

# Silica Nanowires Fabricated with Layer-by-Layer Self-Assembled Nanoparticles

Yi Liu and Tianhong Cui\*

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

In this paper we demonstrate an approach to fabricate silica nanowires by combining “top-down” e-beam lithography and “bottom-up” layer-by-layer (LbL) nano self-assembly techniques. The simple and low-cost LbL self-assembly technique is used to grow silica nanoparticle thin film, while the e-beam lithography based lift-off technique is implemented to pattern the self-assembled thin film to nanometer scale. The silica nanowires fabricated by this method have an average width of 90 nm, while the minimum width obtained is 63 nm. Our experimental results indicate a new approach to fabricate nanowires that can be used in nanoelectronic devices and circuits.

**Keywords:** Silica Nanowire, Layer-by-Layer Self-Assembly, Nanoparticle.

## 1. INTRODUCTION

Nanotechnology is concerned with materials, structures, components, and systems that exhibit novel and improved physical, chemical, and biological properties due to their nanoscale sizes. The objective is to gain control of structures and devices at atomic, molecular, and super-molecular levels in order to efficiently manufacture and exploit such devices. Recently, organized thin films of nanoscale particles have received much attention because they exhibit unique electronic, catalytic, and optical properties that differ from the bulk material, so that interesting scientific and technological applications could arise from such novel materials.<sup>1</sup> The applications of using nanoparticles as building blocks have been found in electronic devices,<sup>2</sup> microelectromechanical system (MEMS) devices,<sup>3</sup> gas sensors,<sup>4</sup> and biosensors,<sup>5</sup> etc.

Nanowires are considered to be the promising building blocks for nanoelectronics so that they are an extension of Moore’s law from silicon industry. The past few years have witnessed tremendous growth to fabricate nanowires in two ways: “top-down” and “bottom-up” approaches. The “top-down” method begins with patterns or thin films generated on a large scale, and then their lateral dimensions are reduced to fabricate nanostructures. Many silicon or metal nanowires have been fabricated using this approach.<sup>6</sup> The “bottom-up” method starts with atoms, molecules, or nanoparticles, and builds up to nanostructures. One well-known “bottom-up” approach is the vapor-liquid-solid (VLS) method.<sup>7,8</sup> Many applications based on

nanowires have also been developed, such as transistors,<sup>9</sup> and biosensors,<sup>10</sup> etc.

Recently, there is an emerging interest to fabricate nanowires based on nanoparticles. For example, Tang et al. demonstrated luminescent nanowires with self-organized CdTe nanoparticles.<sup>11</sup> Hassenkam et al. reported gold nanowires made of a Langmir-Blodgett gold nanoparticle thin film produced by phase separation phenomena.<sup>12</sup> Wang et al. introduced the antimony nanowires formed by chemically self-assembled Sb nanoparticles.<sup>13</sup> However, the above methods have the disadvantage of either long growing time (7 days for Ref. [11], and 8 days for Ref. [13]), or non-controllable growing of nanowires.<sup>12</sup> In this paper, we demonstrate a simple, time-saving, and controllable method to fabricate nanowires combining “top-down” e-beam lithography and “bottom-up” layer-by-layer nano self-assembly techniques. Previously, our group has reported the patterning of LBL self-assembled nanoparticle thin film with optical lithography and lift-off approach.<sup>14–16</sup> When combined with e-beam lithography, this method could be a generic approach to fabricate nanoparticle-based nanowires, provided the nanoparticle thin film can be grown using layer-by-layer nano self-assembly technique.

## 2. EXPERIMENTAL DETAILS

In order to self-assemble silica nanoparticle thin films, several commercially available chemical solutions were used, including silica nanoparticle dispersion and polyelectrolyte. The silica nanoparticle dispersion (with particle diameters of 40 ~ 60 nm) was from Nissan Chemical Corporation. The polyelectrolytes used in the fabrication process

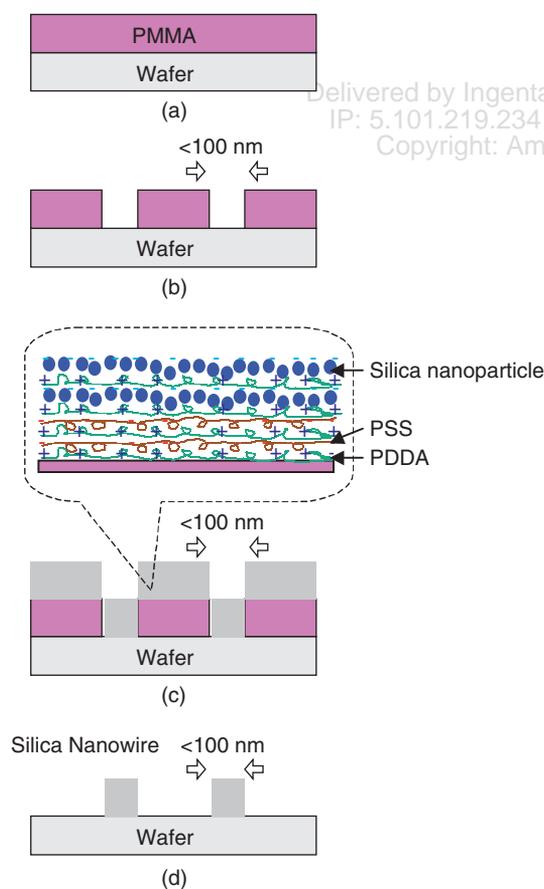
\*Author to whom correspondence should be addressed.

were poly(dimethyldiallyl- ammonium chloride) (PDDA) (MW 200 K and 300 K, from Sigma-Aldrich Corp.) and poly(styrenesulfonate) (PSS) (MW 70 K, from Sigma-Aldrich Corp.), respectively. The concentration of PDDA and PSS aqueous solutions were 5 mg/mL and 3 mg/mL, respectively. Both solutions were doped with 0.5 M NaCl to increase their ionized strength. The thin film growth process was monitored by the research quartz crystal microbalance (QCM) system from Maxtek Inc. Raith 150 e-beam lithography system (from Raith GmbH) was used to write the polymethyl methacrylate (PMMA) photoresist.

The fabrication process was done on standard 4-inch silicon wafers. These wafers were cleaned using the standard Radio Corporation of America (RCA) cleaning procedure prior to fabrication. The nanowire fabrication procedure is shown in Figure 1. First, the silicon wafer was pre-baked on a hotplate at 115 °C for 90 seconds. Next, a layer of hexamethyldisilazane (HMDS) adhesion promoter was deposited and spin-coated at 3000 RPM for 30 seconds to improve the adhesion of photoresist to the surface of the wafer. PMMA photoresist was then deposited and spin-coated on top of the wafer at the same spin-coating condition. Before the e-beam lithography, the silicon wafer was

baked in an oven at 175 °C for 30 minutes. After baking, e-beam lithography was used to write the pre-defined wire patterns with nanoscale width (from 50 nm to 100 nm) and microscale length (from 1  $\mu\text{m}$  to 500  $\mu\text{m}$ ). The shaped electron beam energy was 20 kV with a dose of 215  $\mu\text{C}/\text{cm}^2$ . After the e-beam lithography, the wafer was then immersed into the methyl isobutyl ketone (MIBK) and isopropanol (IPA) solution (ratio 1:3) for 30 seconds to develop the exposed PMMA photoresist. After cleaning with IPA and DI water each for 30 seconds, the wafer was ready for the layer-by-layer nano self-assembly of silica nanoparticle films.

The LbL nano self-assembly process started with the immersing the wafers into the PDDA solution for 10 minutes. Next, the wafers were rinsed with DI water for 1 minute, and dried with a nitrogen flow. The wafer was then immersed into the PSS solution for 10 minutes, rinsed and dried, as in the previous step. The cycle was repeated in a sequence of {[PDDA (10 minutes) + PSS (10 minutes)]<sub>2</sub> + PDDA (10 minutes)}. At this step, the outermost layer was positively charged PDDA. Following that, the wafer was immersed into the negatively charged silica nanoparticle solution for 5 minutes to grow the self-assembled silica nanoparticle thin film. This was also followed by the steps of rinsing with DI water for 1 minute and drying with a nitrogen flow. Two layers of silica nanoparticle thin films were grown in the sequence of [silica (5 minutes) + PDDA (10 minutes) + silica (5 minutes)]. After all of the LbL self-assembly process, the outermost layer was negatively charged silica nanoparticle thin film. The last step was to use acetone to remove the remaining photoresist with the assistance of an ultrasonic bath.



**Fig. 1.** The fabrication procedure of the self-assembled silica nanowires: (a) spin coating a layer of PMMA on the wafer; (b) patterning PMMA with e-beam lithography; (c) LbL self-assembly of silica nanoparticle thin film; (d) lift-off with acetone and form the silica nanowire.

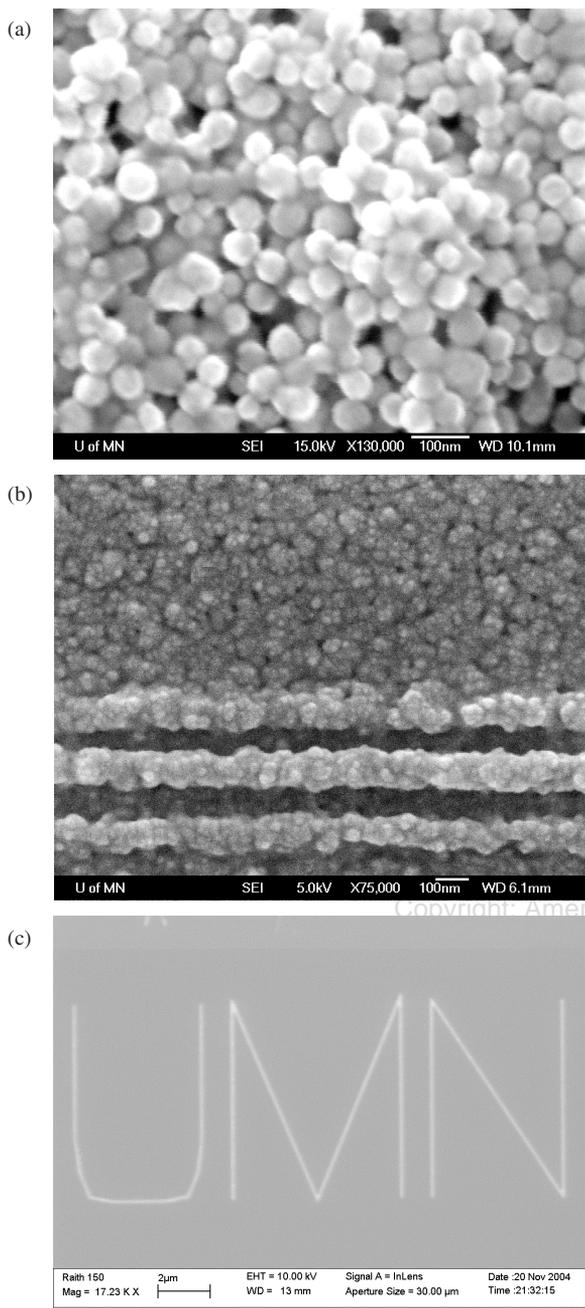
### 3. RESULTS AND DISCUSSION

Figure 2a shows the SEM image of LbL self-assembled silica nanoparticle thin film, which is made of closely packed silica nanoparticles. The SEM images of fabricated nanowires are shown in Figure 2b and 2c. In Figure 2b, it can be seen clearly that the nanowire made of silica nanoparticle is about 90 nm in width. Figure 2c illustrates a logo of “UMN” made of silica nanowires. In our experiment, the minimum width of the fabricated silica nanowire is 63 nm. However, the minimum of the silica nanowire width could be further reduced with optimal e-beam lithography process and control parameters.

A QCM was used to monitor the growing process of the LbL self-assembly thin films. The QCM is an extremely sensitive sensor capable of measuring mass changes in nanogram/cm<sup>2</sup> with a wide dynamic range extending into the 100  $\mu\text{g}/\text{cm}^2$ . The simple equation is shown below:

$$\Delta f = -C_f \times \Delta m \quad (1)$$

where  $\Delta f$  is the frequency change in Hz,  $C_f$  is the sensitivity factor of the crystal in Hz/ng/cm<sup>2</sup>, and  $\Delta m$  is

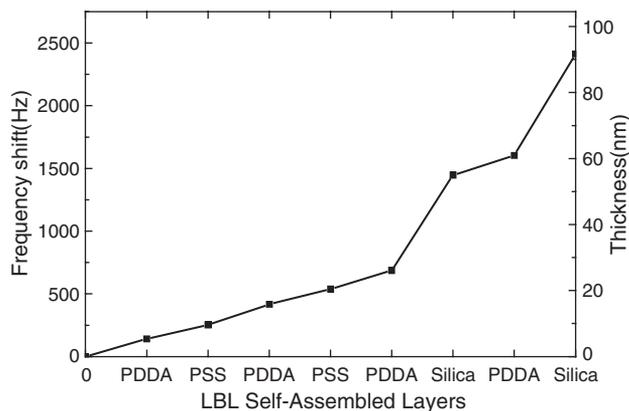


**Fig. 2.** The SEM images of (a) LbL self-assembled silica nanoparticle thin film; (b) silica nanowires with average width of 90 nm. (c) UMN logo made of silica nanowires.

the change in mass per unit area in  $\text{g}/\text{cm}^2$ . The  $C_f$  for the crystal used in the experiment is  $0.1834 \text{ Hz}/\text{ng}/\text{cm}^2$ . The density of the silica/PDD multilayers is  $1.43 \pm 0.05 \text{ g}/\text{cm}^3$ . The diameter of the quartz crystal is 1 inch. Therefore, the thickness of the polyelectrolytes/silica films can be decided using the following relationship within  $\pm 5\%$  error.

$$d(\text{nm}) = -0.038(\text{nmHz}^{-1})\Delta f(\text{Hz}) \quad (2)$$

Figure 3 shows the change of the frequency and corresponding thickness of the LbL thin films during the LbL

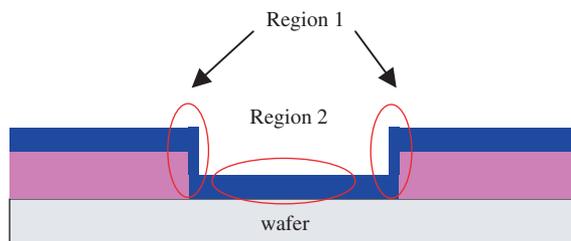


**Fig. 3.** LbL self-assembly progress monitored by QCM.

progress. It can be seen that the final thickness of the silica nanoparticle thin film is about 90 nm.

Several factors influence the final width of the silica nanowire. The first influencing factor is the resolution of the e-beam lithography system. The Raith 150 e-beam lithography system used in the fabrication has a resolution of 30 nm. Therefore, the minimum theoretical width of the nanowire could be close to 30 nm. However, due to the proximity effect during the e-beam writing, the final patterned PMMA would normally be wider than the designed pattern. The second factor that affects the width of nanowire is the dose parameter during the e-beam writing. Higher dose will result in wider exposed area, which results in wider nanowires. To obtain the narrower nanowires, the dose parameter should be as small as possible. However, a smaller dose will also result in the under-exposure of PMMA, hence lead to weak or even no pattern formation. Therefore, the dose parameter should be optimized for the specific thickness of the PMMA.

The general lift-off procedure only uses the acetone without the aid of an ultrasonic bath. This is normally possible when the thickness of the objective thin film is 1/3 of the photoresist. However, the thickness of PMMA photoresist is found to be about 200 nm, which makes it very difficult to lift-off the 90 nm silica nanoparticle thin film without ultrasonic bath. In our experiments, it was found that without the ultrasonic aid, the final silica nanowires could not be lifted-off even after 24 hours soaking time into acetone. The use of ultrasonic bath during the acetone lift-off is indispensable, and very important for the



**Fig. 4.** A magnified schematic of the LbL silica nanoparticle thin film before lift-off.

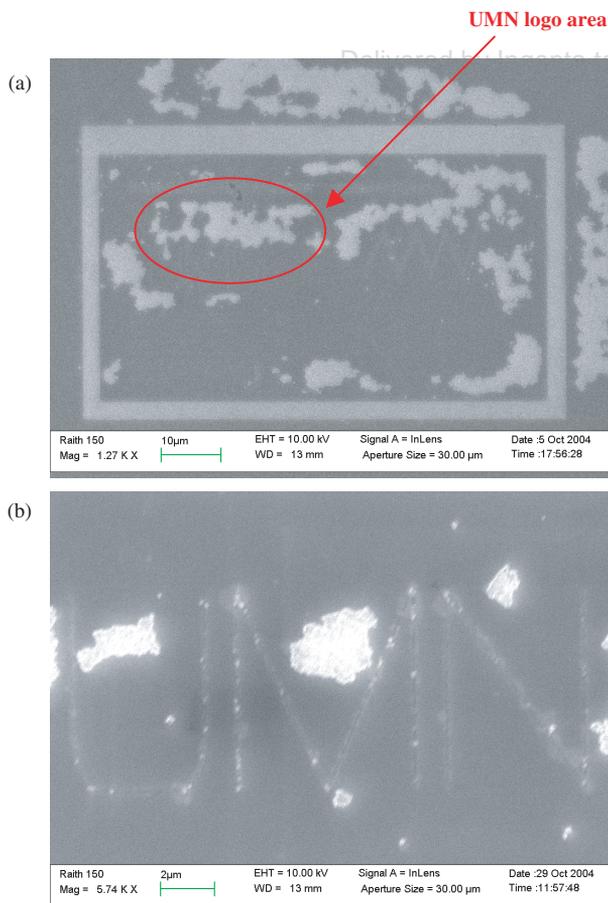
**Table I.** The control experiments to optimize the lift-off time and power.

Power	2 minute	5 minutes	10 minutes
40%	Inadequate lift-off	Inadequate lift-off	Inadequate lift-off
50%	Inadequate lift-off	Good lift-off	Over lift-off
60%	Inadequate lift-off	Over lift-off	Over lift-off

final formation of the nanowires. The ultrasonic bath's power and time have to be optimized to get a successful lift-off procedure. Figure 4 shows magnified schematic view of the LbL self-assembled nanoparticle thin film prior to the lift-off procedure. If the power of the bath is too high, the ultrasonic force will totally break the internal electrostatic connection between the silica nanoparticles and the PDDA polycations within the nanowires itself ( $P_{\text{region}2}$ ). If the power of the bath is too low, the ultrasonic force could not break the connection between the exposed area and the un-exposed area ( $P_{\text{region}1}$ ). Therefore, the ultrasonicating power for lift-off ( $P_{\text{lift-off}}$ ) must fall in the following regions:

$$P_{\text{region}1} < P_{\text{lift-off}} < P_{\text{region}2}$$

The amount of time when the devices are placed in the ultrasonic bath also needs to be optimized to get good

**Fig. 5.** The SEM images of the UMN logo made of silica nanowires at (a) inadequate lift-off situation and (b) over lift-off situation.

lift-off patterns. If the ultrasonic time is too small, the acoustic wave energy is not enough to break the interconnection in region 1 or the minimum breaking-energy at the edge ( $E_{\text{region}1}$ ). On the other hand, too long ultrasonic time will result in superfluous acoustic wave energy that even breaks the electrostatic connection in region 2, or the maximum internal energy  $E_{\text{region}2}$ . Therefore, the following relationship is also required:

$$E_{\text{region}1} < \text{time} \bullet P_{\text{lift-off}} < E_{\text{region}2}$$

In our investigations, we varied the ultrasonic bath power and lift-off time conditions. The results of these experiments are summarized in Table I. The optimal power and time, 50% power for 5 minutes, produced the good silica nanowires shown in Figure 2b and 2c. Some poor lift-off results are also shown in Figure 5. Figure 5a shows an example of inadequate lift-off, where most of the UMN logo edges are connected. Figure 5b is an example of over lift-off, where most of the nanoparticles on the UMN logo pattern have gone.

## 4. CONCLUSION

An approach to fabricate silica nanowires based on e-beam lithography and layer-by-layer nano self-assembly has been demonstrated. The average width of the fabricated silica nanowire is about 90 nm, and the minimum width is 63 nm. This fabrication approach has the advantages of low processing temperature, good compatibility with different substrates, and simplicity. Two disadvantages also exist for this approach, the low-throughput and high cost due to the e-beam lithography process. Soft-lithography using polydimethylsiloxane (PDMS) stamps form with e-beam PMMA as the mold at nanoscale could be introduced to replace the e-beam lithography, and hence overcome these two shortcomings. This alternative approach is still under development in our group.

This approach demonstrated in this paper appears generic, and various types of nanoparticles can be implemented. Currently, nano self-assembled semiconductive nanowires made of *n*-type  $\text{In}_2\text{O}_3$  nanoparticle is under development and would be further applied to the fabrication of  $\text{In}_2\text{O}_3$  nanowire field-effect transistors. With the development of diverse nanoparticle production and characterization, our approach for nanowire fabrication will provide various applications for the nanoelectronics.

## References and Notes

1. B. Raguse, J. Hermann, G. Stevens, J. Myers, G. Baxter, K.-H. Muller, T. Reda, A. Molodyk, and V. Braach-maksvytis, *J. Nanopart. Res.* 4, 137 (2002).
2. F. Hua, J. Shi, Y. Lvov, and T. Cui, *Nanotechnology* 14, 453 (2003).
3. S. B. Fuller, E. J. Wilhelm, and J. M. Jacobson, *J. Microelectromech. S.* 11, 54 (2002).

4. H. Lin, B. Wei, S. Pan, S. C. Tsai, and H. Lin, *J. Nanopart. Res.* **5**, 157 (2003).
5. X. Luo, J. Xu, W. Zhao, and H. Chen, *Sensor. Actuat. B-Chem.* **97**, 249 (2004).
6. Y. D. Park, K. B. Jung, M. Overberg, D. Temple, S. J. Pearton, and P. H. Holloway, *J. Vac. Sci. Technol. B* **18**, 16 (2000).
7. A. M. Morales and C. M. Lieber, *Science* **279**, 208 (1998).
8. C. Li, D. Zhang, S. Han, X. Liu, T. Tang, and Chongwu Zhou, *Adv. Mater.* **15**, 143 (2003).
9. X. Duan, C. Niu, V. Sahi, J. Chen, J. W. Parce, S. Empedocles, and J. L. Goldman, *Nature* **425**, 274 (2003).
10. Y. Cui, Q. Wei, H. Park, C. M. Lieber, *Science* **293**, 1289 (2001).
11. Z. Tang, N. A. Kotov, and M. Giersig, *Science* **297**, 237 (2002).
12. T. Hassenkam, K. Norgaard, L. Iversen, C. J. Kiely, M. Rust, and T. Bjornholm, *Adv. Mater.* **14**, 1126 (2002).
13. Y. Wang, B. H. Hong, J. Y. Lee, J. Kim, G. H. Kim, and K. S. Kim, *J. Phys. Chem.* **108**, 16723 (2004).
14. F. Hua, Y. Lvov, and T. Cui, *J. Nanosci. Nanotechnol.* **2**, 357 (2002).
15. F. Hua, J. Shi, Y. Lvov, and T. Cui, *Nano Lett.* **2**, 1219 (2002).
16. F. Hua, T. Cui, and Y. Lvov, *Langmuir* **18**, 6712 (2002).

Received: 27 May 2005. Revised/Accepted: 3 February 2006.

Delivered by Ingenta to: Main CID is 80004805 (JPP)  
IP: 5.101.219.234 On: Sat, 18 Jun 2016 21:40:37  
Copyright: American Scientific Publishers