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Polymer-Confined Colloidal Monolayer: A Reusable Soft Photomask for Rapid Wafer-Scale Nanopatterning

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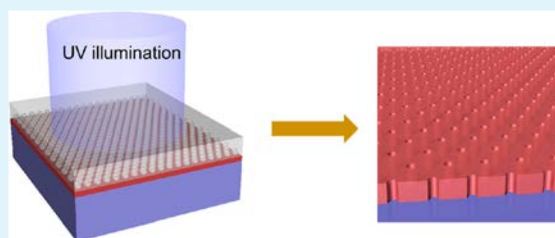
S *Supporting Information*

ABSTRACT: We demonstrate the repeated utilization of self-assembled colloidal spheres for rapid nanopattern generations. Highly ordered micro-/nanosphere arrays were interlinked and confined by a soft transparent polymer (polydimethylsiloxane, PDMS), which can be used as light-focusing elements/photomasks for area-selective exposures of photoresist in contact. Because of the stiffness of the colloidal spheres, the photomasks do not encounter feature-deformation problems, enabling reliable production of highly uniform patterns over large areas. The geometrical feature of the patterns, including the size, pitch, and even the shape, can be finely tuned by adjusting the mask design and exposure time. The obtained patterns could be used as deposition or etching mask, allowing easy pattern transfer for various applications.



KEYWORDS: *colloidal monolayer, reusable, soft photomask, wafer scale, nanopatterning*

1. INTRODUCTION

Ordered nanostructure arrays have been extensively explored for various technological applications, ranging from data storage,[1,2] photovoltaics,[3−5] and plasmonics[6−8] to functional coatings.[9] So far, fabrications of these nanostructures mainly rely on the techniques emerging from the microelectronics industry, including deep ultraviolet (UV) photolithography, electron beam lithography, and focused ion beam milling.[10,11] However, these processes are generally expensive and time-consuming, especially when large-area (e.g., a few square inches) patterns are generated. Therefore, it is of significant importance to develop new technologies that allow nano-patterning in both high speed and low cost. New methods such as nanoimprinting and soft lithography may be usable as inexpensive alternatives, but they still encounter mask deformation/damaging problems. Besides, the printing templates are still fabricated using the aforementioned expensive techniques. Recently, a bottom-up approach, based on self-assembled colloidal nanoparticles, namely, nanosphere lithography (NSL), has attracted huge research attention and been widely employed for fabrication of various highly ordered nanostructure arrays.[12−14] However, in most cases, the nanospheres served as sacrificial masks and cannot be reused, which is unfavorable for scalable cost-effective fabrications. To solve the problem, we recently proposed a novel photolithographic method by first replicating the geometrical features of self-assembled nanospheres onto the surface of a soft polymer film and then employing the film as reusable photomasks for nanopattern generations.[15] At the same time, Jeon et al. proposed another mask fabrication approach in which colloidal nanoparticles are embedded in soft polymer films by applying a spin-coated encapsulation layer.[16] Nevertheless, these methods still involve relatively complicated fabrication processes. Moreover, in the later method, deep burying of nanospheres may cause increased difficulty in light profile control, resulting in distortions of the generated patterns.

Here, we report a single-casting method for facile fabrications of reusable colloidal masks and demonstrate their applications for rapid nanoscale patterning through UV illuminations. Because of the stiffness of the colloidal spheres and shallow burying depth, the photomask does not encounter any feature-deformation problems, enabling reliable production of highly uniform pattern arrays on a wafer scale.

2. EXPERIMENTAL SECTION

The process of mask fabrication and pattern generation is illustrated in Scheme 1. A thin layer (30 nm) of Cu was first coated on a piece of a clean silicon wafer by direct current (d.c.) magnetron sputtering at 50 W in Ar gas (2.3×10^{-3} Torr, 50 sccm) in a MGS-600 Sputtering System from JunSun Tech Co., Ltm. For a large-sized sample, a thin layer of Ti (3−5 nm) was sputtered under the same condition before the Cu deposition to enhance the adhesion between the Cu and the Si substrate. Highly ordered monolayers of polystyrene (PS) colloidal

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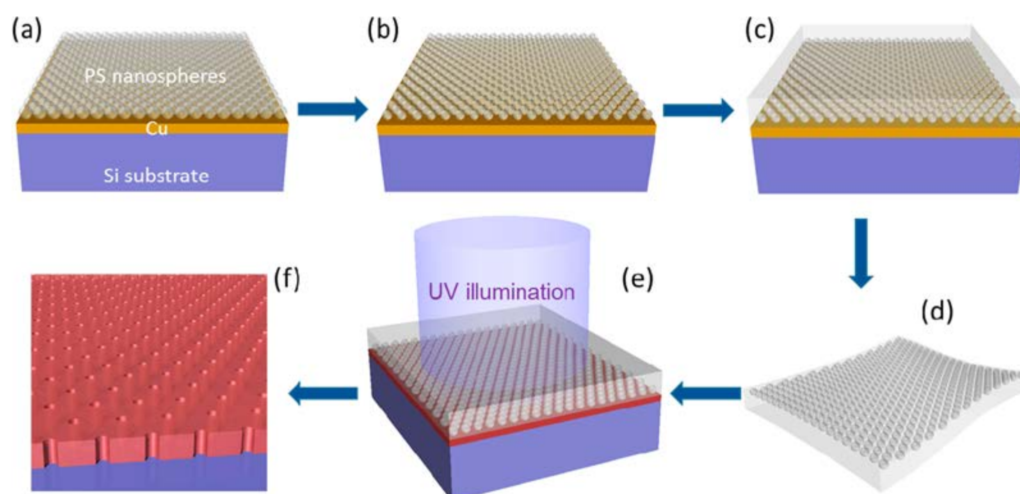
Scheme 1. Process of Masks Fabrication and Pattern Generation[a]



[a](a) Deposition of PS nanospheres monolayer on Cu-coated silicon substrate. (b) Shrinking the nanospheres by oxygen plasma etching. (c) Casting PDMS prepolymer over the nanospheres. (d) Peeling off the cured PDMS film with the confined nanospheres monolayer. (e) Attaching the PDMS soft mask to a photoresist layer and illuminating with flood UV light. (f) Detaching the PDMS mask and developing the exposed photoresist to obtain nanopatterns.

spheres were assembled on water surface via a modified Langmuir–Blodgett method by Moon et al.[17] Specifically, monodispersed polystyrene (PS) colloidal suspensions (microParticles GmbH, see Table S1, Supporting Information, for details) were mixed with proper amounts of ethanol and phosphoric acid (see Table S2, Supporting Information, for details) and slowly dropped into deionized (DI) water through a tilted glass slide (pretreated with piranha solution) by using a micropipette. The floating PS spheres were further compressed on the water surface by adding a few drops of 5% aqueous solution of sodium dodecyl sulfate. The Cu-coated Si substrate was inserted underneath the close-packed monolayer, and raising the Si substrate enabling transfer of the monolayer from the water surface to the substrate. The transferred monolayer was left dry naturally in ambient environment and then treated with oxygen plasma to induce a ∼100 nm reduction in diameters (see Figure S1, Supporting Information, for details). Polydimethylsiloxane (PDMS) prepolymers (Sylgard 184 form Dow Corning, 1:10 by weight of the curing agent and monomer) was mixed in a plastic beaker, vacuum debubbled, and subsequently casted over the treated sample in a Petri dish and cured at 60 °C for 2 h. Finally, the cured PDMS film was peeled off manually from the substrate after cutting the edge using a blade. The thickness of the PDMS film was controlled to be 1−2 mm (by using a proper amount of PDMS prepolymer) for better handling as well as achieving conformal contact with photoresist. Typically, 11 g of the prepolymer (10 g of base and 1 g of curing agent) cured in a plastic Petri dish (diameter of 4.5 in.) gives a film with thickness of about 1 mm.

The photolithography/nanopatterning was conducted in a class 100 clean room at ambient conditions. First, a layer of photoresist (positive photoresist 5206E from AZ Electronic Materials Ltd., or negative photoresist ma-N from micro resist technology GmbH) was coated on a silicon wafer by spin coating (3000−6000 rpm) and soft baking at 90 °C (5−10 min). The PDMS soft mask was gently pressed against the surface of the photoresist layer to allow conformable contact. The sample was then illuminated by parallel UV light with a power intensity of 7.7 mW cm^{-2} at 365 nm via flood exposure in a SUSS MicroTec Mask Aligner. After the exposure, the soft mask was detached, and the exposed sample was developed, rinsed with DI water, and dried with nitrogen gas.

3. RESULTS AND DISCUSSION

PDMS is soft polymer that can conformably attach to a flat surface. Also, it is quite robust and chemically stable, and optically transparent from 240 to 1100 nm. More importantly, the processing/curing condition for PDMS is totally compatible to PS, causing no damage (such as dissolving and melting) to PS spheres. These excellent properties make PDMS a perfect candidate matrix material for our study.

As PDMS adheres much more strongly to Si substrates than to PS spheres, directly casting PDMS on Si may cause problems in the following process for the film peeling-off (Figure S2, Supporting Information). Our previous study shows the Cu can serve as an efficient interfacial layer for PDMS release.[15] Thus, in this work, a thin sputtered Cu layer was coated on the substrate before loading the nanospheres. We also applied plasma treatment to the spheres before PDMS casting, to enhance the mechanical robustness of the composite film by increasing the filling ratio of the PDMS material among the PS spheres and enhancing the bonding of the spheres to the matrix through the plasma-induced polar groups on the spheres. The enhanced bonding was further revealed by scanning electron microscope (SEM) investigations (Figure S3, Supporting Information). From the same SEM image, it can also be observed that the spheres were embedded at the near surface of the peeled film, suggesting that the spheres adhered well with the Cu layer during the PDMS curing. As will be shown later, this shallow burying is important to ensure effective exposure of the photoresist and reducing pattern distortions.

As the refractive index of PS (1.59) is larger than that of PDMS (1.4), from geometrical optics, it is possible to utilize the spheres as tiny ball lens to focus the incident light. Finite-difference time-domain (FDTD) simulations were employed to further investigate the optical properties of the fabricated composite films. Figure 1 shows the simulated light (UV *i*-line, 365 nm) intensity profile for the masks with PS sphere diameters from 500 to 1100 nm. It clearly reveals that the incident light can be efficiently focused underneath the spheres, confirming that it is feasible to utilize these soft polymer films as photomasks to produce subwavelength patterns. As the light-focusing ability tends to be weakened with the decrease of the sphere diameter, we mainly utilize PS spheres with diameter at 500−1200 nm for our lithography purpose.

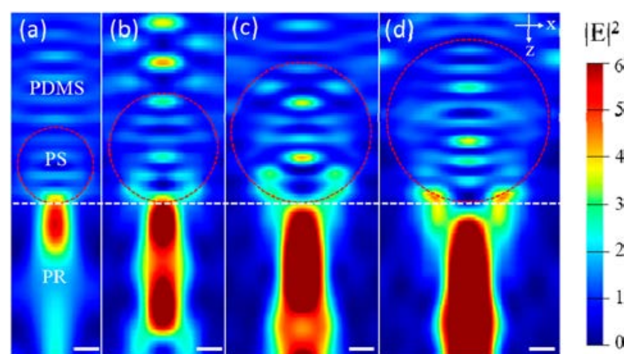


Figure 1. FDTD calculations of the electric field intensity ($|E|^2$) distributions. The light illuminates along the Z direction. The diameters of the PS spheres in (a), (b), (c), and (d) are 500, 700, 900, and 1100 nm, respectively; and the corresponding pitches are 600, 800, 1000, and 1200 nm, respectively. The regions inside the red dashed circles denotes PS spheres while those outside circles and above the white dash-dotted lines are PDMS matrix. The regions below the dash-dotted lines are photoresist (PR). All scale bars are 200 nm.

Since the assembly of the nanosphere monolayer can extend unlimitedly, we can make masks large enough for wafer-scalable patterning. Figure 2a shows a photograph of positive photoresist (5206-E, AZ) patterned on a 4-in. wafer by using an 1150/1280 (diameter/pitch, nm) colloidal mask. The patterned sample exhibits a grating-like diffraction color, indicating the long-range ordered arrangement of structures. Figure 2b−d displays typical SEM images of arrays of nanoholes by using positive photoresist, which further shows that the patterns are uniform and highly ordered. Actually, we can obtain uniform, defect-free nanohole arrays over ~100 μm, with very small (2.1%) coefficient of variation in diameter (Figure S4, Supporting Information). Moreover, the feature size and geometry can be finely tuned by changing the exposure time. Specifically, with the increase of the exposure time, the size of holes became enlarged, and meanwhile, the shape changed from round to hexagonal. The shape change may result from the multiple light scattering among the spheres that were well-packed in a hexagonal lattice. The inset of Figure 2d shows the FDTD calculated light-intensity distribution in a horizontal plane at the depth of 300 nm below the photoresist surface. As can be seen, in addition to the high-intensity circular spot in the center, there is another hexagonal shell in the surroundings which has much weaker intensity, which suggests that, with the increase of illumination time, the scattered light (hexagonal shell) could eventually expose the photoresist and cause hexagonal holes. Similarly, when negative photoresist (ma-N) was used, arrays of nanodisks were obtained, and the shape could be tuned as well by adjusting the exposure time (Figure S5, Supporting Information). Besides, it is also possible to vary the pattern features by applying different masks during the UV illumination. Figure 2e−h displays the SEM images of patterns fabricated through use of masks of smaller colloidal particle sizes (700/800 and 500/600, diameter/pitch, nm) and different exposure parameters, showing excellent control of sizes/pitches of the features over wide dimension ranges. Moreover, these masks were found to be quite robust against repeated usage, with no noticeable distortions and cracks observed after being used at least 50 times (Figure S6, Supporting Information).

Recently, self-assembled colloidal spheres have been employed to generate three-dimensional (3D) nanostructure.[16,18] Based on these studies, we suggest that it is also possible to utilize our polymer-confined colloidal mask for 3D nanofabrications, in an even more rapid and reproducible way. Nevertheless, systematic explorations are still required to make it applicable.

Ordered nanostructure arrays may find applications in many fields. In particular, highly ordered silicon nanostructures such as pillars, cones, and holes are highly desirable active materials for photovoltaic and artificial photosynthesis systems due to their unique synergic advantages in light trapping and charge separation.[3,19−21] Unfortunately, fabricating these nanostructures often involves high costs for both patterning and etching. Here, we show that our colloidal mask assisted lithographic method coupled with metal-assisted chemical etching (MaCE) could offer a practical, low-cost solution to the problem. In a typical process, photoresist patterns were first fabricated on a (100) silicon wafer and utilized as a shadow mask for the deposition of patterned metal catalyst (2 nm Ti and 20 nm Au)

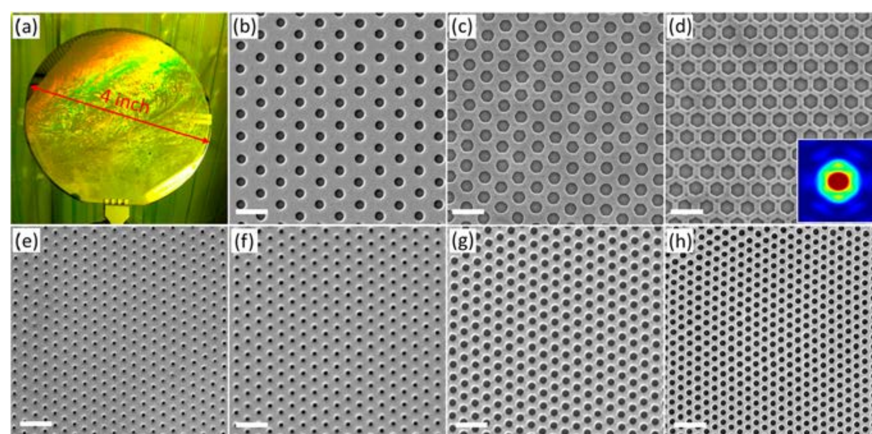


Figure 2. Colloidal mask assisted optical patterning using positive photoresist (AZ5206E). (a) Digital photograph and (b)−(d) SEM images of photoresist patterns fabricated using an 1150/1280 (diameter/pitch, nm) colloidal mask. Exposure time for (b), (c), and (d) are 1, 3, and 5 s, respectively. Inset: calculated electric field intensity distribution at a depth of 300 nm under the photoresist surface. (e)−(g) SEM images of patterns fabricated using a 700/800 colloidal mask, with exposure time of 1, 2, and 4 s, respectively. (h) SEM image of pattern fabricated using a 500/600 colloidal mask, with exposure time of 4 s. Scale bars in (b)−(h) are 2 μm.

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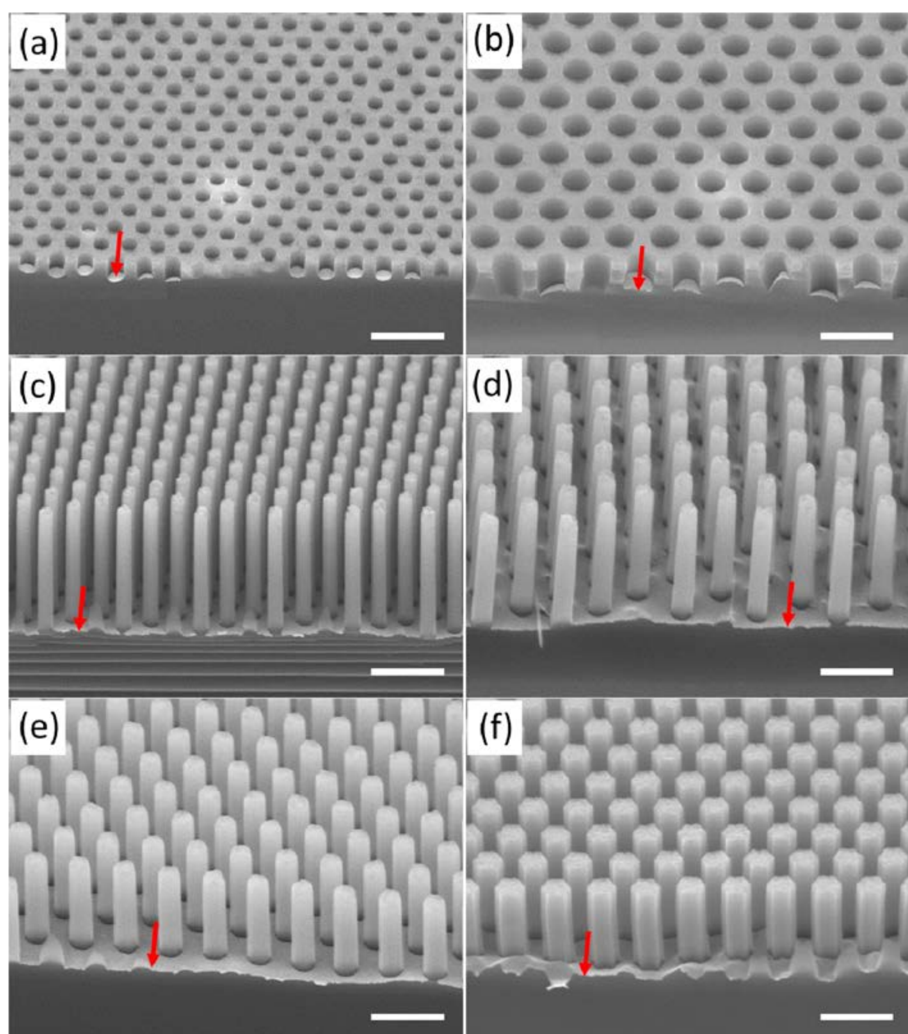

Figure 3. SEM images of silicon nanostructure arrays fabricated through MaCE with the catalyst patterned by our lithographic method. (a), (b) Nanohole arrays obtained by using disklike metal catalysts. (c)−(f) Nanopillar arrays obtained by using meshlike metal catalysts. All scale bars are 2 μm. The catalysts are marked by the red arrows.

by vacuum evaporation and liftoff; and the catalyst-loaded wafer was then immersed in a HF/H_2O_2 solution to perform catalytic etching, resulting in pillared or holelike structures.[22] Figure 3 displays typical SEM images of the obtained silicon nanostructures with retained metal catalysts at the etching fronts. The silicon structure showed complementary cross sections to the catalyst patterns. For meshed catalyst, pillared structures were obtained, while with disklike catalyst, holes were produced. These results demonstrate that the obtained photoresist patterns could be effectively transferred into useful nanostructures. Also, the vertical pillars could be converted into tapered structures by further treating the samples in $AgNO_3$/HF/HNO_3 mixtures,[23] providing more flexibility for structure design for targeted applications.

4. CONCLUSIONS

In conclusion, we have presented a simple yet reliable method to make full use of self-assembly monolayers of colloidal nanospheres by confining them in a PDMS matrix through a single casting process and using them as photomasks for rapid, parallel fabrications of nanopatterns. Specially, applying a thin Cu interfacial layer on the substrate could effectively avoid the crack problem during the film peeling-off. Also, oxygen plasma treatment of the spheres can sufficiently improve the mechanical robustness of composite film for repeated uses. By adjustment of the mask design or exposure time, the size, pitch, and even the shape of the patterns can be finely tuned. Moreover, the obtained patterns could easily be transferred into other materials or derived into 3D nanostructures. We believe that as demonstrated mask fabrication and lithographic method may serve as a reliable, low-cost alternative to the existing nanopatterning techniques for building various nanostructures for practical applications.

■ ASSOCIATED CONTENT

Supporting Information

Product information about the PS spheres, recipe of colloidal suspension for preparing PS monolayer, SEM images of PS spheres, PDMS films, and obtained large-area defect-free nanohole arrays and nanodisk arrays. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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