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Short communication

Template-directed formation of functional complex metal-oxide nanostructures by combination of sol–gel processing and spin coating

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Abstract

We report the template-based formation of functional complex metal-oxide nanostructures by a combination of sol–gel processing and spin coating. This method employs the spin-coating of a sol–gel solution into an anodic aluminum oxide membrane (SSAM). Various metal-oxide nanowires and nanotubes with a high aspect-ratio were prepared. The aspect-ratios of the PbO_2 nanowires and $Pb(Zr_{0.52}Ti_{0.48})O_3$ nanowires were about 300 and 400, respectively, and their diameters were about 50 nm. The fabricated $PbTiO_3$ nanotubes have a relatively constant wall thickness of about 20 nm with an outer diameter of about 60 nm. The deposition time for all of the fabricated metal-oxide nanowires and nanotubes is less than 120 s, which is far shorter than those required in both the sol–gel dipping and sol–gel electrophoretic methods. These results indicate that the SSAM method can be a versatile pathway to prepare functional complex metal-oxide nanowires and nanotubes with a high aspect-ratio. The possible formation process for the one-dimensional nanostructures by SSAM is discussed.

Keywords: Complex metal-oxide nanowires and nanotubes; Spin-coating technique; Sol–gel method; Anodic aluminum oxide membrane

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1. Introduction

In recent years, increasing efforts have been made to synthesize functional complex metal-oxide nanostructures, because of their expected peculiar physical properties, such as their finite size effects or unusual phase transitions, and because of their wide range of potential applications in nanoscale piezoelectric actuators, force and acceleration sensors, ultrasonic transducers, and nonvolatile memory devices [1,2]. Nanowires and nanotubes composed of complex oxides, such as $PbTiO_3$ (PT), $BaTiO_3$, and $Pb(Zr,Ti)O_3$ (PZT), have been fabricated using the hydrothermal reaction [3], sol–gel electrophoretic deposition [4], polymer wetting [5], solution phase decomposition [6], and sol–gel dipping methods [7,8]. Among these methods, the sol–gel based synthesis is considered to be one of the most powerful approaches for preparing complex oxide nanostructures, because well aligned monodisperse complex oxide nanowires and nanotubes can easily be synthesized using these methods [4,7–9]. This is accomplished by filling sols into the nanopores of various templates/membranes such as polycarbonate template/membranes or anodic aluminum oxide (AAO) templates/membranes.

However, there are some limitations to these techniques when it comes to achieving a high aspect-ratio with a small diameter, which is desirable for nanoscale applications in electronics [10]. In the case of the sol–gel dipping method, capillary action drawing the sol into the nanopores of the templates/membranes is the only driving force leading to the formation of the nanowires and nanotubes and, thus, it is very difficult to achieve a high aspect-ratio. PZT nanowires with a diameter of 45 nm were recently prepared within an AAO template by the sol–gel dipping method, but their length was only about 6 μm [8]. In the case of sol–gel electrophoretic deposition, Limmer et al. reported that they successfully synthesized PZT with a diameter of 70 nm, but they noted that the synthesis of PZT nanorods below 70 nm in diameter is very difficult due to the size effect [4]. They also noted that the diffusion of the sols might be very slow in the pores of the polycarbonate membrane, even with an applied electric field. Therefore, it is necessary to seek a more versatile method for the fabrication of functional complex metal-oxide

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nanowires and nanotubes with a high aspect-ratio, good crystallinity, and stoichiometric composition. Fabricating complex oxide nanowires and nanotubes with smaller diameters, particularly down to 10 nm, is desirable in order to better understand the fundamental issues surrounding physical phenomena on the nanoscale, such as finite size effects [2].

In this work, we report a versatile method of fabricating various complex metal-oxide nanowires and nanotubes. Functional metal-oxide PbO_2 (PO) nanowires, PT nanotubes, and PZT nanowires were successfully fabricated via the spin-coating of a sol–gel solution on an anodic aluminum oxide membrane (SSAM)[1].

2. Results and discussion

AAO templates/membranes with various pore diameters (20–100 nm) were prepared by adjusting the electrolyte, anodization time and temperature, applied voltage, and pore widening treatment [12]. A quality AAO template with a desirable pore diameter was obtained using 0.3 M oxalic acid as an electrolyte at 40 V for the anodization process, which corresponds to the optimum condition given by Masuda et al. [11]. The surface view scanning electron microscopy (SEM) image of the AAO membrane (Fig. 1(a)) shows an array of highly ordered, hexagonally distributed pores within domains with a size of one to two microns, where each domain is separated from the neighboring domains with the different orientation of the pore lattice. The cross-sectional view SEM image of the AAO membrane (Fig. 1(b)) shows straight and parallel nanopores.

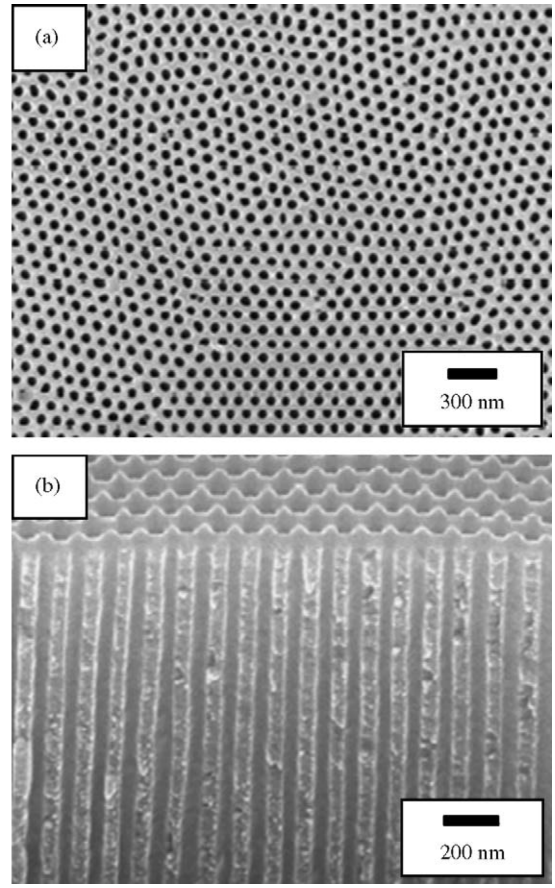

Fig. 1. SEM images of a typical AAO membrane fabricated by the two-step anodization method and subsequent removal of Al metal by applying a saturated $HgCl_2$ solution: (a) the surface view; (b) the cross-sectional view.

It was found that the AAO membranes are advantageous for synthesizing high aspect-ratio nanowires as compared to AAO templates. Fig. 2(a) shows the field-emission SEM image of the PO nanorods, which were fabricated by using the spin-coating of a sol–gel solution into an AAO template, rather than an AAO membrane. Only a few standing PO nanorods were observed on the PO film, which was deposited on one side of the AAO template during the spin-coating process. The diameters of the PO nanorods range from 40 to 60 nm, and their lengths are of the order of several hundreds of nanometers. A high magnification field-emission SEM image of the PO film reveals many small hills, identified by the white circles in Fig. 2(b). This indicates that most of the PO sol penetrates less than a few tens of nanometers into the template pores. This may be because the air inside the pores of the AAO template hinders the penetration of the PO sol [13]. In order to let the air out of the pores, we substituted the AAO template with an AAO membrane, and then the number of resultant PO nanowires, not PO nanorods, was drastically increased, as shown in Fig. 2(c). The large white one on the left side in Fig. 2(c) is the PO film, which was formed during the spin-coating process. The free-standing PO nanowires were collected on a silicon substrate for detailed SEM analysis, as shown in Fig. 2(d). The inset of Fig. 2(d) shows the higher magnification images of two different diameter nanowires. This demonstrates that the PO nanowire with a diameter of about 80 nm (on the left-hand side) appears to be a step-like feature (identified by the white arrow) consisting of two PO nanowires, that is, overlapped PO nanowires, while the other with a diameter of 60 nm (on the right-hand side) features the smooth surface morphology of an individual PO nanowire. This kind of difference in diameter is closely related to the incomplete etching of the AAO membrane between the PO nanowires. This problem was resolved by using a longer etching time. It should be noted that the PO nanowires are about 20 μm in length, and their aspect-ratios are about 300. This higher aspect-ratio demonstrates that the impeding of the penetration of the PO sol solution into the nanopores was resolved by substituting the AAO template with the AAO membrane. The increase in the number of PO nanowires with a high aspect-ratio suggests that using AAO membranes during the spin-coating process is more effective to fabricate high aspect-ratio PO nanowires.

Fig. 3 shows the transmission electron microscopy (TEM) images of the PO nanowires annealed at 650 °C. The diameters

[1] Experimental procedure: porous AAO membranes with a pore diameter of ∼60 nm are synthesized in-house using a well-known two-step anodization procedure described previously [11]. Pb oxide and Pb titanate nanostructures are synthesized in AAO pores using a spin-coating deposition technique. Briefly, an AAO membrane is placed on a lab-made Teflon support, which is placed on a spin coater chuck. The PbO_2, $PbTiO_3$, and $Pb(Zr,Ti)O_3$ sol–gel precursor solutions are dropped on the AAO membrane using a micro pipette and then spin-coated. In order to obtain free-standing nanowires, the aluminum oxide in the AAO membrane is selectively etched in 6 wt.% phosphoric acid solution.