Polymer inking as a micro- and nanopatterning technique

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A polymer inking technique was developed to form micro- and nanopatterns on a substrate. In this process, a polymer thin film is spin coated on a patterned mold. After contacting the substrate at a suitable temperature and pressure, the polymer on the protruded surfaces of the mold is transferred to the substrate and a positive image of the mold is obtained. A selective surface treatment method has been developed to improve the edge smoothness of the inked pattern. During selective surface treatment, the protruded surfaces of the mold are first treated with a flat poly(dimethylsiloxane) stamp impregnated with a silane that has medium surface energy. The mold is then immersed into the solution of another silane with very low surface energy to treat the trenches of the mold. Because the surface energy of the sidewalls is lower than that on the protrusions, polymer dewetting from the sidewalls is promoted, which makes the polymer film discontinuous along the edges of patterns. Therefore, inked polymer patterns from the protrusions of the mold show very smooth edges and smaller dimensions compared to that of the mold. The dimension change of the inked pattern is dependent on the selection of polymer materials. It was found that patterns inked from poly(carbonate) showed larger dimension shrinkage (∼75%) compared to that from poly(methyl methacrylate) (∼30%). This offers a viable approach to obtain predictable submicrometer features using a mold with much larger feature sizes.
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I. INTRODUCTION

In recent years, a number of new patterning techniques have been developed to overcome the resolution limit of photolithography. Among these methods, microcontact printing (μCP)[1–3] and nanoimprint lithography (NIL)[4,5] are two high throughput and low cost patterning techniques. Microcontact printing utilizes a soft poly(dimethylsiloxane) (PDMS) mold to print self-assembled monolayer (SAM) patterns using appropriate small molecule inks. On the other hand, NIL forms thickness contrast in a thermoplastic polymer film by deforming the polymer under high pressure at an elevated temperature. Because significant polymer flow is required during imprinting, relatively high temperatures and pressures are needed in the NIL process.[6]

We have developed an alternative patterning technique called polymer inking. This process is similar to the stamping process in μCP, in which the ink on the protrusions of the stamp is transferred to the substrate. However, different from small molecule inks, a polymer is used as the ink in this process, and the polymer ink is transferred to the substrate at an elevated temperature and pressure. Figure 1 shows the idealized polymer inking process. A thin polymer film is first applied to the patterned hard mold, usually by spin coating. The polymer coated mold is then brought into contact with the substrate and suitable temperature and pressure are applied. Because the protruded surfaces of the mold have been treated to have a lower surface energy than that of the substrate, the polymer film on the protrusion of the mold is transferred to the substrate upon mold separation. This polymer inking technique has several important advantages compared to other high throughput patterning techniques, such as μCP and NIL. The inking polymer can be chosen to have higher dry etch resistance than that of a SAM layer. In addition, because of the absence of large scale polymer flow during inking, much lower temperatures than those required by NIL can be used. Finally, while NIL requires an additional etching step to remove the residual film in the imprinted region,[4,5,7] only the material on the protrusions of the mold is

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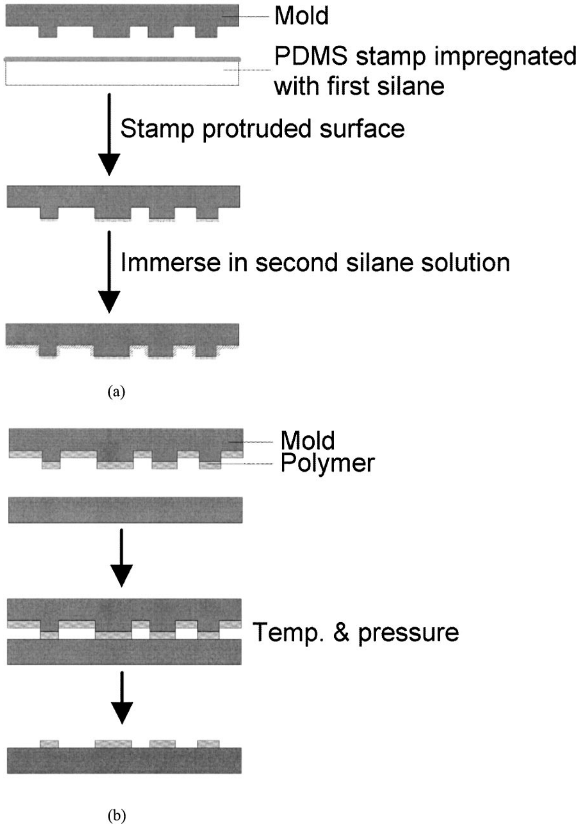

FIG. 1. Schematic illustration of the inking process with selective surface treatment of a patterned mold: (a) selective surface treatment and (b) polymer inking process.

transferred to the substrate in polymer inking, which simplifies subsequent pattern transfer. We have systematically studied the process of polymer inking, with the emphasis on material selection and surface treatment for obtaining optimal results.

II. INKING PROCESS WITH SELECTIVE SURFACE TREATMENT

We have demonstrated the concept of polymer inking in a previous publication, in which a reversal imprinting method was described.[8,9] During reversal imprinting, a polymer film is spin coated onto a patterned mold and then transferred to the substrate at suitable temperature and pressure. When the mold surface is not planarized after spin coating, the polymer film on the protruded surfaces of the mold can be inked to the substrate. However, because a polymer film has continuous coverage over a patterned mold after spin coating, the inked patterns usually display ragged edges due to rupture of the polymer film along the feature sidewalls. Although this problem can be alleviated by using a deep mold coated with a relatively thin coating,[8,9] improvement of the technique is required to reduce edge roughness.

We have recently developed a selective surface treatment to improve the edge smoothness of the inked patterns. In a selective surface treatment, the protruded surfaces and trenches of the mold are treated to have different surface properties as shown in Fig. 1. The purpose of such a treatment is to promote polymer dewetting near the sidewalls of a feature. To achieve this, the protruded surfaces of the mold are first treated by a flat PDMS stamp impregnated with a silane that has medium surface energy. The PDMS stamping of silane leaves a SAM film on the protruded surfaces of a Si or SiO_2 mold.[10,11] After stamping, the mold is immersed into the solution of another silane with very low surface energy. If the reactive sites on protruded surfaces have been completely silanized after PDMS stamping, the second silane should react only with the recessed area during immersion. Different surface properties are thus achieved for the protruded surfaces and trenches. A schematic of this selective surface treatment process is shown in Fig. 1(a). The low surface energy of the trenches causes a polymer thin film to dewet easily from the sidewalls when heated to above the glass transition temperature (T_g) while the film on the protrusions dewets less severely due to the relatively high surface energy. Therefore, the polymer film becomes discontinuous along the edges of the patterns and can be inked to the substrate with smooth edges.

III. EXPERIMENT

The molds used here are made in 2 μm thick SiO_2 on a Si wafer and are patterned by photolithography. The flat PDMS stamps for surface treatment were formed by curing Sylgard® 184 siloxane prepolymer in a plastic Petri dish. In a typical selective surface treatment experiment, the flat PDMS stamp is immersed in a 20 mM toluene solution of the appropriate silane for 15–30 s. After it is removed from the solution and dried under a stream of nitrogen, the stamp is brought into contact with the mold for 2 min. The elastomeric stamp intimately contacts the mold without any need of external pressure. After separation from the stamp, the mold is rinsed, dried, and immersed into the solution of 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS) dissolved in heptane (~ 10 mM). The FDTS reacts with recessed surfaces of the mold and forms a SAM layer with extremely low surface energy.[12]

After surface treatment, the mold is spin coated with a polymer solution. Two polymers are used in this study, poly(methyl methacrylate) (PMMA) ($M_w = 15$ K, $T_g = 105\,°C$) and polycarbonate (PC) ($M_w = 18$ K, $T_g = 150\,°C$). A concentration of 4.5% PMMA and 1% PC in their respective solvents is used to obtain a film thickness of 100–120 nm. The coated mold is then baked at an appropriate temperature to remove residual solvent or to induce controlled dewetting of the polymer film. Finally, the film on the mold is inked to a flat Si wafer at a temperature close to T_g under 5 MPa pressure. The topography of a spin coated mold and the inked patterns are studied by contact mode atomic force microscope (AFM) or scanning electron microscope (SEM).

TABLE I. Surface properties of Si wafers treated with different silanes.

Sample information	Contact angle (°)		Surface energy (mJ/m^2)
	Water	Diiodomethane	
O_2 plasma cleaned wafer	26.9	47.7	65.2
PETS stamp	108.1	69.9	23.4
PETS stamp, then FDTS solution	106.2	72.5	21.6
MOPTS stamp	73.6	58.7	34.6
MOPTS stamp, then FDTS solution	92.8	38.7	30.8
FDTS solution	103.0	99.8	11.7

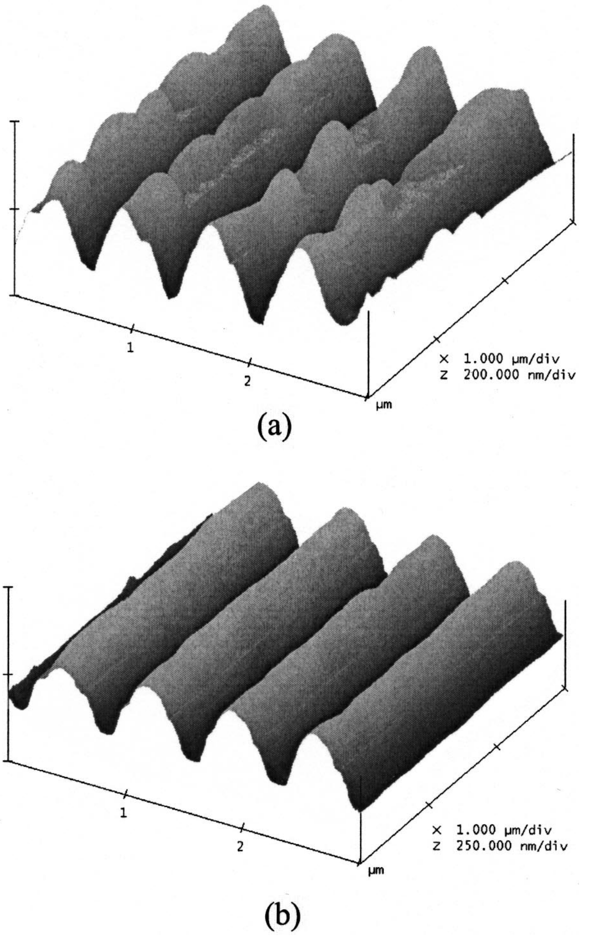

FIG. 2. Dewetting behavior of PMMA film after annealing at 130 °C for 5 min on a 700 nm period grating mold with: (a) FDTS solution treatment and (b) PETS/FDTS selective treatment.

IV. RESULTS AND DISCUSSION

A. Controlled polymer dewetting after selective surface treatment on mold

In our selective surface treatment, the trenches of the mold are treated with FDTS, which forms a SAM film with very low surface energy. The protruded surfaces have been previously treated with a silane with medium surface energy, so that a polymer thin film dewets more easily from the trench surfaces than on protrusions. Two silanes are used to treat the protruded surfaces in this study, phenethyltrichlorosilane (PETS) and methacryloxypropyltrichlorosilane (MOPTS). The contact angle and surface energy of Si wafers treated with different silanes are listed in Table I. The surface energy of a solid is the sum of the nondispersive and dispersive surface energy, which can be calculated using the measured contact angles in two different liquids.[13] As one can see, after the Si surface has been treated by PDMS stamping with PETS or MOPTS, the surface energy reduces. With the additional FDTS solution treatment, slight changes of the surface energy were measured, indicating a possibility of the insertion of FDTS into the loose-packed silane sites formed in the stamping process. However, rather different surface properties are still obtained on the protrusions and inside the trenches after selective surface treatment.

Figures 2(a) and 2(b) demonstrate PMMA dewetting on a patterned mold, in which the mold has been treated with surfactants. A 700 nm period grating mold with a depth of 350 nm is spin coated with a 4.5% PMMA solution in toluene and then annealed at 130 °C for 5 min. The annealing process usually assists polymer dewetting along sidewalls. In Fig. 2(a), the mold is treated with FDTS only. Because of the low surface energy of FDTS treated surface, the PMMA film dewets on the protruded surfaces and breaks up into elongated droplets. In contrast, the mold in Fig. 2(b) has been given selective PETS/FDTS treatment. As the surface energy of the sidewalls is very low, the film dewets near the edges of the protrusions. However, because of the higher surface energy of the PETS treated top surface, the film remains continuous on the protrusions. Apparently, due to dewetting of the polymer film near feature edges, the polymer dimensions on the mold are smaller than those of the mold. This is because when a thin polymer film is annealed at a temperature above T_g, the polymer film gradually relaxes to a lower free energy state, which is determined by the surface properties of the polymer and substrate and the entropic state of the polymer. When the thickness of the PMMA film is comparable to the lateral dimensions of the submicrometer feature, the corresponding dewetted polymer dimensions are smaller (~10%) than those of the mold as shown in Fig. 2(b). Further investigation of the PMMA dewetting on protrusions of micrometer-sized mold shows that such pattern shrinkage after annealing starts from the edges of the features, and the resulting dimension change is around 20%.

The AFM scan in Fig. 3 shows the profiles of dewetted PMMA on a mold with protruded circles (with selective MOPTS/FDTS treatment). A raised rim surrounds the PMMA island on top of the protrusions. Similar behavior is also observed on PETS/FDTS treated molds. The raised rim is likely formed by material retracting from the edge of the feature. During annealing at 130 °C, the thin PMMA film on the sidewalls starts to dewet first. The film retracts toward both the bottom of the trench and the protruded surface. Because of the higher energy of the protruded surfaces, the

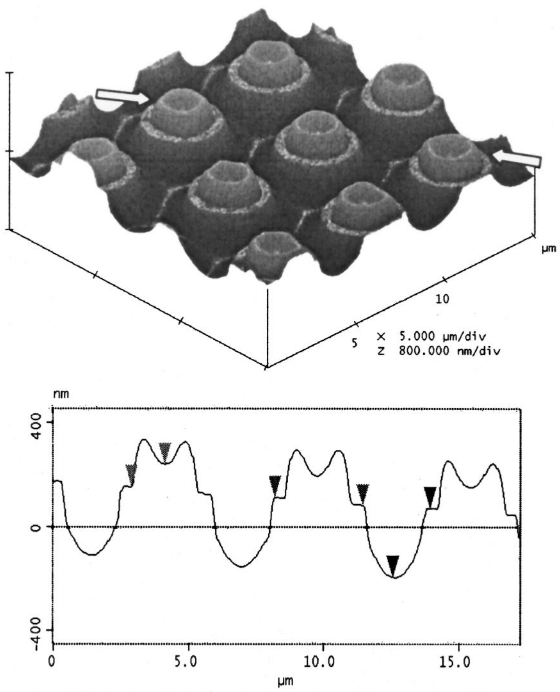

FIG. 3. Dewetting behavior of PMMA film after annealing at 130 °C for 5 min on a 450 nm deep mold with MOPTS/FDTS selective treatment.

PMMA at the interface with the protrusions is immobilized. The retracted film thus piles up near the edge of the feature until the least interaction potential between PMMA and the surface is reached. Dewetting with this mechanism causes the film to shrink into a plateau surrounded with a rim and a pattern dimension change of ∼20% before inking.

When a 1% PC solution in chloroform is spin coated onto selective PETS/FDTS treated micrometer-sized molds, continuous PC film covers the 500 nm deep mold. When a relatively deep mold is used, however, isolated polymer islands are formed on the protrusions directly after spin coating. Figure 4 compares the AFM scans of PC coated 500 and 720 nm deep molds. Isolated PC islands form on the protruded surfaces of the 720 nm deep mold. When a deep mold is coated with a polymer solution, the coating thickness on the sidewalls is likely very small if it exists at all. Spontaneous dewetting could occur on the sidewalls during spin coating, resulting in discontinuous coverage as shown in Fig. 4(b).

In contrast to the dewetting of PMMA during annealing, the PC films on protrusions not only dewet along the feature edges during annealing (170 °C), but also retract over the whole area of protruded surfaces until a low energy state is reached. Dewetting with this mechanism causes the film to shrink into a dome and a large pattern dimension change of ∼60% before inking.

B. Inking after controlled dewetting on selective surface treated molds

The polymer features in Fig. 2(b) can be easily transferred to a Si wafer at 105 °C and 5 MPa. Figure 5(a) is the SEM image of the transferred PMMA grating pattern. The inked

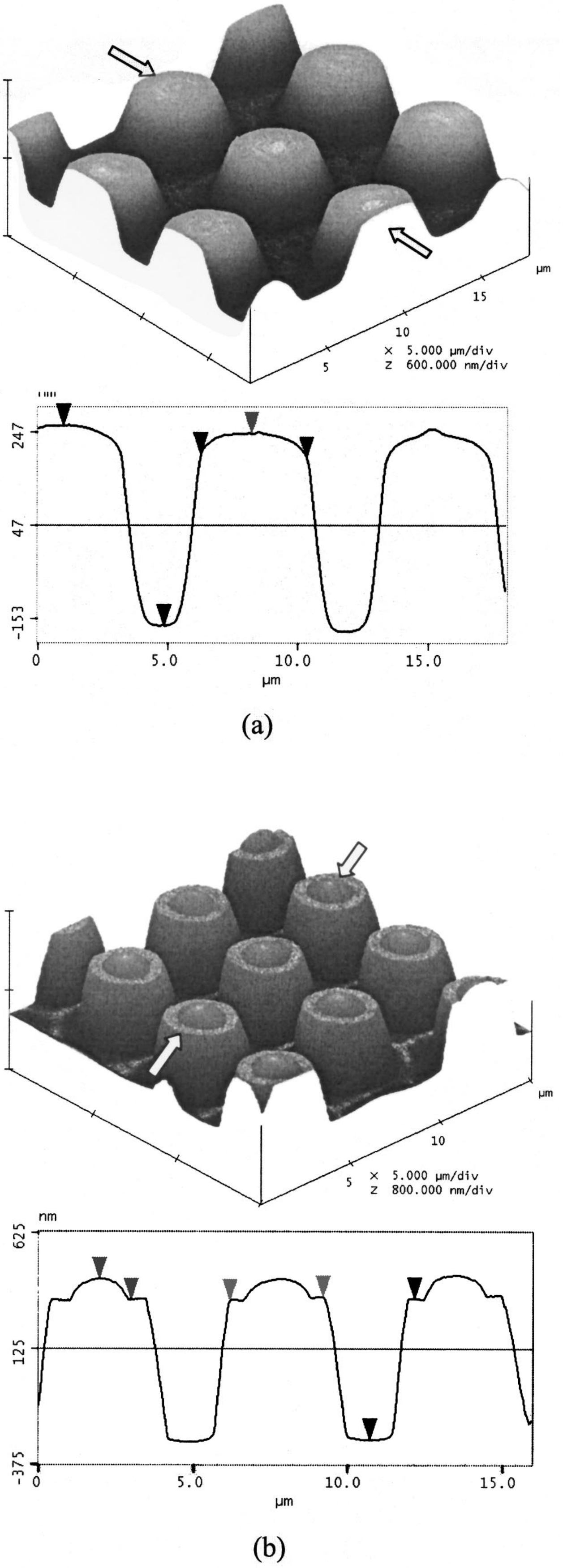

FIG. 4. PC coverage on: (a) 500 nm and (b) 720 nm deep molds.

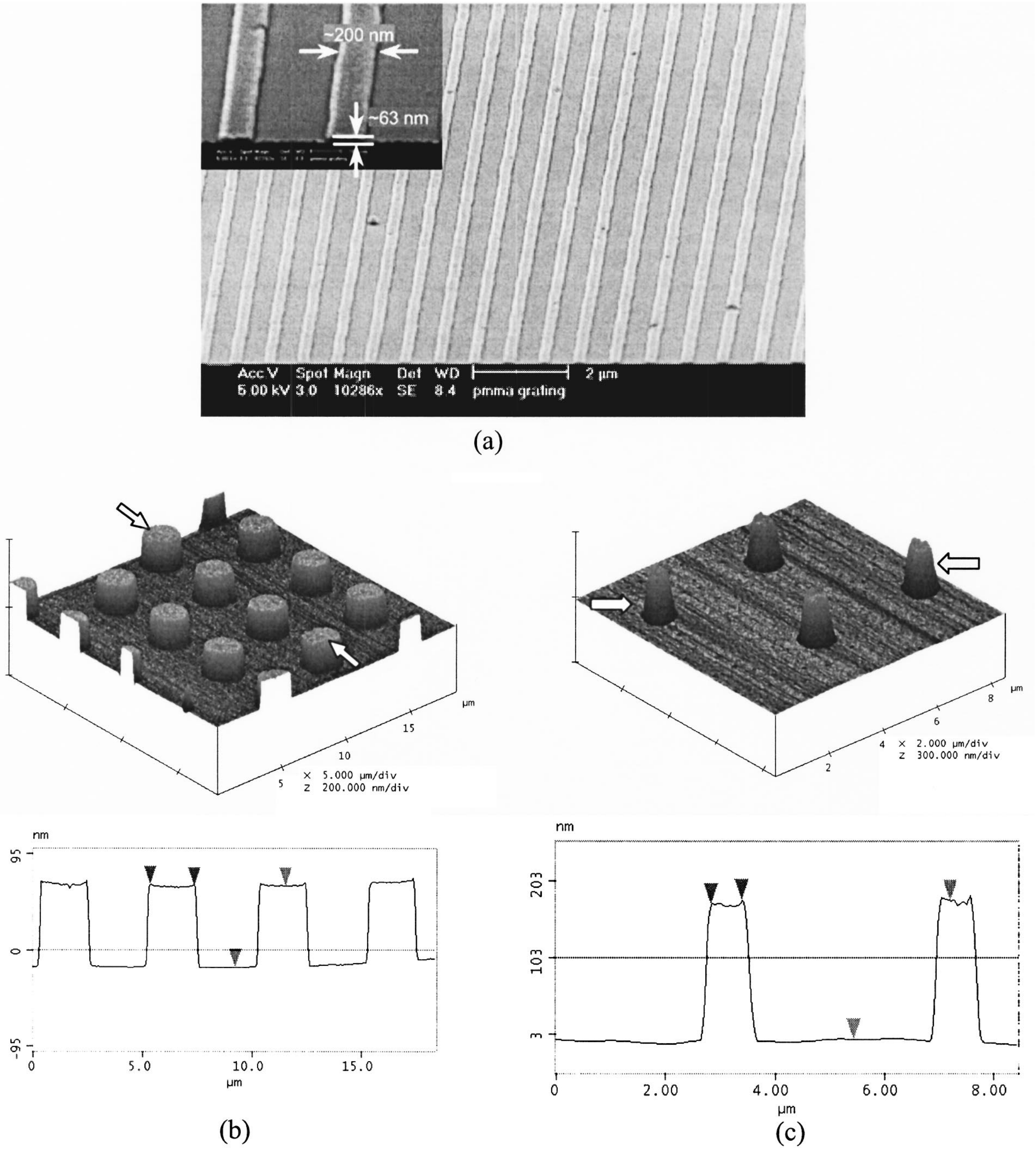

FIG. 5. (a) PMMA grating pattern formed by inking the PMMA film in Fig. 2(b) onto a Si wafer at 105 °C, 5 MPa; (b) PMMA pattern formed by inking the PMMA film in Fig. 3 onto a Si wafer at 115 °C, 5 MPa; and (c) submicrometer PC pattern formed by inking the PC coated mold with 2 μm protruded circles at 150 °C, 5 MPa. The PC was inked without annealing.

PMMA lines have straight and smooth edges. While the PMMA film on the protrusions of the mold as shown in Fig. 2(b) has a very slight variation in polymer thickness, such variations are significantly reduced after inking under elevated pressure. The inked PMMA lines are 200 nm in width compared to the 350 nm lines in the mold. The micrometer scale PMMA islands in Fig. 3 can also be transferred to the substrate at 115 °C under elevated pressure of 5 MPa. An inking temperature slightly higher than T_g is required to flatten the raised rim and ensure good contact between the PMMA film and substrate. Figure 5(b) is an AFM scan of the transferred pattern. Smooth feature edges are obtained with controllable changes in the dimensions of the features. The inked patterns are 2 μm in diameter compared to the 3 μm protruded circles in the mold.

Compared to PMMA inking at 105–110 °C, PC is inked at a temperature of 150 °C and shows easier dewetting during the imprinting process. Thus, the polymer pattern can also be inked without the need for annealing before inking. Figure 5(c) presents such an example. Polycarbonate dots with a diameter of 500–600 nm can be obtained using a mold with 2 μm diam protruded circles without annealing before inking. Very similar pattern profiles and dimensions are obtained for the inked PC with the annealing process. This indicates that despite the high pressure of 5 MPa applied during inking, the material on protrusions of the mold can still dewet and shrink for unannealed polymer films. The significant dimension shrinkage of inked PC also offers a viable method to obtain submicrometer features using a mold with much larger feature sizes.

Since the surface energy of PMMA (33–41 mJ/m^2)[14] is in a very close range to that of PC (39 or 45 mJ/m^2),[13] it is useful to speculate on why the two polymers exhibit different behaviors. A plausible reason is that the entanglement density in PC is higher than that in PMMA. Entanglement density is a measure of the number of entanglement points per unit volume. Critical entanglement molecular weight characterizes the minimum distance between two entanglement points. The smaller the critical entanglement molecular weight, the more entanglement points in a unit volume, and the higher the entanglement density. Though the polymers are similar in molecular weight, their entanglement molecular weights are quite different. For PC it is 1300, while for PMMA it is 10 000.[15] Thus the PC used has a more entangled network which would cause it to retract more strongly from the molecular orientation produced by the spin coating process. This reason as well as other factors must be studied in order to gain better dimensional and geometric control over the process.

V. SUMMARY

A polymer inking technique is developed in which a thermoplastic polymer is used as the ink. In polymer inking, a polymer film is first spin coated onto a patterned hard mold. By contacting the mold and substrate at a suitable temperature and pressure, the polymer film on the protruded surfaces of the mold is transferred to the substrate, forming a positive image of the mold. A selective surface treatment strategy is developed to improve edge smoothness of the inked pattern. In this method, the protruded surfaces are treated with a silane with medium surface energy, while the trenches are treated to have very low surface energy. This difference in surface energies promotes polymer dewetting from the sidewalls. This selective surface treatment technique is very versatile since the interaction between the mold and polymer ink can be fine tuned by choosing different silanes and polymers. Several examples of polymer inking using various selective surface treatments and polymer inks are demonstrated. It was found that patterns inked from poly(carbonate) showed larger dimension shrinkage (~75%) compared to that from poly(methyl methacrylate) (~30%). This offers a viable approach to obtain submicrometer features using a mold with much larger feature sizes.

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