

SUB-WAVELENGTH OPTICAL LITHOGRAPHY VIA NANOSCALE POLYMER LENS ARRAY

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ABSTRACT

For the first time, under exposure is employed to fabricate the patterned photoresist templates with hemispherical cross-sectional profile. The long-range highly regular polymer lens array is replicated from the photoresist templates. The polymer lens array is utilized as the soft phase shift element to produce nearly perfectly periodic nanostructures with sub-100 nm feature size across centimeter-scale areas for the first time. The light focusing capabilities of the nanoscale polymer lens are verified by both simulation and experiment. The polymer lens arrays are repeated used for many times without obvious deterioration of their structures. By adjusting the size of polymer lens and the exposure dose, the metal and negative photoresist nanostructures with the smallest feature sizes of 80 and 200 nm are generated respectively. The advantages of this nanopatterning route lie in low-cost, high yield, long-range periodicity, programmable feature size, geometry and composition.

INTRODUCTION

Periodical nanostructures have wide applications in the various fields, including plasmonics, metamaterials, nanoelectronics, solar cells and chemical/biological sensors [1, 2]. These nanostructures are generally generated by either top-down or bottom-up lithography strategies. Top-down approaches, such as deep-ultraviolet (UV) photolithography, nanoimprint lithography, electron-beam lithography (EBL) and scanning probe based lithography (SPL), ensure long range regular pattern arrangement, but impose tradeoffs between low-cost, high-resolution and high-throughput [3, 4]. Bottom-up strategies such as colloidal lithography and block copolymer (BCP) lithography enable small feature size and high feature density in a cost-effective manner, while long range ordered pattern arrangement is hard to maintain [5]. Recently, self-assembled colloid nanospheres have been employed as optical masks/lenses in photolithography to generate both 2D and 3D sub-wavelength nanostructures over wide areas, which opens a new avenue for various applications, such as surface-enhanced Raman scattering and surface-enhanced infrared absorption [2]. The nanospheres can work as optical lenses to focus incident light below the center of nanospheres, generating sub-wavelength nanostructures. Furthermore, the polydimethylsiloxane (PDMS) nanostructures replicated from the self-assembled nanospheres or imbedded with nanospheres can also be employed as reusable and portable photomasks to produce sub-wavelength nanostructures due to phase shift effect [6]. However, there are two problems associated with this self-assembly nanofabrication strategy. First, the existence of defects is an intrinsic problem in self-assembly crystallization process. Second, the feature geometries achieved by self-assembly method are mainly

limited to dot-based shapes, precluding other functional feature geometries, such as continuous lines. Until now, an optical lens based lithographic strategy that enables the generation of sub-100 nm long-range ordered nanopatterns with diversified feature geometries still needs to be developed.

In photolithography, the produced photoresist structures with vertical sidewalls are usually desired, since these photoresist patterns can be easily transferred to other materials with fidelity in both size and morphology [3, 7]. In our previous work, we also employed metal-coated PDMS photomasks to produce variously shaped sub-100 nm photoresist nanostructures with vertical sidewalls [3, 7]. However, in this work, we find that positive photoresist nanopatterns with hemispherical cross-sectional profile can be generated by employing under exposure (Figure 1a). The generated photoresist nanopatterns can be exploited as templates to replicate highly ordered PDMS lens array with inverted hemispherical cross-section, which can function as optical lens to focus incident light beneath the apex, producing sub-100 nm nanopatterns with nearly perfect periodicity over centimetre-scale areas (Figure 1b-c).

EXPERIMENTAL METHODS

Fabrication of Photoresist Templates

Our previously reported metal-coated elastomeric photomasks were utilized to fabricate positive photoresist trench nanopatterns with hemispherical cross-sectional profiles via under exposure [3]. Si/SiO₂ (100) wafers were coated with 500 nm thick Shipley1805 (MicroChem) photoresist. A Dolan-Jenner MI-150 Fiber Optic Illuminator with adjustable exposure energy was deployed as the light source to expose underlying photoresist through the PDMS lens array. The exposure energy of 250 mw/cm² was utilized. For the Au-coated elastomeric photomask with 100 and 300 nm wide openings, the exposure time should be less than 7 and 6 s respectively in order to form positive photoresist nano-trenches with hemispherical cross-sectional profile. After exposure, the samples were developed in MF319 (MicroChem) for 20 s, leading to the generation of photoresist nano-trenches based template with hemispherical cross section. By casting the mixture of Sylgard 184 PDMS precursor and cross-linker on the produced photoresist templates, followed by curing at 80 °C for 3 h, the PDMS lens array was replicated from the photoresist templates.

Sub-Wavelength Photolithography with PDMS Lenses

For sub-wavelength photolithography with PDMS lenses, 1:5 (v/v) diluted or un-diluted positive photoresist was spin coated on Si/SiO₂ wafer with speed of 2500 rpm for 30 s, generating photoresist layers with the thickness of 40 and 500 nm, respectively. The PDMS lenses were manually brought to contact with the photoresist coated

Si/SiO₂ wafers. Due to the Van der Waals' force between PDMS surface and photoresist surface, the intimate and conformable contact occurred between the two surfaces across centimetre-scale area. For sub-wavelength photolithography on 40-nm-thick photoresist, the exposure energy of 55 mW/cm² was utilized. The exposure time could be adjusted from 6 to 15 s to change the produced feature size. After exposure and development, 10 nm thick Cr or 4 nm thick Cr/11 nm thick Au was coated on positive photoresist nanopatterns surface to transfer the obtained photoresist nanopatterns to metal nanostructures by lift off process. For the generation of deep nanostructures on 500 nm thick photoresist surface, the light source with the energy of 250 mW/cm² was employed. For fabrication of negative photoresist SU-8 nanopatterns, the 20% (v/v) diluted SU-8 2002 photoresist was coated on silicon wafers with the spin-coating speed of 4,000 rpm for 30 s, generating a 50 nm thick negative photoresist layer. The SU-8 coated Si wafer was soft-baked at 95 °C for 60 s. After exposure using the aforementioned halogen light source with the energy of 250 mW/cm² for 2 s, the samples were post baked at 95 °C for 120 s, followed by development of the photoresist in SU-8 developer for 5 s.

Scanning electron microscope (FE-SEM, JEOL JSM-7600 F) and atomic force microscope (AFM) (Park Systems) were employed to characterize various nanostructures. Finite Difference Time Domain (FDTD) simulations were performed based on commercial software FDTD Lumerical version 8.6.3. The PDMS lens was set in intimate contact with photoresist surface during the simulation. The refractive indices of PDMS tips and photoresist were set to be 1.4 and 1.66 respectively.

RESULTS AND DISCUSSION

FDTD Simulations

FDTD simulations are employed to investigate the light focusing properties of PDMS hemispherical structures for guiding the selection of PDMS lens with proper size (Figure 2). The simulations demonstrate that the PDMS hemispherical nanostructure can function as optical lens by focusing UV light (400 nm wavelength) into tiny beam below the apex of PDMS lens, exposing nanoscale regions at underlying photoresist. Furthermore, the 250 nm high PDMS lens produces smaller light beam than the 500 nm high PDMS lens does. It demonstrates that the 250 nm high PDMS lens is capable of generating smaller feature size.

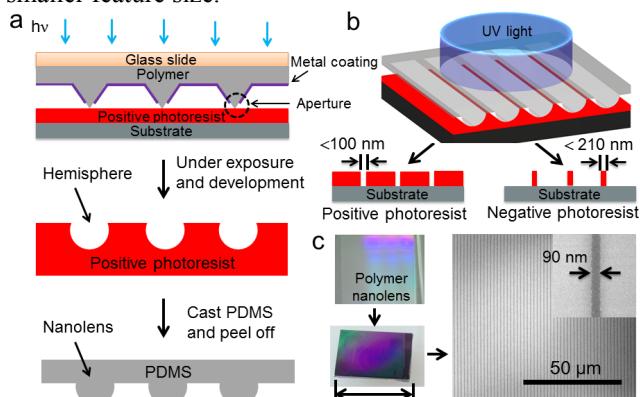


Figure 1: (a) Schematic illustrating the steps involved in

generating a nanoscale PDMS lens array. Under exposure is employed to produce positive photoresist trenches with hemispherical cross-sectional profiles, from which the PDMS lens array is replicated. (b) Scheme illustration of exploiting PDMS lenses to fabricate sub-wavelength positive (left) and negative (right) photoresist nanopatterns respectively. (c) Experimental obtained centimeter-scale sub-wavelength nanopatterns. Left: optical image of centimeter-scale PDMS lenses (top) and correspondingly produced 90 nm wide positive photoresist line patterns (down). Right: SEM image of large-area 90 nm wide Cr lines produced from the positive photoresist nanopatterns after Cr evaporation and photoresist lift off.

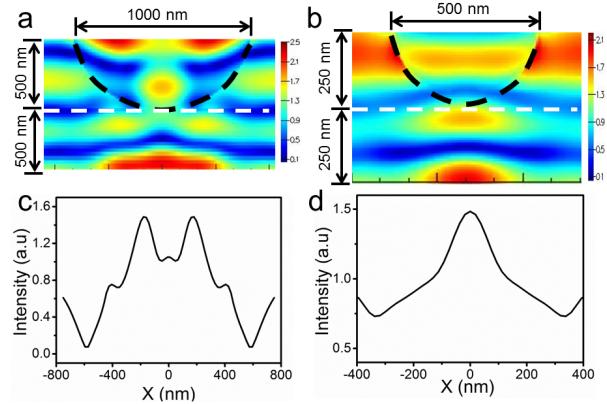


Figure 2: FDTD simulation. (a) and (b) FDTD-calculated electric field distributions below the PDMS lens arrays with the lens heights of 500 and 250 nm respectively. (c) and (d) The light intensity profile obtained at the top surface of photoresist layer that is in contact with the PDMS lenses in (a) and (b) respectively.

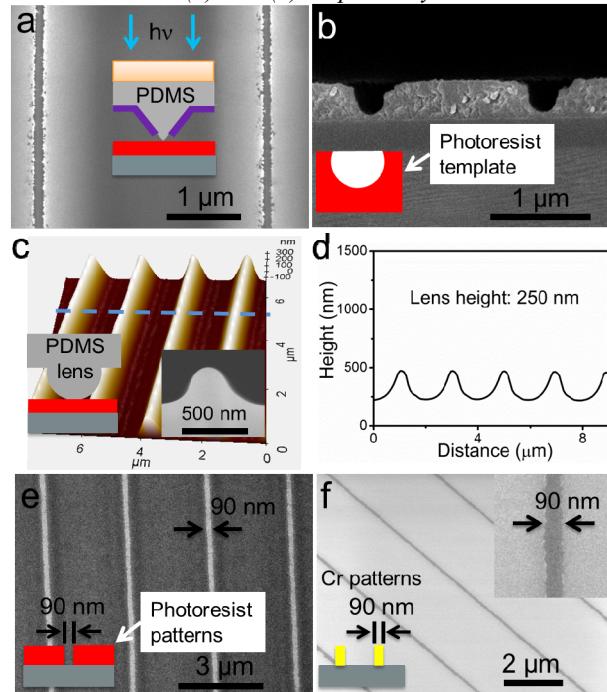


Figure 3: (a) Top-down SEM image of prism-shape Au-coated PDMS photomask with 300 nm wide openings made at the end of tips. (b) Cross-sectional SEM image showing hemispherical cross section of positive photoresist nano-trenches, which were made by the PDMS photomasks in (a). (c) 3D AFM topography image of 250 nm high PDMS lens array that replicated from the positive photoresist patterns.

photoresist nano-trenches in (b). (d) AFM height profile across the structures in (c) along the blue line. (e) SEM image of 90 nm wide positive photoresist lines fabricated using the PDMS lenses in (c). (f) SEM image of 90 nm wide Cr lines produced from the photoresist nanopatterns in (e).

Sub-100 nm Photolithography with PDMS Lens Array

The photoresist trenches with hemispherical cross-sectional profiles can be obtained by controlling the exposure dose in near-field photolithography (Figure 3a-b). The PDMS lenses with the height of 250 nm can be replicated from the photoresist molds and utilized as phase shift elements in near-field photolithography (Figure 3c-d). The intimate contact between photoresist surface and PDMS lens introduces near-field effect, leading to the generation of sub-wavelength photoresist nanostructures. As such, 90 nm wide recessed photoresist patterns across the areas of $1.5 \times 2 \text{ cm}^2$ were produced (Figure 1c and Figure 3e). After metal evaporation and photoresist lift off, 90 nm wide Cr lines across centimetre-scale areas were obtained (Figure 1c and Figure 3f).

Diversified Feature Geometries Both on Positive and Negative Photoresist Surface

One unique characteristic of the nanoscale PDMS lenses replicated from photoresist templates is their capability of producing sub-wavelength nanostructures with diversified feature shapes while maintaining the long range regularity (Figure 4). For previously reported sub-wavelength photolithographic strategies based on lens structures, the shapes of both surface-textured lenses and correspondingly produced nanostructures are limited to dot only [2]. Nevertheless, the feature geometries of polymer optical lenses and correspondingly produced nanoscale features in this work can be diversified and flexibly designed. This is because the horizontal geometry of PDMS lens is defined by the feature shapes on the initial chromium-based hard photomasks. Thus, in addition to the line patterns, nanostructures with other shapes such as dot and connected ellipse could also be produced by the PDMS lenses with corresponding shapes. For example, recessed photoresist dot array was produced when the PDMS lens array with uniformly textured hemispherical dots was employed as near-field phase shift element (Figure 4a-b). The photoresist nanostructures can be transferred to Au dot array with the average diameter of 98 nm (Figure 4c). Furthermore, the produced dot size can be programmed conveniently by adjusting the exposure time (Figure 4d). For example, Au dot array with the diameters of 98, 390 and 560 nm were manufactured using the PDMS lens array with the exposure time of 6, 10 and 14 s respectively. Furthermore, the PDMS nanoscale lens array with the shape of connected ellipse can be employed to fabricate the same shaped Cr nanostructures with the line width of 200 nm (Figure 4e-g). In principle, the feature shapes enabled by this strategy could be extended to any other arbitrary shapes just by designing the original traditional photomask with corresponding feature shapes, indicative of the flexible feature geometry provided by this lithographic approach.

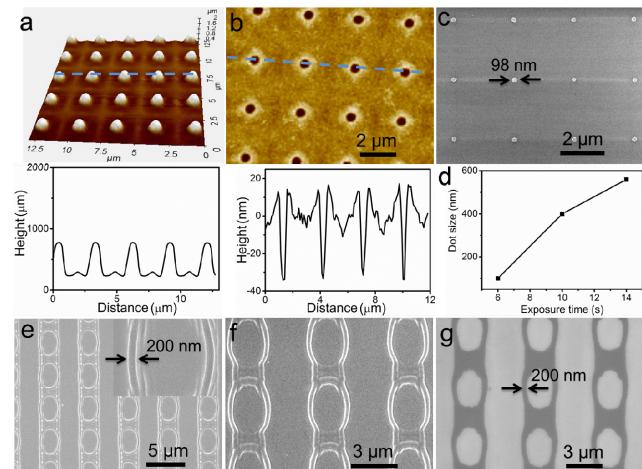


Figure 4: (a) 3D AFM image of the PDMS lenses textured with dot array. (b) AFM images of recessed dot-shape positive photoresist nanopatterns created by the polymer lenses in (a). (c) SEM image of 98 nm Au dot array generated from (b). (d) Plot of Au dot size versus exposure time. (e, f and g) SEM images of initial ellipse-shape photoresist template, the correspondingly replicated PDMS lenses from the template and the fabricated ellipse-shape Cr nanostructures.

In addition to the generation of sub-wavelength nanopatterns on positive photoresist surface, the nanoscale lenses can also be deployed to produce sub-wavelength nanostructures on negative photoresist SU-8 surface (Figure 5). The 250 nm high polymer lenses can focus incident light and therefore make the negative photoresist below the apex of lens be selectively exposed and polymerized, generating sub-wavelength raised SU-8 nanostructures with diversified feature geometries. For example, 300 nm SU-8 dot array, 200 nm wide SU-8 line and grid nanopatterns can be produced by employing PDMS lens array with corresponding geometries as phase shift element in near field photolithography. The Fourier transform of produced large-area SU-8 nanostructures indicated the long-range regular periodicity of these nanopatterns (Insets of Figure 5a and c).

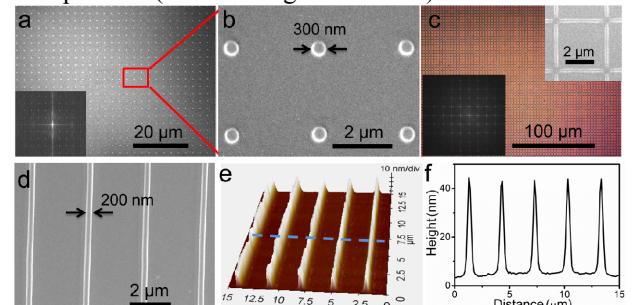


Figure 5: (a-b) Low and high magnified SEM images of 300 nm SU-8 dot array respectively. (c) Large-area optical image of SU-8 grid nanopatterns. Insets in left bottom of (a) and (c): Fourier transform of these images. (d-e) SEM image and AFM topography images of 200 nm wide SU-8 lines. (f) AFM height profile of the 200 nm wide SU-8 lines in (e) along the blue line.

Note that both the photoresist templates and the PDMS lenses can be repeatedly used, making this strategy cost-effective. For instance, no obvious degradation of the

photoresist mold was found after utilization of it for five times in replication of PDMS lens array (Figure 6a-b). Furthermore, the PDMS lens array can be repeatedly utilized for many times without noticeable distortions in the lens array itself. Note that no appreciable variation of produced feature size is observed after utilization in optical patterning for 40 times (Figure 6e-f). These results demonstrate the good reusability of both the photoresist templates and the PDMS lens array. Our previous results also demonstrate that the initial metal-coated PDMS photomasks are reusable. It is noteworthy that photoresist molds are more cost-effective than traditional silicon molds in terms of materials made of them and the fabrication process. For example, the fabrication of photoresist molds is completed in a one-step photolithographic process, bypassing the silicon etching process as used in fabrication of conventional silicon based templates. Note that this nanolithography strategy is not only capable of generating nanostructures on thin photoresist surface for transfer of the photoresist nanostructures to other materials, but also enables the production of deep nanostructures on thick photoresist, which are useful for many devices fabrication. Possibly this method of fabricating photoresist template structures with hemispherical cross-section can also be extended to other lithographic strategies that based on delivery of energy, which will be investigated in future work.

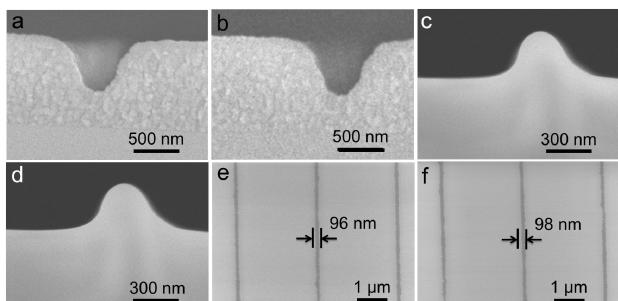


Figure 6:(a-b) Cross-sectional SEM images of the profile of positive photoresist templates before and after being used for 5 times respectively. **(c-d)** Cross-sectional SEM images of hemispherical PDMS lenses before and after near-field photolithography for 40 times respectively. **(e)** and **(f)** SEM images of 96 and 98 nm wide Cr line patterns respectively that were generated by employing the PDMS lenses in **(c)** and **(d)** respectively.

CONCLUSIONS

In summary, a facile and cost-effective nanofabrication strategy is developed to produce sub-100 nm nanostructures with long-range nearly perfect periodicity by using highly ordered PDMS lens array as the soft phase shift element in photolithography. For the first time, under exposure is employed to fabricate photoresist nanostructures with hemispherical cross section, from which the PDMS lens array is replicated. Because of the soft and sticky property of PDMS lens structures, the apex of PDMS lens can contact with underlying photoresist intimately, bypassing the air gap and the diffraction limit. The near-field optical effect ensures the generation of sub-wavelength nanostructures. Consequently, the metal and negative photoresist nanostructures with the smallest

feature sizes of 80 and 200 nm are generated respectively. Furthermore, the produced feature size can also be adjusted conveniently by controlling the size of polymer lens and the exposure dose. Compared with other reported lithographic strategy based on optical lenses, this surface patterning strategy improves in diversifying the feature geometries and ensuring the long-range periodicity of patterns. In future work, this sub-wavelength lithographic strategy can be employed in various practical applications, such as high-performance transparent conducting electrodes, photovoltaics, cell-matrix adhesion and source/drain electrodes for organic thin film transistors [1, 3, 5].

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