Novel techniques for modifying microtube surfaces with various periodic structures ranging from nano to microscale

Zhaoqian Liu, Jinxing Li, Bingrui Lu, Yifang Chen, Ran Liu, Gaoshan Huang, and Yongfeng Mei

Citation: Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena **31**, 011806 (2013); doi: 10.1116/1.4772769
View online: https://doi.org/10.1116/1.4772769
View Table of Contents: http://avs.scitation.org/toc/jvb/31/1
Published by the American Vacuum Society

Novel techniques for modifying microtube surfaces with various periodic structures ranging from nano to microscale

Zhaoqian Liu, Jinxing Li, Bingrui Lu, Yifang Chen, and Ran Liu[a)]
State Key Lab of ASIC and System, Fudan University, Shanghai 200433, China

Gaoshan Huang and Yongfeng Mei[b)]
Department of Materials Science, Fudan University, Shanghai 200433, China

(Received 30 June 2012; accepted 6 December 2012; published 4 January 2013)

Two dimensional (2-D) structured membranes have been well developed and widely studied to find potential applications in broad realms like optics, mechanics, fluidics, and electronics. In this work, the authors have successfully combined the top–down patterning techniques with the roll-up process to convert various structured flat membranes into three dimensional (3-D) microtubes with textured tube-walls. These 3-D textured microtubes may exhibit novel properties different from the original 2-D films and, thus, can be applied in wider research disciplines such as modern material sciences, biology, electrochemistry, etc. Depending on the parameters of the periodic templates including nanoscale porous anodic alumina and microscale imprinted templates in this work, the authors can curve these textured films into 3-D microtubes with structures on the tube-walls by the rolled-up nanotechnique. The specially designed microtubes here have the potential of interesting optical, electrical, and mechanical characteristics as well as possible applications in micro/nanoelectronics, optics, fludics, and bioengineering. © *2013 American Vacuum Society*.
[http://dx.doi.org/10.1116/1.4772769]

I. INTRODUCTION

At present, two dimensional (2-D) periodic structures have been successfully fabricated through various techniques and shown unique properties that can be applied in micro/nanoelectronic systems, optics, fluidics, and mechanics.[1–4] Among all these techniques for patterning thin films; e.g., laser interference lithography,[5] UV lithography, electron beam lithography (EBL), focused ion beam (FIB) milling, block copolymer lithography;[2,6] the top–down methods of nanoimprint and electrochemical anodization of aluminum foil were used in this work to fabricate micro/nano ordered templates with the benefits of low-cost, high efficiency, and a large effective patterned area. It is worth nothing that the templates used here comprised of imprinted polymer and anodized porous alumina also work as sacrificial layers in the subsequent rolling process.

Rolled-up nanotechnology[7] has been rapidly developed in recent years to fabricate versatile micro/nanostructures such as tubes and wrinkled membranes as well as springs, and widely applied in optical resonators, metamaterials, micro/nanorobots, energy storage, electrical devices, cell scaffolds, etc.[8–12] The novelty of this technique includes good controllability of the parameters of the micro/nanocurved structures such as diameter, the number of rotations, rolling direction, and the capability to roll up various material composites after selectively removing the underlying prepatterned sacrificial layer. The composites of nanomembranes include materials deposited via widely applied deposition techniques; e.g., atomic layer deposition (ALD), electron beam (E-beam) evaporation, molecular beam epitaxy (MBE), sputtering and so on.

In this work, by combining nanoimprint/electrochemical anodization and the rolling technique, we have successfully converted structured flat membranes into three-dimensional microtubes with ordered micro/nanostructures on the tube walls. It can be anticipated that these specially designed microtubes could have interesting properties that are promising for application in micro/nanoelectronics, optics, fluidics, bioengineering, and mechanics.[12]

II. EXPERIMENT

In this section, the details of modifying the microtubes with micro- and nanostructures are described separately since the templates used to form ordered structures are different.

A. Microtubes with nanopillared tube walls via anodic aluminum oxide

Nanoporous templates were fabricated via two-step anodization[13] of pure aluminum foil (99.99%) in 0.5 M oxalic acid under 40 V at 3 °C after polishing the cleansed foil in a mixture of $HClO_4$ and ethanol (1:5 in volume) under 18 V for 3 min. To make the nanopores periodically distributed, the first anodization was prolonged to 3 h, and subsequently, the anodized porous alumina was removed by immersion in a mixture of 6 wt. % phosphoric acid and 1.8 wt. % chromic acid (1:1 in volume) at 85 °C for 45 min.[14] The second anodization should be carried out under the same conditions as the first one. It should also be noted that the thickness of the porous layer increased with the duration time of the second anodization process. To avoid the collapse of slim pillars during the rolling process and thus confine the length of channels in the nanoporous templates to the nanoscale, 5 min anodization is sufficient here.

a)Electronic mail: rliu@fudan.edu.cn
b)Electronic mail: yfm@fudan.edu.cn

As shown in Fig. 1(b), to thoroughly replicate the nanochannels in the anodic aluminum oxide (AAO) templates, ALD was employed to grow ~5 nm HfO_2 after 50 cycles. HfO_2 was chosen because of its inertia in the etchant of aqueous KOH solution. After the process of Ebeam evaporation of 10 nm of Ti and 10 nm of Cr as shown in Fig. 1(c), the three stacked layers are released from the substrate and rolled up into a 3-D tubular structure after the removal of the porous alumina in KOH solution, as presented in Fig. 1(d).

B. Microtubes with micro/nanostructured tube walls via nanoimprint

In our earlier work, nanoimprint was employed to investigate the effect of imprinting on ferro/piezoelectric materials such as P(VDF-TrFE)[15] and $Pb(Zr_x,Ti_{1-x})O_3$,[16] and their possible applications in data storage,[16,17] ferroelectric lithography,[18] wave guiding, and micro/nanofluidic systems.

In this work, silicon templates covered by a layer of trichloro(1H, 1H, 2H, 2H-perfluorooctyl) silane were used to imprint P(VDF-TrFE)films into desired micro/nanostructures. Both Si templates and substrates were ultrasonically cleaned in acetone for 5 min and then blown dry with nitrogen. The P(VDF-TrFE) gel was spin-coated on the substrates followed by a heat treatment on a hotplate at 137 °C for 3 min. Transfer of the micro/nanostructures from templates to P(VDF-TrFE) was carried out under the pressure of 5.8 MPa at 137 °C for 20 min.

To transfer the 2-D imprinted structures to the tube wall of the 3-D microtubes, strained bilayers were first deposited onto the imprinted polymer and subsequently rolled up into a tubular structure with a textured tube wall by etching the underlying sacrificial layer. As presented in Fig. 3(a), 2 nm of Cr and 18 nm of Au were grown on the imprinted P(VDF-TrFE) film via Ebeam evaporation in a high vacuum of 7.0×10^{-4} Pa. After rinsing the as-deposited sample in acetone, the metallic bilayer rolled up into a microtube with the tube wall replicating the imprinted structures.

Next, all the rolled up tubes were rinsed in an aqueous etchant and dried in a critical point drier (CPD) to avoid collapse caused by surface tension. A scanning electron microscope (SEM) and optical microscope (OM) were used to visualize the tubular structures and the micro/nanostructured tube-walls.

III. RESULTS AND DISCUSSION

Figure 2 exhibits the morphology of the nanopillared microtube, where the inset shows the magnified tube-wall to clearly show the highly ordered pillars. ALD was adopted here to conformally deposit a thin layer of HfO_2 onto the ordered AAO template and replicate the AAO nanostructures with complete fidelity prior to the deposition of strained metallic layers via Ebeam evaporation. To get periodic structures on the tube-walls, an AAO template fabricated by a two-step anodization was employed. Analogous to other pretreatments used to eventually achieve a perfectly ordered pore array, like atomic force microscope nanoindetation[19] and focused ion beam lithography,[20–22] the second anodization in the two-step anodization process can guide the nanochannels to grow along the ordered indentation left on the Al foil after the first long-time anodization. Two-step anodization is also highly efficient and widely used in recent relevant works.[23,24] However, some HfO_2 pillars with ultrathin walls were damaged, possibly during the subsequent etching process or drying process, as can be seen in Fig. 2 and the inset. To reduce such defects, a smaller nanopillar length might be preferred. Therefore, a 5 min second anodization, which is sufficient to confine the length of the nanochannels in the template (i.e., nanopillars on microtube) to hundreds of nanometers, was selected to avoid pillar damage. The

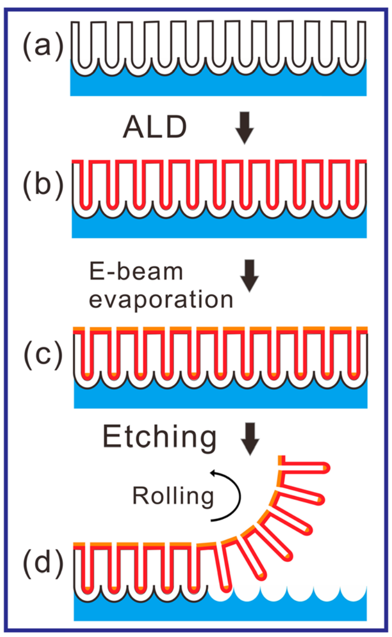

FIG. 1. (Color online) Fabrication flow of the nanostructured microtube: HfO_2 was deposited onto the alumina template with highly ordered pores (a) by the ALD technique (b). 10 nm of Ti and 10 nm of Cr were evaporated via Ebeam evaporation (c). After rinsing in KOH solution for several minutes, the stacked layers are released from the substrate to roll into a tubular structure (d).

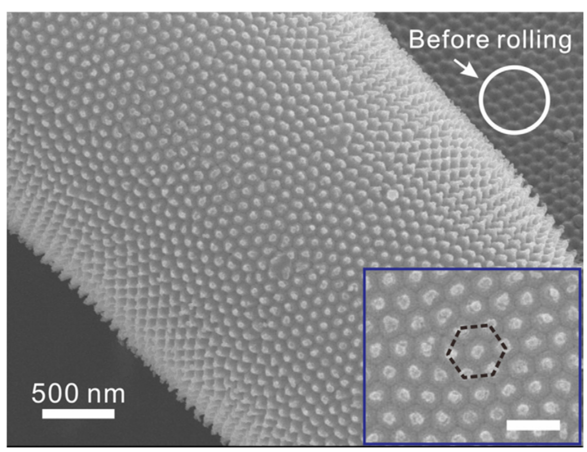

FIG. 2. (Color online) SEM images: The image clearly shows the nanopillar array on the outer surface of the microtube. The inset magnified the microtube wall to present the nanopillar array. The scale bar in the inset is 200 nm.

HfO_2 layer grown via ALD and the strained metallic layers deposited by Ebeam evaporation precisely replicated the porous structure in the AAO template, as can be seen in the unrolled part of the film in the upright corner (white circle part) in Fig. 2. This is also the morphology of stacked layers on the AAO template before the rolling process. On the other hand, it is well known that the nanopores and nanochannels on an ordered AAO template made by two-step anodization are hexagonally distributed;[13] therefore, from the hexagonal dashed curve in the inset it can be inferred that the ordered hexagonally distributed pillars on the outer surface of the rolled up microtube are induced by the exact replication of nanochannels on the AAO templates after conformal deposition in the ALD process. In this case, the parameters of the structures, i.e., the aspect ratio of the pillars on the tube-wall, depend on the parameters of the anodic templates, which can be simply adjusted through pre- and post-treatments as well as changing anodization conditions. In addition, the ultrathin HfO_2 layer and metallic strained layers only diminished the pore diameters without changing the interpore distance of the original porous alumina template.

For the rolling process, the tube diameter can be adjusted by adjusting film thickness as well as deposition parameters that can affect the internal stress of films such as deposition rate, vacuum, and temperature.[7,12] As long as the diameter can be determined conventional lithography can be employed to control the rolling path and direction and, therefore, both the diameter and rotations of rolled up tubes can be optimized in this technique in order to find applications in different realms. Such novel structures with high-dielectric pillars on the outer surface might have applications in rolled-up supercapacitors,[10] micro/nanofluidic systems, optical devices,[7] as well as micro/nanoenvironmental remediation.

Since there are some limitations in the modification of tubes with microstructures by electrochemical anodization, nanoimprint was adopted to fabricate templates with microscale structures. Figure 3 displays optical images of structured metal microtubes rolling from imprinted P(VDF-TrFE) as both the template and sacrificial layer. Imprinted structures with a wide range of scale can be realized depending on the size of hierarchic structures on the silicon templates. In addition, the imprinting conditions could be easily changed to tune the imprinted depth[16] and subsequently alter the aspect ratio of micro/nanostructures transferred from silicon templates to the polymer. Therefore, depending upon the imprinted structures as well as the aspect ratio of the structures on the templates, the deposited metallic films in the following Ebeam evaporation process will form a different morphology on the backside (i.e., the outer surface of microtubes rolled upward). The low aspect ratio structures can be easily covered by evaporated atoms with good conformity. In contrast, the evaporated atoms will grow along the walls of micro/nanochannels or pillars but will not connect to the atoms at the bottom or top due to the high aspect ratio. For the high aspect ratio channels, evaporated atoms will diffuse along the channel walls[14] and cause disordered spikes around the holes on the outer surface after rolling up, as displayed in Fig. 3(c). Moreover, the parameters during

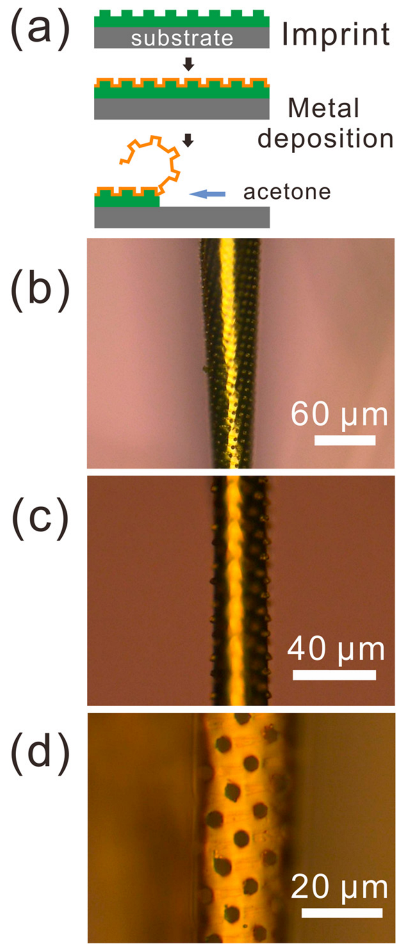

FIG. 3. (Color online) (a) Fabrication process: After the pattern is transferred from the imprint template, 20 nm of Au was deposited and then rolled into a microtube using acetone to selectively remove the polymer. Microtubes with different periodic structures are shown in (b)–(d).

deposition process will also affect the entrance of atoms into channels and thus alter the outer surface. Figure 3(d) illustrates a smooth porous tube-wall with a period of approximately 15 μm, which rolled up from a high aspect ratio pillared template after the same deposition process.

To clearly observe the structures on tube-walls, SEM was carried out as exhibited in Fig. 4. Figure 4(a) is an image of structured metallic bilayers after deposition onto an imprinted polymer with a dot array with a low aspect ratio. Figure 4(b) shows the microtubes rolling from patterned membranes, though an incomplete rolling process will wrinkle the membrane[25] and give rise to the hollow channel below, as shown in Fig. 4(c). Figure 4(d) presents an SEM image of another microtube rolling from the same pillared polymer as the one in Fig. 3(d), which was captured by an optical microscope. It is obvious that the combination of nanoimprint and rolled up nanotechnology can readily modify microtubes with versatile microstructures.

IV. SUMMARY AND CONCLUSIONS

In summary, we have successfully demonstrated two novel techniques to incorporate periodic structures from the nano to the microscale onto microtubes by rolling up

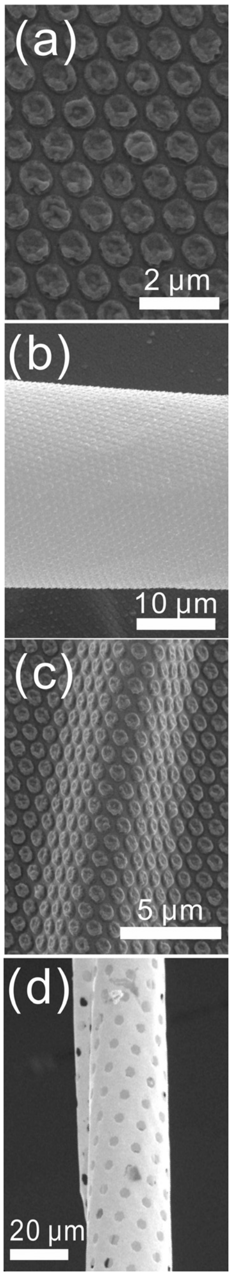

FIG. 4. SEM images of the imprinted polymer covered with strained layers (a), a rolled-up microtube with a dot array (b), a wrinkling surface (c), resulting from an incomplete rolling process, and a rolled up tube with a pore array (d) on the tube-wall.

structured and prestressed membranes deposited on porous alumina and a nanoimprinted polymer, respectively. The parameters and textures of patterned templates, initially controlled by the anodization and imprint conditions, determine the morphology of the outer surface of the rolled up microtubes. It is worth noting that the novel techniques developed here of combing the top–down and the roll-up can assemble various periodic structures ranging from the nano to the microscale onto microtubes. These well-defined hybrid microtubular structures are still under investigation to find their unique optical, mechanical, electrical, and biological properties, which will propel them into a broad realm of applications such as energy storage systems, supercapacitors, metamaterials, micro/nano/optical fluidic devices, and labs-on-a-chip.

ACKNOWLEDGMENTS

This work was financially supported by the Chinese National Key Basic Research Program (NKBRP) (2011CBA00600), the National Science Foundation of China (61171010), and the 985 Micro/Nanoelectronics Science and Technology Innovation Platform at Fudan University.

[1]A. Sinitskii and J. M. Tour, J. Am. Chem. Soc. **132**, 14730 (2010).
[2]J. Bai, X. Zhong, S. Jiang, Y. Huang, and X. Duan, Nat. Nanotechnol **5**, 190 (2010).
[3]E. Gavartin, R. Braive, I. Sagnes, O. Arcizet, A. Beveratos, T. J. Kippenberg, and I. Robert-Philip, Phys. Rev. Lett. **106**, 203902 (2011).
[4]J. N. Coleman *et al.*, Science **331**, 568 (2011).
[5]T. Jia, M. Baba, M. Suzuki, R. A. Ganeev, H. Kuroda, J. Qiu, X. Wang, R. Li, and Z. Xu, Opt. Express **16**, 1874 (2008).
[6]H. Y. Hsueh, Y. C. Huang, R. M. Ho, C. H. Lai, T. Makida, and H. Hasegawa, Adv. Mater. **23**, 3041 (2011).
[7]Y. F. Mei *et al.*, Adv. Mater. **20**, 4085 (2008).
[8]V. A. Bolaños Quiñones, G. Huang, J. D. Plumhof, S. Kiravittaya, A. Rastelli, Y. Mei, and O. G. Schmidt, Opt. Lett. **34**, 2345 (2009).
[9]A. A. Solovev, Y. Mei, E. Bermúdez Ureña, G. Huang, and O. G. Schmidt, Small **5**, 1688 (2009).
[10]H. Ji, Y. Mei, and O. G. Schmidt, Chem. Commun. **46**, 3881 (2010).
[11]G. Huang, Y. Mei, D. J. Thurmer, E. Coric, and O. G. Schmidt, Lab Chip **9**, 263 (2009).
[12]G. Huang and Y. Mei, Adv. Mater. **24**, 2517 (2012).
[13]G. S. Huang, X. L. Wu, Y. F. Mei, X. F. Shao, and G. G. Siu, J. Appl. Phys. **93**, 582 (2003).
[14]Z. Liu, G. Huang, M. Li, J. Li, Y. Chen, Y. Mei, R. Liu, Microelectron. Eng. **97**, 147 (2012).
[15]J. R. Fang, Z. K. Shen, S. Yang, Q. Lu, J. Li, Y. F. Chen, and R. Liu, Microelectron. Eng. **88**, 2033 (2011).
[16]Z. Shen, Z. Chen, Q. Lu, Z. Qiu, A. Jiang, X. Qu, Y. Chen, and R. Liu, J. Vac. Sci. Technol. B **28**, C6M28 (2010).
[17]Z. Shen, Z. Chen, Q. Lu, Z. Qiu, A. Jiang, X. Qu, Y. Chen, and R. Liu, Nanosc. Res. Lett. **6**, 474 (2011).
[18]Z. Shen, G. Chen, Z. Chen, X. Qu, Y. Chen, and R. Liu, Langmuir **27**, 5167 (2011).
[19]S. Shingubara, Y. Murakami, K. Morimoto, and T. Takahagi, Surf. Sci. **317**, 532 (2003).
[20]C. Y. Liu, A. Datta, and Y. L. Wang, Appl. Phys. Lett. **78**, 120 (2001).
[21]N. W. Liu, A. Datta, C. Y. Liu, and Y. L. Wang, Appl. Phys. Lett. **82**, 1281 (2003).
[22]C. Y. Liu, A. Datta, N. W. Liu, C. Y. Peng, and Y. L. Wang, Appl. Phys. Lett. **84**, 2509 (2004).
[23]G. Huang, T. Qiu, X. Wu, P. K. Chu, and H. Nalwa, Encyclopedia Nanosc. Nanotechnol. **11**, 171 (2011).
[24]A. Santos, V. S. Balderrama, M. Alba, P. Formentín, J. Ferré-Borrull, J. Pallarès, and L. F. Marsal, Adv. Mater. **24**, 1050 (2012).
[25]Y. Mei, S. Kiravittaya, S. Harazim, and O. G. Schmidt, Mater. Sci. Eng. R **70**, 209 (2010).