A novel lithography technique for formation of large areas of uniform nanostructures

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ABSTRACT

With nanotechnology becoming widely used, many applications such as plasmonics, sensors, storage devices, solar cells, nano-filtration and artificial kidneys require the structures with large areas of uniform periodic nanopatterns. Most of the current nano-manufacturing techniques, including photolithography, electron-beam lithography, and focal ion beam milling, are either slow or expensive to be applied into the areas. Here, we demonstrate an alternative and novel lithography technique—Nanosphere Photolithography (NSP)—that generates a large area of highly uniform periodic nanoholes or nanoposts by utilizing the monolayer of hexagonally close packed (HCP) silica microspheres as super-lenses on top of photoresist. The size of the nanopatterns generated is almost independent of the sphere sizes and hence extremely uniform patterns can be obtained. We demonstrate that the method can produce hexagonally packed arrays of hole of sub-250 nm size in positive photoresist using a conventional exposure system with a broadband UV source centered at 400 nm. We also show a large area of highly uniform gold nanoholes (~180 nm) and nanoposts (~300nm) array with the period of 1 μm fabricated by the combination of lift-off and NSP. The process is not limited to gold. Similar structures have been shown with aluminum and silicon dioxide layer. The period and size of the structures can also be tuned by changing proper parameters. The technique applying self-assembled and focusing properties of micro-/nano-spheres into photolithography establishes a new paradigm for mask-less photolithography technique, allowing rapid and economical creation of large areas of periodic nanostructures with a high throughput.

Keywords: micro-spheres, super-lenses, photoresist, lift-off, and nanostructures

1. Introduction

As nanotechnology being developed widely, there is an increasing demand for rapid and massively parallel fabrication strategies for large areas of uniform periodic subwavelength structures. Arrays of the nanostructures have been potentially found to have many important applications such as surface plasmonics[1], data storage[2], optoelectronic devices[3], and nano-filtration[4]. To fabricate the nanostructures, standard lithography techniques, such as x-ray lithography[5], electron-beam lithography[6], and focal ion beam milling[7] methods, have high enough resolutions to be applied. However, x-ray lithography is too expensive because of the expensive instruments used and the e-beam lithography and focal ion beam milling methods are too slow because of their inherent serial nature. Low-cost and high throughput methods such as self-assembly are another class of fabrication techniques. Generally, the self-assembly methods can be defined as the spontaneous formation processes which lead to complex hierarchical structures from pre-designed building blocks. The self-assembly methods, such as Copolymer lithography[8] and Nanosphere lithography (NSL)[9], have a lot of advantages for certain applications, but they are not as fully developed as the standard lithography methods. The development of alternative parallel lithography methods is still necessary for different applications.

Here we will present an alternative method, Micro-/nano-sphere Photolithography (NSP), for fabrication of large areas of uniform periodic nanopatterns using a monolayer of silica micro-spheres to focus UV light. Recent theoretical and experimental data show that spheres with certain refractive index can produce "photonic-jets", over a wide

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wavelength range, to generate a beam waist much smaller than the wavelength of light[10][11][12]. Using this effect, we introduced a new subwavelength nano-patterning process that is based on the conventional UV light sources widely used in photolithography industry, such as g-line (405 nm), i-line (365 nm), or other deep-UV light. Since the FWHM of the focused light is a very weak function of the diameters of the micro-spheres, a very uniform array of nanopatterns can be generated by this method. Compared with other nanolithography techniques, NSP is a maskless technique. The microspheres can be assembled as monolayer on top of photoresist by many methods, such as drop-coating[13], spin-coating[14] and convective assembly[15]. NSP has the advantages of being fast, high throughput and low-cost. It utilizes both the self-assembled property of micro-spheres and parallel advantage of photolithography. It can also be widely applied into many areas, since it generates nanopatterns in photoresist, which have been widely studied and used. It is also a tunable process. The sizes of the nanopatterns generated can be changed by different exposure dose and development of photoresist, while the period of the array can be tuned by the diameters of micro-spheres.

The combination of NSP technique with other standard processes such as lift-off and etching greatly broadens NSP into the fabrication of nanopillars and nanoholes in other materials. Applying the lift-off with the nanoholes in positive photoresist or nanopillars of negative photoresist, we produced a large area of periodic uniform nanoposts of gold or nanoholes perforated in gold film. Different metals, dielectrics or multi-stacks with the nanoholes perforated can also be generated. Using a broadband wavelength light source centered around 400 nm we have produced the nanoholes of the diameter of about 250 nm in positive photoresist and the nanopillars of the diameter of about 200 nm with negative photoresist. The nanopillars generated have a high aspect ratio and under-cut shape for lift-off. As small as 180 nm nanohole arrays perforated in titanium/gold films were produced. The nanohole arrays perforated in aluminum and silicon dioxide films were also shown.

2. Simulations

The UV light propagation through the silica micro-sphere has been studied and simulated by 3D-FDTD modeling methods. The basic model for the simulations is the silica micro-sphere standing on top of the photoresist with the substrate below, as shown in figure 1(a). The variables in the simulations are the diameters of the micro-spheres, the indices of the spheres (different materials), and different input wavelengths of UV light. During the simulations, we changed one variable while keeping other variables constant. Figure 1(b) shows one example of the focus process by the silica micro-sphere. We are using the plane wave from the light source. With the diameter of micro-sphere of about 1 μm and the UV light's wavelength of 365 nm, the FWHM value of the focused light is about 150 nm and the intensity is about 30 times stronger than the input one.

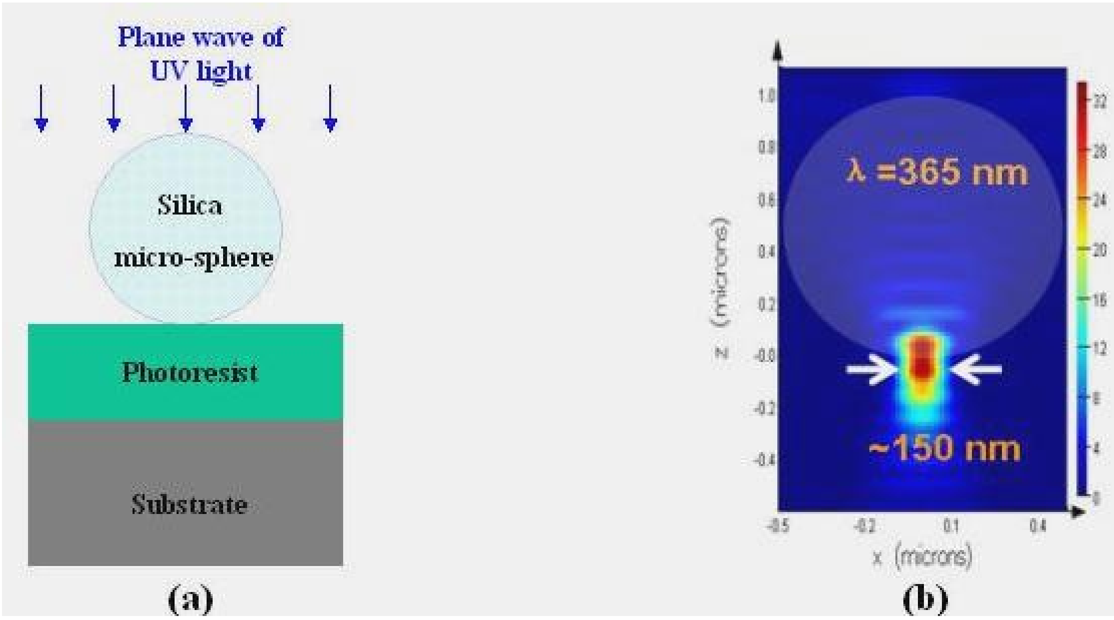

Figure 1 (a) the basic simulation model, (b) one example of the focus process by 1 μm silica micro-sphere

Changing the diameters of the spheres from about 0.5 μm to about 5 μm, we found that the FWHM values of the focused light were almost unchanged. Figure 2 is the normalized intensity of the focused light versus the position in the plane of the light's propagation with different diameters of micro-spheres. The variation of the FWHM values of the focused light versus the spheres diameter is less than 1% considering a linear relationship. The FWHM value can be approximately used as the sizes of nano-features generated in photoresist since it is the threshold value between the exposed and unexposed area. In hence, the nanopatterns array generated would be very uniform.

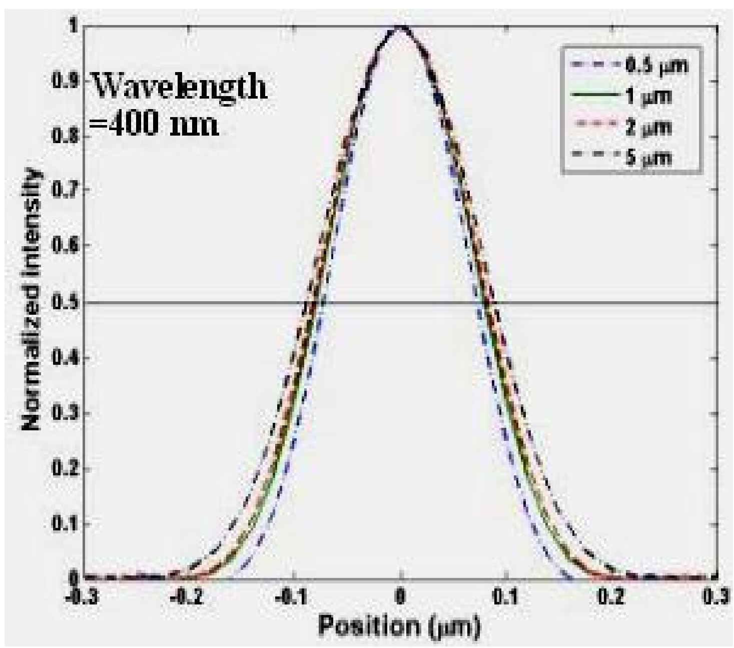

Figure 2 The normalized intensity of the focused light versus the position with different diameters of micro-spheres

By changing different wavelengths of the UV light while keeping the diameter of the microspheres as 1 μm, we found that the FWHM of the focused light would get smaller as the wavelengths get smaller. In figure 3, it shows the normalized intensity distribution of the focused light with different wavelengths. The FWHM values of the light change from about 203 nm to 121 nm when the wavelengths are from 500 nm to 300 nm. So, NSP is a scalable process. With a shorter wavelength, smaller nano-features can be generated.

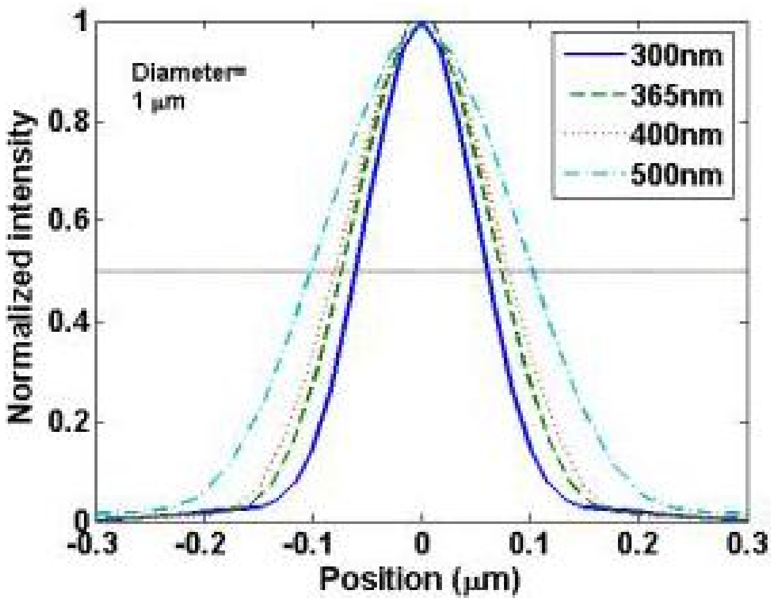

Figure 3 The normalized intensity of the focused light versus the position with different wavelengths of UV light

3. Experiment

The basic process flow is shown in shown in figure 4. Photoresist was spun on the substrate. Either positive or negative photoresist can be applied. A monolayer of micro-spheres was formed on top of the photoresist. Silica micro-spheres were bought from Bangs Lab. The sample with the monolayer of micro-spheres on the photoresist was exposed with a conventional Quintel exposure instrument with broadband wavelength centered about 400 nm. The micro-spheres were removed by ultrasonication method in D.I. water after exposure. An array of periodic uniform nanoholes was formed after the development of positive photoresist. The nanoposts made of Ti/Au layer were formed by electron-beam evaporation of Ti/Au and lift-off. Similar processes were done with aluminum layer. For negative photoresist, an array of periodic uniform nanopillars was formed. The nanoholes perforated in Ti/Au films were formed by lift-off.

The whole process of NSP was quite similar as the standard photolithography techniques. But since it is a maskless process, it avoids using the expensive masks in the photolithography method. It also uses a longer wavelength to fabricate the nanopatterns with the same resolutions compared with the standard photolithography.

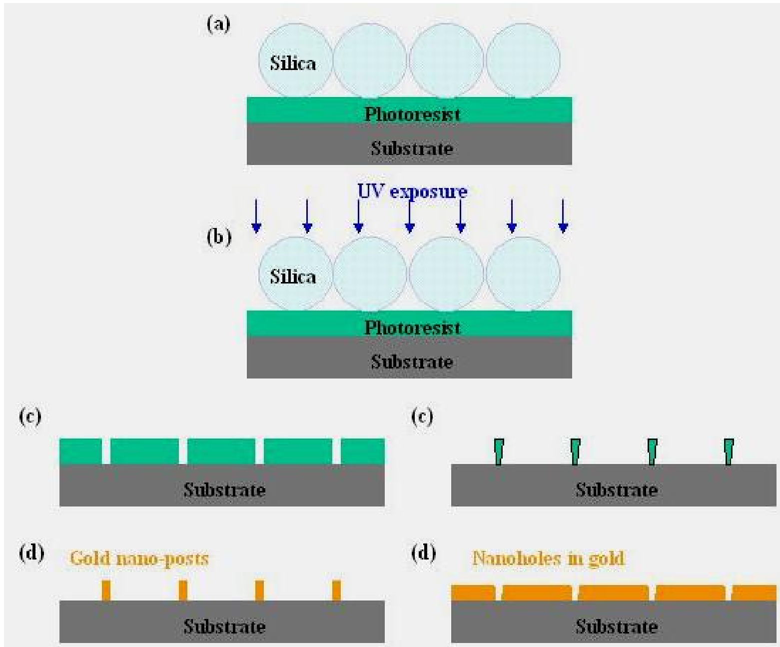

Figure 4 The schematic process of NSP for fabrication of nanoposts in Ti/Au layers and nanoholes perforated in the films, from (b) to (c), it switches to two different processes with two different kinds of photoresist used

4. Results

Figure 5(a) is a Scanning Electron Microscope (SEM) image showing that a HCP monolayer of silica micro-spheres was formed on top of the photoresist. Figure 5(b) is the enlarged view of the micro-spheres on top of the photoresist. These micro-spheres are close packed.

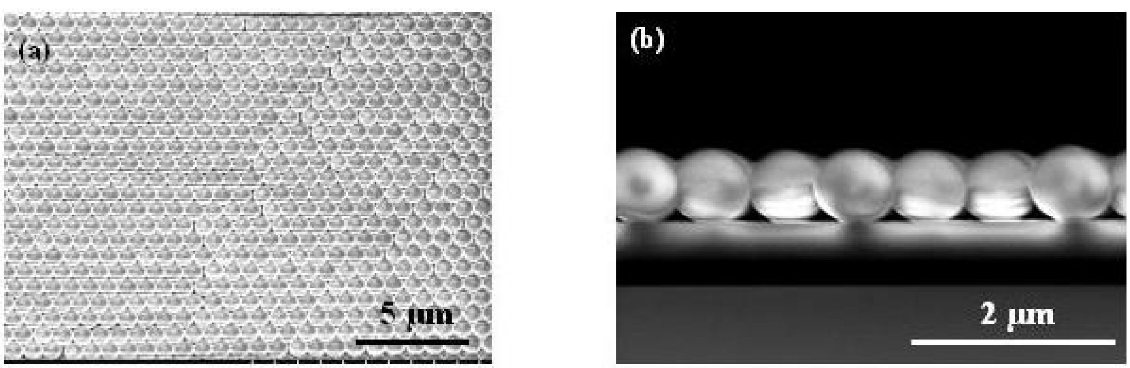

Figure 5 (a) SEM image of HCP monolayer of silica micro-spheres, (b) Enlarged cross-section view of micro-spheres on top of the photoresist

Using the UV light with λ centered about 400 nm to expose the positive photoresist with silica micro-spheres, we produced a periodic uniform nanohole array with the diameter of about 250 nm shown in figure 6(a). The period of the array is about 1 µm, which is the same as the diameter of the microspheres used. Figure 6(b) is the cross section view of the nanohole. It shows about 1:2 aspect ratio and almost vertical sidewall. It can be further used for lift-off and etching process. As you can see, at the bottom of the nanohole the diameter is even smaller and it can be potentially used for generating smaller features by etching-transfer the nanopatterns. To show the tunable ability of NSP, we also used different diameters of silica micro-spheres to produce the nanohole arrays. As expected, we have generated the nanoholes of almost the same sizes but with different periods. Figure 7(a) and (b) show the nanohole arrays with the periods of about 2 and 4 μm and the nanohole sizes are around 300 nm. Using the negative photoresist in NSP, we produced a periodic uniform array of nanopillars. The nanopillars can also be tuned with different sizes and sidewalls in the cross section. Figure 8(a) and (b) show an array of periodic uniform nanopillars of photoresist with different sizes and cross section shapes. With controlled parameters, the size of the nanopillars in figure 8(a) is about 250 nm and the sidewall is almost vertical; the nanopillars in figure 8 (b) have the size of about 200 nm and it shows a very strong undercut shape. As you can see, the nanopillar fallen down shows a clear undercut cross-section shape of the pillar.

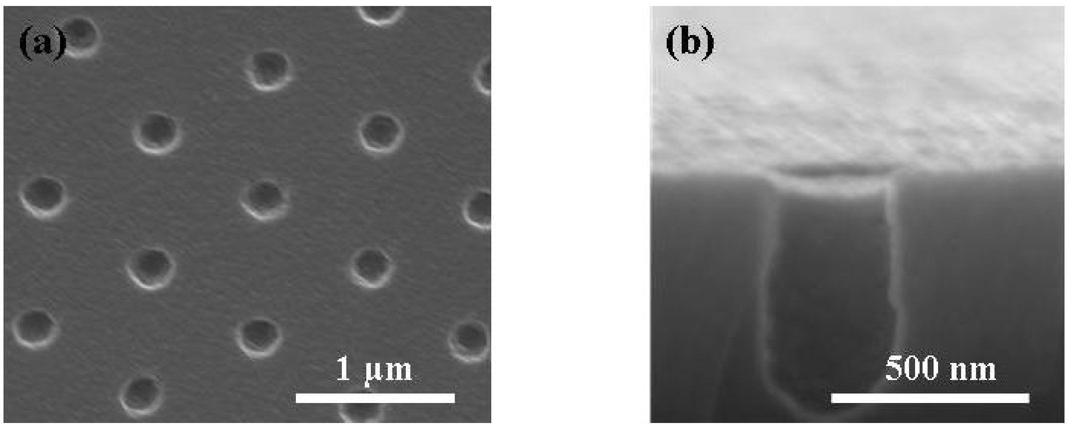

Figure 6 (a) A uniform nanohole array in photoresist with the period of about 1 um, (b) the cross section view of a single nanohole

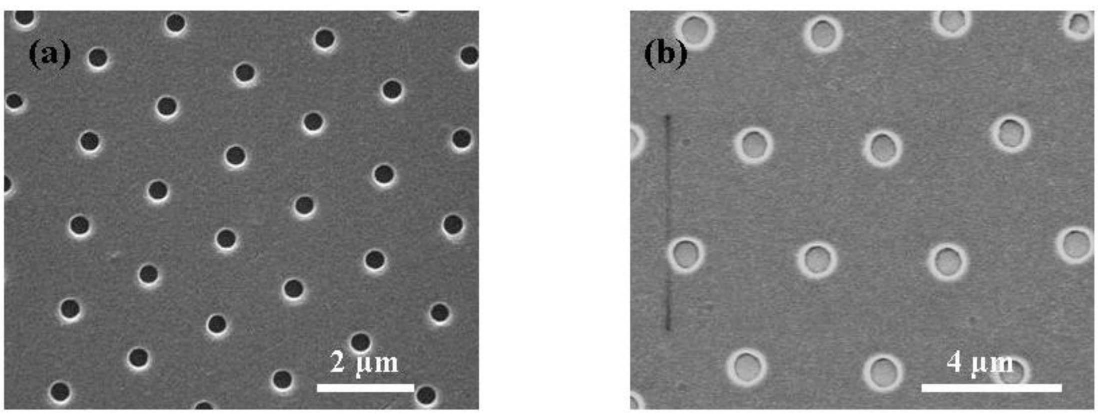

Figure 7 (a) A uniform nanohole array in photoresist with the period of about 2 um, (b) a uniform nanohole array in photoresist with the period of about 4 um

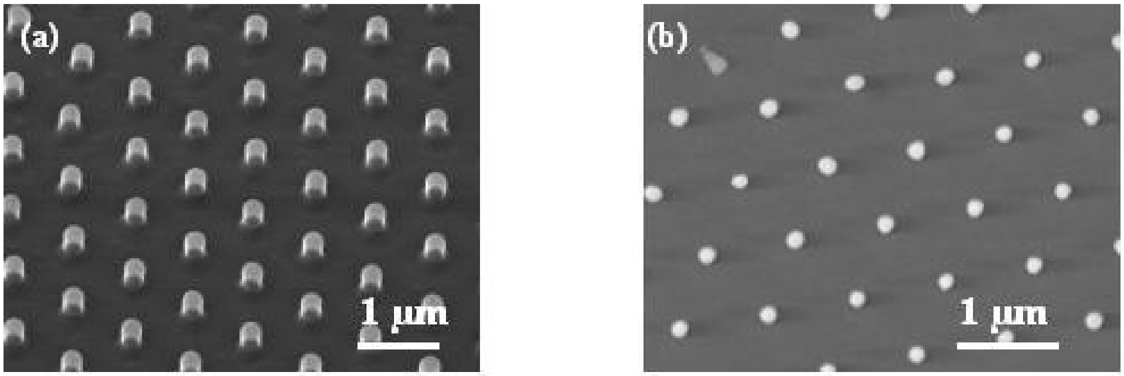

Figure 8 A uniform nanopillar array in negative photoresist with the period of about 1 um (a) the nanohole size of about 250 nm with a vertical sidewall, (b) the nanohole size of about 200 nm with a strong undercut

Using the nanoholes and nanopillars produced by NSP, we successfully produced a uniform array of gold nanoposts and nanoholes. Figure 9(a) shows an array of hexagonally distributed nanoposts of Ti/Au and figure 9(b) shows the array of hexagonally distributed nanoholes perforated in Ti/Au films. The diameter of nanoposts and nanoholes in figure 9(a) and (b) are about 300 nm and 180 nm separately, and the periods are both about 1 um. All these parameters can be tuned since NSP is a tunable process. Similar results can also be obtained with the use of aluminum, as shown in figure 10 (a). The diameter of the nanoholes perforated in the Al film is about 250 nm. The edge of the nanoholes is a little rough because aluminum deposited by e-beam evaporation is not as uniform as other metals. Besides lift-off process, using Reactive Ion Etching (RIE) and the metal layer with the nanoholes as mask, we also produced a similar nanohole array in the dielectric of silicon dioxide (SiO_2) film in figure 10(b). It is a tilted cross section image. There are clearly two layers of materials on top of the substrate, which are SiO_2 and Al thin films. The size of the nanohole is almost the same as the one in the metal films.

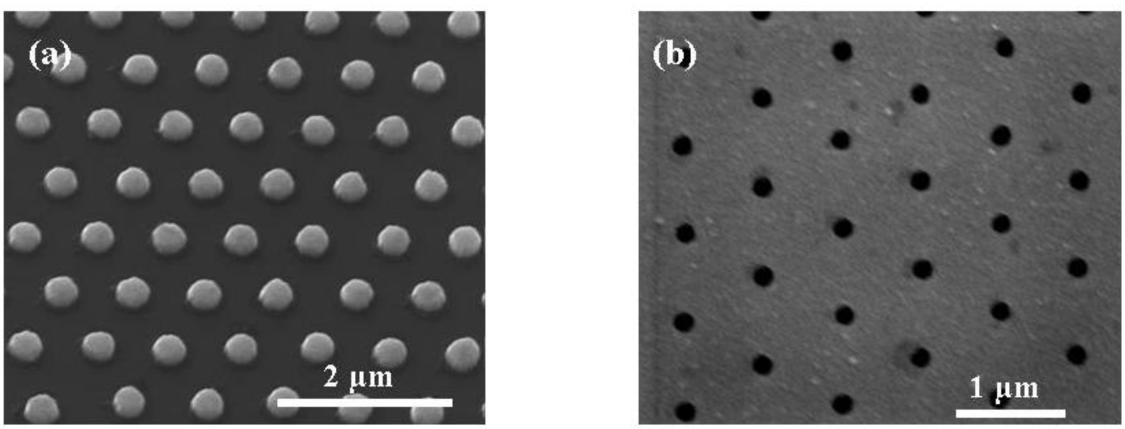

Figure 9 (a) An array of hexagonally distributed uniform nanoposts of Ti/Au, (b) an array of hexagonally distributed uniform holes perforated in Ti/Au films

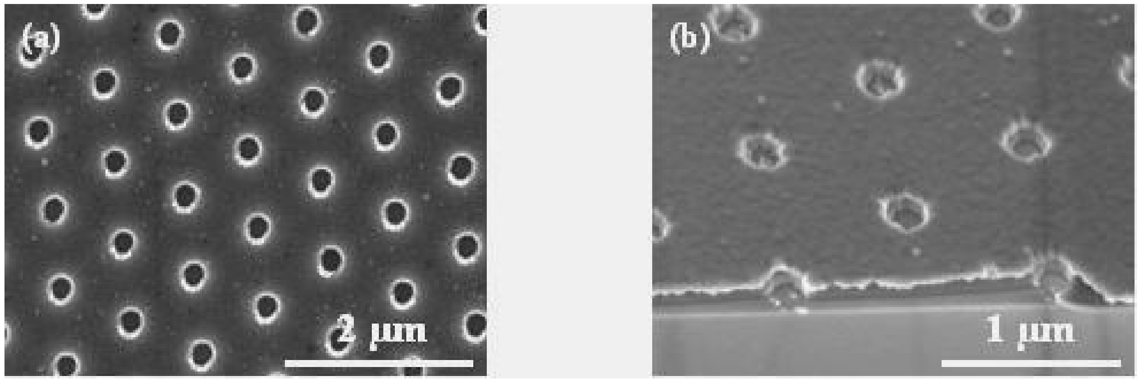

Figure 10 (a) An array of hexagonally distributed uniform nanoholes perforated in aluminum layer, (b) using RIE to transfer the nanoholes patterns in the SiO_2 film below

5. Conclusions

We have demonstrated a maskless photolithography method to generate subwavelength structures. The method utilizes the self-assembled monolayer of silica micro-spheres as super-lenses to focus UV light into photoresist and generated highly uniform arrays of nanoholes or nanopillars. We also presented the similar nanostructures in different metals and dielectrics using the method with other standard processing methods. The technique is a controllable process. We believe that it can be used for many areas, such as fabrication of electronic and optoelectronic devices.

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