

Photolithographic Approaches for Fabricating Highly Ordered Nanopatterned Arrays

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Abstract In this work, we report that large area metal nanowire and polymer nanotube arrays were successfully patterned by photolithographic approach using anodic aluminum oxide (AAO) templates. Nanowires were produced by electrochemical deposition, and nanotubes by solution-wetting. The highly ordered patterns of nanowire and nanotube arrays were observed using scanning electron microscopy (SEM) and found to stand free on the substrate. The method is expected to play an important role in the application of microdevices in the future.

Keywords Pattern · AAO · Photolithographic approach · Nanowire arrays · Nanotube arrays

Introduction

Recent innovations in the areas of micro- and nanofabrication have created a unique opportunity for patterning surfaces with features, the lateral dimensions of which span over the nano- to millimeter range. Micro- and nanometer scale patterns can be obtained by photolithography [1–4], electron beam lithography [5, 6], soft lithography [7], micro-contact printing (μ CP) [8–11]. These techniques above have partially the same process: they can transfer patterns onto the surface

of a substrate. With the development of nanotechnology, a variety of industries, such as biosensor [12], proteomic arrays [13], and multifunctional coatings [14], have focused on obtaining patterns with the smallest possible lateral dimensions [15]. Photolithography is one of the most successful techniques available in large-scale microfabrication [16]. The method is effective, of low cost, simple to implement, and suitable for patterning various nanomaterials [17, 18].

Herein, we report an effective procedure for the fabrication of patterned nanostructure arrays with micro scale features. This process starts with the fabrication of patterned anodic aluminum oxide (AAO) templates. An AAO template was spin-coated with a layer of photoresist to seal the pores of the AAO template, and then “soft baked” at low temperature to remove the solvents from the photoresist and improve photoresist–AAO template adhesion. This composite was covered with a photolithographic mask and exposed to UV, and then “hard baked” at higher temperature to further active cross-linking processes and improve the mechanical stability of the pattern [19]; it was subsequently developed in a developer to make the pores of AAO selectively open only in those exposed areas.

Then the designed template was used for a secondary template to synthesize metal, semiconductor, and polymer one-dimensional nanoarrays. We explain this useful method by an example of patterning copper (Cu) nanowire and polystyrene (PS) nanotube arrays.

Electrodeposition of Cu Nanowires

The same side of the secondary template was sputtered with a layer of Au and regarded as a work electrode. In a tri-electrode system, the electrodeposition was carried out using platinum as the anode and a calomel electrode as the reference electrode, and the Cu nanowires were selectively

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deposited into the open pores. Finally, the patterned nanowire arrays were revealed by the removal of AAO in a sodium hydroxide solution.

Solution-Wetting of Polymer Nanotubes

A drop of PS solution was placed on a microscope slide, and then an AAO membrane with patterned side downward was quickly placed on it. The solution entered completely into the template pores along their inner wall. Then the composite was placed in a sodium hydroxide solution to dissolve the template after the solvent completely evaporated. PS nanotube arrays were obtained.

Figure 1 clearly shows that the nanowire arrays are regular and the nanowires are parallel to each other and completely free standing after the AAO template is removed. Those patterns were completely copied from those of the masks. It is observed from Fig. 1a, that highly ordered large area QDU patterns are obtained using the above method. The QDU patterns are very ordered, and the distance between the three letters is equal, about 4 μm . The whole rows and lines are also regular in arrangement, and the distance between lines and between rows is about 50 μm .

The pattern was tilted to reveal the length of the vertical nanowires. From Fig. 1b, the length is measured to be approximately 50 μm (the depth of AAO is 60 μm), and can be controlled to satisfy application by controlling the deposition time. The line width of the patterns is about 15 μm , and can also be changed by changing the line width in the masks. The diameter of a single wire is about 300 nm, the same as the pores of AAO template, which are well proportioned in diameter (Fig. 1c).

In the same way, Fig. 2a presents highly ordered PS nanotube arrays with QDU patterns obtained from solution-wetting method. Each letter is vertical, and the distance between rows, lines, and letters is just the same as mentioned in Fig. 1a. The width and length of letters is, respectively, 50 and 70 μm .

Figure 2b shows that the length of the PS nanotubes is about 45 μm , and can be controlled by controlling the synthesis time or polymer solution amount. The line width of the patterns is the same as Fig. 1b.

Figure 2c shows the characteristic of nanotubes more clearly, from which we can see their open mouths. The free standing nanotubes have very strong mechanical temperament, and an outer diameter of about 300 nm and a wall thickness of about 50 nm. The outer diameter is a bit larger than that of the AAO pores, because PS nanotubes may be swollen when AAO template is removed in the sodium hydroxide solution [20].

The explanation for forming nanotubes is as follows. Because the inner surfaces of the template nanopores have a very high surface energy, when polymeric solution goes

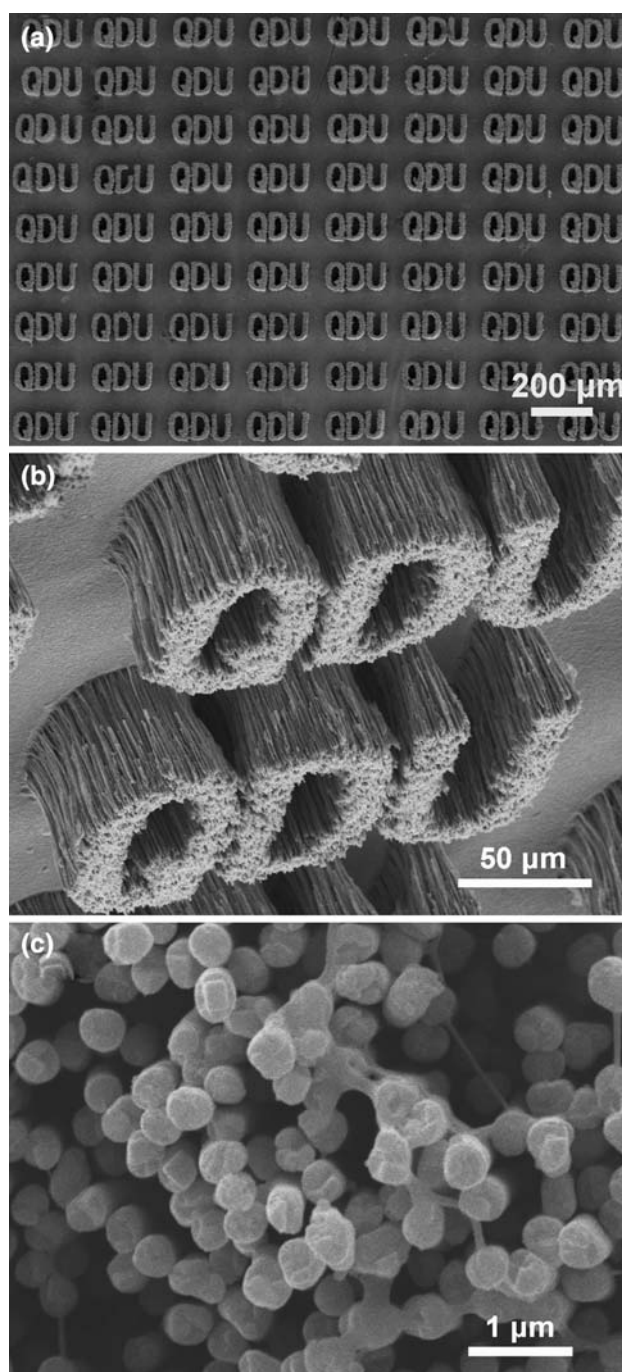


Fig. 1 SEM images of Cu nanowire arrays with QDU patterns (**a**, **b**): **a** large area QDU patterns. **b** The side image shows that the length of the Cu nanowires is about 50 μm . **c** Higher magnification image shows that the nanowires are parallel to each other, and the diameter of the nanowires is about 300 nm

through the open nanopores, it will wet the nanoporous wall first and form a wetting layer. The wetting layer extends along the porous wall to cover the whole template surface. The wetting process is carried on repeatedly and does not stop until the solvent completely evaporated [21]. Thus the nanotubes are formed.

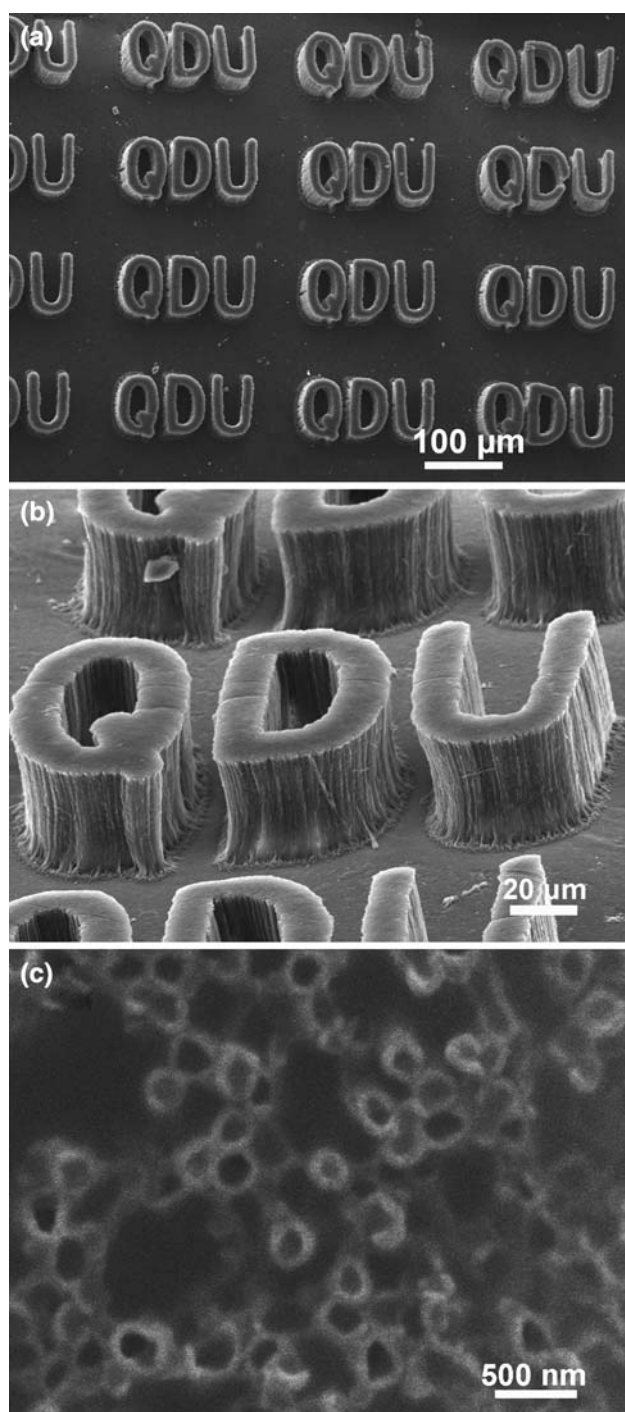


Fig. 2 SEM images of PS nanowire arrays with QDU patterns (**a**, **b**): **a** large area QDU patterns. **b** The side image shows that the length of the PS nanowires is about 45 μm . **c** Higher magnification image shows the PS nanotubes with clear mouths

In summary, we obtained highly ordered free standing patterns of metal nanowire and polymer nanotube arrays with secondary templates at room temperature. They have uniform structures and can be applied in microdevices and integrated circuits in the future. Various patterns can be made

using this method according to demands. Different kinds of materials, such as metal nanowires, semiconductor, and polymer one-dimensional nanoarrays, can be also fabricated. In addition, our group has made Ni and other polymer non-patterned nanowire arrays by the AAO template [20–23], and further research in the field of photolithography is under way. Our group is trying to use the photolithographic method to combine metal nanowires with polymer nanotubes to synthesize patterned coaxial nanocables, which can be used in microdevices, and will report the application of the method in microdevices in our next work.

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References

1. F. Li, M. Zhu, C. Liu, W.L. Zhou, J.B. Wiley, *J. Am. Chem. Soc.* **128**, 13342 (2006). doi:[10.1021/ja0647856](https://doi.org/10.1021/ja0647856)
2. B.D. Gates, Q.B. Xu, M. Stewart, D. Ryan, C.G. Willson, G.M. Whitesides, *Chem. Rev.* **105**, 1171 (2005). doi:[10.1021/cr030076o](https://doi.org/10.1021/cr030076o)
3. M. Rothschild, *Mater. Today* **8**, 18 (2005)
4. B. Ziaie, *Langmuir* **20**, 21 (2004)
5. H. Elsner, H.G. Meyer, *Microelectron. Eng.* **291**, 57 (2001)
6. K. Yamazaki, H. Namatsu, *Microelectron. Eng.* **85**, 73 (2004)
7. M. Denoual, L. Griscom, H. Toshiyoshi, H. Fujita, *Jpn. J. Appl. Phys.* **42**(Part 1), 4598 (2003). doi:[10.1143/JJAP.42.4598](https://doi.org/10.1143/JJAP.42.4598)
8. L.B. Goetting, T. Deng, G.M. Whitesides, *Langmuir* **15**, 1182 (1999). doi:[10.1021/la981094h](https://doi.org/10.1021/la981094h)
9. H. Schmid, B. Michel, *Macromolecules* **33**, 3042 (2000). doi:[10.1021/ma982034l](https://doi.org/10.1021/ma982034l)
10. P.M. St. John, H.G. Craighead, *Appl. Phys. Lett.* **68**, 1022 (1996). doi:[10.1063/1.116216](https://doi.org/10.1063/1.116216)
11. E.S. Györfv, *Nano. Lett.* **3**, 315 (2003). doi:[10.1021/nl025936f](https://doi.org/10.1021/nl025936f)
12. K. Kuwabara, M. Ogino, S. Motowaki, A. Miyauchi, *Microelectron. Eng.* **752**, 73 (2004)
13. K.L. Christman, M.V. Requa, V.D. Enriquez-Rios, S.C. Ward, K.A. Bradley, K.L. Turner, H.D. Maynard, *Langmuir* **22**, 7444 (2006). doi:[10.1021/la0608213](https://doi.org/10.1021/la0608213)
14. H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, *Science* **318**, 426 (2007). doi:[10.1126/science.1147241](https://doi.org/10.1126/science.1147241)
15. G.M. Wallraff, W.D. Hinsberg, *Chem. Rev.* **99**, 1801 (1999). doi:[10.1021/cr980003i](https://doi.org/10.1021/cr980003i)
16. S. Erika, G. Alan O'Riordan, A.J. Quinn, G. Redmond, D. Pum, U.B. Sleytr, *Nano. Lett.* **3**, 315 (2003). doi:[10.1021/nl025936f](https://doi.org/10.1021/nl025936f)
17. X. Zhang, J.Q. Pham, N. Ryza, P.F. Green, K.P.J. Johnston, *Vac. Sci. Technol. B* **22**, 818 (2003). doi:[10.1116/1.1676502](https://doi.org/10.1116/1.1676502)
18. H. Sato, Y. Houshi, S. Shoji, *Microsyst. Technol.* **10**, 440 (2004). doi:[10.1007/s00542-004-0400-9](https://doi.org/10.1007/s00542-004-0400-9)
19. A. del Campo, E. Arzt, *Chem. Rev.* **108**, 911 (2008). doi:[10.1021/cr050018y](https://doi.org/10.1021/cr050018y)
20. G. Song, D. Chen, Z. Peng, X. She, J. Li, P. Han, *J. Mar. Sci. Technol.* **23**, 427 (2007)
21. X. She, G. Song, J. Li, P. Han, S. Yang, S. Wang, Z. Peng, *Polym. J.* **38**, 639 (2006). doi:[10.1295/polymj.PJ2005208](https://doi.org/10.1295/polymj.PJ2005208)
22. X. She, G. Song, J. Li, P. Han, S. Yang, Z. Peng, *J. Mater. Res.* **21**, 1209 (2006). doi:[10.1557/jmr.2006.0161](https://doi.org/10.1557/jmr.2006.0161)
23. X. She, G. Song, Z. Peng, J. Li, C.T. Lim, E.P.S. Tan, L. Lv, X.S. Zhao, *Polym. J.* **39**, 1025 (2007). doi:[10.1295/polymj.PJ2007008](https://doi.org/10.1295/polymj.PJ2007008)