

Patterning of Layer-by-Layer Self-Assembled Multiple Types of Nanoparticle Thin Films by Lithographic Technique

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ABSTRACT

A lithographic approach to generate clean patterns of multiple types of nanoparticles on one 4-inch silicon wafer is demonstrated in this paper. Each type of nanoparticle is precisely directed to the desired location. The process is mainly based on conventional microelectronic techniques with extremely high reproducibility. This enables the possibility of industrial applications to fabricate devices made of nanocrystals. A thin film of polystyrene spheres, 150 nm in diameter, was first coated on the silicon wafer with layer-by-layer self-assembly, followed by a layer of aluminum deposited on the thin film. A layer of positive photoresist was spun on the surface of aluminum and then patterned by lithographic technique. The unprotected aluminum was removed by wet etching until the polystyrene thin film underneath was exposed to the air. Oxygen plasma was employed to etch the polystyrene thin film all the way to the silicon surface. Subsequently, a thin film of another type of nanoparticle, silica particle 78 nm in diameter, was adsorbed onto the surface with layer-by-layer self-assembly. Eventually, aluminum and photoresist were removed and each type of nanoparticle was located next to each other as the pattern was designed. A scanning electron microscope was used to produce the image of the pattern.

Introduction. Nanoparticles have been the focus of many material researchers due to their unique properties in the microelectronics, optoelectronics, and chemical fields.^{1,2} A great deal of attention has been attracted to the various potential applications of nanoparticles to complex nanoelectronic devices, photonic crystals, and biochemical sensors.^{3–7} Among numerous nanoparticle deposition techniques, layer-by-layer (LbL) self-assembly, since its introduction by Decher et al.,^{8,9} has become, due to its simplicity and versatility, an increasingly popular technique, which enables adsorption of colloidal nanoparticles onto almost any material. The alternate immersion of substrate in oppositely charged solutions allows thin films of nanoparticles, enzymes, or protein in nanometer scale to be coated by electrostatic interaction.^{10–13}

However, before the LbL self-assembled nanoscale colloidal structure is applied to real devices, an approach must be developed to easily generate complex and distinct patterns on the multilayer films. Recently, some results have been reported for the creation of spatially resolved nanoparticle films. These works are mostly based on the microprinting technique in which a template is first fabricated by stamping two functional chemicals on the flat substrate, then directing nanoparticles onto adhesion-promoting regions while they

are repelled by adhesion-resisting regions.^{14–21} This method is quite successful but is restrictive in application by the necessity of special microstamps and the deliberate selective deposition. They are all chemical methods in principle. Another challenge prior to device fabrication is to pattern two or more types of nanoparticles on one wafer. Hammond and T. Vossmeier groups demonstrated their approaches to introduce two types of nanoparticles in the matrix by selective deposition technique.^{17,22}

In our early reports,^{23,24} two methods based on the combination of traditional lithography and LbL assembly were presented to pattern one type of nanoparticle film. One is referred to by authors as the “modified lift-off”, the other as the “metal-mask method”. The strategy completely differs from the microprinting technique, thus avoiding the difficult selective deposition. The patterns created by this strategy are illustrated in Figure 1. Since the standard 4-inch wafer process was adopted to pattern the LbL assembled nanoparticle films, dramatically high reproducibility is obtained on the whole wafer surface. In addition, each step of LbL self-assembly can be automatically controlled; therefore, this idea may find wide industrial application in the future. The schemes of both methods are illustrated in Figure 1.

In this paper, an approach to generate patterns composed of two types of nanoparticles is presented. The approach is the combination of metal-mask and lift-off. It provides a

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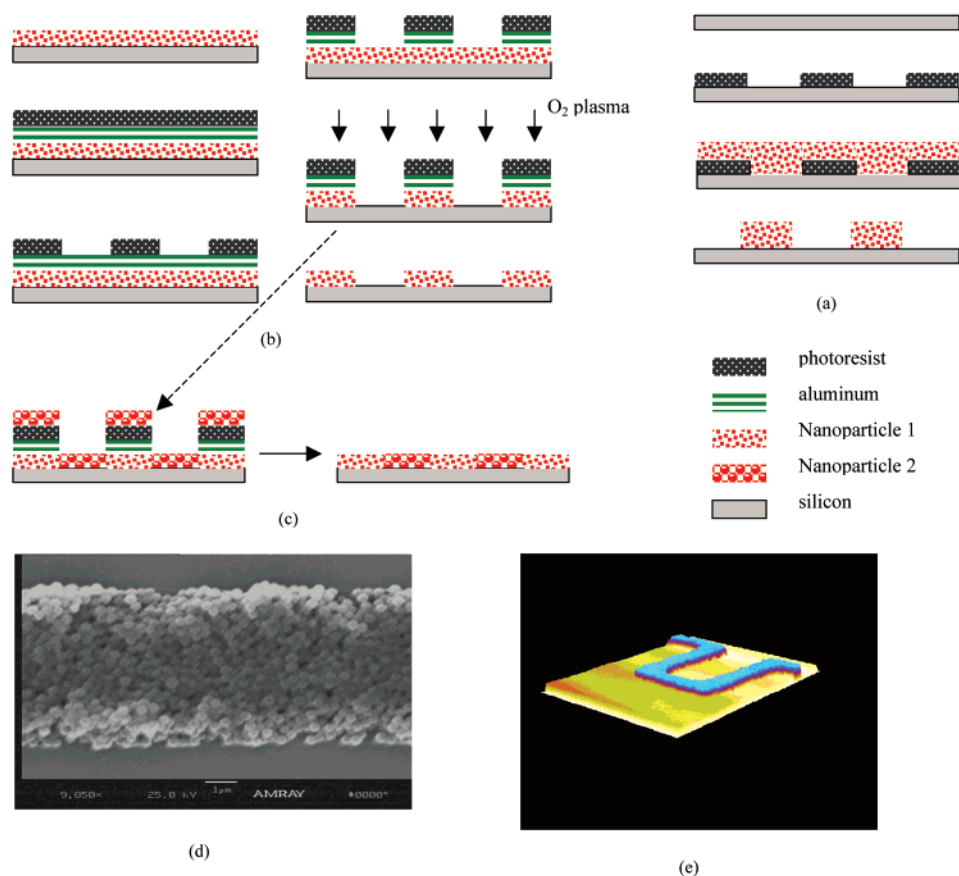


Figure 1. Schematic of the patterning approaches: (a) lift-off method, (b) metal-mask method, (c) combination of “lift-off” and “metal-mask” to pattern two types of nanoparticles, (d) a 5 μm strip composed of 300 nm silica nanoparticles created by lift-off, (e) 3-D plot of a U-turn pattern composed of 300 nm silica nanoparticles created the by metal-mask method.

capability to fabricate varieties of microdevices or systems that consist of more than one type of nanocrystals. UV light lithography, etching, and lift-off, which are all mature processes in the semiconductor industry, are used in the method. They ensure the remarkable reliability of the method. The flexibility of traditional lithographic technique may lead to other methods that may be developed to fulfill the same target. In this work, a 4-inch silicon wafer served as the substrate. The thin film of polystyrene nanoparticles, 150 nm in diameter, were coated on the wafer with LbL self-assembly and patterned by the metal-mask method, but the aluminum and photoresist layers above the pattern were not removed immediately. Subsequently, a layer of silica nanoparticles, 78 nm in diameter, was deposited above all these layers. Eventually, the photoresist and aluminum were dissolved in series and the silica particles that attached on photoresist were also removed during this lift-off process. The scheme is illustrated in Figure 1(b) and (c).

Experimental Method. Polyelectrolytes were obtained from Aldrich-Sigma and were used as follows: (1) poly(dimethyldiallylammonium chloride) (PDDA) aqueous solution, MW 200 to 300 K, 3 mg/mL, 0.5 M NaCl, (2) sodium poly(styrenesulfonate) (PSS) aqueous solution, MW 70 K, 3 mg/mL, 0.5 M NaCl. The blue-dyed carboxylate modified polystyrene particles, 150 nm in diameter, were obtained from Seradyn Inc. The polystyrene aqueous solution was made in dispersion to water volume ratio of 1:9. The silica

nanoparticles dispersion (8 mg/mL) was diluted from Snow-Tex colloidal silica (40.9 wt %, PH 9.6, 78 nm in diameter) which was made by Nissan Chemical Industries, Ltd. The photoresist is Shipley AZ1813. 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. Dry etching was carried out using an 800 series micro RIE system from Technics Inc. Ultrasonication was performed using an 8892 Cole-Parmer ultrasonic cleaner.

Initially, the 4-inch silicon wafer was put into sulfuric acid and hydrogen peroxide solution (volume ratio 3:7) at 70 $^{\circ}\text{C}$ for 1 h, after which LbL assembly of 150 nm polystyrene particles was carried out on the silicon wafer. The sequence of the alternate immersion was: [PDDA (10 min) + PSS (10 min)]₂ + PDDA (10 min) + polystyrene (10 min). The intermediate rinsing and drying after each immersion are necessary. The rinsing was done by purging the wafer in the DI water flow for 1 min. The wafer was placed on a spinner and spun to remove water by centrifugal force. The maximum rotating speed was set at 1300 rpm for a time of 45 s. It should be heated at 100 $^{\circ}\text{C}$ for 10 min to completely remove moisture in the films, after which aluminum was deposited by thermal evaporation. The deposition of aluminum was carried out at a pressure of 10^{-5} mTorr with a deposition rate of 2 $\text{\AA}/\text{S}$ until a thickness of 2500 \AA was reached. After it was taken out of the vacuum chamber, a

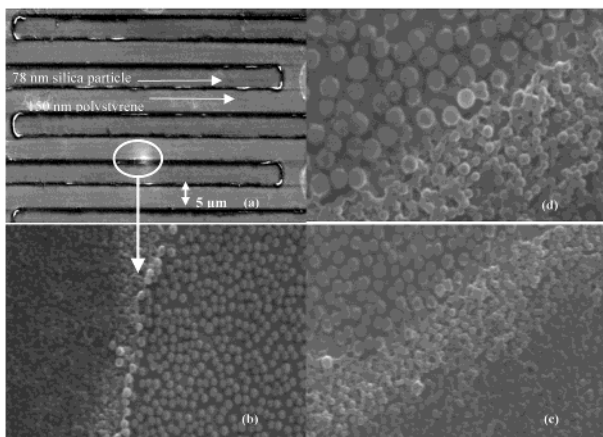


Figure 2. SEM pictures of two types of patterned nanoparticle films: (a) strips filled with 78 nm silica and 150 nm polystyrene nanoparticles alternately; (b–d) magnified images of the interface between silica and polystyrene particles.

photoresist (AZ 1813) layer of 1 μm thick was spun on the aluminum at the maximum speed of 2000 rpm for 40 s. The photoresist was baked at 115 $^{\circ}\text{C}$ on a hotplate for 1 min. Then the silicon wafer was placed on a mask aligner to be exposed under UV light irradiation in order to transfer the pattern on the chrome mask to the photoresist. The time of exposure was set at 6 s. Later, the photoresist was developed using a MF-319 developer for 30 s and rinsed with DI water. The wafer was then placed under UV light for another 6 s to expose the remaining photoresist. The aluminum etchant, phosphoric acid and nitric acid (136 g H_3PO_4 + 5.5 g H_3NO_3 per 100 mL), was used at 70 $^{\circ}\text{C}$ for 2 min to remove aluminum. It was then put in the vacuum chamber of the reactive ion etching system to etch the polystyrene particle film. The etching conditions were the following: an oxygen flow rate of 8 sccm, a pressure of 110 mTorr, and an electric power of 250 W. The etching time was 5 min. To this point, the thin film of polystyrene nanoparticles had been patterned and remained covered by the aluminum and photoresist. Scraps sticking to the silicon surface remained, which resulted from the oxygen bombardment upon the nanoparticle layer. The wafer was immersed in ultrasonic cleaner for 1 min to clean all of these scraps.

Next, a layer of 78 nm silica nanoparticle thin film was adsorbed on the surface using LbL self-assembly. The sequence of immersion was [PDDA (10 min) + PSS (10 min)]₂ + PDDA (10 min) + silica (10 min). The intermediate rinsing and drying were still necessary and were carried out as described above. The wafer was soaked in developer solution MF-319 for 10 min to dissolve photoresist and aluminum and during the first minute, the ultrasonic bath was introduced for roughly 3 s to improve the lift-off. Eventually, the pattern was obtained with two types of particles located next to each other.

The wafer sample was fixed on the stage of 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 scanning electron microscope was set up at 25 kV and maximum magnification of 30 K. The SEM pictures are illustrated in Figure 2.

Results and Discussion. As shown in SEM pictures, clear patterns of 5 μm feature size were created with a sharp border between 78 nm silica and 150 nm polystyrene nanoparticles. The upper left part is composed of 150 nm polystyrene nanoparticles, and the lower right part is 78 nm silica nanoparticles. Figure 2c was taken at the magnification of 30 k from which we can see that two types of particles are thoroughly separated by this method. UV light lithography, wet etching, dry etching, and lift-off are all ordinary microelectronic processes. We can see that an optimized combination of them can offer a strong capability to apply the conventional lithography to the LbL self-assembled nanotechnology. The high reproducibility of the process ensures that almost all the patterns on the 4-inch wafer are of similarly high quality. However, because the LbL self-assembled nanoparticle films are unlike the conventional thin films in many respects, modification and optimization of the traditional process is required. Some issues during the process must be emphasized.

The drying step is critical for LbL self-assembled films. It can improve the adhesion and thickness of the films by enhancing the linkage between the materials that compose the film and removing the moisture. In the laboratory, drying was realized with a nitrogen gun that was operated by hand. The random fashion of this operation often makes the films nonuniform over the broad area of the wafer surface. An efficient way was found to use a spinner to spin off the water on the wafer surface. The rotation movement results in a much more uniform film, which makes the subsequent process easier. The rotating speed is set at 1300 rpm, and a higher speed is not considered beneficial because it may drive the water drops away from the center too quickly so that the assembled materials will be carried away with them. Apparent radius traces created by liquid and solid flows can be observed on the wafer surface at higher rotating speed.

When the lift-off was executed, acetone was not used to dissolve the photoresist, mainly because acetone was sometimes found to be detrimental to LbL assembled thin films, although the damage is not very severe. In fact, the remaining resist was exposed again and later removed by developer solution. The developer is also able to etch aluminum at a lower but controllable rate. Therefore, it also works as the aluminum etchant after the photoresist is dissolved.

After the RIE dry etching of the nanoparticle thin film, tiny scraps were observed sticking to the channel, which was supposed to be a smooth and clean silicon surface. The scraps must be removed prior to the next LbL self-assembly of silica nanoparticles and lift-off. Otherwise the scraps may be dissolved from the surface during the lift-off and leave defects on the nanoparticle films. They can be removed after the wafer is shaken in an ultrasonic cleaner for 1 min.

During the lift-off, it is better to introduce ultrasonic treatment for 3 s when the wafer was soaked in developer solution. Within the nanoparticle film structure, polyion multilayers such as PDDA and PSS were sandwiched between the nanoparticle film and photoresist as a kind of “chemical glue”. The structure of the polyion is like a long thread which strongly links the polyion film as a whole. It

is hard to break them up during the lift-off so that at some areas the nanoparticle and polyion multilayer cannot be removed when the photoresist is dissolved. On the contrary, they just come down and re-attach to the film underneath. The ultrasonic treatment is introduced to disconnect the linkage between polyion branches and to obtain a more distinct pattern with higher reproducibility.

Conclusions. An approach based on the conventional lithographic process to pattern two types of nanoparticles on the same silicon wafer was developed. The pattern feature size can be continuously downsized to the submicron level. The combination of LbL assembly with the mature lithography process offers the opportunity to avoid extra effort necessary to develop a new process in our research, although some modifications are necessary. The process itself has the advantages of low cost, low process temperature, and simplicity. It also provides extreme reliability and flexibility. Moreover, the modern semiconductor industry provides numerous simple and reliable processes other than lift-off or dry etching. A reasonable combination of them may give rise to more approaches with unique advantages to realize the patterning of multiple types of nanoparticles on one wafer.

A wide array of potential applications exists for the fabrication of conventional devices using nanobricks, as well as lowering the price and reducing the complexity of some traditional processes. Keeping in pace with the development of nanoparticle production and characterization, the process of nanoparticle arrangement on a silicon wafer can provide a way to produce devices or systems in microscale or nanoscale in the future.

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References

- (1) Chen, G. *J. Nanoparticle Res.* **2000**, *2*, 199.
- (2) Takeda, Y.; Gritsyna, V. T.; Umeda, N.; Lee, C. G. *Nucl. Instrum. Methods Phys. Res., B* **1999**, *148*, 1029.
- (3) Bezryadin, A.; Dekker, C. *J. Vac. Sci. Technol. B* **1997**, *15*, 793.
- (4) Baur, C.; Bugacov, A.; Koel, B. E. *Nanotechnology* **1998**, *9*, 360.
- (5) Vargo, T. G.; Calvert, J. M. *Supramol. Sci.* **1995**, *2*, 169.
- (6) Rogach, A.; Susha, A.; Caruso, F.; Sukhorukov, G.; Kornowski, A.; Kershaw, S.; Möhwald, H.; Eychmüller, A.; Weller, H. *Adv. Mater.* **2000**, *12*, 333.
- (7) Ozin, G. A.; Yang, S. M. *Adv. Funct. Mater.* **2001**, *11*, 95.
- (8) Decher, G. *Science* **1997**, *227*, 1232.
- (9) Lvov, Y.; Decher, G.; Möhwald, H. *Langmuir* **1993**, *9*, 481.
- (10) Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *Langmuir* **1997**, *13*, 6195.
- (11) Takeshi, S.; Satoko, K. *Colloids Surf.* **2000**, *164*, 237.
- (12) Yoo, D.; Shiratori, S.; Rubner, S. *Macromolecules* **1998**, *31*, 4309.
- (13) Lvov, Y. In *Handbook of Surfaces and Interfaces of Materials*, H. S. Nalwa, H. S., Ed.; Academic Press: New York, 2001; Chapter 4, p 170–189.
- (14) Chen, K.; Jiang, X.; Kimerling, L.; Hammond, P. *Langmuir* **2000**, *16*, 7825.
- (15) Jiang, X.; Hammond, P. *Langmuir* **2000**, *16*, 8501.
- (16) Jiang, X.; Zheng, H.; Gourdin, S.; Hammond, P. *Langmuir* **2002**, *18*, 2607.
- (17) Zheng, H.; Lee, I.; Rubner, M.; Hammond, P. *Adv. Mater.* **2002**, *14*, 681.
- (18) Kim, E.; Xia, Y.; Whitesides, G. *Adv. Mater.* **1996**, *8*, 245.
- (19) Torsten, M.; Annamaria, G. *J. Phys. D: Appl. Phys.* **1996**, *29*, 340.
- (20) Haynes, C.; Van Duyne, R. *J. Phys. Chem. B* **2001**, *105*, 5599.
- (21) Hulteen, C.; Treichel, A. *J. Phys. Chem. B* **1999**, *103*, 3854.
- (22) Vossmeier, T.; Jia, S.; DeIonno, E.; Diehl, M.; Kim, S. H. *J. Appl. Phys.* **1998**, *84*, 3664.
- (23) Hua, F.; Lvov, Y.; Cui, T. *J. Nanosci. Nanotechnol.* **2002**, *2*, 357.
- (24) Hua, F.; Cui, T.; Lvov, Y. *Langmuir* **2002**, *18*, 6712.

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