Research Letter

A Method for Fabricating Arrays of Nanopatterns with the Feature Size beyond Diffraction Limit

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A convenient lithographic technique is proposed in this paper, which can be used to produce subdiffraction-limit arrays of nanopatterns over large areas (about several square centimeters). An array of polystyrene spheres (PS) is arranged on the surface of a layer of silver which has a thickness of about tens of nanometers. With the normal illumination light of wavelength 365 nm perpendicular to the substrate, PS can generate an array of optical patterns with high intensity at their contact points with silver. By designing the silver slab, the evanescent waves that carry subwavelength information about the optical patterns are substantially enhanced, while propagating components are restrained. In the photoresist which is on the other side of silver, the optical intensity is redistributed and subdiffraction-limit patterns are obtained after exposure and development. Simulation by finite-difference time-domain (FDTD) and experiments were carried out to verify the technique. The results show that by using PS with diameter of 600 nm, nanopatterns with dimension of less than 80 nm can be obtained.

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1. INTRODUCTION

Arrays of nanopatterns are useful for a wide range of applications such as chemical sensors [1], optical filters [2–4], photonic crystals [5], digital optical systems [6, 7], and displays [8]. Conventional photolithography [9] cannot be used to fabricate arrays of nanopatterns because of the diffraction limit. Holographic lithography [10], E-beam lithography [11], and laser pattern writing [12] are currently used to fabricate them. Although high-quality patterns can be produced with those techniques, they require the expensive facilities, and the multistep processing is required normally. In 2002, the group of Whitesides proposed a lithographic technique by which the simple, repetitive micropatterns over large area can be produced [13]. However, the technique can only be used to fabricate patterns with dimensions larger than 100 nm. In 2005, Zhang Xiang's group proposed a method to produce subdiffraction-limited optical imaging with a silver superlens [14]. However, masks fabricated by focused-ion-beam lithography or E-beam lithography are needed in this method.

To obtain nanopatterns for the potential applications, we demonstrate a convenient process to produce subdiffraction-

limit arrays of nanopatterns over large areas in this paper. An array of PS is placed on the surface of a layer of silver and forms contact points of medium and metal. When there is illumination light, PS can generate an array of optical patterns with high intensity at these contact points. Evanescent waves that carry subwavelength information of the optical patterns can be enhanced when they are transmitted through the silver layer to form intensity distribution in photoresist on the other side of silver. Meanwhile, propagating components are restrained. Therefore, subdiffraction-limit nanopatterns can be obtained in photoresist after development. In this technique, the nanopattern masks produced by E-beam lithography can be omitted. The contact points of PS and silver layer can be considered as the mask, where PS diameter is about hundreds nanometers which can be easily produced. Nanopatterns with dimensions below 80 nm can be obtained by this technique, which are about one-fifth of the illumination wavelength.

2. PRINCIPLE AND SIMULATION

The schematic view of this technique is shown in Figure 1(a). Figure 1(b) shows the location of PS in the PDMS

FIGURE 1: (a) The scheme of the technique; (b) PS embedded in PDMS membrane; (c) the arrangement of PS.

membrane, where PS cannot be enwrapped completely by PDMS because of the capillary effect. Figure 1(c) shows that the PS is arranged in hexagonal arrays.

We begin the process by making a mask constituted by PS embedded in PDMS membrane. Then, the mask is put onto the surface of a silver layer, where a photoresist (PR) layer is placed on the other side. Here, PS converges the incidence light to the limited area, where optical patterns with relatively high intensity are generated on the surface of the silver. At the nanoscale contact points of PS and silver layer, some of the light in optical patterns can be coupled into evanescent waves with wave vector k_x , where $k_x \gg k_0$ (k_0 is the wave vector in the vacuum). Here, evanescent waves and propagating components are included in the optical patterns, where evanescent waves carry the subwavelength information. When the real part of the metal permittivity equals the dielectric of adjacent medium, most of the evanescent waves that carry subwavelength information can be transmitted by extremely amplifying in the silver layer. Meanwhile, the propagating components are restrained by reflecting and absorbing of the silver slab. Therefore, in the photoresist on the other side of silver, the optical intensity is redistributed and subdiffraction-limit patterns are obtained after exposure and development.

To verify the feasibility of this technique, simulation with FDTD method was carried out to obtain the intensity distribution in the photoresist. The permittivities of PS, PR, and silver are 2.5281 [13], $2.886 + i0.059$ [15], and $-2.4012 + i0.2488$ [15], respectively. The results are shown in Figure 2. The wavelength of the illumination light is 365 nm, and the diameter of PS is 600 nm.

The left part of Figures 2(a) and 2(c) is the simulated schemes with and without a layer of silver on the surface of photoresist, respectively, where the thicknesses of optimum silver slab and photoresist are 30 nm and 100 nm. The right parts in these two figures are the intensity distributions in photoresist within 40 nm away from the surface. Figures 2(b) and 2(d) are the normalized intensity distributions on the surface of photoresist according to Figures 2(a) and 2(c),

from which we can see that the full width half maximums (FWHMs) are 57 nm and 247 nm. Here, we consider the FWHM as the size of photoresist which is exposed and can be dissolved in the development process. In the above two situations, the dimensions of the patterns to be obtained in photoresist are 57 nm and 247 nm, respectively.

From above simulation, we can know that with silver slab in the exposure procedure, the dimension of the obtained patterns is extremely reduced. The reason is the amplifying ability of the silver to the evanescent waves and restrained to the propagating components.

3. EXPERIMENTS AND RESULTS

To clean the Si substrate completely, it was dipped in a $3 : 1$ (v:v) mixture of H_2SO_4 (98%) and H_2O_2 (30%) for about an hour in the temperature of 80°C . Then, it was processed to be hydrophilic by dipping in a $1 : 1$ (v:v) mixture of H_2O_2 (30%) and NH_4OH (20%) for an hour. Then, a monolayer of PS (from Duke Scientific Corporation, Calif, USA) with diameter 600 nm was spin-coated onto the surface of the substrate Si. It was worth mentioned that the PS was arranged in hexagon which could be seen in Figure 3.

The substrate was placed in a plastic petri dish. A $10 : 1$ (v:v) mixture of PDMS-Sylgard Silicone Elastomer 184 and Sylgard Curing Agent 184 (Dow Corning Corp. Midland, Mich, USA) was poured into the petri dish. The PDMS cured at room temperature in the laboratory ambient for 30 – 60 minutes. This cure was followed by additional curing at 65°C for approximately 1 hour or until the polymer was rigid. After cooling to room temperature, the PDMS was carefully peeled from the dish and substrate. The membrane of PDMS embedded with PS was obtained.

Silicon was taken as the substrate material and photoresist AZ3100 as the exposure material. The resist was spin-coated onto the substrate with rotation speed of 4000 rad/s. Process parameters of coating time, prebake temperature, prebake time, and resist thickness were 30 seconds, 100°C , 5 minutes, and 100 nm, respectively. A layer of silver with optimum thickness 30 nm was then deposited to the surface of the photoresist. The PDMS membrane was put onto the surface of silver with the PS contacted with silver. Then, the above structure was exposed from the top of the PS by illumination light source with central wavelength of 365 nm. The exposure time was 7 seconds.

After exposure, the PDMS membrane embedded with PS was peeled off from the surface of silver. The substrate was dipped in the solution of HNO_3 (30%) to wipe off the layer of silver. After developing for about 20 seconds, the nanopatterns with dimension of about 75 nm were obtained in photoresist as shown in Figure 4(a), which is a little larger than the theory value 57 nm we got in the part principle and simulation. The reason may be the infection of the PS not contacting with silver tightly and the miss control in the development process.

Control experiment was also carried out. There was no silver layer on the surface of photoresist. The optimum process parameters of exposure time and development time were 1 second and 5 seconds, respectively. The obtained

FIGURE 2: The simulation results: (a) the intensity distribution in photoresist with a layer of silver on its interface; (b) the normalized intensity distribution on the surface of photoresist according to the scheme in (a); (c) the intensity distribution in photoresist without silver on its interface; (d) the normalized intensity distribution on the surface of photoresist according to the scheme in (c).

FIGURE 3: Monolayer of PS on the surface of substrate Si.

FIGURE 4: Experiment results: (a) patterns in photoresist obtained with silver in the exposure procedure; (b) patterns in photoresist obtained without silver in the exposure procedure.

patterns in photoresist are shown in Figure 4(b) from which we can see that the dimension of holes is about 260 nm.

From the above results, we can know that the pattern's dimension we got with silver layer in the exposure procedure is much smaller than that without silver layer. The effect of silver can be proved.

4. CONCLUSIONS

This paper demonstrates a technique which can be used to fabricate nanopatterns. The technique does not require the use of masks made by expensive optical facilities. It provides a convenient method for fabricating subdiffraction-limit nanopatterns. By reasonably choosing the size of PS, the arrangement of PS array, the kind of the photoresist, and different kinds of nanopatterns can be obtained. Nanostructures generated by this technique can be useful for the fabrication of optical elements. The research group in our laboratory is carrying out deep research about the technique. Nanopatterns with other periods and arrangement arrays are in fabricating.

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