A novel self-assembled and maskless technique for highly uniform arrays of nano-holes and nano-pillars

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ABSTRACT

We present a low-cost and high-throughput process for realization of two-dimensional arrays of deep sub-wavelength features using a self-assembled monolayer of HCP silica and polystyrene microspheres and well-developed photoresist lithography. This method utilizes the microspheres as super-lenses to fabricate highly uniform nano-holes and nano-pillars arrays over large areas on conventional positive and negative photoresists, and with a high aspect ratio. The period and diameter of the holes and pillars formed with this technique can be controlled precisely and independently. We also present our 3-D FDTD modeling, which shows a good agreement with the experimental results. The technique is simple, fast, economical, and is a convergence of bottom-up and top-down lithography.

Keywords: lithography, microspheres, nanoholes and nanopillars

1 INTRODUCTION

Nowadays, nanostructures and nanopatterns can be formed by top-down and bottom-up methods. Top-down methods mostly make use of lithography techniques to generate small patterns/structures in polymers of high sensitivity and then transfer them into other materials. Bottom-up methods assemble the identical building blocks into the desired structures. Top-down methods have been used in industry for a very long time and they are still the mainstream methods. However, they are expensive or inefficient to be applied into certain areas. For example, to generate a large area of periodic uniform nanoholes and nanopillars, using photolithography method requires expensive exposure instruments and mask sets [1] while e-beam lithography and focal ion beam milling methods will be extremely time-consuming [2]. With bottom-up methods being developed more and more widely, they have shown many advantages compared with the top-down methods, such as lower-cost, higher-efficiency, and easier-operation. However, it is still not as mature-developed as the top-down methods. The convergence of both methods has become an important research direction of nanoscale lithography [3][4].

Here we present an unconventional lithography method using the colloidal microspheres as nano-lenses to focus UV light in photoresist. We simulated that microspheres of silica have a strong focus ability to get a small focused beam size with high intensity and they can be self-assembled into a large hexagonally closed packed (HCP) monolayer [5]. So, using the technique, a large area of nanoscale patterns or structures can be generated in photoresist. Our simulations show that the focused beam waist is a very weak function of the sphere diameters and in hence extremely uniform pattern size can be achieved. By changing the exposure energy and development time of the photoresist we are also able to control the sizes of the patterns as well as changing the periodicity of the patterns by using spheres of different diameters. This method is a low-cost and high-throughput technique for realization of two-dimensional arrays of deep sub-wavelength features with high uniformity. The arrays of nanoholes and nanopillars generated by the method can be potentially applied in many areas, such as photonic crystals [6], storage devices [7], solar devices [8] and ion pumps [9].

2 SIMULATIONS

We used 3D-Finite-difference time-domain (3D-FDTD) method to simulate how the UV light was propagating through silica microspheres and photoresist. We tested four different sizes of silica microspheres and the simulation results were shown in figure 1 (a). By comparing the full-width at half-maximum (FWHM) of the focused beams by four different spheres, we found that the focused beam sizes have a very weak function with the sizes of spheres. As shown in figure 1(b), the cross-section distribution of light intensity after being focused showed that the FWHM of the focused beam almost didn't change with the spheres' sizes. Besides silica spheres, we found that polystyrene spheres (PS) also had a similar focus property as the silica ones because of the close refractive indices. In fact, FWHM of the focused light intensity is a good indication of the photoresist exposure, since the developing rate usually changes by almost an order of magnitude for a 50% optical intensity change around the photoresist threshold dose [10].

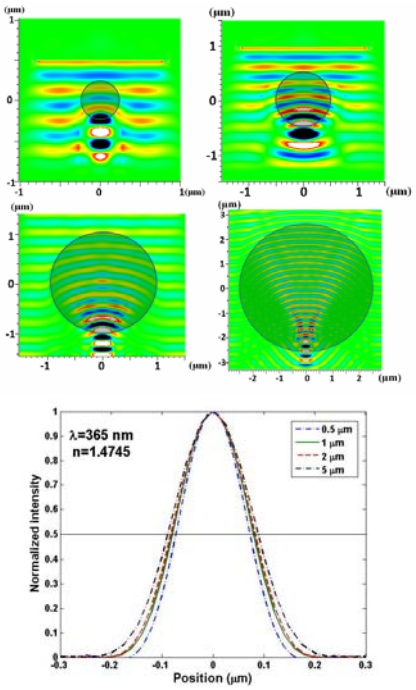

Figure 1: (a) 3D-FDTD simulations of light's electrical field profile of being focused by silica microspheres with different sizes; (b) normalized light intensity distribution after being focused by silica microspheres.

3 EXPERIMENT

All experiments are done in a class-100 clean room. Two kinds of photoresist, positive photoresist AZ 5214-E and negative photoresist ma-N 405, were used. 10 wt.% aqueous suspensions of transparent silica microspheres were bought from Bangs Lab Inc. for formation of HCP monolayer. We spin photoresist on GaAs substrate at 3000 rpm for 60 seconds and prebaked the sample at 95 degrees for 1 minute. We used the convective self-assemble method to form a large area of HCP monolayer of silica spheres on top of the photoresist. The samples with photoresist covered with a single microspheres layer were exposed by conventional photolithography instrument (Quintel Q-4000) under low exposure energy with a broad wavelength centered at about 400 nm. Before development, the spheres were removed by either HF acid solution or ultrasonication in D.I. water. The photoresist was developed using AZ-300 MIF developer. We deposited metal films in high vacuum using Edwards Electron Beam Evaporator. Figure 2 is the process chart for the technique.

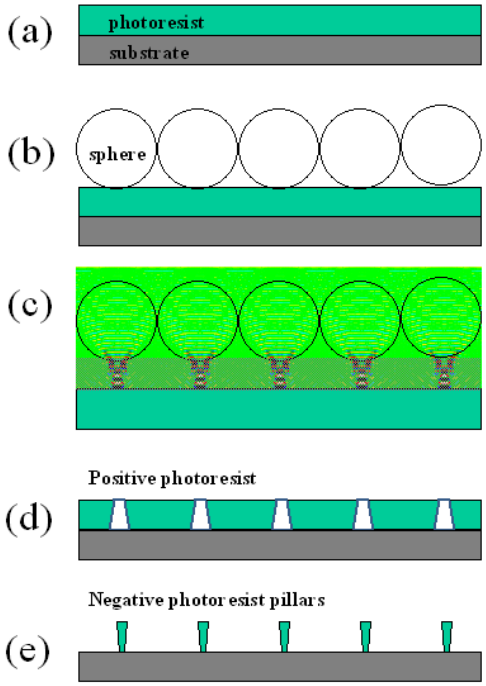

Figure 2: processing chart for our technique: (a) spin-on deposition of photoresist on a substrate, (b) a monolayer of microspheres formed on top of the photoresist, (c) UV light exposure of the photoresist covered with the particle lenses, (d) nanoholes formed after development of positive photoresist, (d) nanopillars of negative photoresist formed after being developed.

4 RESULTS

Figure 3(a) shows the SEM image of a typical monolayer of silica spheres with diameter of ~0.97 um formed on top of the negative photoresist. A monolayer of HCP microspheres is easy to form under optimized conditions of the temperature, humidity and the concentration of spheres. Figure 3(b) shows the top view of SEM images of the developed positive photoresist. The diameter of the holes is about 250 nm. The periodicity of these holes is 0.97 um: almost identical to the diameter of the spheres. The ratio of the feature size to the wavelength used is about 0.625. As shown in figure 3(c), we used another negative photoresist, ma-N 405 to fabricate the photoresist nanopillars. Figure 3 (d) is the enlarged image of the negative pillars. The diameter of the nanopillars is about 250 nm and the thickness of the photoresist is about 500 nm. The nanopillars have a high aspect ratio and it is good for the lift-off process using these nanopillars.

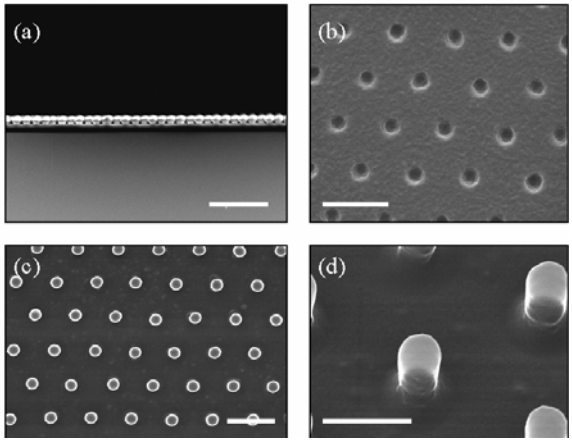

Figure 3: (a) SEM images of a single layer of microspheres (~0.97 μm diameter) on top of photoresist, the scale bar is 5 μm; (b) AZ5214 photoresist nanoholes after microspheres removal and photoresist development, the scale bar is 1 μm; (c) ma-N 405 photoresist used as negative photoresist to form nanopillars of photoresist, the scale bar is 1 μm; (d) high aspect ratio of nanopillars of negative photoresist, the scale bar is 500 nm.

We are also able to change the size of the holes and the lattice periods of the photoresist nanoholes array precisely and independently. The diameters of these nanoholes have been controlled with different exposure and development time, while the lattice periods were changed using different sizes of spheres. Figure 4 shows a uniform HCP arrays of photoresist holes with the diameters of about 300, 500, and 700 nm and lattice periods of about 500, 1000, 2000, and 4000 nanometers. In each line of the figure, the hole arrays have almost the same sizes with different periods. In each column, the array of holes has the same periods with different diameters.

Using the nanoholes and nanopillars of photoresist, we successfully produced a large area of highly uniform hexagonally packed metal nanoposts and nanoholes in multi-layers of metals by lift-off process, as shown in figure 5. As shown in figure 5 (a), we produced an array of gold posts with a thickness of 70 nm and 5 nm Cr as the adhesion layer. Figure 5 (b) is the enlarged view of the posts, which clearly shows the hexagonal distribution and the surface is very smooth. Figure 5 (c) and (d) are the nanoholes with the 100 nm gold and 5 nm Ti as the adhesion layer. The holes are perfectly circular and the edge of these holes is very smooth. These metal nanoposts and nanoholes can be potentially applied into photonic crystals, and also for further processing as metal masks.

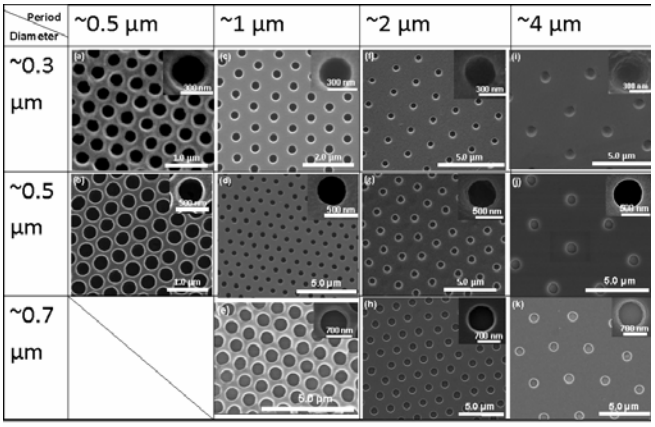

Figure 4: SEM images of uniform HCP arrays of nano-holes with controllable diameters and periods in the positive photoresist.

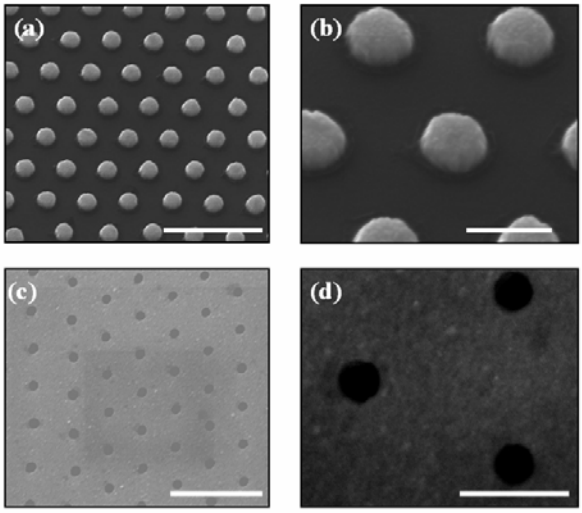

Figure 5**:** SEM images of (a) an array of gold nanoposts with a thickness of 70nm by lift-off process with 5nm Cr as the adhesion layer, the scale bar is 2 μm; (b) the enlarged view of the gold nanoposts, the scale bar is 500 nm; (c) gold nanoholes with a thickness of 100nm by lift-off process with 5nm Ti as the adhesion layer, the scale bar is 2 μm; (d) the enlarged view of the nanoholes in gold films, the scale bar is 500 nm.

5 CONCLUSIONS

We have successfully developed a novel mask-less and self-assembled sub-wavelength photolithography technique for forming highly uniform nano-holes and nano-pillars. The technique utilizes the self-assembled and super-focusing property of silica microspheres and applies them into the maturely developed photolithography system. It is a convergence of the bottom-up and top-down methods with the advantages of being simple, fast, economical, and compatible with current photolithography sources and photoresist. In hence it can be alternatively applied into some areas.

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[10] See for example Shipley 1800 series photoresist development curves at http://cmi.epfl.ch/materials/Data_S1800.pdf