

A lithographic approach of spatial separation for multiple types of layer-by-layer self-assembled nanoparticles

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

^a*Institute for Micromanufacturing, Louisiana Tech University, 911 Hergot Ave, Ruston, LA 71272, USA*

^b*Department of Mechanical Engineering, University of Minnesota, Minneapolis, MN 55455, USA*

Received 26 March 2003; received in revised form 3 October 2003; accepted 19 October 2003

Abstract

A lithographic approach is presented to pattern two types of nanoparticles on one 4 inch silicon wafer. The different nanoparticles are separated completely according to the designed pattern. The process is applicable to all types of nanoparticles, which may enable its application in complex device fabrication that requires more than one type of functional nanoparticles. The process is quite simple, consisting of only two consecutive lift-offs, and there is no high requirement for the equipments. 150 nm and 64 nm polystyrene particles were selected in the experiment as two different particles. A scanning electron microscope was used to observe the patterns comprised of two types of polystyrene nanoparticles.

© 2003 Elsevier B.V. All rights reserved.

Keywords: Adsorption; Nanostructures; Layer-by-layer self-assembly; Spatial patterning

1. Introduction

Nanoparticles are exciting materials because they exhibit novel electronic, 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 process of device fabrication. It is shown that extensive research efforts are attracted on their optical, electrical, and magnetic properties and devices based on them [11–13].

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 semiconductive particles. Techniques must be developed to pattern these particles before they are integrated into a device or a system at a micro or nanometer level. Recently, reports have been presented

on how to pattern multiple types of self-assembled nanoparticle thin films. Hammond's and Vossmeier's groups 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 [14–17]. 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 the 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]. LbL self-assembly is one of the popular techniques used to coat the colloidal nanoparticles, introduced by Decher et al. [19–21]. The advantage of this technique is the precise

*Corresponding author. Tel.: +1-318-257-5122; fax: +1-318-257-5104.

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

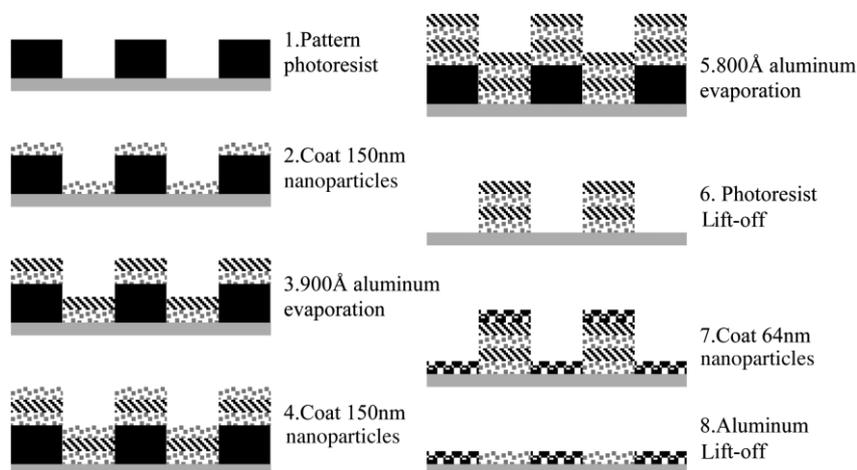


Fig. 1. Flow chart of patterning two types of nanoparticles in which the aluminum layer is divided into three parts.

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 [18]. However, expensive etching equipments were required and one of the particles must be organic can be etched by oxygen reactive ion etching. In addition, contamination 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 patterning all types 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, this 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. 1. The process starts with the patterning of a layer of photoresist as step 1. Next, at step 2 150 nm polystyrene nanoparticles are coated on the entire surface without concerning with the directed adsorption. At step 3, one layer of aluminum is evaporated on it. At step 4, 150 nm polystyrene nanoparticles are again coated. At step 5, another layer of aluminum is evaporated. Two layers of aluminum will serve as the sacrificial material layer. The reason why they are evaporated separately is to generate a distinct pattern, which will be explained in the discussion section. At step 6, the resist at the bottom is dissolved so that the nanoparticles and aluminum on it are peeled off. Subsequently, at step 7, the 64 nm polystyrene nanoparticles are coated on the entire

surface, some of which are filled into the blank areas next to the 150 nm particles. Finally, at step 8, the second lift-off is done by dissolving the aluminum and removing the above 64 nm particles.

2. Experimental method

Polyelectrolytes were obtained from Aldrich-Sigma and were used as follows: (1) poly(dimethyldiallyl ammonium chloride) (PDDA) aqueous solution, MW 200 to 300 K, 3 mg/ml, 0.5 M NaCl, (2) sodium poly(styrenesulfonate) (PSS) aqueous solution, MW 70K, 3 mg/ml, 0.5 M NaCl. The colloidal carboxylate modified polystyrene particles, 150 nm 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.

The wafer was immersed in the PDDA, PSS, and 150 nm polystyrene nanoparticle solutions alternately in a sequence of: two cycles of (PDDA + PSS) and three cycles of (PDDA + polystyrene). Each immersion time is 10 min. 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 cycles of 150 nm particles and PDDA were coated. After that, another layer of aluminum 800 Å thick was evaporated. To this point, the multilayer can be described from

bottom to top as 2 layers of (PDDA + PSS) + 3 layers of (PDDA + polystyrene) + (900 Å Al) + 3 layers of (PDDA + polystyrene) + (800 Å Al). The wafer was soaked in the acetone solution to do the lift-off during which ultrasonication was introduced to help in removing the polyion thin films.

Sixty-four nanometer polystyrene nanoparticles were coated on the entire surface in a sequence of two cycles of (PDDA + PSS) and one cycle of (PDDA + polystyrene). Finally, the wafer was put into MF-319 solution (volume ratio 1:6) to dissolve the aluminum and to 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. 2, two types of nanoparticles, 64 and 150 nm polystyrene, were successfully settled in different regions as desired. The designed patterns consisted of regularly arranged squares with a side and distance of 5 μm . After the process, the 64 nm nanoparticles were filled into the tiny squares with 150 nm particles surrounding them. Under the conditions of adsorption in our experiment, the nanoparticle thin films have a dense structure, therefore the monolayer thickness of the film is the diameter of the nanoparticle.

The ultrasonication must be introduced during the lift-off to break the linkages among the polyion layers. The LbL self-assembled nanoparticle thin films are sandwiched between oppositely charged polyion films, which could be regarded as a cross-linked net that is not readily cut off. They cannot be removed when the materials under them are dissolved. On the contrary, they tend to come down and reattach to the places where the dissolved materials used to occupy. In this case, the nanoparticles between two polyion layers also cannot be removed. The ultrasonication provides a way to break off the polyion net when the materials underneath are dissolved and completely lift off the nanoparticles.

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 dissolving under control.

The aluminum thickness is a factor needed to be taken into consideration in the process. It is found that dissolving a thick aluminum layer may peel off many desirable parts of the 150 nm nanoparticle films under it. However, 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 shown in Fig.

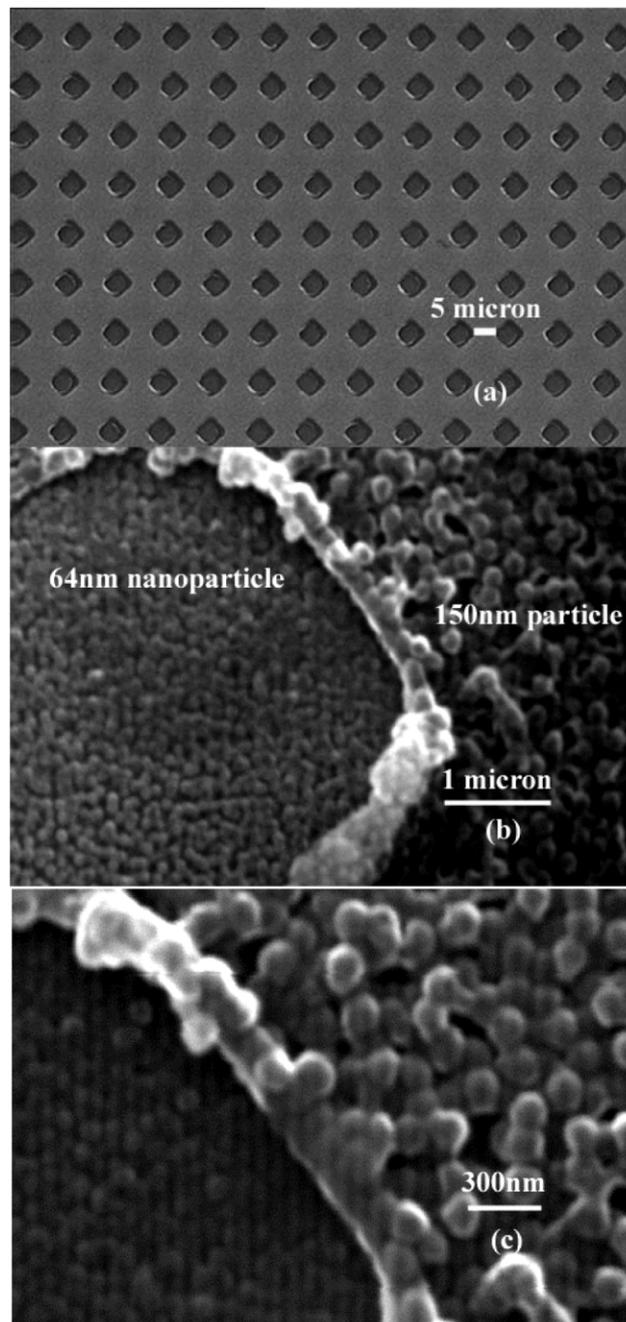


Fig. 2. Two types of nanoparticles are separately located on wafer. (a) pattern on photoresist comprised of 5 μm squares. (b), (c) 64 nm nanoparticles were filled in the square and 150 nm ones surrounding them.

1. As described in the experiment section, 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 thickness 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 can not peel off from the

150 nm nanoparticle films and a total thickness of 1700 Å can lift off the 64 nm nanoparticles completely.

4. Conclusions

A simple and effective approach is found, which is compatible to patterning 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 to the fabrication of novel devices or systems made from a variety of nanobuilding blocks.

Acknowledgments

This work is partially supported by NSF/LEQSF(2001–04)-RII-02 foundation. Any opinions, finding, 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. We also acknowledge the assistance of Dr Naidu Seetala at Grambling State University for the scanning electronic microscopy pictures.

References

- [1] B. Bezryadin, C. Dekker, *J. Vac. Sci. Technol.* 15 (1997) 793.
- [2] C. Baur, A. Bugacov, B.E. Koel, *Nanotechnology* 9 (1998) 360.
- [3] T.G. Vargo, J.M. Calvert, *Supramol. Sci.* 2 (1995) 169.
- [4] Rogach, A. Susha, F. Caruso, G. Sukhorukov, A. Kornowski, S. Kershaw, H. Möhwald, A. Eychmuller, H. Weller, *Adv. Mater.* 12 (2000) 333.
- [5] G.A. Ozin, S.M. Yang, *Adv. Funct. Mater.* 11 (2001) 95.
- [6] Mitsuyoshi, N. Hiroshi, Y. Takahiro, Y. Katsumi, *Jpn. J. Appl. Phys.* 36 (1997) 5322.
- [7] Onitsuka, A.C. Fou, M. Ferreira, B.R. Hsieh, M.F. Rubner, *J. Appl. Phys.* 413 (1996) 395.
- [8] J. Halls, C. Walsh, N. Greenham, E. Marseglia, R. Friend, S. Moratti, A. Holmes, *Nature* 376 (1995) 498.
- [9] G. Chen, *J. Nanopart. Res.* 2 (2000) 199.
- [10] Y. Takeda, V.T. Gritsyna, N. Umeda, C.G. Lee, *Nucl. Instrum. Methods Phys. Res. B* 148 (1999) 1029.
- [11] N.I. Kovtyukhova, B.R. Martin, J.K.N. Mbindyo, P.A. Smith, B. Razavi, T.S. Mayer, T.E. Mallouk, *J. Phys. Chem. B* 105 (2001) 8762.
- [12] T. Cassagneau, J.H. Fendler, T.E. Mallouk, *Langmuir* 16 (2000) 241.
- [13] N. Saito, H. Haneda, T. Sekiguchi, N. Ohashi, I. Sakaguchi, K. Koumoto, *Adv. Mater.* 14 (2002) 418.
- [14] X. Jiang, P. Hammond, *Langmuir* 16 (2000) 8501.
- [15] X. Jiang, H. Zheng, S. Gourdin, P. Hammond, *Langmuir* 18 (2002) 2607.
- [16] H. Zheng, I. Lee, M. Rubner, P. Hammond, *Adv. Mater.* 14 (2002) 681.
- [17] T. Vossmeier, S. Jia, E. DeIonno, M. Diehl, S.H. Kim, *J. Appl. Phys.* 84 (1998) 3664.
- [18] F. Hua, J. Shi, Y. Lvov, T. Cui, *Nano Lett.* 2 (2002) 1219.
- [19] G. Decher, *Science* 227 (1997) 1232.
- [20] Y. Lvov, G. Decher, H. Möhwald, *Langmuir* 9 (1993) 481.
- [21] Decher, E. Michel, J. Schmitt, B. Struth, *Colloidal Interface Sci.* 3 (1998) 77.