Spatial Patterning of Colloidal Nanoparticle-Based Thin Film by a Combinative Technique of Layer-by-Layer Self-Assembly and Lithography

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A novel approach to generating clear patterns of different types of nanoparticles is presented in this paper. Nanoassembly in the vertical direction was combined with planar micropatterning. This provides industrial applications of a popular layer-by-layer method to produce multilayers of polymers, nanoparticles, and proteins organized on the nanometer scale. A thin film of organic polystyrene spheres was first coated on the pretreated silicon wafer with layer-by-layer self-assembly. Then a layer of aluminum was deposited on the thin film. A layer of positive photoresist was spun on the surface of aluminum and then illuminated with UV light. The exposed parts of the resist were removed and windows were opened above the aluminum. The subsequent etching removed exposed aluminum and left a polystyrene thin film in the open windows. Oxygen plasma was employed to remove the polystyrene thin film on the bottom. Eventually, aluminum and photoresist were removed and only the desired pattern remained. This approach was also employed for the patterning of the silica nanoparticle thin film, a widely used material in various applications. In this case, wet etching was demonstrated to etch silica particles. A scanning electron microscope was used to produce the image of the pattern.

Keywords: Layer-by-Layer Self-Assembly, Nanoparticle, Lithography, Metal Mask, Patterning.

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1. INTRODUCTION

In recent years, technologies for the production of metallic, semiconducting, and insulating nanocrystals have been able to provide nanoparticles that function similarly to the high-grade materials used by the modern microelectronics industry.[1,2] Because of their unique properties and versatility, nanoparticles have become the focus of material research for applications in microelectronics, optoelectronics, and catalysis and for fundamental research in solid-state physics.[3–5] For example, semiconductive nanoparticles are technologically important materials that are expected to have numerous potential applications including nanoelectronic, photovoltaic, and chemical. More and more results have shown that nanoparticles may play an important role in future technologies. Prior to integrating various functional nanoparticles into electronic and photonic devices and catalytic reactions, the development of techniques for the precise control of the spatial arrangement of the individual building block on the nanometer and subnanometer levels is crucial to the design and fabrication of advanced devices. Many approaches, such as microprinting, have been demonstrated in this field, and many of them depend on the template fabrication and subsequent template-based selective deposition with certain selectivity.[6–10]

This paper demonstrates a patterning technique based on layer-by-layer self-assembly in combination with traditional lithography. It is referred to by the authors as the metal mask approach. By using this method, we avoid selective deposition, which demands strict control and consequently obtain extremely high reproducibility and a simplified process. Because layer-by-layer self-assembly and lithography techniques are mature processes and lithography is widely applied in the modern semiconductor industry, a combinative technique will be economical and suitable for mass production. By just following the traditional process, the nanostructures composed of nano-building blocks can be realized. As it is used in the semiconductor industry, the process results in such a high reproducibility that distinct patterns (in this experiment 10 μm) can be created in almost all of the dies on the wafer. Commercial electronic and photonic devices, such as MOSFET or solar cells with nanostructure are expected to be fabricated by this method at considerably lower cost and temperature. Layer-by-layer self-assembly was employed to deposit the nanoparticle-based thin film on a substrate, and a semiconductor process was used to pattern the thin film.

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Nanoparticle assemblies on certain substrates have been widely investigated by many researchers with different techniques. In particular, colloidal adsorption onto silicon substrates is of great interest because of its potential applications in the future. Layer-by-layer self-assembly appears to be a promising technique for the application of nanoparticles because it only involves the alternate immersion of a charged substrate into oppositely charged polymer aqueous solutions.[11–15] The technique is also called molecular beaker epitaxy. With simple instruments, one can produce molecularly organized films similar to the ones obtained with the highly sophisticated and expensive molecular beam epitaxy technology used for metals and semiconductors. The versatility, relative ease of preparation, and potential for scale-up have made self-assembly a viable colloid chemical approach for the fabrication of nanostructured devices. A rational control of the structure based on the ultrathin particle film is also achieved by layer-by-layer self-assembly. It can also help adsorption of particles to almost all of the substrates in nature.

After layers of nanoparticle-based thin film were deposited on a 4-inch silicon wafer, a conventional lithographic technique was employed to open windows above the nanoparticle layer while the remaining area was covered by metal. Then the nanoparticle thin film exposed to the air would be removed by an appropriate etching method so that a desired pattern was created. UV spectrum irradiation, wet etch, and dry etch were involved in this process. In this paper, 300-nm polystyrene particles were used as the nano-material. It is easier to manipulate particles with smaller diameters because of their better adhesion to the substrate. Particles with a diameter of 300 nm were chosen because they were imaged more easily with a scanning electron microscope.

This paper describes the fabrication of a patterned structure composed of polystyrene or silica nanoparticles, which can represent organic and inorganic materials, respectively. The technique can be applied to most of the nanoparticle thin films as long as it succeeds on these two spheres. At the beginning, a 4-inch silicon wafer was immersed in a solution of sulfuric acid and hydrogen peroxide for 1 h to make the surface strongly negatively charged. It was soaked in a positively charged poly(dimethyldiallyl ammonium chloride) (PDDA) solution to be coated with a layer of cationic polyelectrolyte. An alternate immersion of the substrate was then carried out in a negatively charged poly(styrenesulfonate) (PSS) solution. The surface of the substrate was covered with a layer of anionic polyelectrolyte. This cycle would be repeated until the whole silicon surface was uniformly covered and the outermost layer was positively charged. Next, nanoparticles, in this case polystyrene particles 300 nm in diameter with a carboxylated modified surface, were coated by putting the substrate into its aqueous solution. After that, a layer of aluminum was coated entirely on the surface about 2500 Å thick. A layer of 1 μm photoresist was then spun on and, with the use of a chrome mask, exposed to UV spectrum light. The exposed photoresists were dissolved by developer because the photon-sensitive polymer in the resist would become aqueous soluble after UV light irradiation. The predesigned pattern on the mask was now transferred to the surface of the resist. Subsequently, the substrate was put into an aluminum etching solution until the aluminum was etched and parts of the polystyrene thin films began to open to the air. It was taken into a vacuum chamber and etched by oxygen plasma, which would remove the polystyrene particles. Eventually, the aluminum and resist were removed by their etching solutions, shown in Figure 1. In some cases, the aluminum can remain to work as the electrodes of the device.

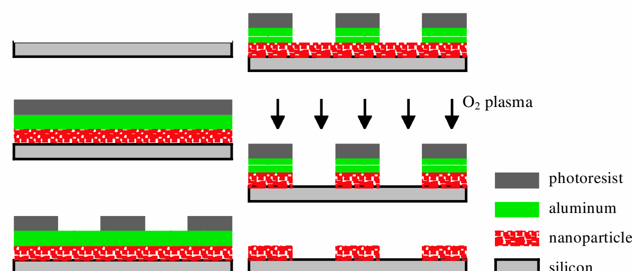

Fig. 1. Schematic of the metal mask approach to generate patterns on thin films composed of nanoparticles.

When the dry plasma etching facility is not available, a traditional wet etching is still on hand to implement the etching step. For this paper, the authors selected another important material in electronic devices, silica particles 300 nm in diameter with a carboxylated modified surface, to demonstrate the process of patterning. The whole process is similar to that of polystyrene, except that chrome was used as the metal mask and liquid hydrofluoric acid was the etchant of silica particles.

2. EXPERIMENTAL DETAILS

2.1. Patterning Polystyrene Nanoparticle-Based Thin Film with Plasma Dry Etching

2.1.1. Materials and Equipment. The polyelectrolytes involved were poly(dimethyldiallyl ammonium chloride) (PDDA) aqueous solution, MW 200 to 300 K, 3 mg/mL, 0.5 M NaCl and sodium poly(styrenesulfonate) (PSS) aqueous solution, MW 70 K, 3 mg/mL, and 0.5 M NaCl. They were obtained from Aldrich-Sigma. A dispersion of blue-dyed carboxylate-modified polystyrene particles 300 nm in diameter was obtained from Seradyn Inc. The photoresist was Shipley AZ1813. An Electronic-Vision dual side mask aligner EV420 from Electronic Visions, Inc., was used as the UV light illuminator. Aluminum layers were deposited by a DV-502A high-vacuum evaporator from Denton Vacuum, Inc. A Wyko RST white light

interferometer microscope was the instrument for surface measurement. An 800 series micro RIE system from Technics, Inc., was the etching device used to remove organic nanoparticles.

The 4-inch silicon wafer was first put into sulfuric acid and hydrogen peroxide solution (volume ratio 7 : 3) at 70 °C for 1 h. It was immersed in 50 mL of PDDA solution for 20 min. After that, it was rinsed in DI water for 1 min and dried by nitrogen flow. It was then immersed in 50 mL of PSS solution for 10 min, rinsed, and dried as in the previous step. The cycle was repeated in a sequence of {PDDA (20 min) + [PSS (10 min) + PDDA (10 min)]$_2$}. The intermediate rinsing and drying are necessary. Finally, the outermost layer was positively charged PDDA. Then, it was immersed in 50 mL of diluted polystyrene aqueous solution for 10 min (aqueous solution was made in a dispersion to water volume ratio of 1 : 9), rinsed, and dried, followed by another cycle of PDDA (10 min) + polystyrene (10 min). Therefore the complete sequence of adsorption was {PDDA (20 min) + [PSS (10 min) + PDDA (10 min)]$_2$} + polystyrene (10 min) + PDDA (10 min) + polystyrene (10 min). It was heated at 100 °C for 10 min to get rid of the moisture in the films, and then aluminum was deposited by thermal evaporation. The deposition of aluminum was carried out at a pressure of 10^{-5} mtorr and a deposition rate of 2 Å/S until a thickness of 2500 Å was reached. After it was taken out of the vacuum chamber, a photoresist (AZ 1813) layer 1 μm thick was spun on the aluminum at a maximum speed of 2000 rpm for 40 s. The photoresist was baked at 115 °C on a hotplate for 1 min. Then the silicon wafer was put on a mask aligner, which is a UV light irradiation instrument with a chrome mask between the light source and the wafer. The time of exposure was set at 6 s. Later, it was developed with MF-319 developer for 30 s and rinsed with DI water. The aluminum etchant, phosphoric acid and nitric acid (136 g H_3PO_4 + 5.5 g H_3NO_3 per 100 mL), was used to remove aluminum at 70 °C for 2 min. It was put in the vacuum chamber of the reactive ion etching system. The etching conditions were an oxygen flow rate of 8 sccm, a pressure of 110 mTorr, and an electric power of 250 W. The etching time is 5 min. The remaining photoresist was removed by acetone. The aluminum can be either removed by its etching solution or just left as an electrode.

Two samples of polystyrene nanoparticles were prepared by this process. One was fixed on the stage of a scanning electron microscope (SEM) for observation. Before the picture was taken, TiPt alloy was sputtered on the sample surface for 40 s at a pressure of 0.1 Torr and a current of 12 mA. The SEM was set up at 25 kV and a maximum magnification of 20 K. The SEM pictures are illustrated in Figure 2. The other sample was measured by WYKO roughness stepper testing (RST) for its surface characteristics, including average roughness (R_a), rms roughness (R_q), and surface topography. An area of

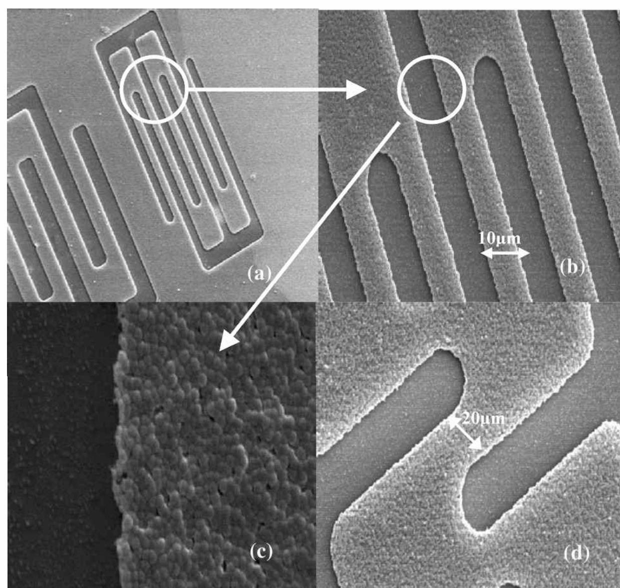

Fig. 2. SEM pictures of particle thin film. (a) Full-size pattern of 300 nm polystyrene particle thin film, width of the line is 10 μm. (b) Amplified circle area in (a). (c) Amplified circle area in (b). (d) A pattern made of 300 nm silica particle.

213.7 μm by 317 μm was selected at a block area to measure the roughness at VSL mode, and a 3-D plot was produced on a U-like pattern, shown in Figure 3.

2.2. Patterning Silica Nanoparticle-Based Thin Film with Wet Etching

2.2.1. Materials and Equipment. The polyelectrolytes involved were the same as in experiment 1. The silica particles, 300 nm in diameter, were obtained from

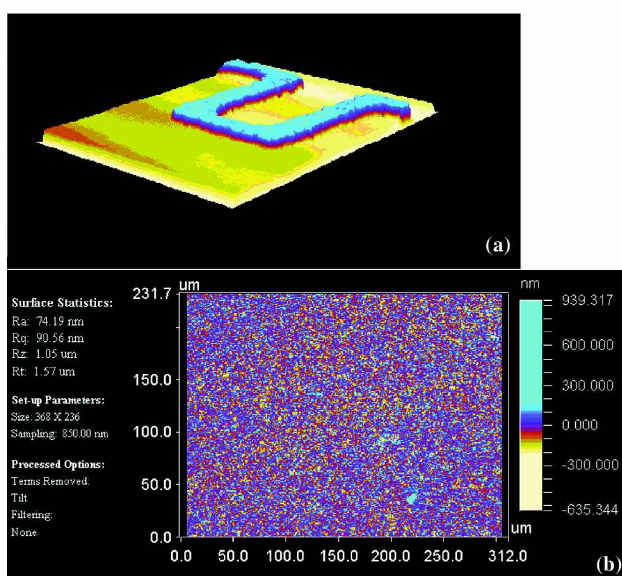

Fig. 3. (a) 3-D plot of a U-turn pattern made of 300-nm polystyrene particles. The width of the line is 25 μm. (b) Surface statistics of latex film with an area of 213.7 μm by 317 μm.

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Polyscience, Inc. A buffer of hydrofluoric acid (BHF) was made as a mixed solution of hydrofluoric acid and ammonium fluoride with a volume ratio of 1 : 6. Chrome was deposited with a PVD-300 sputtering system from Uniform Technology. The chrome etching solution was a mixture of 83 g ceric ammonium nitrate, 2 mL perchloric acid, and 50 mL DI water. The analytic instruments are the same as in experiment 1.

The wafer was pretreated and silica particles were coated on it as in experiment 1. Then a layer of chrome 2500 Å thick was sputtered on in the high-vacuum chamber of the PVD-300 sputtering system at a rate of 800 Å/min. Photoresist was patterned in a similar way as in experiment 1, and then the chrome was etched by an etching solution. Finally, the silica particles were removed by immersing in BHF solution for 20 s instead of dry etching. Photoresist and chrome were subsequently dissolved by acetone and etching solution.

3. RESULTS AND DISCUSSIONS

The image on the mask was transferred to the nanoparticle layer quite well by the metal mask approach. As illustrated in Figure 2, a comb-shaped pattern was generated, with the particle occupied area and the blank area separated clearly and sharply. Figure 2a–c contains pictures of one image at different magnifications. In Figure 2c, a sharp border along the blank area and particle-covered area can be seen. It is quite interesting that many of the spherical particles along the border are observed to be cut in half. This is due to the oxygen plasma, with high kinetic energy, which etches the particles that are not covered by the metal mask. This factor will improve the sharpness of the pattern. Meanwhile, in the picture with the highest magnification, along the border tiny defects about one particle diameter in size can be observed. This may result from the roughness of the particle surface. The aluminum patterning is not carried out on the smooth silicon surface as in the usual case. On the contrary, it is deposited on the rough surface of the polystyrene particles. This may affect the uniformity of aluminum deposition and photoresist coating. The straightness of the border that results from a series of the process of deposition, UV exposure, and development is not as satisfactory as that on the smooth substrate. The approach is applied to both organic and inorganic particles so that it is supposed to be able to be compatible with most of the important nanoparticles.

Another main advantage of this method is its significant reliability. Because the conventional lithography has already reached the nanometer scale, the patterning of nanoparticle thin films can be done at the same level. In this paper the smallest size is 10 μm, but we can continuously downscale the features if the mask has a smaller size.

The principle of this approach is to use a metal layer as a mask when etching the nanoparticle layers underneath. The selection of metal is flexible. In our experiments, aluminum and chrome were chosen. Certainly, another optional material of mask over nanoparticles is photoresist, and it may simplify the process greatly. A reason not to choose it is that photoresist is not suitable to the ultimate target of three dimensional nanoscale architecture fabrication. The first layer of resist that remains as the mask would be irradiated by the UV light when the second layer of photoresist is exposed. It would be dissolved with the second layer of photoresist during the second developing. Thus, a metal mask layer is the best way to avoid the issue addressed above.

In Figure 3, the 3-D plot and surface roughness of the created pattern are illustrated. The rms roughness and average roughness are defined by

$$R_q = \left[\frac{1}{L} \int_0^L Z^2(x)\, dx \right]^{1/2}$$

and

$$R_a = \frac{1}{L} \int_0^L |Z(x)|\, dx$$

where $Z(x)$ is the difference in the surface coordinate and the mean value.

As shown in Figure 4, the roughness should approximate one-fourth of the diameter, that is, 75 nm in theory when the particles are all uniformly coated and closely packed. Our experimental result is in agreement with this and implies a quite closely packed structure. To some extent, the roughness might be reduced by using smaller particles. But on the other hand, smaller particles usually have a wider size distribution which may result in more serious irregularity. In the situation where a perfect surface is necessary, for example when a 3D platform is to be built, this is the factor that must be taken into consideration. Any defect like pinholes also must be avoided to prevent short-cuts between top and bottom layers and to enhance the conductivity of the conductive layers. A higher concentration of particle solution is recommended. In addition, the thickness of the metal mask can be a little larger, to keep the particle layer from damage during the etching process.

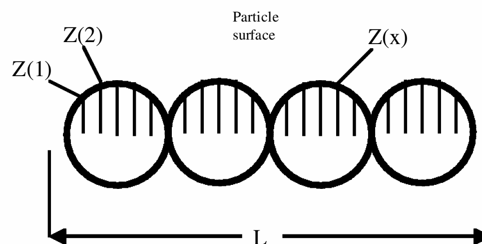

Fig. 4. Surface roughness profile $Z(x)$.

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4. CONCLUSIONS

In this work, we demonstrate a microfabrication method applied to the layer-by-layer nanoassembly. A layer-by-layer assembly allows construction in the vertical to a support direction with a resolution of 1 nm, and we added to this ability patterning of the films in plane with micron resolution with a metal mask approach. It provides a potential method for 2-D or 3-D nanostructure fabrication, combining the versatility and ease of layer-by-layer self-assembly and traditional lithography. Different metallic materials can be chosen as the mask to protect covered nanoparticle layers from being etched. The free choice of wet etching with nanoparticles as a substitute to dry etching when a dry etching facility or recipe is not available increases the flexibility of this approach. A rather sharp edge and flat surface are available with high reproducibility. The approach appears quite general, and various types of particles can be patterned on substrates such as glass or silicon. Three-dimensional nanostructures made of nanoscale building blocks are currently under investigation, as are nanoelectronic devices such as capacitor and MOSFET. This patterning technique is expected to fully or partially replace the conventional process with the advantages of significantly lower cost, lower temperature, and a simpler process.

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