

Lithographic approach to pattern multiple nanoparticle thin films prepared by layer-by-layer self-assembly for microsystems

Tianhong Cui^{a,b,*}, Feng Hua^a, Yuri Lvov^a

^a Institute for Micromanufacturing, Louisiana Tech University, 911 Hergot Avenue, P.O. Box 10137, Ruston, LA 71272, USA

^b Mechanical Engineering, University of Minnesota, 111 Church Street SE, Minneapolis, MN 55455, USA

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Abstract

We report a lithographic approach to pattern multiple types of layer-by-layer (LbL) self-assembled nanoparticle thin films. Polystyrene particles (150 and 64 nm) are spatially separated in desired patterns with a feature size of 5–20 μm . The process is technically simple, consisting of only two consecutive lift-off steps, and can be applied to various types of nanoparticles. This method can be applied to various types of nanoparticles. Since it is based on the conventional lithographic technique, it provides a simple, reliable, and cheap method to pattern nanoparticles into two-dimensional patterns of microscale pitches for the fabrication of complex microsystems which is composed mainly of functional nanoparticles for the applications to sensing and actuation.

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1. Introduction

Nanoparticles are brand new and exciting materials due to their novel electronic, biomedical, chemical, catalytic, and optical properties [1–8]. The physical properties of nanoparticles can vary significantly as the particle sizes change [9,10]. This new class of materials becomes the focus of the material research not only due to their controllable optical and electrical properties through the variation of particle size, but also due to the greatly reduced sintered temperature in the fabrication of devices. Currently, the extensive research efforts are attracted on their optical, electrical, and magnetic properties and corresponding devices [11–13]. Therefore, the nanoparticles will be promising building blocks to microsensors and microactuators.

In most cases, the practical devices and systems are comprised of more than one type of functional nanoparticles, for example, an LED using nanoparticles as the building blocks may include metal, hole, and electron supplying semi-conductive particles. Techniques must be developed to pattern these particles before they are integrated into a device or a system at a micro or nano meter level. Recently, re-

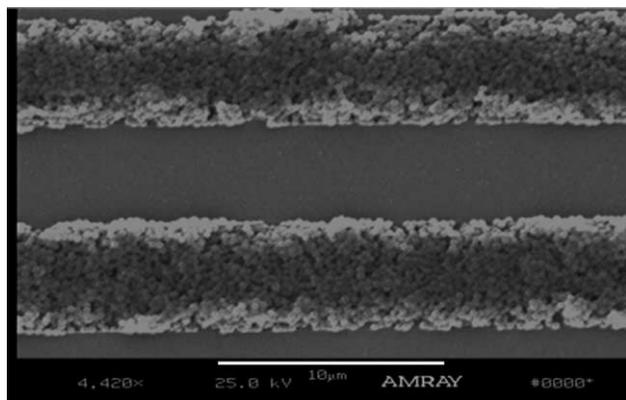
ports have been presented on how to pattern multiple types of self-assembled nanoparticle thin films. Hammond and co-workers [14–16] and Vossmeier et al. [17] demonstrated their approaches to introduce two types of nanoparticles in the matrix by selective deposition in which chemically adhesion promoting and resisting regions must be formed in order to direct the nanoparticles only onto the adhesion promoting regions. These processes include the micro-patterning of the adhesion promoting and resisting regions and the subsequent directed adsorption of the nanoparticles. They are quite successful at adsorbing two types of nanoparticles onto specified regions. However, a template must be prepared as the first step by micro-printing or lithography. The following selective deposition is complicated, demanding the strict control of the adsorption parameters as well as many preparing steps.

In our early report, a strategy combining the conventional lithography technique with layer-by-layer (LbL) self-assembly was presented, in which the lithographic technique was directly employed to pattern the nanoparticle-based thin films, therefore, the delicate selective deposition was avoided [18]. Fig. 1 shows the SEM images based on the lift-off approach and the conventional lithography to pattern one type of silica nanoparticle thin film. The patterns are long lines, 5 μm wide and 5 μm interval. LbL self-assembly is one of the popular techniques used to coat the colloidal nanoparticles, introduced by Decher and co-workers [19,20].

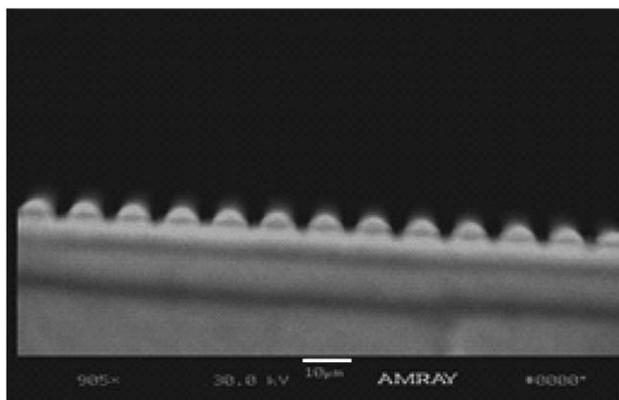
* Corresponding author. Tel.: +1-612-626-1636/318-257-5122;

fax: +1-612-625-9395/318-257-5104.

E-mail address: tcui@me.umn.edu (T. Cui).



(a) Top View



(b) Section View

Fig. 1. (a and b) SEM images of silica nanoparticle patterns by the modified lift-off.

The advantage of this technique is the precise control of step growth to even 1 nm, as well as its low temperature, versatility, and simplicity. Polystyrene particles, 150 nm, and silica particles, 78 nm in diameter, were demonstrated to be spatially separated on a 4 inch silicon wafer in that report. However, expensive etching equipments were required and one of the particles must be organic which can be etched by oxygen reactive ion etching. In addition, contamination also remained after the treatment of the oxygen plasma.

In this paper, a new method based on conventional lithography and LbL self-assembly is demonstrated. Its capability is extended to pattern all kinds of nanoparticles without any etching process. The process consists of merely two ordinary lift-off processes. It is therefore simple, cheap, and clean. Because most of the process takes place by immersing the wafer in two beakers of oppositely charged polyion solutions, the wafer does not have to undergo high temperatures and the requirements of equipment are basic. Compared to the selective deposition process shown by Hammond and co-workers, our method employs the lithography directly, and as a result, avoids the complex preparation and operation of the selective deposition. The schematic of the process is shown in Fig. 2. The process starts with the patterning of a layer of photoresist. Next, 150 nm

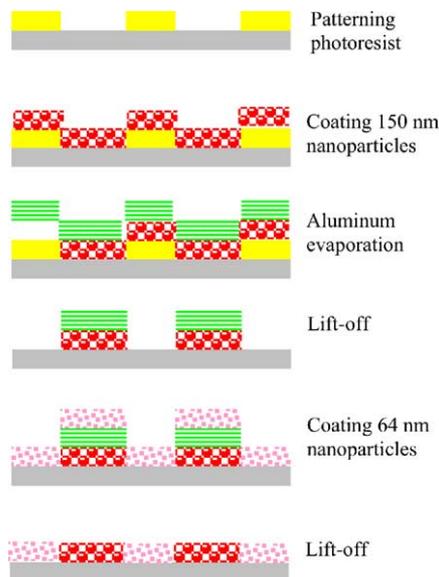


Fig. 2. Procedure to pattern nanoparticles thin film with different sizes or types.

polystyrene nanoparticles are coated on the entire surface without concerning about the directed adsorption. A layer of aluminum is coated, following which, a lift-off is done to create nanoparticle-aluminum columns on the blank wafer surface. Subsequently, the 64 nm polystyrene nanoparticles are coated on the entire surface, some of the nanoparticles are filled into the blank areas next to the 150 nm particles. Finally, the second lift-off is done by dissolving the aluminum and removing the above 64 nm particles.

2. Experimental methods

Polyelectrolytes were obtained from Aldrich–Sigma and were used as follows: (1) poly(dimethyldiallyl ammonium chloride) (PDDA) aqueous solution, MW 200–300 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 colloidal carboxylate modified polystyrene particles, 150 and 64 nm in diameter, were obtained from Seradyn Inc. They were diluted to 8 mg/ml. The photoresist is NPR-1500 negative resist from Futurrex. MF-319 solution from Shipley was diluted to 1:6 (volume ratio) to dissolve the aluminum. EV420 UV light illuminator was from Electronic Visions, Inc. Aluminum layers were deposited by DV-502A high-vacuum evaporator from Denton Vacuum, Inc. An 8892 Cole-Parmer ultrasonic cleaner was used during the lift-off.

Initially, the 4 in. silicon wafer was put into sulfuric acid and hydrogen peroxide solution (volume ratio 3:7) at 70 °C for 1 h. It was baked by a hotplate at 150 °C for 3 min. The negative photoresist was dropped onto the wafer and spun at a speed of 1000 rpm for 40 s. It was baked by the hotplate at 150 °C again for 80 s. Then it was placed under a mask and exposed by the UV light irradiation for 26 s. It was baked

by the hot plate at 100 °C for 85 s and developed for 12 s. At this point, the patterns on the mask have been transferred onto the resist.

The wafer was immersed in the PDDA, PSS, and 150 nm polystyrene nanoparticle solutions alternately in a sequence of: [PDDA (10 min) + PSS (10 min)]₂ + [PDDA (10 min) + polystyrene (10 min)]₃. The intermediate rinsing (1 min in DI water) and drying steps must be involved to ensure a strong and clean film. Thin films of PDDA, PSS, and polystyrene particles were adsorbed layer-by-layer by the electrostatic interaction because they were all oppositely charged. A layer of aluminum 900 Å thick was evaporated onto the nanoparticle thin film. Next, three layers of 150 nm particles were coated once more in a sequence of [PDDA (10 min) + polystyrene (10 min)]₃. After that, another layer of aluminum 800 Å thick was evaporated on. The wafer was put in the acetone solution to do the lift-off during which ultrasonication was introduced to help remove the polyion thin films.

64 nm polystyrene nanoparticles were coated on the entire surface in a sequence of [PDDA (10 min) + PSS (10 min)]₂ + [PDDA (10 min) + polystyrene (10 min)]₁. Finally, the wafer was put into MF-319 solution (volume ratio 1:6) to dissolve the aluminum and remove the smaller particles above it. Ultrasonication was necessary during the lift-off to remove the polyion and smaller nanoparticles.

3. Results and discussions

As shown in Fig. 3, two types of nanoparticles, 64 and 150 nm polystyrene, were successfully deposited into spatially different regions as desired. The designed patterns consisted of regularly arranged squares with a side length of 5 μm. After the process, the 64 nm nanoparticles were deposited within the lithographically patterned squares, while the 150 nm particles were deposited into the region surrounding the squares.

The ultrasonication process must be introduced during the lift-off to cleave the linkages among the polyions. The LbL self-assembled nanoparticle thin films are sandwiched between two oppositely charged polyion films, forming a cross-linked net that is not readily cleaved. Without ultrasonication, the polyion films cannot be removed when the materials under them are dissolved, and tend to come down and reattach to the substrate. Therefore, the nanoparticles between two polyion layers also cannot be removed. The ultrasonication provides a way to cleave the polyion net when the materials underneath are dissolved and to lift-off the nanoparticles completely.

The negative photoresist and aluminum were selected as the lift-off materials in this experiment. The photoresist is a common lift-off material. Of course, other substitutes can be selected instead of aluminum. MF-319 served as the aluminum solvent due to the slow dissolving rate that can put the material dissolution under control.

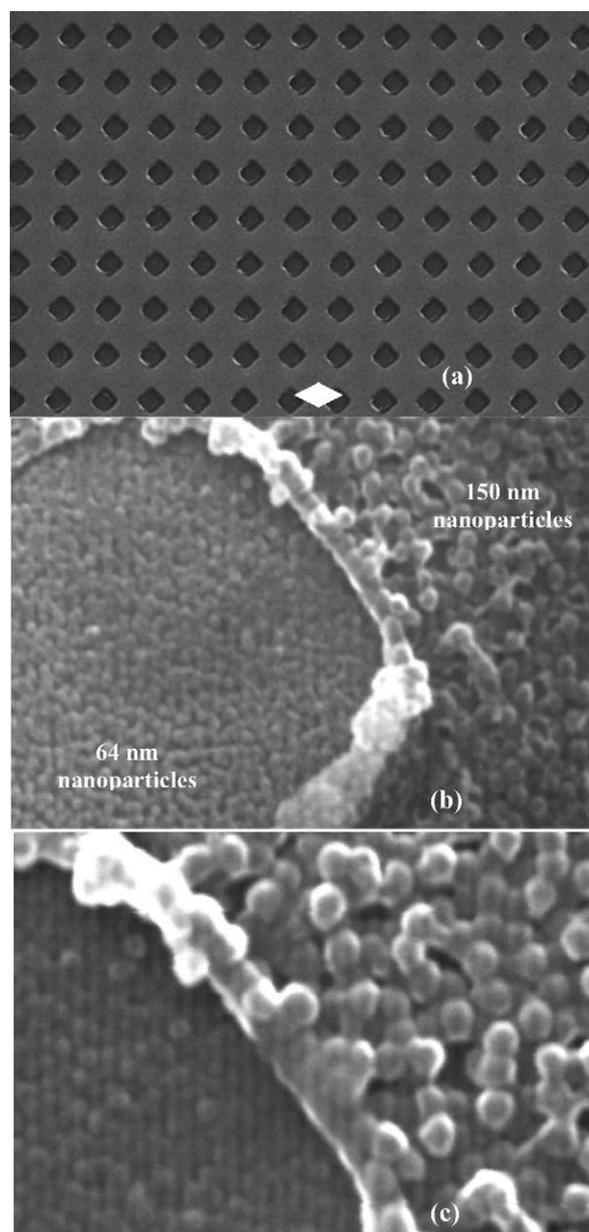


Fig. 3. (a–c) SEM images of patterned two nanoparticles at different magnification.

The aluminum thickness is a factor needed to be taken into consideration in the process. It is found that a thick aluminum layer may peel off many desirable parts of the 150 nm nanoparticle films under it. On the other hand, a thin aluminum layer is not enough to lift-off all 64 nm nanoparticles on it. Our solution is to split the aluminum into two layers and insert three layers of 150 nm nanoparticle films in between. As described in Section 2, the first layer of aluminum deposited is 900 Å which is right above the 150 nm nanoparticle film. The second aluminum layer which is 800 Å in thick is separated from the first layer by three layers of weakly attached 150 nm nanoparticle films. When the aluminum is being dissolved, the 900 Å aluminum is too thin to remove the 150 nm nanoparticle films on the substrate,

while the aluminum with a total thickness of 1700 Å can lift-off the 64 nm nanoparticles completely.

4. Conclusions

A simple and effective approach is presented to pattern all types of nanoparticles on a silicon wafer. It adopts the well-established semiconductor process directly to pattern the nanoparticle thin films without the demand of intermediate micro-stamp or directed adsorption. The pattern can be more distinct and clear. The number of chemicals involved in the process is significantly reduced except the commonly used ones in the semiconductor industry. The equipments used just consist of the basic lithographic tools. It is expected to find wide applications in the fabrication of novel micro devices or microsystems based on varieties of nano building blocks.

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References

- [1] A. Bezryadin, C. Dekker, Nanofabrication of electrodes with sub-5 nm spacing for transport experiments on single molecules and metal clusters, *J. Vac. Sci. Technol. B* 15 (1997) 793–799.
- [2] C. Baur, A. Bugacov, B. Koel, Nanoparticle manipulation by mechanical pushing: underlying phenomena and real-time monitoring, *Nanotechnology* 9 (1998) 360–364.
- [3] T. Vargo, J. Calvert, Patterned polymer multilayer fabrication by controlled adhesion of polyelectrolytes to plasma-modified fluoropolymer surfaces, *Supramol. Sci.* 2 (1995) 169–174.
- [4] A. Rogach, A. Susha, F. Caruso, G. Sukhorukov, A. Kornowski, S. Kershaw, H. Möhwald, A. Eychmüller, H. Weller, Nano- and micro-engineering: three-dimensional colloidal photonic crystals prepared from submicrometer-sized polystyrene latex spheres pre-coated with luminescent polyelectrolyte/nanocrystal shells, *Adv. Mater.* 12 (2000) 333–337.
- [5] G. Ozin, S. Yang, The race for the photonic chip, opal-patterned chips, *Adv. Funct. Mater.* 11 (2001) 1–10.
- [6] M. Onoda, H. Nakayama, T. Yamaue, K. Tada, K. Yoshino, Properties of light-emitting diodes fabricated from self-assembled multilayer heterostructures of poly (*p*-pyridyl vinylene), *Jpn. Appl. Phys.* 36 (1997) 5322–5328.

- [7] O. Onitsuka, A.C. Fou, M. Ferreira, B.R. Hsieh, M.F. Rubner, Enhancement of light emitting diodes based on self-assembled heterostructures of poly (*p*-phenylene vinylene), *J. Appl. Phys.* 413 (1996) 395–400.
- [8] J. Halls, C. Walsh, N. Greenham, E. Marseglia, R. Friend, S. Moratti, A. Holmes, Efficient photodiodes from interpenetrating polymer network, *Nature* 376 (1995) 498–499.
- [9] G. Chen, Particularities of heat conduction in nanostructures, *J. Nanoparticle Res.* 2 (2000) 199–204.
- [10] Y. Takeda, V. Gritsyna, N. Umeda, C. Lee, Optical properties of nanoparticle composites in insulators by high-flux 60 keV Cu implantation, *Nuclear Instrum. Meth. Phys. Res. B* 148 (1999) 1029–1034.
- [11] N.I. Kovtyukhova, B.R. Martin, J.K.N. Mbindyo, P.A. Smith, B. Razavi, T.S. Mayer, T.E. Mallouk, Layer-by-layer Assembly of rectifying junctions in and on metal nanowires, *J. Phys. Chem. B* 105 (2001) 8762.
- [12] T. Cassagneau, J.H. Fendler, T.E. Mallouk, Optical and electrical characterizations of ultrathin films self-assembled from 11-aminoundecaic acid capped TiO₂ nanoparticles and polyallylamine hydrochloride, *Langmuir* 16 (2000) 241–246.
- [13] N. Saito, H. Haneda, T. Sekiguchi, N. Ohashi, I. Sakaguchi, K. Koumoto, Low-temperature fabrication of light-emitting zinc oxide micropatterns using self-assembled monolayers, *Adv. Mater.* 14 (2002) 418–420.
- [14] X. Jiang, P. Hammond, Selective deposition in layer-by-layer assembly: functional graft copolymers as molecular templates, *Langmuir* 16 (2000) 8501–8509.
- [15] X. Jiang, H. Zheng, S. Gourdin, P. Hammond, Polymer-on-polymer stamping: universal approaches to chemically patterned surfaces, *Langmuir* 18 (2002) 2607–2615.
- [16] H. Zheng, I. Lee, M. Rubner, P. Hammond, Two component particle arrays on patterned polyelectrolyte multilayer templates, *Adv. Mater.* 14 (2002) 681.
- [17] T. Vossmeier, S. Jia, E. DeIonno, M. Diehl, S.H. Kim, Combinatorial approaches toward patterning nanocrystals, *J. Appl. Phys.* 84 (1998) 3664–3670.
- [18] F. Hua, J. Shi, Y. Lvov, T. Cui, Patterning of layer-by-layer self-assembled multiple types of nanoparticle thin films by lithographic technique, *Nano Lett.* 2 (2002) 1219–1222.
- [19] G. Decher, Fuzzy nanoassemblies: toward layered polymeric multicomposites, *Science* 227 (1997) 1232–1237.
- [20] Decher, G. E. Michel, J. Schmitt, B. Struth, Layer-by-layer assembled multicomposite films, *Colloidal Interf. Sci.* 3 (1998) 77.

Biographies

Tianhong Cui is currently serving as Nelson associate professor, the Richard and Barbara Nelson chair, at Department of Mechanical Engineering and Nanofabrication Center at University of Minnesota. Prior to joining the University of Minnesota, he has been an assistant professor of electrical engineering and Institute for Micromanufacturing at Louisiana Tech University from 1999 to 2003. Prior to that, Dr. Cui was at the National Laboratory of Metrology in Japan as a research fellow under STA fellowship, and previous to that, served as a postdoctoral research associate at the University of Minnesota from 1997 to 1998 and Tsinghua University from 1995 to 1997. He received his PhD from Chinese Academy of Sciences in 1995. His current research interests include MEMS, nanotechnology, and polymer micro/nanoelectronics.