pressed into a thermally softened polymer thin film at a controlled temperature and pressure, thereby duplicating the pattern into the polymer film after separation at low temperature. As thermal NIL is performed at high temperature and high pressure, precise alignment is difficult due to thermal expansion mismatch between the mold and the substrate [3]. As an alternative, UV-curing NIL is becoming more popular in recent years because it is carried out at room temperature and low pressure [4,5]. The process involves pressing a transparent mold into a low-viscosity photo-curable thin film spin-coated on the substrate and then solidifying the liquid film by UV exposure. Quartz is the most widely used mold material due to its ease of fabrication and UV transparency. However, quartz mold can only be used on a flat substrate; and an applied pressure, though much lower than that involved in thermal NIL, is still needed to assure an intimate contact between the rigid mold and substrate. In addition, vacuum is necessary to eliminate the trapped air that will cause un-patterned area due to the gap between the mold and substrate, as well as poisoning of the free-radical photoinitiator in typical UV-resist [6].

To pattern on non-flat surface, soft NIL mold using flexible poly(dimethylsiloxane) (PDMS) that can form intimate contact with curved surface is developed. However, due to its low Young's modulus, it is suitable only for patterning features with size larger than ~100 nm [7,8]. Bi-layer mold consisting patterns in a hard thermoplastic material such as PMMA coated on soft PDMS has been investigated [9], yet the PMMA is not compatible with mold release agent treatment necessary for repeatable and reliable imprinting. Hard PDMS on top of regular (soft) PDMS was also studied [10], but the modulus of the hard PDMS is still very low (by ~2 orders) compared to rigid polymers like PMMA.

Recently, Li et al. demonstrated the so-called hybrid nanoimprint-soft lithography [11] using molds in a rigid UV-cured resist on soft PDMS, which is capable of high resolution patterning in nitrogen ambient without the need of applied pressure or vacuum. For the fabrication of the molds from a master mold, one remaining critical issue is the surface energy of the master mold relative to the liquid UV resist: if it is too high, the resist will wet the mold and thus the de-molding will be difficult; if it is too low, the liquid UV resist cannot fully fill the trenches and holes in the master mold or even forms droplets on the master mold. The solution has been partial treatment (forming sub-monolayer) of the master mold by exposing it for reduced time in (1H,1H,2H,2H)-perfluorooctyltrichlorosilane (FOTS), but with narrow process window and low yield. A more robust solution would be to use a sacrificial master mold that the resist wets well, and dissolve the master mold after the resist is UV-cured. In this work, we propose to duplicate the mold from a sacrificial mold fabricated in poly(dimethyl

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doi:10.1016/j.mee.2010.12.107

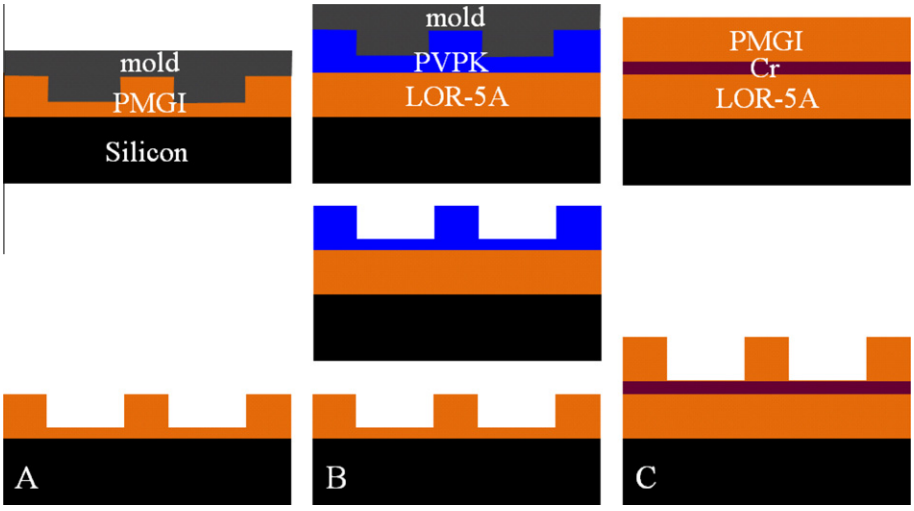


**Fig. 1.** Three methods for the fabrication of sacrificial mold in PMGI (or LOR-5A that is based on PMGI). (A) Direct imprint into PMGI at high temperature; (B) imprint into PVPK at reduced temperature, then RIE transfer the pattern into LOR-5A; (C) electron beam lithography using PMGI as positive resist.

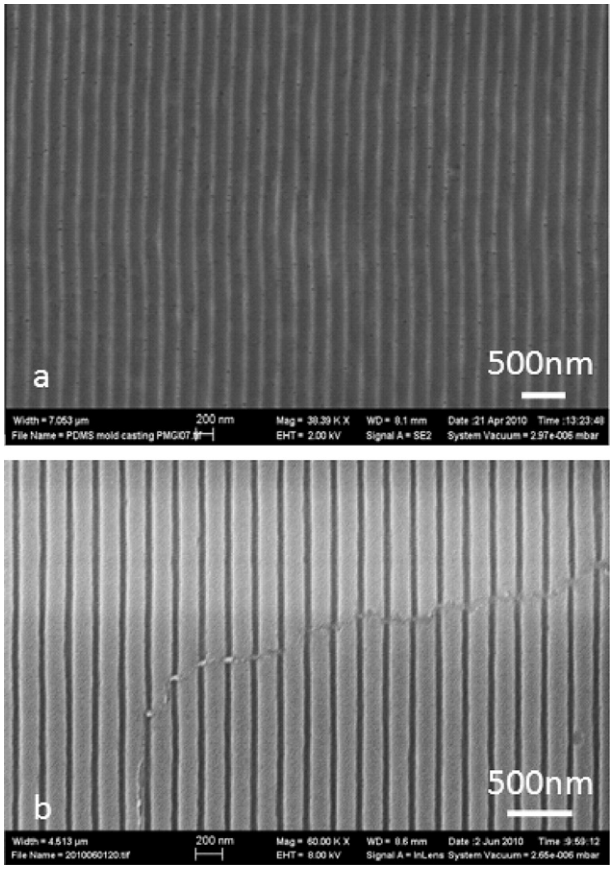


**Fig. 2.** (a) SEM image of a mold in UV-cured resist on PDMS duplicated from a PMGI sacrificial mold that was patterned using the method as shown in Fig. 1a; (b) SEM image of a grating imprinted into UV-curable resist using this mold.

glutarimide) (PMGI, MicroChem Corp.). The UV-curable resist wets well the PMGI and can thus fully fill the trenches and holes in it. After UV curing of the resist, PMGI can be dissolved by aqueous basic solution that, unlike most organic solvents, does not swell and deform the PDMS [12]. More importantly, PMGI is resistant to most solvents, so the pattern will not be affected (dissolved or swelled) by the solvent of the UV-curable resist.

## 2. Experiment

The fabrication process is similar to that detailed in Ref. [6], except that the master mold is fabricated in PMGI rather than in silicon. Briefly, to fabricate the mold for hybrid nanoimprint-soft lithography, the UV-curable resist was absorbed into the PDMS elastic support several times, as well as spin-coated onto the master mold. The absorbed elastic support was then placed against the resist-covered master mold and exposed to UV radiation. The PMGI was subsequently dissolved by AZ 300 developer that contains 0.22 M tetra-methyl ammonium hydroxide (TMAH). After $O_2$ plasma treatment, the mold was coated with FOTS anti-adhesion layer. For hybrid nanoimprint-soft lithography, a silicon substrate was first coated with PMMA as adhesion and liftoff layer, and then with UV-curable resist onto which the mold was laid down. Next, the mold-substrate stack was placed in a plastic bag that was flushed with nitrogen gas, and the stack was exposed to UV light of 365 nm wavelength until the resist is fully cured. Here we carried out the UV-curing in nitrogen environment only as a preventative measure, since in principle the UV-cured resist on PDMS should be able to inhibit oxygen in air from getting into the liquid resist layer through PDMS that is air permeable.

To fabricate the PMGI sacrificial master mold, we developed three methods as shown in Fig. 1. In the first method, we imprinted directly into a thick PMGI layer (spun three times to attain 200 nm thickness) with 1.2 MPa and 230 °C that is 41 °C higher than the glass transition temperature of PMGI. In the second method, to avoid the use of high temperature of >200 °C that is unachievable for some commercial imprint tools, we carried out imprint on poly(vinyl phenyl ketone) (PVPK) at 90 °C and 1.2 MPa. The pattern in PVPK is then transferred into the underlying 700 nm-thick LOR-5A (based on PMGI, MicroChem Corp.) using low-pressure oxygen RIE that etched LOR-5A faster than PVPK by approximately 2×. To further improve the adhesion of PMGI/LOR-5A to the silicon substrate, an anti-reflection coating (ARC, Brewer Science) may be coated and baked before spinning PMGI/LOR-5A. In the third method, as PMGI is a high resolution resist for electron beam lithography (EBL) [13], it can be patterned readily by EBL. A silicon wafer was first coated with a thick LOR-5A layer that dissolves faster than a thin PMGI layer by AZ 300, then 20 nm e-beam evaporated Cr conduction layer that also separates the LOR-5A and PMGI layer,

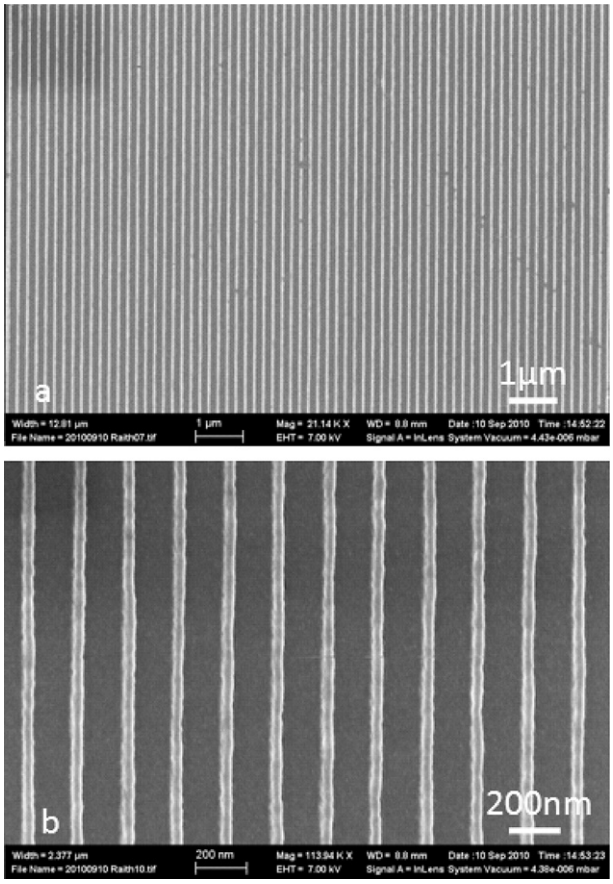


**Fig. 3.** SEM image of a grating imprinted into UV-curable resist using a mold in UV-cured resist on PDMS, which was duplicated from a PMGI sacrificial mold that was patterned using the method as shown in Fig. 1b. (a) Overview; (b) zoom-in image.

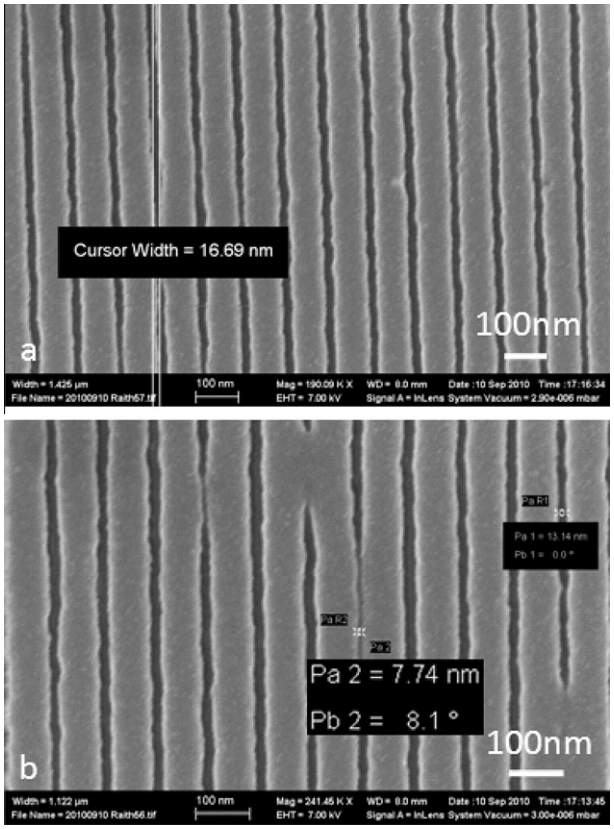


**Fig. 4.** SEM image of a grating imprinted into UV-curable resist using a mold duplicated from a PMGI sacrificial mold that was patterned using the method as shown in Fig. 1c. (a) Grating of 100 nm period with a trench-width ~17 nm; (b) a collapsed grating shows features down to 8 nm.

and finally 70 nm PMGI layer (thin PMGI layer reduces pattern collapse due to capillary force during developer drying). After exposure using Raith 150$^{TWO}$ at 30 kV acceleration voltage and 1.3 nA beam current, the pattern was developed using methyl isobutyl ketone (MIBK):2-propanol = 1:3 for 1 min.

## 3. Results and discussion

Fig. 2 shows the SEM image of a mold duplicated from PMGI sacrificial mold that was fabricated by the first method, and the SEM image of the 200 nm period grating in UV-curable resist imprinted using this mold. As can be seen, the line-width of the mold matches well with the trench-width of the imprinted resist. It was also found that the high imprint temperature of 230 °C made PMGI less soluble in the AZ 300 developer, so the dissolution of the sacrificial mold took hours. The imprint result using the 200 nm period grating mold duplicated from PMGI master mold that was fabricated by the second method is shown in Fig. 3. Due to the low imprint temperature of only 90 °C for PVPK, LOR-5A was not hardened and could be dissolved quickly by AZ 300.

Fig. 4 shows the 100 nm period grating imprinted in UV-curable resist using the mold duplicated from PMGI sacrificial mold that was fabricated by the third method. As can be seen, fine features of 17 nm-width can be created readily. Moreover, the narrow trenches of ~8 nm in PMGI (due to PMGI pattern collapse by capillary force during developer drying) were faithfully duplicated, indicating that features below 10 nm can be replicated. This is not possible for soft mold materials like PDMS.

Lastly, we want to point out that, despite the ultra-fine feature sizes and ease of fabrication (without the need of vacuum, applied pressure and thermal cycle), there are still some critical issues to be addressed before the hybrid nanoimprint-soft lithography can be employed for commercial application. One issue is the life-time of the anti-adhesion layer that may be degraded by the UV-curable resist [14]. Another issue is the crack of the brittle UV-cured resist on the soft PDMS, which is also a major concern for the hard PDMS/regular PDMS combination.

## 4. Conclusion

Hybrid nanoimprint-soft lithography is capable of high resolution patterning without the need of vacuum, applied pressure or high temperature. We fabricated molds consisting of features in rigid UV-cured resist on an elastic PDMS support through using a PMGI sacrificial master mold, which is a more robust process. PMGI was chosen because it can be dissolved using an aqueous basic solution that did not swell the PDMS support, and it is resistant to the solvent in the UV-curable resist. Three methods were developed to fabricate the PMGI sacrificial mold: direct imprint into it at >200 °C, imprint into another polymer layer at sub-100 °C and then RIE transfer the pattern into PMGI, and direct writing by e-beam lithography. The third method is the most flexible, but also the most time-consuming. Using the hybrid nanoimprint-soft lithography process, we demonstrated pattern replication with sub-10 nm features.

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