FABRICATION OF THREE-DIMENSIONAL NANO-PATTERNS BY INCLINED NANOIMPRINTING LITHOGRAPHY

Zhan Liu[1], David G. Bucknall[1], and Mark G. Allen[2]

[1]School of Polymer, Textile and Fiber Engineering

[2]School of Electrical and Computer Engineering

Georgia Institute of Technology, Atlanta, GA, 30332, USA

(Tel: 1-404-894-9906; E-mail: gth825n@mail.gatech.edu)

Abstract: We report a non-conventional nanofabrication approach, **Inclined Nanoimprint Lithography (INIL)**, which can produce three-dimensional (3-D) nano-patterns of varying heights in a single imprinting step with the potential for low cost and high throughput. Such 3-D nano-patterns can be produced using soft lithography without the need for conventional nano-lithography of either the imprinting mold or the substrate, by exploiting the technique of anisotropic de-wetting. We demonstrate the INIL technique using a commercially available nanolithography resist, poly(methyl-α-chloroacrylate-*co*-α-methylstyrene), and demonstrate 3-D pattern transfer to silicon dioxide using reactive ion etching.

Keywords: Inclined Nanoimprint Lithography, De-wetting, Nanofabrication, Soft Lithography.

1. INTRODUCTION

The capability to fabricate three-dimensional (3-D) nano-patterns is a significant technical driver not only toward systems with similar scale and topography to those found in nature, but also in integrated photonics, micro- and nanofluidics, and nanobiochemistry [1]. To these ends, both Nanoimprinting Lithography (NIL) and soft lithography have been recently exploited since they offer not only the ability to form the desired structures, but also the potential for low cost and high throughput. Both of these techniques, however, require fabrication of relatively expensive mold masters with uniform nano-scale patterns over a large area. Furthermore, since mold master preparation techniques such as electron-beam nanolithography typically produce structures of uniform height, an additional challenge for NIL is the fabrication of 3-D nano-patterns of varying heights from a single mold. Additionally, one important research aspect in nano-scale fabrication is pattern transfer from a thin imprinted layer (typically a polymeric system) to an underlying substrate, especially when the layer is substantially 3-D. The layer material must possess both suitable imprinting properties as well as etch selectivity over the substrate [2].

Here we present a non-conventional nano-scale fabrication approach, Inclined Nano- imprinting Lithography (INIL), derived from an anisotropic de-wetting process of polymer thin films [3] utilizing an inclined poly(dimethylsiloxane) (PDMS) mold. INIL can produce 3-D nano-patterns with different heights in a single step, thereby not only maintaining the low cost and high throughput advantages of molding, but also removing the need to directly produce nano-scale soft lithography mold patterns. Additionally, soft lithography stamps of a single imprint height can produce 3-D structures. Various commercially available polymer systems are suitable for INIL. In this paper we demonstrate the use of INIL to build up true 3-D structures in a commercial poly(methyl-α-chloroacrylate-*co*-α-methylstyrene) e-beam resist (ZEP) [4], and subsequent 3-D pattern transfer into a SiO_2 layer on silicon wafer using reactive ion etching.

2. FABRICATION

The INIL fabrication method is outlined in Figs. 1 and 2. A PDMS stamp with a desired pattern was prepared using conventional lithographic methods followed by micromolding techniques. Various patterns were investigated such as trenches (with 1 μm width, 1 μm depth and separated by a lateral pitch of 2 μm) and cylindrical pillars (with 1μm diameter, 1 μm depth and a 2 μm lateral pitch). In order to ensure a high surface energy of the PDMS mold an O_2 plasma treatment was carried out before the INIL process. The mold is then brought into contact with an oxidized silicon wafer bearing a thin ZEP film (~30 nm) (Fig. 1*a*). The entire assembly is then inclined at a small angle, typically 0°~5°, followed by annealing for ~7 hours in vacuum at a temperature (T≈140°C) above the polymer glass transition temperature (T_g=105°C). During the annealing, the polymer can flow and tends to de-wet from the SiO_2 layer, eventually wetting the two nearest available PDMS trench sidewalls. When the inclined angle is 0°, symmetrical polymer flow results in an inverted "U" shape polymer profile in the region between two trenches (Fig. 1*b*). This pattern can then be fixed by cooling the assembly below the polymer T_g. After mold separation, a uniform nano-line pattern is obtained with ~1 μm pitch, but the feature size is much smaller than the PDMS stamp (Fig. 1*c*). Ultimately, the polymer pattern is transferred into the oxide layer on the wafer using anisotropic plasma etching (CHF_3/H_2) (Fig. 1*d*).

As the inclined angle is changed from zero, the polymer flow and consequently the inverted "U" profile become asymmetric (Fig. 2). As a result, a 3-D nano-line pattern with different heights and widths is obtained. When θ is increased to 4°~5°, the profile evolves to only a single side of the inverted "U" shape with the other side absent. Therefore only one nano-line can be observed per 2 μm pitch spacing (Fig. 2*c*).

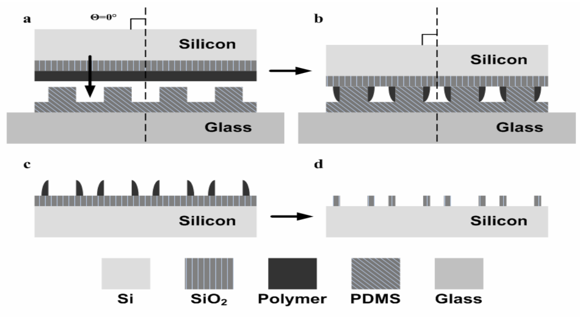


Fig. 1 Schematic illustration of INIL (θ=0°).

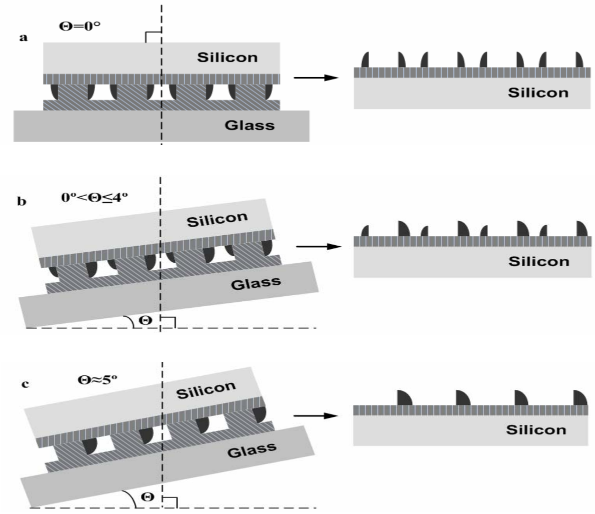


Fig. 2 Schematic illustration of INIL (a) θ= 0°; (b) 0°<θ≤ 4°; (c) θ≈5°.

3. EXPERIMENTAL RESULTS

Fig. 3 shows the AFM images of 3-D nano-line patterns produced by the INIL process in a 30 nm thick ZEP polymer layer. As observed different heights are obtained when the inclined angle is varied from 0° to ~5°. The height of the symmetric line (Fig. 3*a*) is ~100nm, and the full width half-maximum (FWHM) of the lines is ~300nm. It is instructive to calculate the volumes of the film patterns before and after INIL. Since the lines are extruded in one dimension, e.g. y-axis, an area calculation (in the x-z plane) can be performed instead of volume. Based on the symmetric profile, the cross-sectional area occupied by polymer nano-lines over 2μm pitch of the original mold is calculated as 100nm×300nm×2 (line width × line height × line number per 2μm). This is consistent with the cross-sectional area of non-patterned

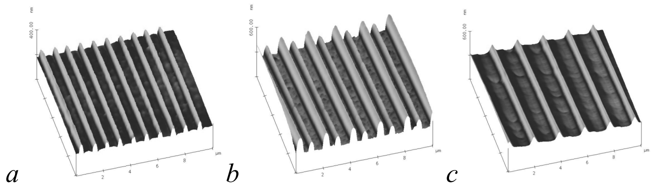


Fig. 3 AFM images of 3-D nano-lines with different heights in various inclined angles (10μm×10μm). (a) θ= 0°; (b) θ=1.4°; (c) θ= 5.7°.

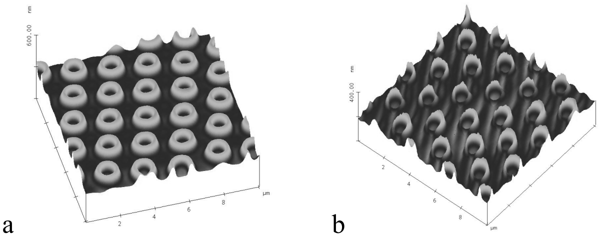


Fig. 4 AFM images of 3-D nano-circles (10μm×10μm).

polymer thin film per 2μm distance, 30nm× 2000nm (film thickness × 2μm pitch). For asymmetric lines, therefore, the height and width are changed due to the geometry, but the volume of polymer is conserved.

The process has also been successfully used to transfer other shapes, such as a PDMS cylindrical pillar stamp. Both symmetric and asymmetric

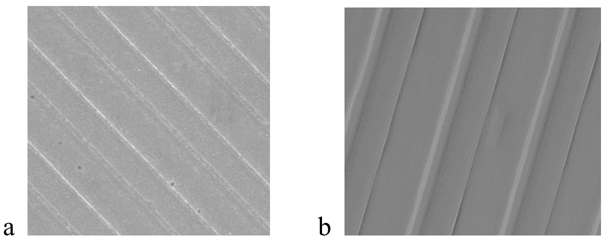


Fig. 5 SEM images of silicon dioxide pattern (a) with the same and (b) different heights respectively, fabricated by anisotropic dry etching.

nano-circles are obtained by INIL. Fig. 4 shows AFM images of 3-D nano-circles. All the polymer patterns have been successfully transferred into the SiO_2 layer by anisotropic plasma etching. Fig. 5 shows SEM images of etched SiO_2 patterns, using polymer nano-line patterns as masks. The SiO_2 patterns retain the 3-D shape of the INIL polymer mask.

4. DISCUSSION

The exact mechanism behind the INIL process is still under investigation. Generally, de-wetting phenomena of polymer thin films can be explained by analyzing the free energy of the system [5-6]. The simplest systems are uniform thin films on horizontally flat surfaces. De-wetting leads to a morphology change into droplets or other patterns. When a PDMS mold with topographic features is introduced to the system normal to the surface (Fig. 1), the film is in contact with two different surfaces, the mold and the substrate. The overall system attempts to reach a minimum free energy by deforming in a 3-D framework.

When the mold is in contact with the surface, as in INIL, the de-wetting of the ultra-thin polymer film is a complex dynamic process. In addition to the surface energy interactions that drive the de-wetting process in INIL two additional force components, gravity and viscous flow, are important factors that affect the morphology evolution of the polymer during the INIL process. The magnitude of these effects may be influenced by various factors, including the inclined angle θ, the film thickness, polymer viscosity, annealing conditions, and direction of the gravity vector.

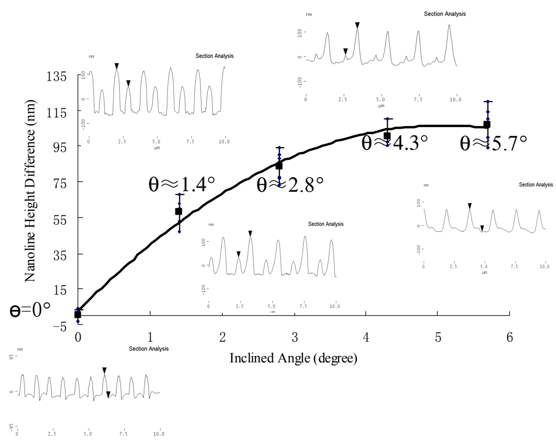
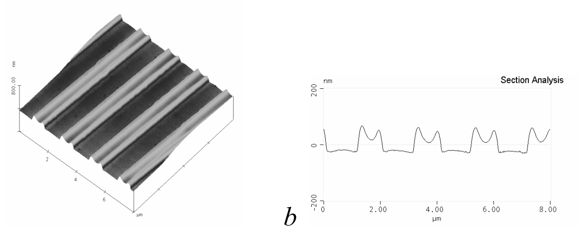


Fig. 6 Plot of nano-line height difference as a function of the inclined angle. The inserted images are representative AFM section analyses corresponding to each testing θ respectively.

In order to understand the effect of the inclined angle θ, a series of polymer films with similar thickness, equal to ~30nm, was studied, using the same trench mold. The experimental conditions were the same in all cases except for the inclined angle. The line height difference as a function of the inclined angle is plotted in Fig. 6. These data show that under these conditions, the height difference of the nano-lines is primarily dependent on the magnitude of the inclined angle θ. When θ is above 4°, the height difference saturates at the point and the extreme asymmetric structure appears, as seen previously in Fig. 3*c*. The asymmetry produced in the INIL process must be a balance of the wetting, gravitational and viscous flow forces. The wetting of the polymer along the PDMS side walls and the viscous forces of the polymer flow in its fluid state (above T_g) are in opposite directions and both parallel to the PDMS wall. However, with increasing inclined angle the gravitational force no longer acts parallel to the wall, and consequently when $\theta \neq 0°$ the balance of forces causes more material to build up on one PDMS face of the mold wall compared to the other.

We have studied the INIL effect both when the polymer coated substrate is placed onto the PDMS mold (as in Fig. 1) and additionally when the system is inverted and the mold is placed onto the substrate. In the “inverted” INIL process the effect of the gravitational force acts in opposing direction relative to the polymer flow direction. An example of the structure that results from an “inverted” INIL process (when the mold is placed on top of the polymer coated substrate) is shown in Fig. 7. The annealing time and temperature are identical to those for the INIL structure shown in Fig. 3*a*. The differences in the structures are evident that the INIL structure (Fig. 3*a*) demonstrates clear separation between the dewetting lines, which does not occur in the “inverted” INIL case (Fig. 7). However, if this latter example is annealed for approximately 14 hours at 195°C a structure that closely resembles Fig. 3*a* is observed. Clearly, inverting the system does not affect the resulting equilibrium structures,



a *b*

Fig. 7 AFM image of nano-line without a complete development from the “inverted” INIL process (8μm×8μm). (a) AFM 3-D image; (b) section analysis result of (a).

but does affect kinetics of the polymer behavior. A possible reason for this is that the gravitational force acts to reinforce the INIL process. In the “inverted” INIL the gravitational force acts against the polymer flow, which is de-wetting the substrate and wetting up the PDMS mold walls. In this case a long time scale at a high temperature and hence polymer viscosity is required to reach.

5. CONCLUSION

In this paper, Inclined Nanoimprinting Lithography (INIL) is demonstrated. By combining the advantages of the high throughput from the soft lithography and the three-dimensionality from the INIL, the possibility of nano-structuring large surface areas with varying nanostructure heights in a single step is enabled. The effects of the inclined angle and the gravity are studied. The underlying mechanism is still being investigated. INIL can be integrated with other techniques to fabricate patterns for the various applications in NEMS and MEMS areas.

REFERENCES

[1] Y. Chen and A. Pépin, “Nanofabrication: Conventional and Nonconventional Methods,” Electrophoresis, Vol. 22, No. 2, pp. 187-207, 2001.

[2] I. Korczagin, S. Golze, M. A. Hempenius, and G. J. Vancso, “Surface Micropatterning and Lithography with Poly(ferrocenylmethyl phenylsilane),” Chem. Mater., Vol. 5, No. 19, pp. 3663-3368, 2003.

[3] H. L. Zhang, D. G. Bucknall, and A. Dupuis, “Uniform Nanoscopic Polystyrene Patterns Produced from A Microscopic Mold,” Nano Lett., Vol. 4, No. 8, pp. 1513-1519, 2004.

[4] D. R. Medeiros, A. Aviram, C. R. Guarnieri, W. -S. Huang, R. Kwong, C. K. Magg, A. P. Mahorowala, W. M. Moreau, K. E. Petrillo and M. Angelopoulos, “Recent Progress in Electron-beam Resists for Advanced Mask-making”, IBM J. Res. & Dev., Vol. 45, No. 5, pp 639-650, 2001.

[5] Reiter G., “Unstable Thin Polymer-films-Rupture and Dewetting Process”, Langmuir Vol. 9, No. 5, pp. 1344-1351, 1993.

[6] J. Leopoldes, A. Dupuis, D. G. Bucknall, J. M. Yeomans, “Jetting micron-scale droplets onto chemically heterogeneous surfaces”, Langmuir, Vol. 19, No. 23, pp. 9818-9822, 2003.