Large areas of periodic nanoholes perforated in multistacked films produced by lift-off

Wei Wu, Dibyendu Dey, Alex Katsnelson, Omer G. Memis, and Hooman Mohseni[a)]
EECS Department, Northwestern University, Evanston, Illinois 60208

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The authors report a low-cost and high-throughput method—nanosphere photolithography, for generating periodic subwavelength holes in metals/dielectrics. By combining the self-assembled and focus properties of micro-/nanospheres, the authors utilized the sphere arrays as lenses to produce large areas of nanopillars with a strong undercut in negative photoresist. Using lift-off with the nanopillars of photoresist, the authors demonstrate a large area of uniform nanoholes of as small as 50 nm in diameter at the bottom of ~160 nm thick metal. The authors also show that the nanohole arrays can be generated in multistacked layers of different materials and these nanoholes can be processed with different sidewall shapes. The technique promises to be an alternative nanopatterning method that is simple, economical, fast, and flexible. © *2008 American Vacuum Society.* [DOI: 10.1116/1.2982240]

I. INTRODUCTION

Subwavelength periodic hole arrays have received great interests since the discovery of enhanced optical transmissions through these arrays at resonant wavelengths.[1,2] The nanohole arrays have applications for exploring the basics of surface plasmons,[3,4] as chemical and biological sensors, and photonic devices.[5–7] At present, most common methods to fabricate these nanohole arrays are based on low-throughput techniques such as focused ion beam (FIB) milling[1] and electron-beam lithography (EBL).[8] Due to the increased research interests and expanded capabilities of nanohole arrays for production purposes, high-throughput and low-cost fabrication methods such as nanoimprint lithography[9] are becoming increasingly attractive.

Recently, we demonstrated the deep subwavelength focusing property of silica microspheres for nanopatterning photoresist.[10] In this work we utilized the method, nanosphere photolithography, to form uniform arrays of nanoholes in multistacked films. We utilized the focusing property of silica microspheres in UV light with negative photoresist to produce controlled nanopillars of photoresist with a strong undercut shape and large aspect ratio. Using lift-off, we fabricated highly uniform nanohole arrays in different metals and dielectrics. The diameter of the nanoholes can be as small as 50 nm. Our method has several advantages over current methods as follows: (1) Simplicity: our method utilizes the self-assembled sphere arrays as lenses, and a large area of spheres can be easily produced by drop coating,[11] spin coating,[12] and the convective assembly method.[13] (2) Lower cost: it avoids the expensive fabrication of masks and all other processes, such as lift-off and photolithography, are all widely used. (3) Parallelism: our method is based on the self-assembled arrays of spheres, so it produces all the holes in the array simultaneously rather than drilling holes in serial process as FIB milling and EBL methods. (4) Flexibility: since the hole arrays are produced by using lift-off process with photoresist pillars, different metals, magnetic materials, or combinations of them can be applied.

II. EXPERIMENTAL DETAILS

The processing scheme is shown in Fig. 1. The negative photoresist ma-N 405 from MicroChem Corporation[14] was spun on top of the GaAs substrate. 10 wt % aqueous suspensions of silica spheres of 0.97 μm diameters were bought from Bangs Laboratory Inc.[15] and diluted down to 0.5 wt % before usage. The hexagonally closed packed (hcp) array of spheres was formed by the convective self-assembled method. The samples were exposed using a conventional photolithography tool (Quintel Q-4000) at center wavelength of 400 nm for low exposure energy. Silica spheres were removed by ultrasonication in water for 1 min. Photoresist was developed in two different developers, AZ-300 MIF or ma-D 331S. They resulted in different undercut angles of photoresist. Also, the experiment show that the photoresist we used is more sensitive to the developer AZ-300 MIF than ma-D 331S. Using AZ-300 MIF, it is easier to produce the nanopillars of photoresist with a strong undercut shape, while ma-D 331S is better for generating nanopillars with a vertical cross section. Scanning electron microscopy (SEM) images were taken by high resolution SEM (Hitachi S4800).

III. RESULTS AND DISCUSSION

Figures 2(a) and 2(b) show SEM images of a typical hcp monolayer of silica spheres on top of photoresist. Using convective assembly method,[13] we can easily form sphere arrays of hundreds of micrometers. However, uniform sphere arrays of several inches are possible by other methods.[12] We can form nanopillars with different sidewall shapes using our controlled processing detailed below. Figures 2(c) and 2(d) show hexagonal arrays of nanopostphotoresist developed by ma-D 331S. Figure 2(d) is the high magnification image of these nanopillars, the size of which can be as small as

a)Electronic mail: hmohseni@ece.northwestern.edu

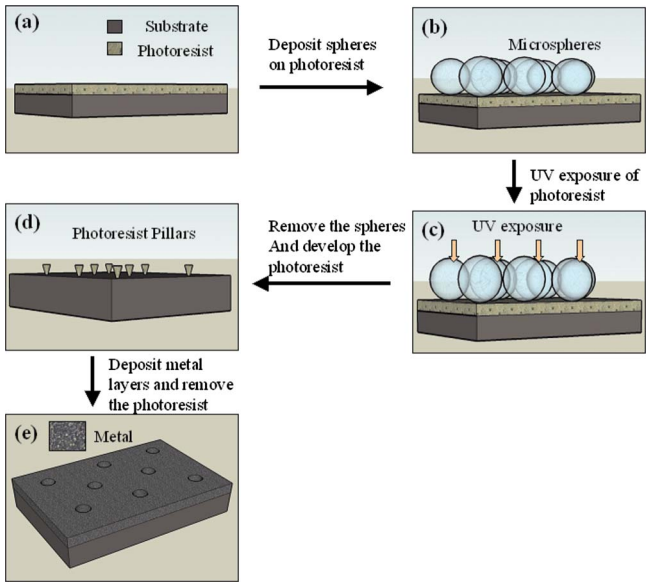

FIG. 1. Schematic illustration for forming perforated hole arrays in metal layer.

~210 nm using a broadband UV light source centered around 400 nm. The inset of Fig. 2(d) shows the side view of a single pillar with a vertical sidewall. By switching the developer to AZ-300 MIF, we produced 180 nm pillars with stronger undercut shape as shown in Figs. 2(e) and 2(f). The inset of Fig. 2(f) is a single pillar with a strong undercut shape. The bottom diameter of the pillar is as small as ~50 nm. The area of the periodic nanopillar arrays can reach hundred of micrometers, which is the same as the size of hcp monolayer of spheres. We observed few lattice defects

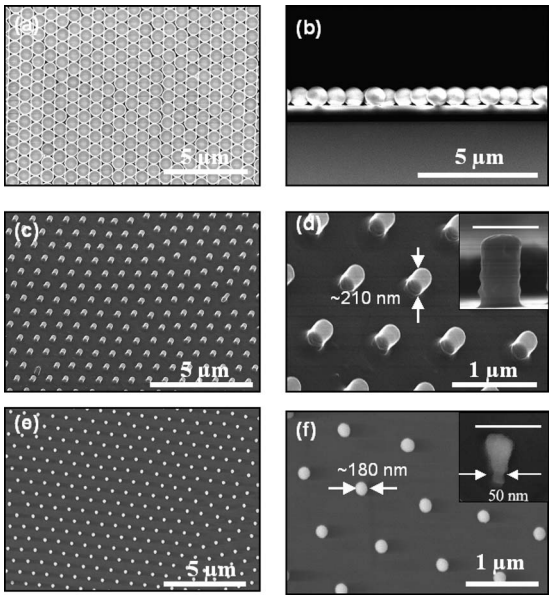

FIG. 2. SEM images: (a) hcp monolayer of spheres on top of photoresist; (b) cross-sectional view of (a); (c) nanopillar arrays of photoresist developed by ma-D 331S; (d) enlarged image of (c); (e) nanopillars of photoresist developed by MIF-300; (f) enlarged view of (e); insets of (d) and (f) show single pillars (the scales are both 400 nm).

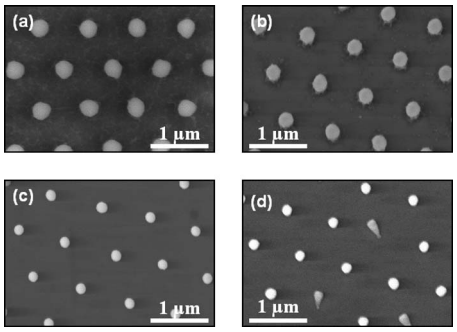

FIG. 3. SEM images of photoresist pillars with different development times of MIF-300: (a) underdeveloped photoresist, the development time is about 30 s; (b) the development time is about 40 s, there is still photoresist around the pillars; (c) the development time is about 50 s, perfectly nanopillars formed; (d) overdeveloped photoresist, the pillars began to fall down, the time is about 60 s.

in the array of nanopillars, which are caused by the irregular distributed microspheres. They show a relatively low density of defects.

We have studied different morphologies of the photoresist nanopillars with different development times. As shown in Figs. 3(a)–3(d), with increased development time by the developer 300 MIF we saw that the photoresist becoming more and more developed. Figure 3(a) shows that at about 30 s development time, the photoresist was still underdeveloped and there was a layer of photoresist covering the surface. With increased development time, the residue began to disappear and nanopillars became separated, but there was still residue around the root of the pillars, as shown in Fig. 3(b). At about 50 s, the nanopillars were perfectly developed as shown in Fig. 3(c). With more development time, the nanopillars began to fall down, since the root of the pillars became so thin.

Using the nanopillars as shown in Fig. 3(c), we produced nanoholes in metal film stacks by lift-off. Figures 4(a) and 4(b) show the SEM images of small holes in titanium/gold bilayer of ~160 nm thickness. Highly uniform holes of ~180 nm diameter were fabricated. Figures 4(c) and 4(d) are aluminum film perforated with nanoholes after lift-off. Using this technique, we can also form nanoholes in other metals, oxides, or combinations of different materials. Figures 4(e) and 4(f) show the aluminum/aluminum oxide bilayer perforated with nanoholes. The nanohole arrays are hexagonal distributed, which depends on the distribution of the microspheres on top of photoresist. At present, most deposition methods of microspheres can only produce a hexagonal shape.

The period of the nanohole arrays is about 1 μm, which is the same as the diameter of the microspheres used. Based on our former simulation and experimental results,[10] different sizes of spheres ranging from 0.5 to 4 μm can be applied in our lithography technique, so different periods of the nanopillar arrays are feasible to be generated. We have produced the nanopillar arrays of photoresist with the period of about 2 μm using the silica microspheres of about 2 μm diameter, shown in Fig. 5(a). Using the nanopillar array for

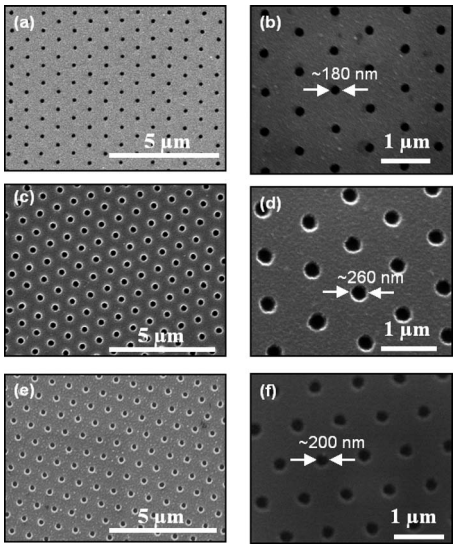

FIG. 4. SEM images: (a) gold hexagonally packed hole arrays; (b) enlarged view of (a); (c) aluminum hole array; (d) enlarged view of (c); (e) aluminum/aluminum oxide hole array; (f) the enlarged view of (e).

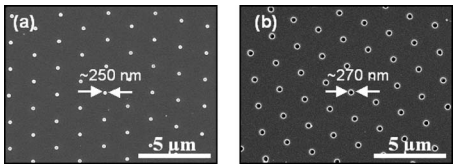

FIG. 5. SEM images: (a) photoresist nanopillar array with a different pitch size (~2 μm); (b) nanohole array perforated in titanium film with a differnt pitch size (~2 μm).

lift-off, the hexagonal nanohole arrays perforated in metal film were also generated. Figure 5(b) shows the nanoholes perforated in the titanium film with a hole diameter of about 270 nm.

Using the nanopillars of photoresist with different undercut angles, we can produce nanoholes with different sidewall shapes. Figure 6(a) demonstrates the cross section of the nanoholes with strong conical shapes in the aluminum layer. Although the size of the hole on the top is about 260 nm, on the bottom it is only about 50 nm. It is generated by the e-beam deposition of aluminum with an evaporation angle combined with a strong undercut of the nanopillars. These nanoholes with this conical shape can be potentially applied for rectifying and pumping ions by the ratchet principle.[16] Figure 6(b) shows the cross-sectional view of nanoholes with vertical sidewalls in silicon dioxide/aluminum layers. The diameter of the nanoholes is about 180 nm.

IV. SUMMARY

In summary, we have demonstrated a novel method with a potentially high throughput for the formation of large areas of deep subwavelength holes in metal/dielectric stacks. This method provides an alternative way to produce large arrays of uniform nanoholes. Using a broadband UV source centered at 400 nm, we demonstrated nanoholes that are half of the exposure wavelength, and using a tailored process we can achieve a diameter of about a quarter of the wavelength at the bottom of the holes.

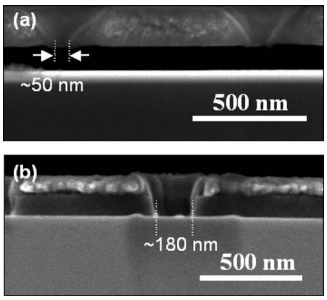

FIG. 6. SEM images: (a) cross-sectional view of holes in aluminum with a strong undercut sidewall, (b) cross-sectional view of holes in silicon dioxide/aluminum with vertical sidewall.

ACKNOWLEDGMENTS

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