

Synthesis and piezoresponse of highly ordered $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ nanowire arrays

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We report the synthesis and characterization of ferroelectric lead zirconate titanate $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) nanowires. The PZT nanowires, with diameters of about 45 nm and lengths of about 6 μm , were fabricated by means of a sol-gel method utilizing nanochannel alumina templates. After postannealing at 700 °C, the PZT nanowires exhibit a polycrystalline microstructure, and x-ray diffraction and transmission electron microscopy study revealed their perovskite crystal structure. The piezoelectric characteristics of individual PZT nanowires were demonstrated by piezoresponse force microscopy. © 2004 American Institute of Physics. [DOI: 10.1063/1.1814427]

Recently, increasing efforts have been made to synthesize and understand ferroelectric nanostructures because of the promise they show in the realization of nanoscale piezoelectric transducers and actuators, ultrasonic devices, and nonvolatility memory devices.¹⁻⁵ As ferroelectricity represents a cooperative phenomenon that relies on the interaction of neighboring permanent electric dipoles in a crystal lattice, there is a size limit, known as the superparaelectric limit, below which ferroelectricity vanishes. Therefore, the synthesis of ferroelectric nanostructures of a controllable size and shape is of great interest not only for future applications but also from a fundamental point of view. Urban and co-workers have reported earlier the synthesis of BaTiO_3 and SrTiO_3 nanorods with diameters ranging from 5 to 60 nm by a solution-phase decomposition of bimetallic alkoxide precursors in the presence of coordinating ligands.⁶ Using a sol-gel template method of synthesis, Hernandez *et al.* have fabricated BaTiO_3 and PbTiO_3 nanotubes within 200 nm alumina templates.⁷ Some interesting properties have also been found in ferroelectric nanowires. For example, BaTiO_3 nanowires as small as 10 nm in diameter still retain ferroelectricity, and nonvolatile polarization domains as small as 100 nm² in size can be induced on BaTiO_3 nanowires. This suggests that ferroelectric nanowires may be used to fabricate nonvolatile memory devices with an integration density approaching 1 terabit/cm².⁸

Lead zirconate titanate $\text{Pb}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3$ (PZT) is a ferroelectric material that possesses a perovskite crystal structure, and shows a high potential for applications in device due to its high dielectric constant, high Curie temperature, and high breakdown strength. PZT nanotubes have been obtained within silicon and nanochannel alumina (NCA) templates by using several different deposition techniques, including misted chemical solution deposition and pore wetting.^{3,9} In this letter, we report the synthesis of the PZT nanowires by using a sol-gel template method. We choose NCA as the template because the pore diameters of the NCA template can be well controlled from several hundreds of nanometers to 5 nm. Ferroelectric properties have been dem-

onstrated in individual PZT nanowires by using piezoresponse force microscopy (PFM).

NCA templates were prepared by means of anodization,^{10,11} and the PZT nanowires were synthesized by sol-gel method utilizing the NCA templates. A PZT sol-gel precursor was prepared according to a previous report,¹² whereby lead acetate hydrate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$, and Zirconium-*n*-propoxide $\text{Zr}(\text{O}(\text{CH}_2)_2\text{CH}_3)_4$ were initially dissolved in 2-methoxyethanol $\text{C}_3\text{H}_8\text{O}_2$, and stirred for 30 min at 70 °C. A precursor with 10% excess Pb composition was prepared in order to compensate the lead loss in the thermal treatment process. After the solution was cooled down to room temperature, the required quantity of tetrabutyl titanate $\text{Ti}(\text{OC}_4\text{H}_9)_4$ was added to the solution. The concentration of the final solution was adjusted to 0.3 M and the pH value to 2–4 by adding 2-methoxyethanol and acetic acid. The NCA templates were immersed into the precursor solution for 5 h. In order to obtain the perovskite phase, the templates containing the precursor were subsequently heated in air at 700 °C for 30 min by using a thermal annealing furnace. The structure and morphology of the PZT nanowires were

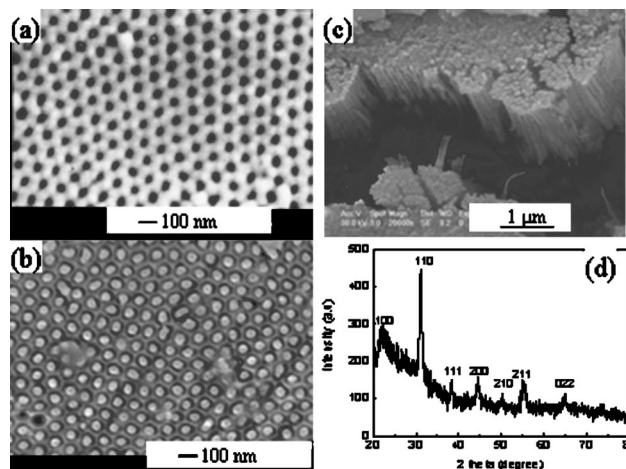


FIG. 1. SEM images of the NCA template and PZT nanowires: (a) nanochannel alumina templates, (b) top view of the nanochannel porous alumina filled with PZT nanowires, and (c) oblique view of the PZT nanowire arrays. (d) XRD pattern of the PZT nanowire arrays.

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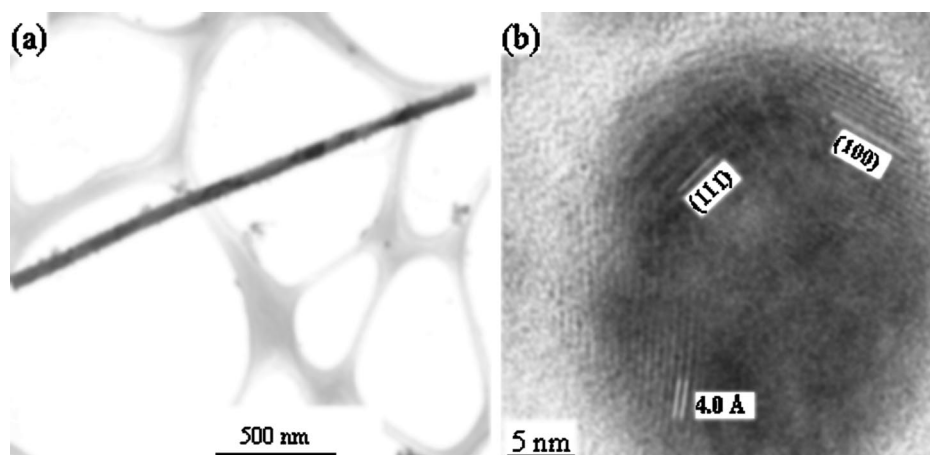


FIG. 2. (a) TEM image of an isolated PZT nanowire after completely dissolving the NCA template, and (b) HRTEM image of the cross-sectional view of a PZT nanowire.

investigated using x-ray diffraction (XRD, D/Max 2250V), a scanning electron microscope (SEM, JEOL JSM-6300), and a high-resolution transmission electron microscope (HRTEM, JEOL-2010). A Raman scattering spectrometer (Spex 1403) with a 514.5 nm incident wavelength and a 200 mW of output power was also brought out for structural characterization. The piezoelectric properties of the PZT nanowires were characterized by a piezoresponse force microscope (nanoscope IV, Digital Instruments) equipped with a conductive tip and a lock-in amplifier (SR830, Stanford Research Systems).

Figures 1(a) and 1(b) show the SEM images of the empty NCA templates and those filled with PZT nanowires. The diameters of the pores and the thickness of the NCA template are about 45 nm and 10 μm , respectively, and it can be seen that almost all of the pores are filled with PZT nanowires. Figure 1(c) is the corresponding SEM image of the free-standing PZT nanowires after etching away the alumina using a 4 M NaOH solution. The PZT nanowires are of uniform diameters and equal height. The XRD spectrum of the PZT nanowires after dissolving away the surface alumina is shown in Fig. 1(d). The reflection peaks are clearly distinguishable, and can be perfectly indexed as perovskite PZT structures.

Figure 2(a) shows the TEM image of a single PZT nanowire after the alumina has been completely dissolved away. The perovskite structure was further confirmed using a cross-sectional high-resolution electron microscopy (HRTEM) image of a single PZT nanowire, as shown in Fig. 2(b), where the well-recognized lattice spacing of 0.40 and 0.23 nm correspond to the $\{100\}$ and $\{111\}$ atomic planes, respectively. Figure 2(b) reveals the polycrystalline structure nature of the PZT nanowires and it shows the presence of multiple domains. Raman spectroscopy was also implemented to further elucidate the ferroelectric phase of PZT nanowires. Figure 3 shows the Raman scattering spectrum of PZT nanowire arrays measured at room temperature. The Raman shift peaks of the PZT nanowires located at around 205, 275, 330, 591, and 740 cm^{-1} match well with the typical Raman peaks of perovskite PZT.^{13,14} The prominently intense, low-frequency modes at 205 and 275 cm^{-1} correspond to one of the $E(2TO)$ modes and to the E_T+B_1 modes, respectively. The peak at 330 cm^{-1} corresponds to the $A_1(2TO)$ mode. The peaks at 591 and 740 cm^{-1} correspond to the $A_1(2TO)$ and $A_1(3LO)$ modes, respectively.

To measure the piezoelectric property of the PZT nanowires, the two surfaces of the PZT-filled NCA templates were

mechanically polished to remove the remaining PZT from the surface until the PZT nanowires emerged. Pt films with a thickness of 100 nm were then coated on one side of the samples as the bottom electrode. An individual PZT nanowire was identified by the AFM imaging and its piezoresponse was measured using the PFM,^{15,16} to which a 16.5 kHz ac electric field plus a biased voltage was applied. Figures 4(a) and 4(b) show the butterfly loop of the piezoresponse amplitude and phase, respectively, as a function of applied dc bias voltage. It can be clearly seen that the PZT nanowires exhibit a significant piezoelectric response, illustrating their ferroelectric behavior. The phase change when the applied voltage changes from +4 to -4 V is about 165°, which is smaller than 180°. This may be due to the difficulty of carrying out polarization switching in a very high aspect ratio nanowire structure. It is interesting to notice that there is a positive shift in the coercive field in the amplitude and phase loops. This shift may be caused by the surface charges at the electrode and PZT interface^{17,18} or the space charges stored in the alumina template walls.¹⁹ It is also worthy noting that even though the amplitude of the piezoresponse is not calibrated, our experiment comparing the piezoresponse of the PZT nanowire with that of the PZT films (the results are not shown here) revealed that the piezoresponse for the PZT nanowire is more significant. For the PZT films, their piezoresponse is usually restricted by clamping effect.²⁰ However, the interfacial strength of the PZT/alumina tem-

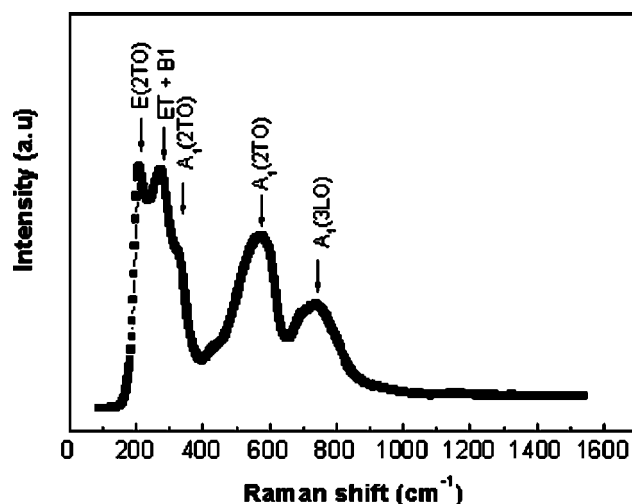


FIG. 3. Raman spectrum of the PZT nanowires.

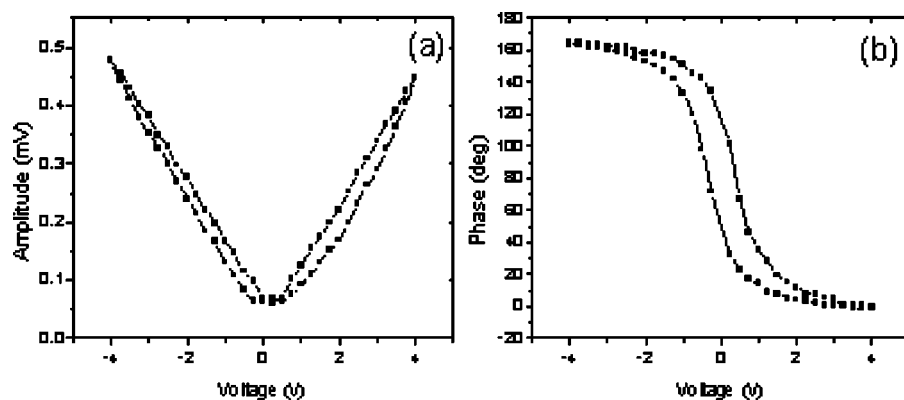


FIG. 4. (a) The piezoresponse amplitude butterfly loop, and (b) the phase loop of a single PZT nanowire piezoresponse.

plate and thus the clamping effect is not clear, and needs to be studied further. A study investigating the influence of the size and shape of the PZT nanowires, such as diameter, and aspect ratio, on the ferroelectric properties of the PZT nanowires is highly desirable.

In summary, highly ordered PZT nanowires have been fabricated using sol-gel synthesis within hexagonal, closely packed, nanochannel alumina (NCA) templates. These highly ordered ferroelectric one-dimensional PZT arrays exhibit a significant piezoresponse and show promise for potential applications.

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