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High order symmetry interference lithography based nanoimprint

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We report on soft nanoimprint lithography using masters obtained by high order symmetry interference lithography. The use of high order symmetry leads to the formation of three-dimensional structures with features smaller than 40 nm. Masters were realized in silicon in a two-step process without transfer layer. Pure silicon masters allow mechanical stability and potential surface functionalization. We further demonstrate the ability of these masters as mold for nanoimprint lithography. High fidelity replication in hybrid sol-gel and pure silica with conservation of both minute features and long distance organization is observed over large areas.   2011 American Institute of Physics. [doi:10.1063/1.3530729]

Large scale controllable nanopatterning is a major issue of the nanotechnology era. Over the past decade, nanoimprint lithography (NIL) appeared as an easy way for surface patterning and at limited cost.¹ The main advantage of this technique is the replication of a pattern with submicrometer resolution over large areas in many different materials: classically thermoplastics or UV-curable resists are used but recent interests have been developed on metal or metal oxides because of their functionalities and stability.^{2,3} Hybrid materials represent an easy way toward metal oxide thin films,⁴ and we have recently demonstrated the formation of pure silica pattern via the sol-gel route.⁵ However, the main problem in NIL is the fabrication of large scale nanopatterned masters, and the compatibility of these masters with the imprint process.

Among large areas patterning method, interference lithography (IL) is a method of choice for the fabrication of masters. It is based on the selective exposure of a photoresist under an interference pattern, usually obtained with two laser beams.⁶ Arrays of dots or gratings with sub-50 nm half pitch are normally obtained using extreme-UV lasers.⁷ To increase the aspect ratio, the pattern is first transferred from the resist to a layer with a low sputtering yield such as Cr (Ref. 7) or Si₃N₄.⁸ This step leads to the formation of two-dimensional structures.

Along the replication of patterns such as gratings or square arrays, there is an emergent need of more complex structures presenting high order symmetry. The use of high order symmetry enables the relative isotropy of the surface properties. For example, such surface patterns can enhance the adhesion or wetting properties,⁹ increase the light output in emitting devices,¹⁰⁻¹² or even induce random lasing.¹³ They may be preferred to the classically proposed random structures because of the higher control on the final properties.

In this study, silicon masters for NIL with original patterns, high order symmetry and three-dimensional (3D) structures were fabricated by IL. The goal of this study was to demonstrate the ability of this technique to obtain few centimeter large masters with the desired structures and the transfer of the realized structures into a silica layer by NIL. It is a promising way to design suitable patterns for various aimed applications.

Figure 1 describes the fabrication procedure starting from the silicon wafer to the silica replica. The first steps rely on holographic patterning. A 360 nm thick positive photore-

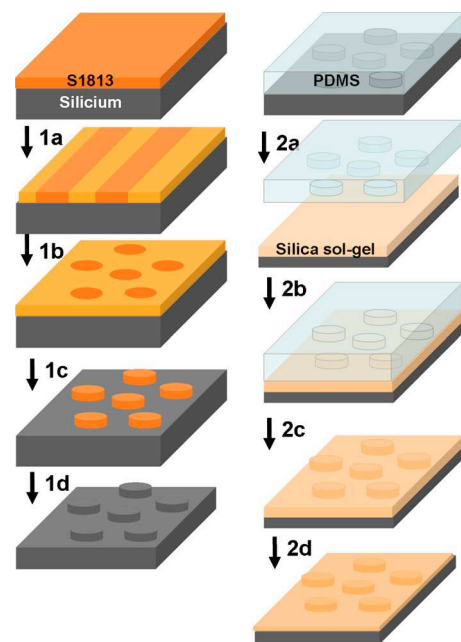


FIG. 1. (Color online) Scheme of the two main processes. 1, IL: (a) first exposure of the resist to the interference pattern, (b) subsequent exposures to obtain higher symmetry order, (c) dissolution of the exposed resist, and (d) transfer of the structures into silicon by RIE. 2) NIL: (a) a PDMS stamp is obtained from the master mold, (b) imprint into a hybrid silica sol-gel layer, (c) demolding, and (d) sintering of the hybrid materials into pure silica.

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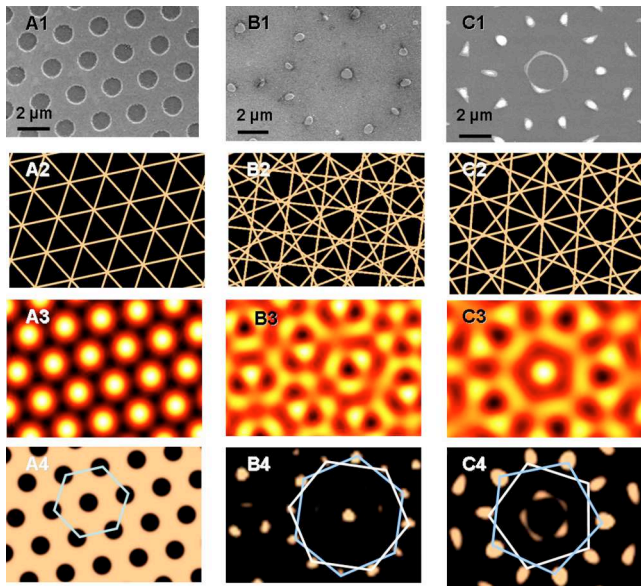


FIG. 2. (Color online) First row: SEM pictures of different silicon masters. Depth of the structures: (a) and (b) 150 nm (c) 450 nm. Symmetry order: (a) 3, (b) 6, (c) 5. Second row: corresponding directions of the interference patterns during the n exposures. Third row: simulated exposure dose on each point of the surface, obtained by summing up the intensity of the n interference patterns. Fourth row: simulated resist height profiles. The results were obtained using the simulated doses and initial layer thicknesses. Pentagons and hexagons are guide for the eyes.

sist (Microposits S1813 from Shipley) was deposited on silicon wafers and subsequently exposed during 2 min to an interference pattern. The interference pattern was obtained with two coherent filtered and expanded laser beams ($\lambda = 442$ nm) under an incident angle $\theta = 7^\circ \pm 1^\circ$. Each 2 cm laser spot has a power of 0.25 mW/cm². Here, the resist was exposed n times during 2 min and the substrate was turned by an angle of π/n between each exposure, where $2n$ is the desired symmetry order for the pattern. In a second step, the exposed resist was dissolved and the pattern transferred into the silicon wafer by reactive ion etching (RIE) using SF₆ and O₂ gases (Fig. 1).

Several silicon masters with various symmetries were fabricated. The obtained masters are presented on Fig. 2. Figure 2(a), is a scanning electron microscopy (SEM) picture of a hexagonal pattern with a maximum structure height of 150 nm. Homogenous dots hexagonal patterns are obtained over several centimeters square. The distance between the holes is 2.20 μm . This value is in agreement with the pitch p , calculated using the grating formula [Eq. (1)]

$$p = \frac{\lambda}{2n \sin \theta}, \quad (1)$$

where λ is the laser wavelength, θ the incident angle, and n the index of the surrounding media. Figure 2(b), presents a silicon master with 12-order symmetry (illustrated with the two hexagons); the longer exposure time and the higher symmetry lead to the formation of structures with reduced lateral size.

The direct transfer from the pattern photoresist to the silicon enables the realization of more complex pattern with 3D features. Figure 2(c), presents a silicon master, obtained

from thicker samples, with ten-order symmetry (evidenced with the two pentagons). The initial layer thickness was 1.07 μm and each exposure time was increased to 4 min. These conditions lead to a maximum structure height of 450 nm. The combination of thicker samples and high order symmetry allows the formation of smaller features, the almost circular pattern in the middle of the decagon is 150 nm high.

The strong versatility of the obtained pattern can be rationalized using simulation. The second row of Fig. 2 shows the direction of the interference patterns for a number n of exposures. The pitch is obtained by the grating formulas and the directions are obtained after rotation of π/n . The third row gives the intensity of the laser illumination on each point of the surface as the sum of the intensities of each exposure. Finally, the fourth row represents the simulated profiles of the resist after multiple exposures and revelation. The resist profile was subsequently extracted from the data sheet of the resist, giving the height of the structures as a function of the intensity. An excellent agreement in the lateral dimensions is observed between the experimental and the simulated profiles. The structures are transferred with high fidelity from the resist to the silicon with only a modification of the height. Comparison between the heights indicates that the etching speed is 2.4 times higher for the resin than for silicon. While a simulation program can be used as a predictive tool for the pattern design (periodicity, symmetry), it also allows for better understanding of the potentiality of IL. An aspect that has been so far neglected is the ability of 3D structuring using planar (two beams) IL. The difference of color intensity on the simulated profile [Fig. 2(c)] shows that the structures are not only different in their lateral size but also different in height. This is due to the intensity profile resulting of high order symmetry exposure.

The replication and imprint process has been described previously:¹⁴ polydimethylsiloxane (PDMS) was spin cast onto the structured silicon wafer. After thermal treatment, a replicate stamp can be demolded from the original silicon master. A hybrid silica layer was deposited from a methyltriethoxysilane sol via the sol-gel route. The imprint was performed with the PDMS stamp at 90 $^\circ\text{C}$ for 20 min under a pressure of 1 bar (Fig. 1). Thanks to its low modulus and its permeability, PDMS is often used for surface patterning: this soft-NIL allows for imprinting over large areas. To improve the stability of the structured coating, the imprinted hybrid silica layer can be subsequently annealed into pure silica. Annealing at 600 $^\circ\text{C}$ for 8 h of the hybrid silica resulted in a crack free pure silica coating.

On Fig. 3, we report the results of the replication of the tenfold symmetry master [Fig. 3(a)]. Figure 3(b) presents a large view of the silica replica of silicon master after annealing. The replication process is faithful over large areas and the features of the initial master are transferred into the hybrid silica layer. An atomic force microscopy (AFM) study of the surface shows that the height of the structures is homogeneously reduced by 40%. This loss is due to the char of the organic moiety. However, the lateral sizes and the organization of the pattern were not affected by the thermal annealing.

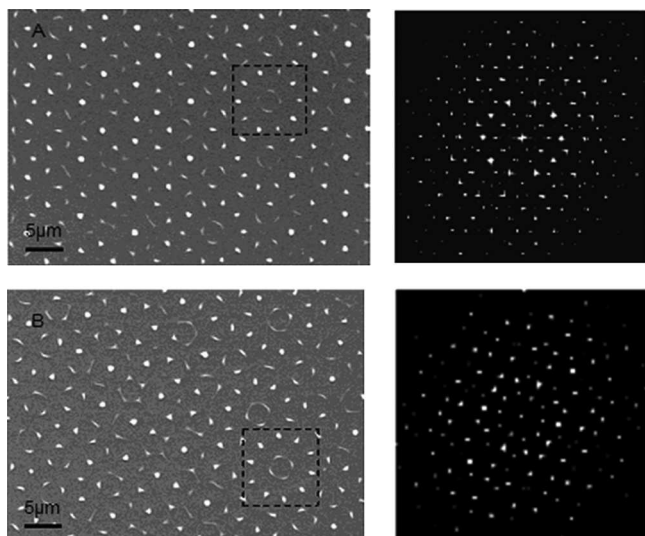


FIG. 3. SEM pictures of the silicon master (a), and of the pure silica imprinted film after sintering (b). The original silicon master presents 450 nm high structures and tenfold symmetry [Fig. 2(c)]. The correlation factor r_p was calculated in the highlighted areas. On the second column, the corresponding FFT are presented.

In order to validate the fidelity of the replica, we estimated the correlation between the master and the silica replica. Using the highlighted area, a correlation factor, r_p as high as 0.73 was obtained. The correlation factor was calculated using the standard formula

$$r_p = \frac{\sum_{i=1}^N (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_{i=1}^N (x_i - \bar{x})^2} \sqrt{\sum_{i=1}^N (y_i - \bar{y})^2}}. \quad (2)$$

Due to the tenfold symmetry of the structure and therefore the absence of long range order, the correlation could only be calculated on restricted area unless one is sure to observe the same area in both images. In order to further confirm the correlation, we compare the two Fourier transform of the SEM images. A fast Fourier transform (FFT) is equivalent to the diffraction pattern and gives the optical response of the surface. They were obtained numerically from the SEM pictures and are presented on the right of Fig. 3. The similitude of the two FFT, at both small and large scales, evidences the ability of the hybrid silica for multilevel patterning by NIL. This is due to the large difference in viscosity of the materials between the liquid state before the imprint and the vitreous state after thermal treatment.¹⁴

This combination of IL and soft-NIL allows also the creation and the replication at the wafer scale of patterns with small features, as evidenced on Fig. 4. Figure 4(a) presents an AFM view of the pattern over a few periods and Fig. 4(b) a SEM closer view of a pentagon like structures from Fig. 2(c). The width of the bridge between the two subunits of the pentagon is less than 40 nm. AFM investigations indicate that these small features present aspect ratio greater than 1.5. After replication and sintering [Fig. 4(c)], they are still present at the surface. They are however not as sharp as the

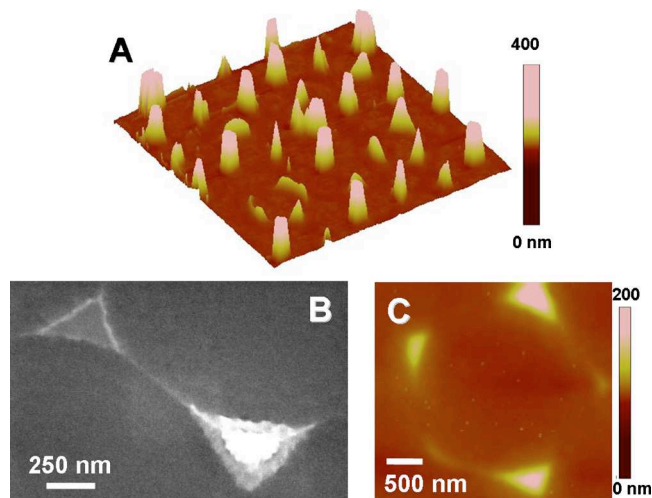


FIG. 4. (Color online) (a) AFM images of a tenfold symmetry silicon master (the size is $12 \times 12 \mu\text{m}^2$). (b) SEM zoom in small features on (a) silicon master, (c) AFM images of the pure silica replica after sintering.

original silicon master and some are missing. This is due to the replication process with the PDMS stamp which smoothes the edges of the pattern.

In summary, high order symmetry NIL has been demonstrated. We have fabricated by IL silicon masters with threefold symmetry and above and 3D structures. The direct transfer into the silicon allows the formation of features with lateral sizes smaller than 40 nm. We further demonstrate the ability of the hybrid silica sol-gel layer as resist for soft-NIL to replicate these multilevel structures. Both long range organization and minute features are replicated with high fidelity.

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