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A Novel Self-aligned and Maskless Process for Formation of Highly Uniform Arrays of Nanoholes and Nanopillars

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Abstract Fabrication of a large area of periodic structures with deep sub-wavelength features is required in many applications such as solar cells, photonic crystals, and artificial kidneys. We present a low-cost and high-throughput process for realization of 2D arrays of deep sub-wavelength features using a self-assembled monolayer of hexagonally close packed (HCP) silica and polystyrene microspheres. This method utilizes the microspheres as super-lenses to fabricate nanohole and pillar arrays over large areas on conventional positive and negative photoresist, 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 demonstrate that the method can produce HCP arrays of hole of sub-250 nm size using a conventional photolithography system with a broadband UV source centered at 400 nm. We also present our 3D FDTD modeling, which shows a good agreement with the experimental results.

Keywords Microspheres · Lithography · Nanoholes · Nanopillars

Introduction

With nanotechnology becoming widely used, there is an increasing demand for rapid, parallel fabrication strategies for nanoholes and nanopillars. Some applications that require repetitive uniform nanoholes and nanopillars over large area are photonic crystals [1], memory devices [2], nanofiltration [3], solar cells [4], artificial kidneys [5], etc. Conventional photolithography techniques cannot satisfy the requirements of the nanopatterns due to the wavelength limit of current light source. Novel techniques like X-ray, electron beam, and focused ion beam are either slow or expensive for fabricating such repetitive patterns over large areas. Micro- and nanospheres that have highly uniform sizes and could easily produce a hexagonally close packed (HCP) self-assembled monolayer have attracted widespread attention for forming large areas of periodic nanostructures. One important example is Nanosphere Lithography (NSL) technique [6], which uses planar ordered arrays of polystyrene micro/nanospheres as a lithography mask to generate ordered nanoscale arrays on the substrate. However, the technique is always used for production of periodic particle arrays and it strictly requires the nanospheres to form a perfect hexagonal closed monolayer.

Here we present a novel photolithography technique, Nanosphere Photolithography (NSP), utilizing the self-assembled planar ordered single layer transparent spheres to generate sub-wavelength regular patterns over a large area on common photoresist. Previous studies show that the silica and polystyrene micro/nanospheres would act as super-lenses for the UV light [7]. The beam waist of the focused light would be much smaller than the wavelength of the light and the intensity would be many times stronger. Our full 3D finite difference time domain (3D-FDTD) calculations show that the beam waist is a very weak function of the sphere diameters and hence extremely uniform pattern size can be achieved. It is also possible to obtain the uniform nanopatterns of tunable sizes by changing the exposure energy and develop time

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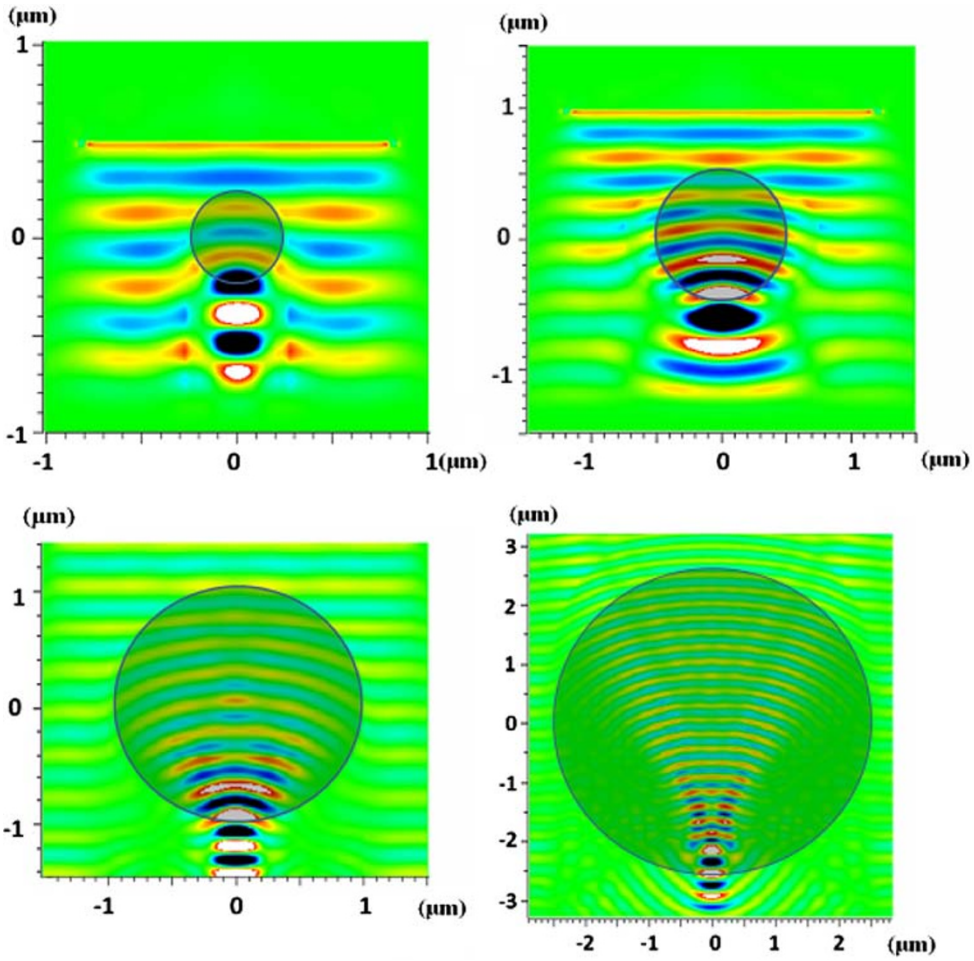

Fig. 1 3D-FDTD simulations of light's electrical field profile for silica micro/nanospheres with different sizes

of the photoresist, as well as controlling the spacing and density of the patterns using spheres of different diameters. NSP technique does not have special requirement for the coverage of the spheres, because the area of photoresist without the spheres or with multilayers of spheres cannot absorb enough photon energy to be developed.

Simulation Results

Figure 1 shows the 3D-FDTD simulations of light's electrical field profile for silica micro/nanospheres with diameters of $D = 0.5$, 1, 2, and 5 μm from left (up) to right (down) for conventional UV lithography i-line ($\lambda = 365$ nm); the centers of spheres are all in position (0,0), and the axis values represent the positions. Figure 2 is the normalized light intensity cross-section after being focused by silica micro/nanospheres with different sizes from 0.5 to 5 μm. It shows that the variation of the FWHM of the focused light is about 0.7% of the change of sphere's diameters. Highly uniform micro- and nanospheres with a standard deviation of about 1.3% can be obtained in the market [8], and hence the standard deviation of the light's FWHM due to the size variation would be less than 0.01%.

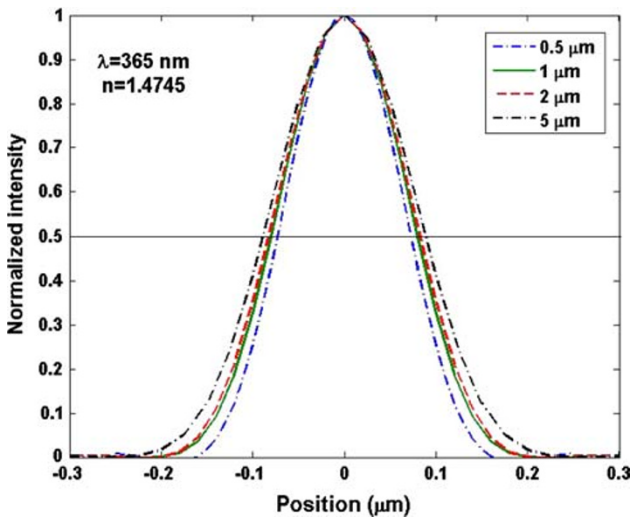

Fig. 2 Normalized light intensity cross-section after being focused by silica micro/nanospheres with different sizes

Similar simulation results could also be obtained for polystyrene (PS) spheres. FWHM of the light intensity is a good measure 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 [9].

Experiment and Results

All experiments are done in class-100 clean room. Two kinds of photoresists, AZ 5214-E and Shipley 1805, and two types of spheres, silica and PS, were used to form HCP arrays on top of the photoresist. About 10 wt.% aqueous suspensions of transparent silica or PS spheres were diluted by DI water down to 0.05 wt.% for both types of the spheres. Based on our simulations, it was found that the focusing intensity of silica spheres was smaller than that of PS spheres of the same sizes on the photoresist. So after using AZ 5214-E for the PS spheres, we considered photolithography with Shipley 1805 using silica spheres. The samples were exposed by a conventional photolithography instrument (Quintel Q-2000) under low exposure energy with a broad wavelength centered at 400 nm. Before development, the spheres can be removed by either HF acid solution or ultrasonication in DI water. The photoresist was developed using an AZ-300 MIF developer.

A large area of HCP monolayer of silica or PS spheres was formed by the self-assembled drop-coating method [10]. To form a good monolayer of micro- and nanospheres on photoresist, we modified the surface property of photoresist by dipping them into the developer solution for a few seconds before being processed, which helps make the surface of the photoresist hydrophilic enough. Figure 3a shows the SEM image of a typical monolayer of silica spheres with $d \sim 0.97$ μm formed on top of the AZ5214 photoresist. A monolayer of HCP microspheres is easy to form under an optimized condition with the temperature, humidity, and the concentration of spheres. Figure 3b shows the top view of SEM images of the developed photoresist. The diameter of the holes is about 250 nm. The periodicity of these holes is 0.97 μm: almost identical to the diameter of the spheres. The ratio of the feature size to the wavelength used is about 0.625. In Fig. 3c we show the cross-section image of a single nanohole in AZ5214 photoresist. It shows a high aspect ratio, which can be potentially used for lift-off and deep dry etching processes.

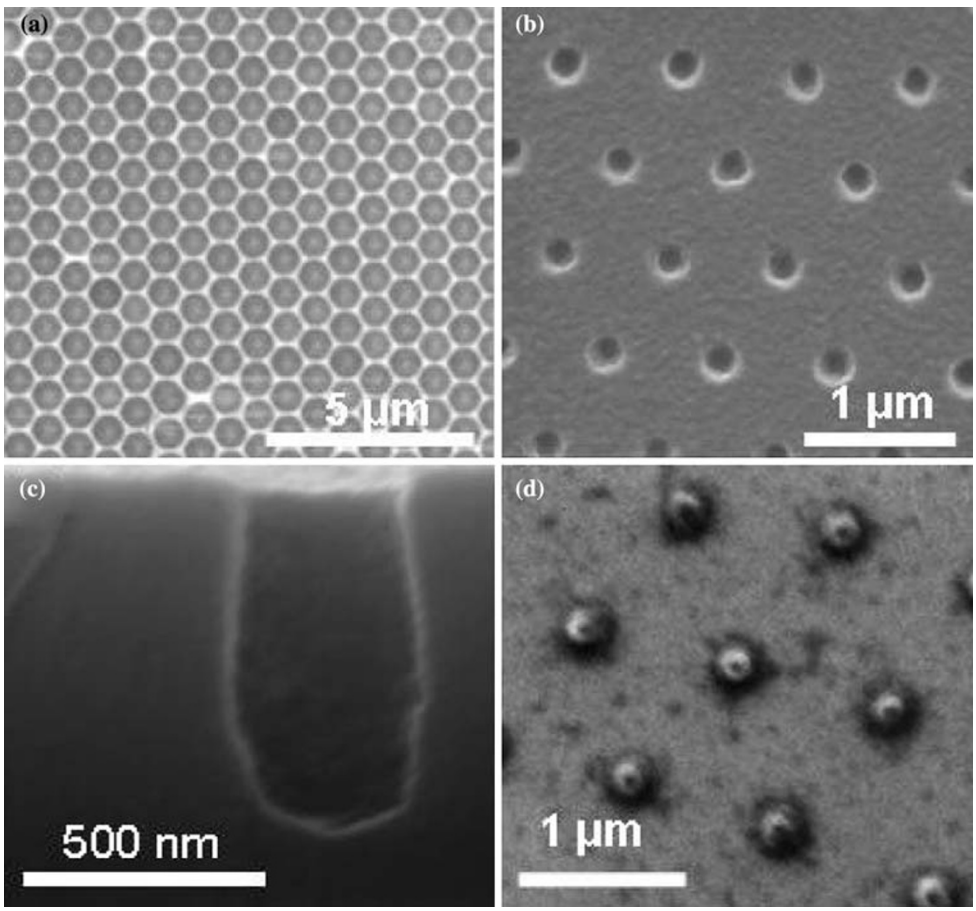

Fig. 3 SEM images of (**a**) a single layer of microspheres (0.97 μm diameter) on top of photoresist; (**b**) AZ5214 photoresist nanoholes after microsphere removal and photoresist development; (**c**) high aspect-ratio cross-section of nanopatterns formed by silica spheres and AZ5214 photoresist; (**d**) Shipley 1805 photoresist used as negative photoresist to form nanopillars of photoresist

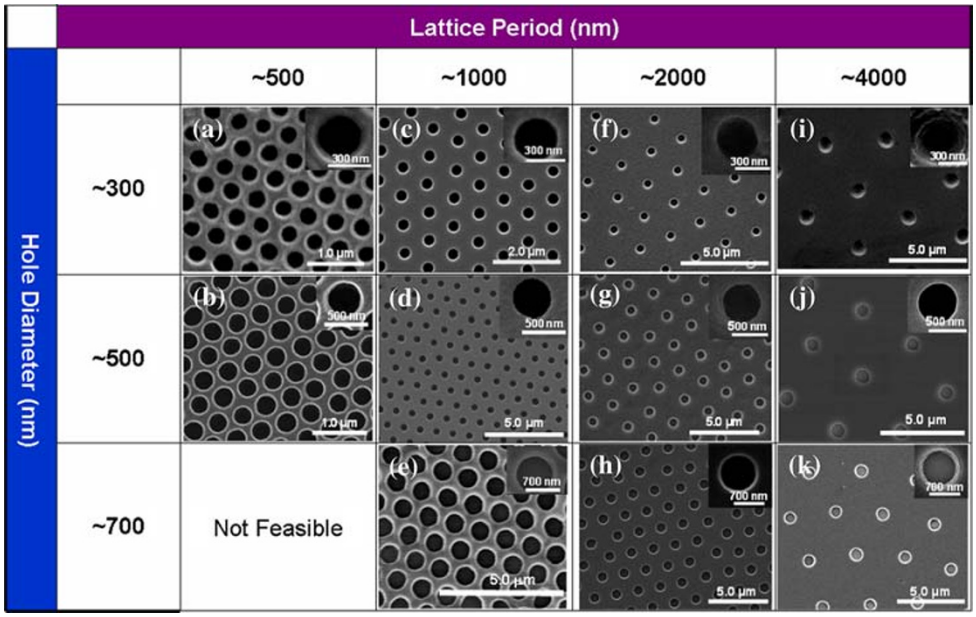

Fig. 4 SEM images of uniform HCP arrays of nanoholes with controlled different hole's diameters and periods in the photoresist

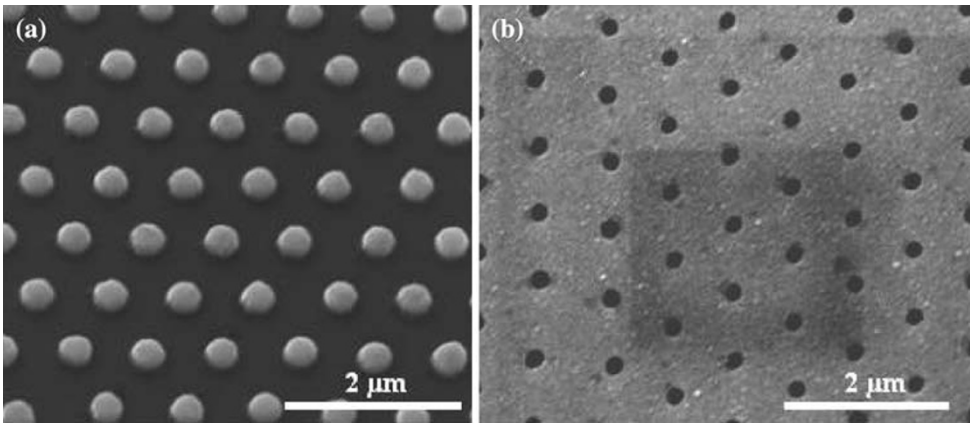

Fig. 5 SEM images of (**a**) a gold nanostructure with a thickness of 70 nm by lift-off process with 5 nm Cr as the adhesion layer; (**b**) gold nanoholes with a thickness of 100 nm by lift-off process with 5 nm Ti as the adhesion layer

As shown in Fig. 3d, we used another photoresist, Shipley 1805, to fabricate the photoresist nanopillars. Shipley 1805 photoresist is normally used as positive photoresist. To convert Shipley 1805 to negative photoresist we treated the samples with the photoresist in ammonia environment at 90 °C for about 1 h, followed by a post-exposure step for about 2 min.

Using NSP technique, we could also change the size of the holes and the periodicity of the array precisely and independently. The hole diameter has been controlled with different exposure and develop time, and the lattice period by different sphere diameters. Figure 4 shows a uniform HCP array of photoresist holes with hole diameters of about 300, 500, and 700 nm and lattice periods of about 500, 1,000, 2,000, and 4,000 nm.

As one application of the technique, we successfully produced a large area of highly uniform hexagonally packed gold nanoposts and nanoholes in gold thin film using the uniform HCP nanoholes and nanopillars of photoresist for lift-off process, as shown in Fig. 5a and b. These metal nanoposts and nanoholes can be potentially applied into photonic crystals, and also for further processing using as metal masks.

Conclusions

We have demonstrated a novel maskless and self-aligned sub-wavelength photolithography technique for forming highly uniform arrays of nanoholes and nanopillars. The technique utilizes the self-assembled property of micro- and nanospheres and applies them into the maturely developed photolithography system. It is simple, fast, economical, and compatible with current photolithography sources and photoresists, and hence it can be alternatively applied into some areas.

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