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Template synthesis and characterization of $PbTiO_3$ nanowire arrays from aqueous solution

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Abstract

Highly ordered $PbTiO_3$ nanowire arrays were first reported by fabricating within the pores of anodic aluminum oxide (AAO) template in the aqueous solution by liquid-phase deposition method. The structure and morphology of $PbTiO_3$ nanowire arrays were characterized by SEM and TEM, respectively. The XRD result shows that desired stoichiometric composition could be easily obtained preparing the treatment solution during post-annealing in order to crystallize the nanowires. TEM analyses confirmed that the obtained nanowires composed of large crystals than others made by sol–gel methods. Finally, a possible growth mechanism of the $PbTiO_3$ nanowires is discussed.

Keywords: Nanostructure materials; Nanofabrication; Chemical synthesis

1. Introduction

During the past few years, inorganic nanotubes and nanowires have attracted much more interest because of their unusual, different properties compared to the bulk counterparts resulting from the larger surface area, and because of their many potential applications in the electric devices, sensors, and others [1–6]. Up to now, many nanostructures (nanowires and nanotubes) made of various oxide materials such as TiO_2, SiO_2, In_2O_3, and other oxide materials have been synthesized [7–12].

Among the numerous oxide materials, broad range of properties of ferroelectric oxide, such as spontaneous polarization, high dielectric permittivity as well as piezo- and pyroelectricity, make ferroelectric nanostructures extremely interesting material class for research, as well as for applications in nanoscale piezoelectric transducers and actuators, ultrasonic devices, and nonvolatile memory devices [13–15]. More and more efforts have been made to synthesize and understand ferroelectric nanostructures. Among the many methods that have been used to prepare one-dimensional ferroelectric nanomaterials, due to the superiority of convenience in experimental equipments and particularly the capability to facilitate the fabrication of complex materials, the sol–gel template method is one of the most common techniques used. Hernandez et al. [12] have fabricated $BaTiO_3$ and $PbTiO_3$ (PTO) nanotubes within 200 nm alumina templates. PZT nanotubes and nanowires have been obtained within silicon and alumina templates by using pore wetting and sol–gel templating, respectively [16,17]. However, in these processes, the templates are usually dipped into the sols directly with the only driving force of capillary action. If a higher-concentration sol is used, filling of the pores will be difficult, especially for small pore diameter templates. Conversely, because of the lower concentration, sol causes in nanomaterials serious shrinkage and cracking during annealing [18]. Although in recent years, Limmer et al. [18] have developed the sol–gel electrophoresis deposition method to synthesise PZT nanowires, the process is more complex than the sol–gel process and requires special equipments. Furthermore, precursors and solvents used to prepare the sol are usually unstable in the ambient air and

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harmful to human body in the experimental procedure. Therefore, a simpler and safer technique becomes desirable for preparation of one-dimensional ferroelectric nanomaterials.

Recently, a novel wet process called liquid-phase deposition (LPD) has been developed for the preparation of metal oxide thin film from aqueous solution [19,20]. It is a very simple process and does not require special equipments. Moreover, it can be applied to deposit thin film on the various substrates with complex morphology. Subsequently, some results have been reported to fabricate periodic nanostructures by LPD method. But all of them are limited to simple oxide materials, such as titania, tin oxide, and iron hydroxide [21–24]. To our knowledge, no one-dimensional nanostructure made of complex oxide ferroelectric materials, such as lead titanate, using LPD method has been reported. In this paper, by combining the concepts of LPD method and template preparation of nanomaterials, we propose a novel general route for fabricating highly ordered and highly crystalline PTO nanowire arrays.

2. Experimental section

PTO nanowires were prepared with an aqueous solution made by mixing 0.025 M ammonium hexafluorotitanate, $(NH_4)_2TiF_6$, 0.025 M lead nitrate, $Pb(NO_3)_2$, and 0.075 M boric acid, H_3BO_3 in the concentration ratio of 1:1:3. Commercially available anodic alumina membranes (Whatman, pore diameter 200 nm) were used as template. Prior to template deposition, one side of the membrane was deposited with OTS-SAMs (octadecyltetrachlorosilane self-assembled monolayer) by contact printing. These SAMs can prevent the deposition of PTO precursor films to the top surface of the membrane. As a result, the PTO thin films can only be deposited along the pore walls but not on the top surfaces of the membrane. These modified anodic aluminum oxide (AAO) templates were put into a vessel vertically with an appropriate amount of the treatment solution. At the end of reaction, the AAO template was taken out and washed by DI water several times, dried with clean nitrogen.

For observing detailed images and the mechanism of transformation of PTO, nanostructures formed in these reactions, the templates were attached to silicon wafer with the SAM-covered side up using quick-dry epoxy. After setting, the sample was placed in the 6 M NaOH solution for 30 min to remove the AAO template. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a TG-DTA instrument (Setsys Evolution 16/18, Setaram, France), under an air flow with a heating rate of 5 °C/min from room temperature to 1000 °C. The structure and the morphology of the PTO nanowires were investigated using an X-ray diffractometer (Rigaku D/MAX 2500 V), a scanning electron microscope (Philip XL-40 FEG), and a transmission electron microscope (Hitachi HF-2000).

3. Results and discussion

In LPD process, metal oxide or hydroxide thin films are formed by means of a hydrolysis equilibrium reaction of a metal–fluoro complex ion and an F^- consuming reaction. In this treatment solution for deposition, a hydrolysis reaction of $[TiF_6]^{2-}$ ion in aqueous solution is presumed (Eq. (1)). Lead(II) ions, Pb^{2+}, in the treatment solution are coordinated by $[TiF_6]^{2-}$ ions to give species $Pb[TiF_6]$ (Eq. (2)). Following F^- release, reaction (Eq. (3)) proceeds leading to PTO precursor film formation:

$$[TiF_6]^{2-} + nH_2O \leftrightarrow [TiF_{6-n}(OH)_n]^{2-} + nHF, \quad (1)$$

$$Pb^{2+} + [TiF_6]^{2-} \rightarrow Pb[TiF_6], \quad (2)$$

$$Pb[TiF_6] + nH_2O \leftrightarrow Pb[TiF_{6-n}(OH)_n] + nHF. \quad (3)$$

However, according to the literature [24], equilibrium reaction (1) could be shifted to the right-hand side by addition of boric acid or alumina oxide, which can react with the F^- ions to form a stable complex. In order to obtain the fixed outer diameter of the nanowires, the role of boric acid was important in our experiment. Not only it can shift the equilibrium reaction (3) to right-hand side but can efficiently slow down the etching rate of the AAO template to maintain the pore size in this process.

The thermolytic behavior of PTO precursor nanowires obtained by LPD method is shown in Fig. 1. The TG curve can be roughly divided into three stages. The first major weight loss of about 8.7% from room temperature to 350 °C, which can be attributed to the evaporation of physically adsorbed water and other chemicals. The second stage weight loss between 380 and 580 °C (about 4.6%) is due to the thermal decomposition of the intermediate complex containing NH_4^+ and F^- in the PTO precursor powders [25]. The final stage is from 600 to 730 °C, where the weight loss is about 1.5%. This can be assigned to the dehydration of the Ti complex. Exothermal peak at 750 °C in DTA curve was observed without weight loss and this can be attributed to the phase change from PTO precursor to crystalline PTO.

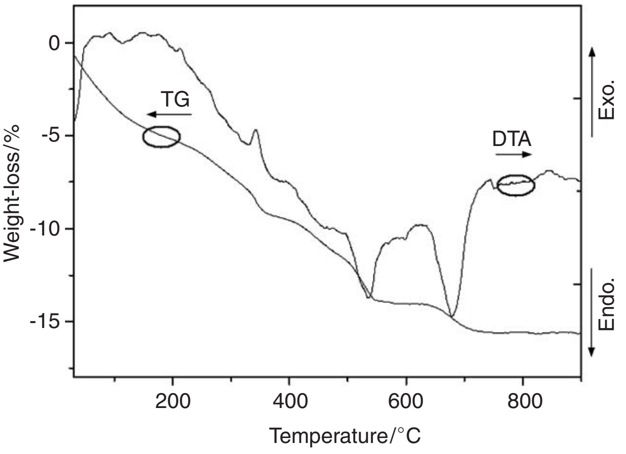

Fig. 1. TG-DTA curve of $PbTiO_3$ precursor nanowires obtained by LPD method.

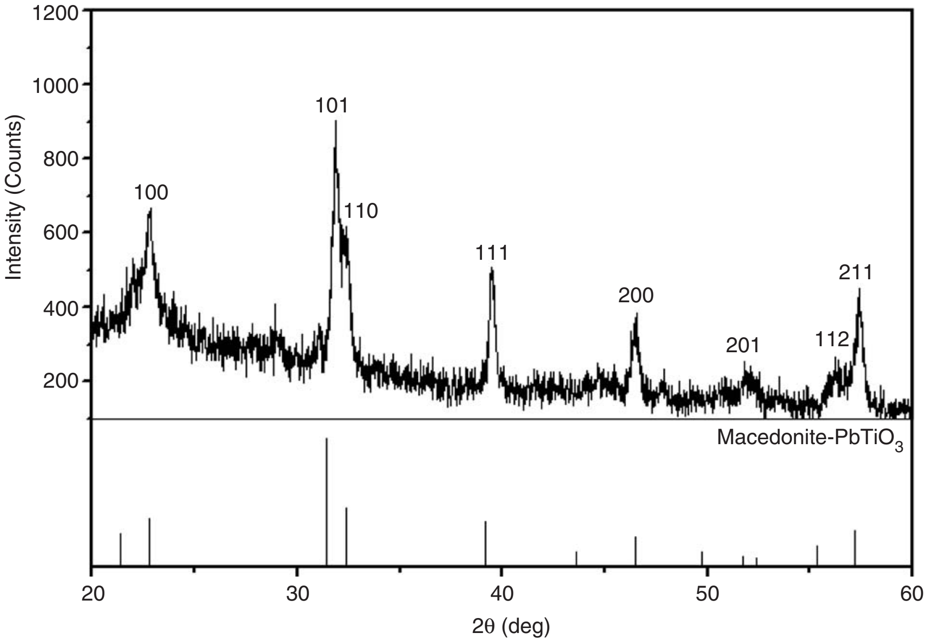

Fig. 2. X-ray diffraction pattern of the $PbTiO_3$ nanowire arrays as annealed at 750 °C.

Crystallographic characterization was performed with X-ray diffraction (XRD) in the grazing incidence mode. Fig. 2 shows the XRD spectrum of the PTO nanowires. After annealing at 750 °C, PTO nanowires consist of only crystalline perovskite phase, and no other secondary phase can be detected. The literatures report that a certain extent of Pb loss would happen as a result its high vapor pressure during the annealing process. That is why an excess amount of lead (5–10 mol%) is always used in the fabrication of the sol in order to compensate the lead loss in the thermal treatment process [12,16]. However, an interesting phenomenon could be observed in this spectrum. In this process, although the starting molar ratio of Pb/Ti in the reacting solution was 1:1, no diffraction peaks corresponding to titania or pyrochole phase could be detected after deposition and annealing at 750 °C for 2 h. This could confirm that nearly no Pb element was lost during the annealing process. This result is in agreement with the earlier experimental observation for $SrTiO_3$ thin film prepared by Gao and other workers [26]. The mechanism could be proposed that the as-prepared PTO precursor solid films deposited on the AAO template should be a compound with stable Pb–Ti–O bonds, rather than a mixture of precipitated Pb- and Ti-containing species. Because the precursor is more stable, these as-prepared precursor solid films can reduce the evaporating amount of lead when they transformed to the crystalline PTO by annealing at 750 °C for 2 h. So, the as-deposited PTO precursor solid was then decomposed into crystalline PTO by annealing could be proposed as

$$Pb[TiF_{6-n}(OH)_n] \leftrightarrow PbTiO_3 + (n-3)H_2O + (6-n)HF \tag{4}$$

Fig. 3a illustrates the top view image of the PTO nanowire arrays grown within an AAO template with 200-nm diameter pores. It can be found that almost all the pores in AAO templates are filled with PTO nanowires. And the pore size does not change a lot even during long-time deposition. This micrograph shows that the nanowires are approximately parallel to each other, vertically oriented on the AAO template to form an array, and the outer diameter of these nanowires is slightly smaller than the pore size of the channels in the AAO template. This could be explained by the shrinkage due to densification and the removal of water and impurities from the as-prepared thin film during annealing. Fig. 3b is a side view image of PTO nanowires, which shows the nanowires bundle together after removing the AAO template by chemical etching. Although it seems that many nanotubes can be seen in this side view, from some fractured nanowires at the left bottom part in this side view, it can be seen obviously that all of them grow through the membrane from one side to the other. Fig. 3c shows the microanalysis by energy dispersive spectroscopy (EDS) for the PTO nanowires after annealing and removing the template by hot NaOH solution. It confirms the presence of Pb and Ti for the nanowires. No peaks attributing to Al and other elements from the reagent and template appeared in this spectrum, thereby confirming that not only the AlOx template but the halogen and other impurities from reactant had been completely removed.

Fig. 4a depicts a transmission electron microscopic (TEM) image of the products, which take the shape of a nanotube obtained by choosing the samples without having enough reaction time to fill the AAO pore completely. It is evident that the boundary of the wall of the nanotubes is quite well defined. The inset of Fig. 4a presents the selected

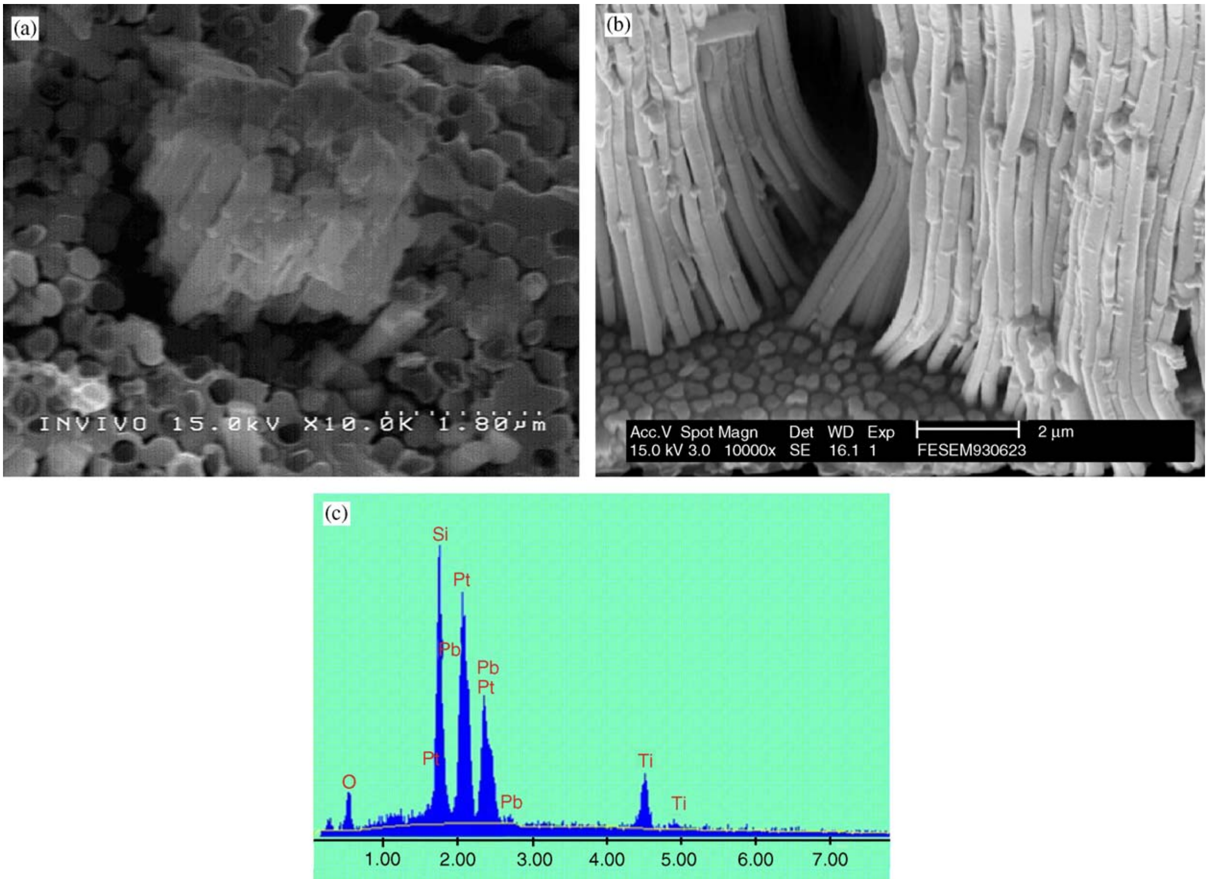

Fig. 3. SEM micrographs of nanowires formed by liquid-phase deposition method using 200-nm alumina template membranes. (a) Top view image of the $PbTiO_3$ nanowire arrays grown within an AAO template. (b) Side view image of $PbTiO_3$ nanowires bundle together after removing the AAO template. (c) Energy dispersive spectroscopy of the bulk nanowire samples after removing the AAO template.

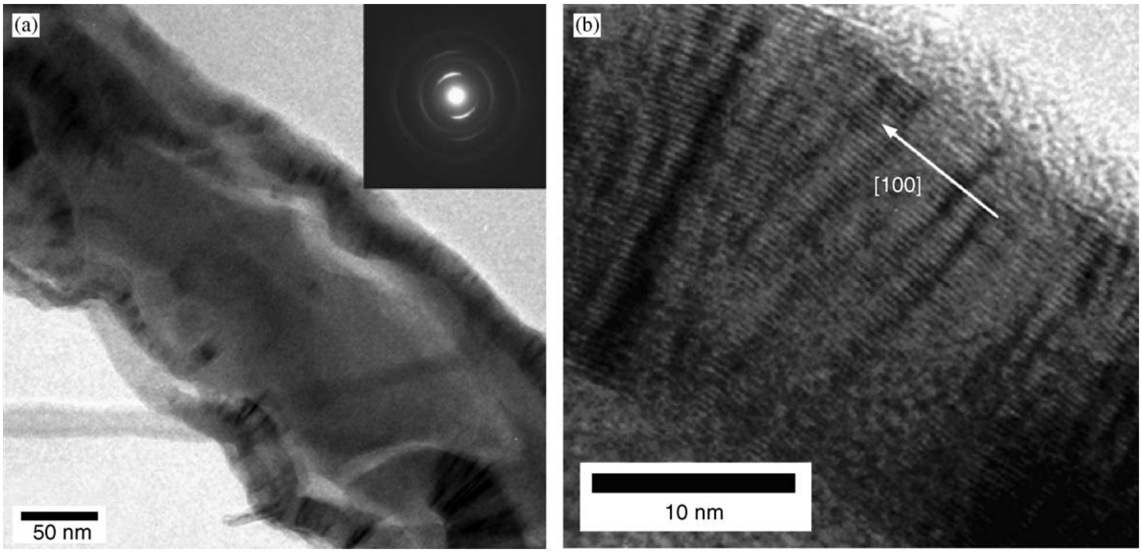

Fig. 4. (a) TEM image of an isolated $PbTiO_3$ nanotube as annealed at 750 °C after dissolving AAO template and the corresponding selected area diffraction pattern of the nanowire (inset). (b) HRTEM lattice image of the nanotube.

area electron diffraction (SAED) pattern taken from this nanotube. The SAED pattern exhibits three bright rings which correspond to the (001)/(100), (110)/(101) and (111) planes of perovskite lead titanate from inside to outside, and the results agree with the XRD pattern. While the presence of the ring pattern evidences the formation of polycrystalline PTO, the strong (100) ring indicates that the crystals do have preferred growth orientation. The

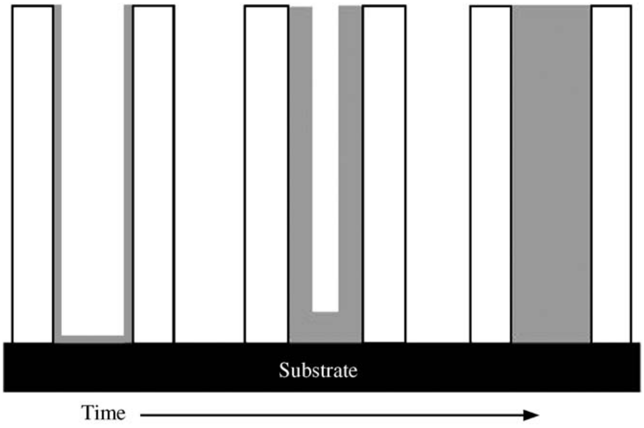

Fig. 5. Schematic illustration of the formation process of $PbTiO_3$ nanowires.

HRTEM image in Fig. 4b can give further insight into the details of the structure. It reveals the wall is made of highly crystalline PTO along the [100] direction. The distance between the parallel fringes is about 0.39 nm, corresponding to the spacing of {100} plane. The fine crystalline of the nanotubes fabricated by our process was identified by this image. Unlike the ferroelectric nanotubes and nanowires prepared by sol–gel method are only composed of small and random nanocrystals with ~3–5 nm diameter [27], the high-quality crystalline PTO nanowires composed of large and preferentially oriented crystals could be easily prepared in our proposed process. Nearly no paper has ever reported so clear HRTEM image before. This image can strongly support this process is a desirable process for fabricating large quantity and high-quality PTO nanowires. A schematic of the possible formation process of PTO nanowires is shown in Fig. 5. In our experiments, the templates were soaked into the reagent solution. Because the viscosity of this regent was lower than that of sol, the aqueous solution was easy to fill the pores of the templates. When the reaction balance was changed by the addition of boric acid, the PTO precursor started to deposit on the wall of AAO templates. Then the thickness of PTO precursor film increased with time. The precursor film extended to the center and completely filled the pores of AAO templates to form the PTO precursor nanowires. These precursor nanowires were then heated to 750 °C to form the crystalline phase.

4. Conclusion

In summary, highly crystalline PTO nanowire arrays were successfully prepared by LPD method. Using this novel technique, large area and near unidirectionally aligned nanowires could be easily prepared from aqueous solution. Transmission electron microscopy and X-ray diffraction demonstrate the PTO nanowire arrays with polycrystalline structure. Desired stoichiometric composition is easily achieved by adjusting the composition of treatment solution, and without the need of regarding the lead loss during the post-annealing at elevated temperature to crystallize the nanowires. By controlling the reaction times, we can obtain aligned lead titanate nanowires or lead titanate nanotubes. Compared with sol–gel electrophoresis and chemical bath deposition technique, the present method shows the advantages of simplicity, high efficiency and low cost. Furthermore, because the reactions occur in aqueous solution, not only the complex process but also toxic solvents are not required, the objectives of reducing the prime cost and waste liquid can be easily procured to protect the ecological environment.

Acknowledgments

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