Nanoimprinting over topography and multilayer three-dimensional printing

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We have developed a simple imprinting technique that allows patterning over a nonflat substrate without the need for planarization. In this process, a polymer film is spin coated onto the mold and then transferred to a patterned substrate by imprinting. By selecting polymers with different mechanical properties, either suspended structures over wide gaps or supported patterns on raised features of the substrate can be obtained with high uniformity. It is found that imprinting at a temperature well above the glass transition temperature (T_g) of the polymer causes the thin residue film between features to dewet from the mold, which can greatly simplify the subsequent pattern transfer process. Multilayer three-dimensional polymer structures have also been successfully fabricated using this new imprinting method. The yield and dimensional stability in the multilayer structure can both be improved when polymers with progressively lower T_g are used for different layers. Compared to existing techniques for patterning on nonflat substrates, the current method has a number of advantages, including simplicity, versatility, high resolution, and low pattern distortion.
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I. INTRODUCTION

In recent years, the requirement for continuous device miniaturization in microelectronics has stimulated the development of new nanofabrication techniques. At the same time, applications in electronics, optics, microelectromechanical systems, and biomedical and tissue engineering also demand the ability to pattern over contoured surfaces and to form three-dimensional structures.[1–4] Among a number of novel lithography methods developed recently, nanoimprint lithography (NIL) is a high-resolution, high-throughput, and low-cost patterning technique.[5–8] However, one major obstacle for fabricating complex three-dimensional (3D) structures using NIL is the difficulty to imprint on nonflat surfaces. Previous efforts to solve this problem often involve multilayer resist approaches with a thick polymer planarization layer on top of the nonflat substrate.[9,10] These techniques not only require complex processes with multiple steps, but also entail deep etching steps to etch through the thick planarization layer, which often degrades the resolution and fidelity of the pattern.

We have developed a simple imprinting method that allows patterning over a nonflat surface without the need for planarization. To achieve this, a polymer layer is first spun on a surfactant-treated mold and the polymer pattern on the mold is then directly transferred to a prepatterned substrate. We found that for a given polymer, the imprint result strongly depends on the dimensions of the substrate pattern, especially the distance between features. By controlling the mechanical properties of the polymer materials used, we can obtain two different imprinting behaviors. Furthermore, multilayer, three-dimensional polymer structures can also be conveniently fabricated using this method. Compared to other methods for patterning on nonflat surfaces,[1,9,11,12] the current method has the advantages of a very simple process, high resolution, and low distortion.

II. EXPERIMENT

The mold used for imprinting is a 350-nm-deep grating with a 700 nm period in SiO_2. To assist polymer transfer to the substrate, the mold was treated by a surfactant, 1H,1H,2H,2H-perfluorodecyl-trichlorosilane, which results in a very low-energy surface.[13] Before imprinting, the mold was first spin coated with a polymer solution. The solution concentration is chosen so that the film thickness after spin coating a flat wafer is between 200 and 300 nm. When the

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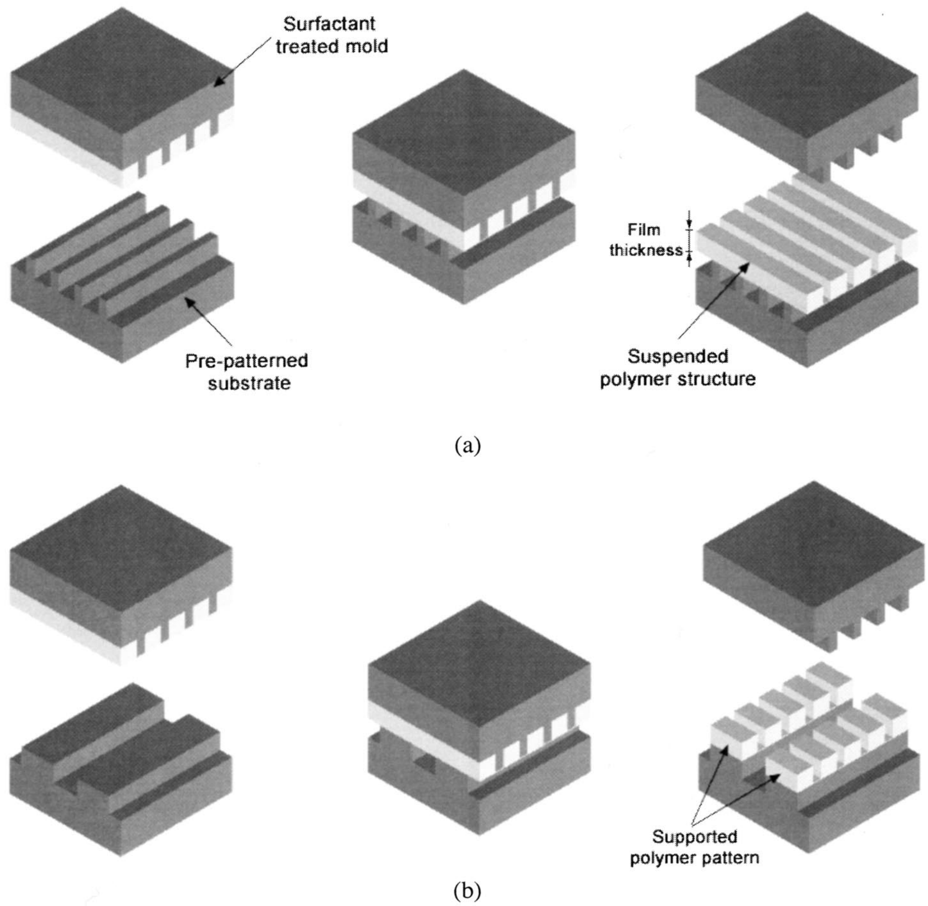


FIG. 1. Schematics of imprinting over topography. Two situations can occur depending on the pattern spacing on the substrate: (a) polymer pattern is imprinted across the raised features on the substrate; (b) polymer pattern is only transferred over the protruded surfaces.

mold is coated with such a film, the surface is significantly planarized. Atomic force microscopy studies indicate that the surface profile of the coated mold consists of oscillating waves with the maximum step height being much less than 100 nm. After spin coating, the mold is soft baked at 80 °C for 5 min to remove residual solvent. The coated mold is then pressed against a prepatterned SiO_2 substrate in a preheated hydraulic press. The typical imprinting pressure is 5 MPa. Cooling is initiated after 5 min and the pressure is sustained until the temperature has decreased to below the glass transition temperature (T_g) of the polymer. The mold is then separated from the patterned substrate, leaving polymer patterns on top of the protrusions on the substrate. The substrates used here have line patterns with various linewidths and spacings ranging from 350 nm to 50 μm.

In the fabrication of multilayer polymer structures, the first layer was formed in a polymer by NIL on a flat Si wafer at a temperature well above T_g. The second layer was then imprinted using the aforementioned method at a temperature below T_g of the first polymer layer. The same process was repeated for the third layer and beyond. In this procedure, when imprinting is done at a temperature close to T_g, a thin residual polymer layer is usually formed in the recessed areas of the imprinted pattern. This residual layer can be removed by O_2 reactive ion etching (RIE) before the next layer is imprinted.

III. RESULT

A. Reversal imprinting onto a prepatterned substrate

Figure 1 illustrates the fabrication process for imprinting over topographies on the substrate. There is no planarization step involved in this process. Instead, a polymer film that is coated on a surfactant-treated mold is directly transferred to the prepatterned substrate under suitable pressure and temperature. Based on the results of our previous study on surface planarization after spin coating,[14] the polymer coating thickness was chosen so that the mold is considerably planarized after spin coating and the entire polymer layer on the mold is transferred onto the prepatterned substrate without significant polymer flow. Furthermore, since little polymer flow is required during imprinting, reliable pattern transfer can be achieved at temperatures as low as 30 °C below T_g. Even at a temperature slightly below T_g, the polymer deformation under the imprinting pressure is sufficient to result in a good contact between the coated mold and the substrate.

When a polymer layer is imprinted onto a patterned substrate with various feature sizes, the imprinting result strongly depends on the ratio between the film thickness being imprinted (namely, the height of the feature being imprinted plus any residue thickness) and the distance between features on the substrate. The imprinting result also depends on the mechanical properties of the polymers used. If a rela-

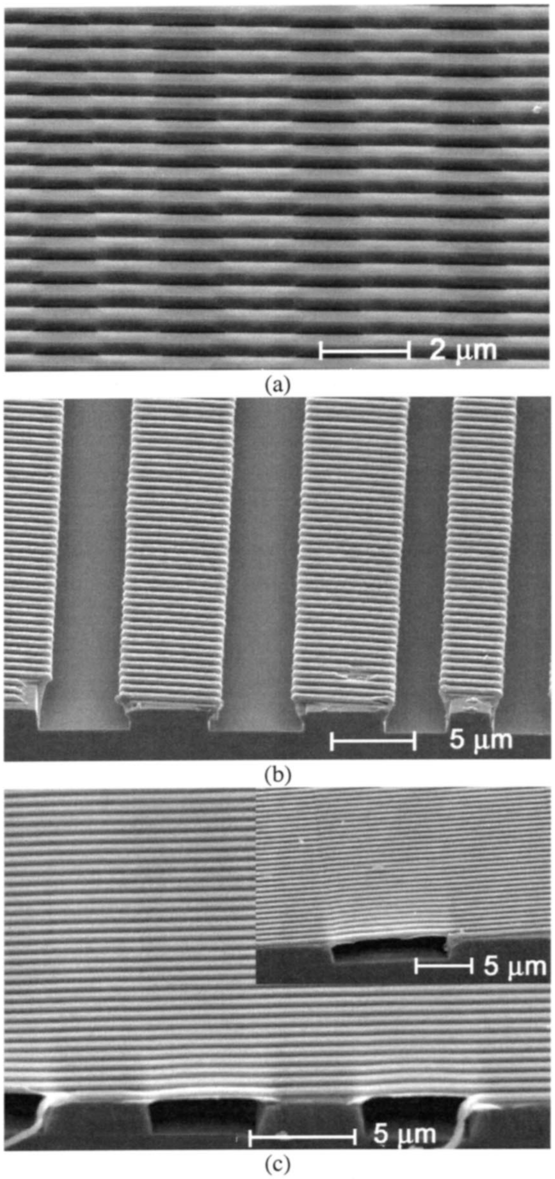


FIG. 2. Imprinting of 700 nm period grating on 2-μm-deep SiO_2 line patterns with various linewidths and spacings. (a) PMMA pattern imprinted across lines with spacings of less than 2 μm. (b) PMMA pattern imprinted on the protruded surfaces for line spacing of greater than 3 μm. (c) PC pattern imprinted across 5 μm gaps, and 10 μm gaps as shown in the inset.

tively brittle polymer is used, two situations may occur after imprinting, as illustrated in Fig. 1. When the distance between features on the substrate is smaller than or comparable to the thickness of the film being transferred, the polymer film can be imprinted across the raised features on the substrate, as shown in Fig. 1(a). In this situation, the pattern is transferred over the entire imprint area and suspended polymer patterns are achieved. On the other hand, when the features on the substrate are separated by a distance much larger than the film thickness on the mold, the suspended part of the film will break during mold separation, leaving the polymer pattern only on the protruded surfaces.

Figures 2(a) and 2(b) demonstrate the imprinted pattern in poly(methyl methacrylate) (PMMA) ($M_w = 15\,000$, $T_g = 105\,°C$), which is a relatively brittle polymer (tensile elongation at break$=2\%$), over SiO_2 lines with different widths and spacings. The imprinting was performed at 145 °C with 5 MPa pressure. Figure 2(a) shows that when the line spacing is below 2 μm, the 700 nm period grating pattern can be uniformly imprinted over the SiO_2 lines. On the other hand, for line spacings above 3 μm, the grating pattern is only formed on top of the protrusions on the substrate. The suspended part of the polymer film adheres to the mold during mold separation. For PMMA, we found that the maximum spacing that a film can be imprinted across is on the order of four times the film thickness. Previously, patterning much larger features over patterned substrates has been attempted by microtransfer molding with a soft elastomer mold using another brittle polymer, epoxy.[11] Similar limitations in the maximum span of a suspended structure were observed. As shown in Fig. 2(b), the breakage near the line edge is very sharp and uniform. Thus, the situation in Figs. 1(b) and 2(b) offers an alternative patterning route in which only the protruded surfaces on a substrate are patterned. This method may find applications in optical and biomedical systems.[12,15]

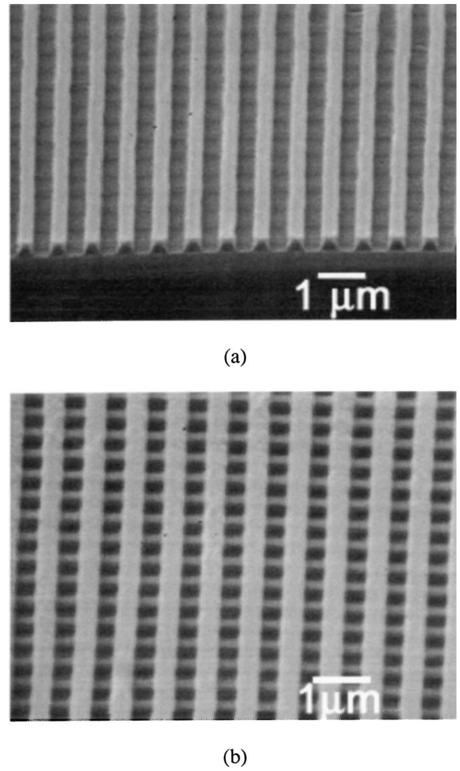
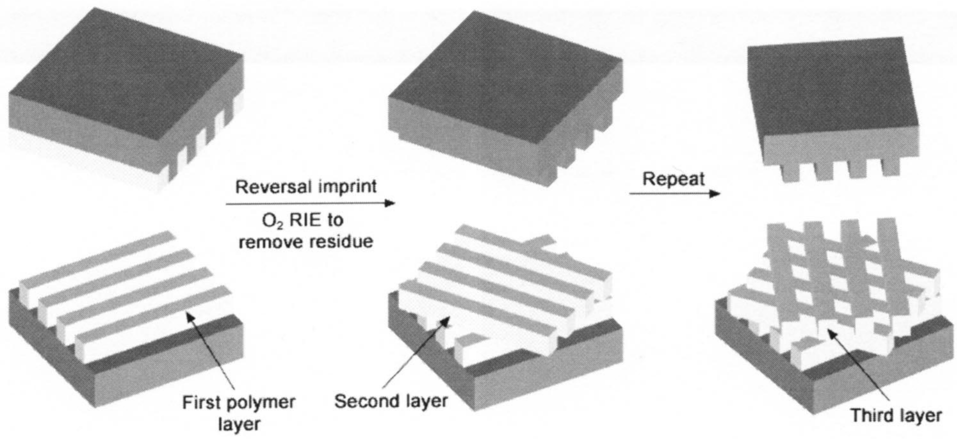
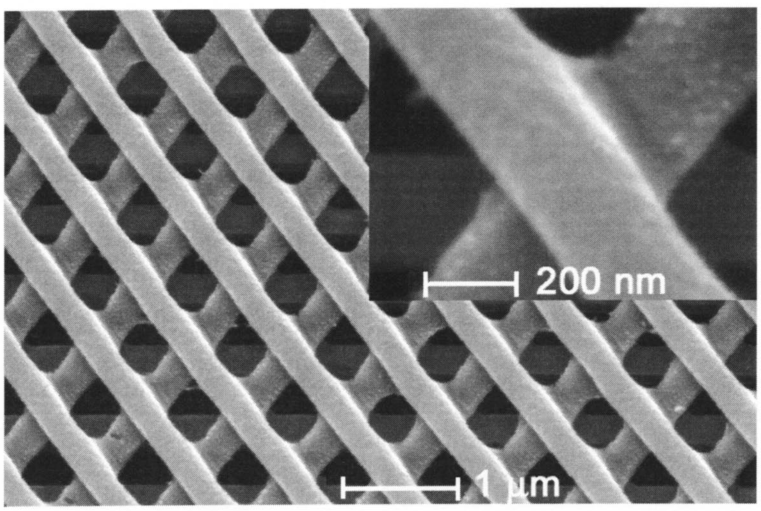


FIG. 3. Imprint of 700 nm period grating in PMMA on another 700 nm period grating in SiO_2. (a) Imprinting at 90 °C, continuous residue is formed between lines; (b) imprinting at 175 °C, dewetting on the mold removes the residue during imprinting.

The maximum width of the suspended structure that can be fabricated using the current technique is determined by the mechanical strength of the polymer. While a brittle polymer can only be imprinted across relatively narrow gaps, the use of a tough material can dramatically extend the scope of the feasible structures. Figure 2(c) demonstrates the effect of polymer selection on the imprint result. In Fig. 2(c), polycar-



(a)



(b)

FIG. 4. (a) Schematic illustration of the imprinting of multilayer polymer structures. (b) Three-layer polymer structure fabricated using the scheme in (a). From the top to the bottom, the polymers used are PBA, PMMA, and PC. After imprinting of each layer, the residue film was removed by O_2 RIE.

bonate (PC) ($M_w = 18\,200$ and $T_g = 150\,°C$), an extremely tough polymer with relatively high ductility (tensile elongation at break$>$110%), was coated on the mold and imprinted at 160 °C under 5 MPa pressure. It was found that the PC film could be imprinted across spacings that are much wider than the thickness of the film. However, because of the extremely low film thickness, the suspended film over wide gaps often sags or deforms if the mold is separated from the substrate at room temperature. We found that if the system is quenched to a low temperature, e.g., liquid nitrogen, before mold separation, the problem of sagging can be minimized. The inset in Fig. 2(c) indicates that the 700 nm period grating pattern can be imprinted across 10 μm gaps with high uniformity—this is more than 20 times the film thickness.

The drastically different imprint behaviors of PMMA and PC demonstrate the importance of material selection in process design. PMMA and PC are only two examples in the wide spectrum of polymer mechanical properties. Because of the large variety of available polymers, the current technique can be utilized to fabricate a wide variety of suspended and supported structures over topography.

A key factor for successful imprinting on a nonflat substrate using this new technique is the ability to planarize the mold with a relatively thin polymer coating. Although this

TABLE I. Material parameters and imprint temperatures of the three-layer structure shown in Fig. 5.

Layer No. (from the bottom)	Material	Weight average molecular weight (g/mol)	T_g (°C)	Imprinting temp. (°C)
1	Polycarbonate	18 200	150 °C	200 °C
2	PMMA	15 000	105 °C	120 °C
3	Poly(*t*-butyl acrylate) (PBA)	100 000	43 °C	50 °C

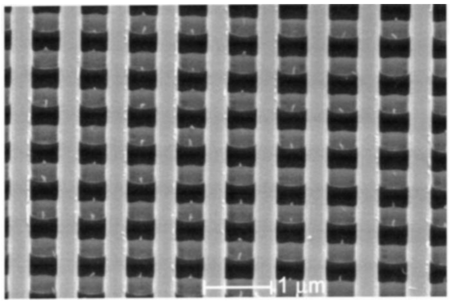


FIG. 5. Two-layer grating structures in PC. The second layer is imprinted at 135 °C. Residual layer has been removed by O_2 RIE.

may be difficult to achieve for a mold with large features (beyond several micrometers), submicrometer and nanometer features can be easily planarized by spin coating.[16–19] Therefore, the current method is especially advantageous for the fabrication of nanostructures on nonflat substrates. Such structures are becoming increasingly important in applications such as photonic devices, and biomedical and tissue engineering. The use of a hard mold enables very high resolution and fidelity of the pattern. Pattern distortion suffered in soft lithography can be minimized. Moreover, this technique is extremely versatile because of our capability of controlling imprint conditions and tailoring the polymer materials.

Another interesting behavior observed in this new imprinting method is the effect of temperature. Figure 3 shows the imprinted PMMA grating pattern on a SiO_2 substrate with 350 nm line spacing at two different imprinting temperatures. At 90 °C, which is 15 °C below the T_g of PMMA, a continuous film is transferred onto the substrate with a thin residue layer (<100 nm) connecting neighboring lines, as shown in Fig. 3(a). On the other hand, if the pattern is imprinted at 175 °C [Fig. 3(b)], the residue film completely disappears. This is caused by the dewetting of an ultrathin film from the surfactant-treated mold at a temperature well above T_g. Similar dewetting behavior is also noticed in Fig. 2(a), in which the residue layer in the suspended portion of the film dewets during imprinting at 145 °C and retracts to the protruded SiO_2 surface, whose surface energy is much higher than that of the mold. The disappearance of the residue film at elevated temperatures simplifies subsequent pattern transfer by eliminating the O_2 RIE step needed to expose the substrate between features.[5]

B. Three-dimensional polymer structures

Besides patterning nonflat substrates, this new imprinting method can also be used to fabricate multilayer, 3D structures. Figure 4(a) illustrates the process of building up 3D structures by imprinting over existing polymer patterns. To prevent deformation and flow in the polymer layer underneath, the imprinting temperature needs to be below the T_g of the underlying polymer structure. In order to achieve high yield at the same time, the polymer being imprinted can be chosen so that its T_g is lower than that of the polymer layer underneath. The thin residue film can be removed by a brief O_2 RIE step after each layer is imprinted. The process can then be repeated to achieve multilayer structures.

Figure 4(b) shows a three-layer structure fabricated using three polymers with progressively lower T_g according to this scheme. The residue layer in each layer has been removed by O_2 RIE. The polymer properties and imprinting temperatures are listed in Table I. During the formation of each layer, the imprinting temperature was chosen to be slightly above the T_g of the material being imprinted, but well below the T_g of the polymer underneath. Under these conditions, the yield of each layer is very high while the deformation in the previous layers is minimized. Although only three polymers are used in this demonstration, this scheme can be used to fabricate structures with a large number of layers because of the wide range of T_g in commercially available polymers.

We have also demonstrated that multilayer imprinting can be performed in a single polymer. In this case, since the substrate and the layer being imprinted are of the same material, the most suitable imprinting temperature was found to be in the range of 10–20 °C below the T_g of the polymer. Imprinting in this temperature range gives high yield without causing severe deformation of the underneath layer. Figure 5 shows a two-layer grating structure in PC. The first layer was formed on flat Si wafer by NIL at 200 °C, and the second layer by the new method at 135 °C under 5 MPa pressure. The residue film in the second layer was removed by a brief O_2 RIE treatment. Since the yield in each imprint is quite high ($>80\%$), this method can be used to fabricate structures with multiple layers. On the other hand, because the imprint temperature is quite close to T_g, the high pressure used during pressing does cause slight deformation of the underneath layer, as seen in Fig. 5. Nevertheless, when dimension stability is not very critical, multiple imprinting in the same polymer still provides a viable technique to fabricate multilayer, 3D structures.

IV. SUMMARY

A new imprinting technique has been developed to enable imprinting onto nonflat substrates. In this method, a polymer film is spin coated on a surfactant treated hard mold and then transferred to the substrate. When polymers with different mechanical properties are used, either suspended structures over wide gaps or supported patterns over the protruded surfaces of the substrate can be obtained with high uniformity. If imprinting is performed at a temperature well above the T_g of the polymer, dewetting from the low surface energy mold naturally removes the thin residue layer on the raised areas of the mold, which simplifies subsequent pattern transfer. This new imprinting method can also be used to fabricate three-dimensional multilayer structures in polymer. In the fabrication of multilayer structures, polymers with progressively lower T_g can be used to improve the yield and dimensional stability of the imprinted structure. The numerous advantages of this technique, e.g., simplicity, versatility by controlling material selection and process condition, high resolution, and high fidelity, suggest great potential in a wide range of applications.

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