

Lithographic Approach to Pattern Self-Assembled Nanoparticle Multilayers

Feng Hua, Tianhong Cui, and Yuri Lvov*

Institute for Micromanufacturing, Louisiana Tech University, Ruston, Louisiana 71270

Received April 22, 2002. In Final Form: June 6, 2002

Nanoassembly of ultrathin films through alternate adsorption of oppositely charged components (linear polyions, nanoparticles, and enzymes) allows formation of layers with component location precision of a few nanometers in the direction perpendicular to the surface. Since its demonstration by Decher et al.,^{1,2} it has found applications in electro-optical devices, biocompatible coverage, and bioreactors.^{1–7} The typical procedure of layer-by-layer self-assembly is as follows: A pretreated silicon substrate is immersed in a cationic solution for 10 min, forming a single layer of cationic polyelectrolytes on the substrate. The substrate is then rinsed. Next, it is immersed in a polyanion solution for 10 min to adsorb a layer of anionic polyelectrolyte. The process can be repeated indefinitely; the only condition is a proper alternation of positive and negative components. Linear polyions frequently used in the layer-by-layer (LbL) assembly are cationic poly(ethyleneimine) (PEI), poly(dimethyldiallylammonium chloride) (PDDA), poly(allylamine hydrochloride) (PAH), polylysine, chitosan, and anionic sodium poly(styrenesulfonate) (PSS) and poly(vinyl sulfate), poly(acrylic acid), and DNA. Enzymes and charged nanoparticles were also used in the LbL assembly.⁵ To use LbL multilayers in devices, one has to provide film ordering not only in a vertical direction but also in the planar direction. This is critical for nanodevice production, such as nanoelectronic chips or NEMS (nanoelectromechanical systems).^{8–15}

There are works on application of the layer-by-layer assembly on two-dimensional (2D) patterns.^{16–21} They are

- (1) Decher, G. *Science* **1997**, *227*, 1232.
- (2) Lvov, Y.; Decher, G.; Möhwald, H. *Langmuir* **1993**, *9*, 481.
- (3) Lvov, Y.; Ariga, K.; Ichinose, I.; Kunitake, T. *Langmuir* **1997**, *13*, 6195.
- (4) Yoo, D.; Shiratori, S.; Rubner, M. *Macromolecules* **1998**, *31*, 4309.
- (5) *Protein Architecture: Interfacial Molecular Assembly and Immobilization Biotechnology*; Lvov, Y., Möhwald, H., Eds.; Marcel Dekker: New York, 2000; pp 1–394.
- (6) Bezryadin, Dekker, C. *J. Vac. Sci. Technol., B* **1997**, *15*, 793.
- (7) Baur, C.; Bugacov, A.; Koel, B. E. *Nanotechnology* **1998**, *9*, 360.
- (8) Lin, X.; Parthasarathy, R.; Jaeger, H. *Appl. Phys. Lett.* **2001**, *78*, 1915.
- (9) Kenausis, G.; Janos, I.; Elbert, D. *J. Phys. Chem. B* **2000**, *104*, 3298.
- (10) Bulthaupt, C.; Wilhelm, E.; Hubert, B. *Appl. Phys. Lett.* **2001**, *79*, 1525.
- (11) Ozin, G.; Yang, S. *Adv. Funct. Mater.* **2001**, *2*, 95.
- (12) Brott, L.; Naik, R.; Pikkas, D. *Nature* **2001**, *413*, 291.
- (13) Vossmeier, T.; Jia, S.; DeFonno, E.; Diehl, M.; Kim, S. H. *J. Appl. Phys.* **1998**, *84*, 3664.
- (14) Haynes, C.; Van Duyne, R. *J. Phys. Chem. B* **2001**, *105*, 5599.
- (15) Hultheen, C.; Treichel, A. *J. Phys. Chem. B* **1999**, *103*, 3854.
- (16) Chen, K.; Jiang, X.; Kimerling, L.; Hammond, P. *Langmuir* **2000**, *16*, 7825.
- (17) Jiang, X.; Hammond, P. *Langmuir* **2000**, *16*, 8501.
- (18) Jiang, X.; Zheng, H.; Gourdin, S.; Hammond, P. *Langmuir* **2002**, *18*, 2607.
- (19) Zheng, H.; Lee, I.; Rubner, M.; Hammond, P. *Adv. Mater.* **2002**, *14*, 569.
- (20) Kim, E.; Xia, Y.; Whitesides, G. *Adv. Mater.* **1996**, *8*, 245.
- (21) Vargo, T.; Calvert, J.; Wynne, K.; Advyanov, J.; MacDiarmid, A.; Rubner, M. *Supramol. Sci.* **1995**, *2*, 169.

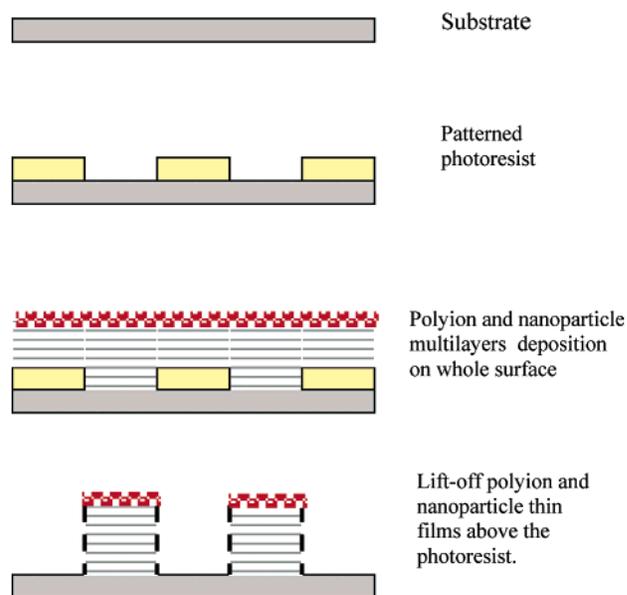


Figure 1. Scheme of patterning of nanoparticle thin films.

based mostly on the microprinting of thiol compounds on gold and further assembly of the polyion multilayers on charged patterns, and they were developed by Hammond et al.^{16–19} This strategy is designed to produce patterns by stamping onto substrates chemicals with different functionalities, that is, polyion adhesive or resisting. The polyions were directed only to charge “attractive” regions and were repelled from the resistant regions. Whitesides et al.²⁰ crystallized latex particles in capillary channels produced by poly(dimethylsiloxane) (PDMS) micromolding and made three-dimensional (3D) ensembles of 450-nm spheres with a resolution of ca. 1 μm . In another approach,²¹ poly(pyrrole) and poly(styrenesulfonate) were LbL-assembled on the 2D charged micropattern produced on a fluoropolymer by plasma treatment. The three methods described were quite successful but restricted in applications by substrate materials (gold, fluoropolymers) or by necessity of special plastic stamps. In this paper, we present an approach to realize 2D patterning of self-assembled multilayers by silicon-based lithographical technology, which is a well-established industrial process.

At the beginning, a photoresist was patterned through a mask by the standard UV-irradiation procedure (Figure 1). Then the substrate was entirely covered with polyion layers with the alternate layer-by-layer method to get the desired multilayer structure. Therefore, polyion film covers the entire surface (not only the adsorption-promoting region as in the work with thiol microprinting¹⁷) followed by removal of part of the film.

By using this strategy (Figure 1), the deliberate selective deposition control is avoided. The photoresist was dissolved, and during the dissolution, polyion multilayers were removed from the substrate at the selected areas. Nanoparticle or polyion multilayers can be micropatterned by this process. The lithographic micromanufacturing approach is widely accepted in industry, and it offers larger versatility of the process and high pattern resolution. Since both lithography technology and the layer-by-layer thin film fabrication are well established, an industrial application of LbL ensembles organized in three directions (3D-LbL) is becoming a feasible target.

Total multilayer film architecture in this experiment was as follows: {PEI + (PSS/PDDA)₃ + (SiO₂/PDDA)₃}. After a seven-layer precursor of PEI + (PSS/PDDA)₃ was coated, the outermost layer was positive. Then the wafer was immersed in negatively charged SiO₂ particles 300 nm in diameter. This layer of SiO₂ was used to make the pattern visible. At this moment, the whole surface of the wafer becomes white due to the entire cover of SiO₂ particles. More silica/PDDA layers were deposited in a similar way. The last manufacturing step was to put the silicon wafer into acetone solution for 20 s to strip off the photoresist together with the above polyion/nanoparticle layers. For this step, ultrasonic treatment was necessary.

Experimental Section

Materials involved are the following: poly(ethyleneimine) aqueous solution, 1 mg/mL, MW = 25K; sodium poly(styrene-sulfonate), 3 mg/mL, MW = 70K, 0.5 M NaCl; poly(dimethyl-diallylammonium chloride), 3 mg/mL, 0.5 M NaCl, pH 7 (all from Sigma-Aldrich); and a dispersion of 300 nm diameter silica nanoparticles in 0.02 M NaCl, 1 mg/mL, pH 9 (Bang Inc.) or 45 nm diameter Fluoresbrite microspheres, 2.5 mg/mL, 0.02 M NaCl (Polyscience Inc.).

Silicon wafers (Silicon Inc.) were used. A spin-coating machine (Brewer Science), a UV lamp, and an Az1813 photoresist were used for the lithography process. For analysis of the pattern structures, we used a scanning electron microscope (SEM, AMRAY), an Olympus epifluorescence microscope, and a Wyko RST white light interferometric microscope.

A silicon wafer was hydrophilized by treatment with H₂SO₄ and H₂O₂ solution (volume ratio 7:3) at 50 °C for 1 h. Then, it was "hardbaked" at 115 °C on a hot plate for 2–3 min to remove the moisture for the subsequent lithography. A photoresist layer of 1 μm was spanned on the silicon wafer. It was exposed under a UV lamp for 1.5 min, and the desired pattern on the photomask was transferred to the surface of the photoresist by developing. The image consists of 5 μm wide strips and spaces. Then the substrate was dipped into PEI, PSS, and PDDA solutions alternately, in the sequence of PEI (20 min) + [PSS (10 min)/PDDA (10 min)]₃. Now the outermost layer is positively charged, and then silica nanoparticles are adsorbed in the sequence of [PDDA (10 min)/silica (2 min)]₃. For the first three steps, the substrate was rinsed by deionized (DI) water for 1 min and dried by nitrogen flow between immersions. After that, the intermediate rinsing was still necessary while the drying was skipped. Finally, the substrate was put into acetone solution with ultrasonic treatment for 20 s to remove the photoresist.

Results and Discussion

On the resulting wafer, we see clear and distinct SEM images (Figure 2a–c). The 5-μm strips containing the polyion precursor with a nanoparticle multilayer are well shaped and have sharp borders. Silica nanoparticles are closely packed with few vacancy defects. An average roughness of the strip borders is less than one particle diameter (in this case 200 nm, but it could be less if smaller particles were used). There are no particles in the areas between the strips. The cross section of the image is very spectacular: strips are evenly separated and shaped and have the same height, 3000 nm. The height of the strip may be controlled with LbL assembly. In the present experiment, we performed three steps of silica/PDDA deposition, and every step gave a 200-nm thickness increase which corresponds to a triple silica layer. One layer thickness can be adjusted by lowering the ion strength of the silica dispersion.^{3,22}

These results indicate that polyion layers are permeable enough to let acetone molecules penetrate inside to dissolve the photoresist and strip off the multilayers from these

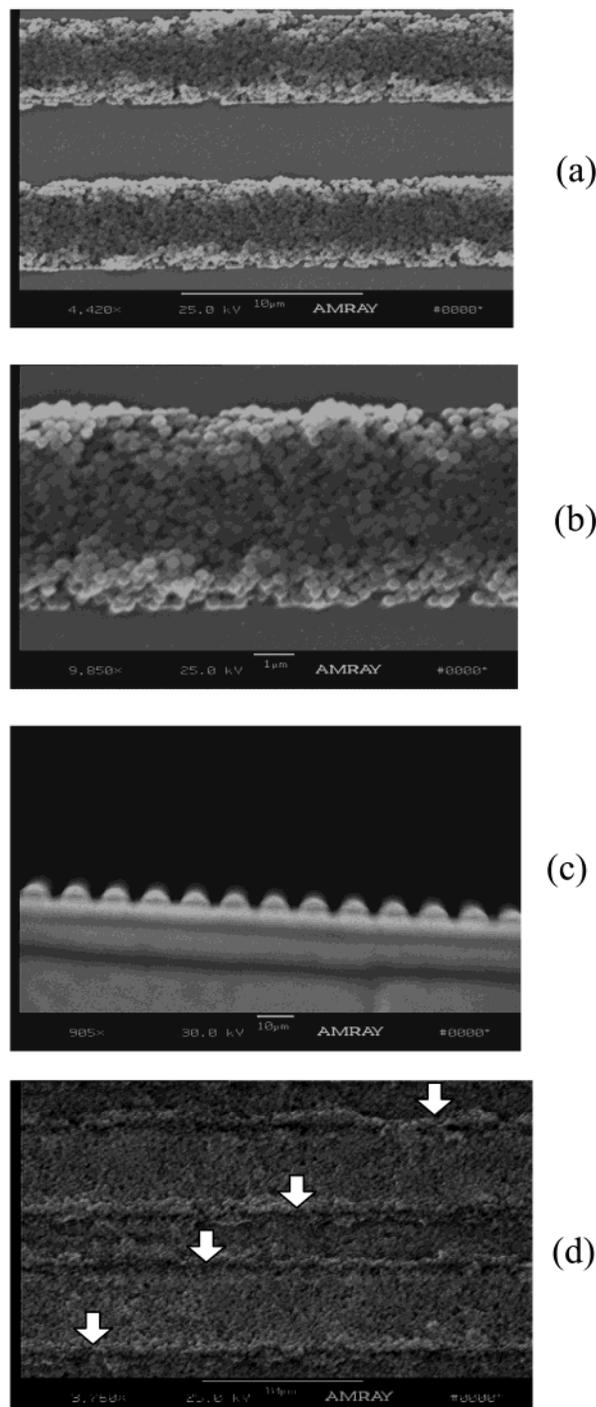


Figure 2. SEM pictures of self-assembly patterns. (a,b) Top view and (c) cross-sectional view, all with SiO₂ particles of 300 nm in diameter at the outermost layers. The line width is 5 μm. (d) SEM picture of the control sample (lift-off technology without sonication). The arrows indicate those particles which were attached on the sidewall.

regions. The strip border sharpness indicates that the intercalation length between neighboring molecules in the polyion layer is less than 200 nm. In the control sample (Figure 2d), which has not been sonicated during photoresist removal with acetone, the silicon wafer remains entirely covered by SiO₂ particles. The polyion layers and the particles above them were not lifted off and collapsed back during drying, which prevents the pattern formation. The collapse of the polyion layers and particles is due to the links not being broken at the edge of the photoresist

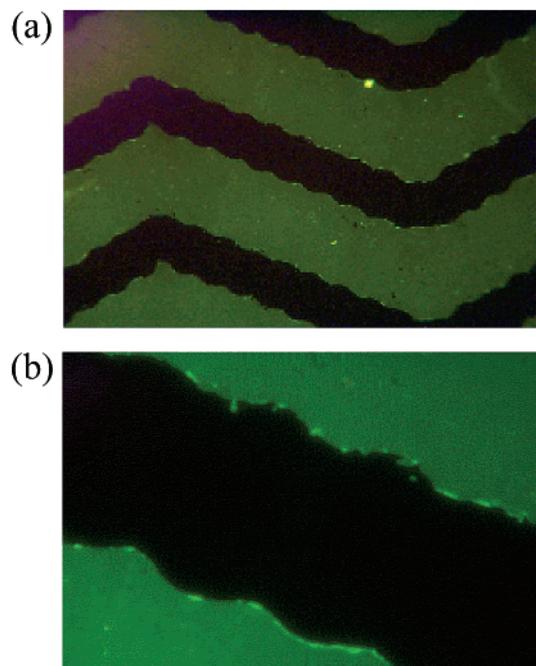


Figure 3. (a,b) Images of patterns of 25 μm width with a fluorescent multilayer of $\{\text{PEI} + (\text{PSS}/\text{PDDA})_3 + (\text{Fluoresbriht}/\text{PDDA})_3\}$ composition produced on silicon with the LbL method (Olympus epifluorescence microscope with a 530-filter and an exposure time of 8 s).

sidewall by the process. Drying at each LbL assembly step also results in poor final patterns. The presence of particle clusters, instead of the pattern, visible in Figure 2d is due to incomplete removal of the polyion film located above the photoresist.

The omission of drying after rinsing and ultrasonic treatment when removing the photoresist are very critical steps to the whole process. Failure to do these two steps will result in an unpatterned area where polyion chains are not completely separated. The drying step in conventional alternate adsorption will help to form stronger connections among polymer molecules. The polymer molecule chains are easy to separate if drying is omitted at the last several cycles. The internal pressure resulting from the dissolving photoresist is not sufficient to remove the polyion layers surrounding the photoresist. It is the ultrasonic wave that breaks the link among polyion chains. Currently, we are working on other samples based on lithography and layer-by-layer assembly combined methods, which may allow electrode fabrication directly on the polyion layers.

In another experiment, negatively charged 45 nm diameter fluorescent nanoparticles were assembled above a similar precursor, $\{\text{PEI} + (\text{PSS}/\text{PDDA})_3 + \text{Fluoresbriht}/\text{PDDA})_3\}$, following the same experimental procedure. We used another mask with wider strips to provide a pattern that was well visible in the optical microscope (Figure 3). One can see a sharp green pattern indicating a permanent coverage with 25 μm wide strips and 12 μm wide dark areas without a fluorescent multilayer.

In Figure 4, the 3D plot and surface roughness of the created U-turn pattern are shown. The root-mean-square roughness and average roughness are defined by the equations

$$R_q = \frac{1}{L} \left[\int_0^L Z^2(x) dx \right]^{1/2} \quad \text{and} \quad R_a = \frac{1}{L} \int_0^L |Z(x)| dx \quad (1)$$

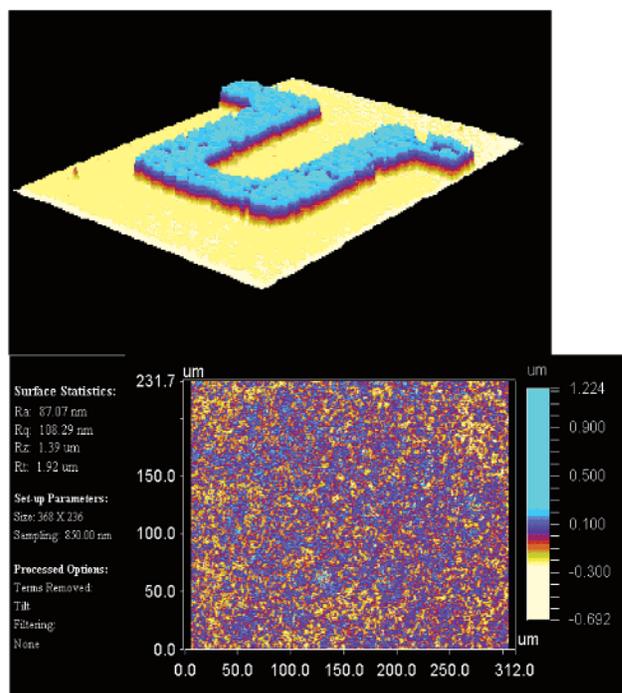


Figure 4. Surface characteristics measured by a Wyko RST interferometric microscope. (a) A 3D image of a U-turn pattern 20 μm in width which is made of $(\text{PDDA}/\text{PSS})_2 + (\text{PDDA}/300\text{-nm latex})_5$ multilayers. Blue is the multilayer, and yellow is the bare silicon surface. (b) The multilayer surface roughness.

where $Z(x)$ is the difference of the surface coordinate and the mean value. If the spherical particles are uniformly coated and closely packed, then the roughness should be approximately 1/4 of the diameter, that is, 75 nm. Our experimental result (87 nm) agreed with this value and implies a closely packed layered structure. The surface roughness can be reduced by using smaller particles in the LbL assembly.

It is interesting to compare our approach on 2D-micro-patterning of polyion/nanoparticle multilayers with thiol compound microprinting of charged patterns on gold supports and further LbL assembly of multilayers developed in last six years by Hammond's group.^{16–19} Both methods give patterns of approximately the same quality with minimal elements of about 1–2 μm , edge roughness of about 0.1–0.2 μm , and clear support surface between the pattern features. One of the advantages of our lithographic approach is that it is compatible with existing silicon micromanufacturing technology. This means that for industrial application one can use existing silicon technology to produce 4 in. diameter silicon wafers completely covered with needed patterns of nanoparticle multilayers. With the microprinting approach, it is difficult to produce a perfect pattern on a surface area more than a few mm^2 . On the other hand, in the microprinting approach one can assemble biological (protein, DNA) multilayers on charged patterns. This is more difficult in the lithographic approach because of the need to use an organic solvent to dissolve the photoresist underlayer at the final stage of the process. In a recent development, polyion stamping on supports other than gold and the possibility to fill gaps between polyion/nanoparticle strips with a second component through hydrogen bonding were elaborated.¹⁶ In the lithographic approach, it is also possible to fill gaps between LbL-assembled strips with a second component using metal mask etching and oxygen

plasma treatment similar to the approach used in the VLSI (very large scale integrated circuits) industry.¹²

In conclusion, the micropatterning of LbL self-assembled layers can be obtained by traditional lithography technology. The advantages of the method include a simpler process with micron feature size and very good reproducibility. It is believed that the feature size can be downscaled to the submicron level. The technique can be applied to almost all charged nanoscale building blocks. One can produce a pattern of thousands of tiny identical elements on a standard 4 in. silicon wafer. This method provides a technology for nanodevices such as nanoelectronic chips

or NEMS, which have varieties of potential applications. It could also allow the patterning of particle-based sensors for use in biomedical applications (bioMEMS production).

Acknowledgment. This work was partially supported by National Science Foundation Grant No. 0092001 "Micro/Nanodevices and Systems". Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the view of the National Science Foundation.

LA025856R