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Yirong Lin, Yingtao Liu, and Henry A. Sodano

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Hydrothermal synthesis of vertically aligned lead zirconate titanate nanowire arrays

Yirong Lin, Yingtao Liu, and Henry A. Sodano

School of Mechanical, Aerospace, Chemical and Materials Engineering, Arizona State University, ECG Building Room 346, Mail Stop 6106, Tempe, Arizona 85287-6106, USA

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A hydrothermal method is employed for the growth of single crystal vertically aligned lead zirconate titanate (PZT) nanowire arrays. The resulting PZT nanowires were grown from a TiO2 film and are shown to be single crystal with growth in the [110] axis. PZT has a coupling coefficient up to two orders of magnitude higher than ZnO, which should provide many opportunities for the creation of active nanodevices and systems. © 2009 American Institute of Physics.

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Piezoelectric materials offer excellent sensing and actuation properties which has led to their wide ranging application in biomechanical devices, sensors, and actuators. With the miniaturization of sensors and systems, these materials have also attracted considerable attention in the field of nanotechnology. When piezoceramics are confined to the nanoscale in one-dimensional, many unique properties can be capitalized upon for energy harvesting,\textsuperscript{1,2} piezoelectric field-effect transistors,\textsuperscript{3,4} piezoelectric-gated diodes,\textsuperscript{5} and nanosensors.\textsuperscript{6-11} In many of these applications it is desirable to grow the one-dimensional piezoelectric nanostructures from a substrate such that their growth is aligned perpendicular to it. This configuration allows for facile interfacing of the nanowires with the electrodes required to apply or remove electrical energy from the piezoelectric material. Almost all studies to date have used vertically aligned ZnO nanowires for this application; however, ZnO exhibits extremely low electromechanical coupling seriously limiting the viability of the resulting devices.\textsuperscript{1,2,3,5} In this letter, we report the growth of vertically aligned lead zirconate titanate (PZT) (PZT or PbZr\textsubscript{0.52}Ti\textsubscript{0.48}O\textsubscript{3}) nanowires, which have a coupling coefficient up to two orders of magnitude higher than ZnO.\textsuperscript{1,4,5} The significantly higher coupling of these piezoelectric arrays will potentially lead to innovative and viable applications for piezoelectric nanostructured arrays.

Many growth techniques have been investigated to create one-dimensional nanostructured ferroelectrics such that their unique properties can be capitalized upon. These techniques include chemical vapor deposition,\textsuperscript{16-18} template methods,\textsuperscript{19,20} and hydrothermal growth.\textsuperscript{21-24} While these techniques have lead to the growth of vertically aligned nanostructures, only template methods have been reported to grow ferroelectrics with high electromechanical coupling coefficients. However, the template method has several limitations, most notably the low yield and polycrystalline nature of the resulting nanostructure. It was shown by Xu et al.\textsuperscript{21} that poly(vinyl alcohol) (PVA) and poly(acrylic acid) (PAA) can restrict the directional growth of ferroelectric materials resulting in freestanding nanowires grown in solution. The PVA and PAA adsorbed on the PZT crystal reducing the surface energy along certain axes, which led to the formation of one-dimensional structures. In this letter, we report the synthesis of vertically aligned single-crystal perovskite PZT nanowires by a hydrothermal process utilizing polymer surfactants. The process uses an oxidized titanium substrate for growth and yields well aligned nanowires.

The PZT nanowire array was grown from a layer of titanium oxide formed on the surface of a titanium foil (0.127 mm, 99.7% metals basis, Aldrich) by a thermal treatment at 600 °C in air for 5 min. The hydrothermal solution used for growth was prepared by dissolving tetrabutyl titanate [(C\textsubscript{4}H\textsubscript{9}O\textsubscript{5})\textsubscript{4}Ti] in ethanol to form a 0.1M solution and zirconium oxychloride (ZrOCl\textsubscript{2}·8H\textsubscript{2}O) was dissolved in deionized (DI) water to form 0.08M solution.\textsuperscript{22} The Ti\textsuperscript{4+} ethanol solution was then added into the Zr\textsuperscript{4+} aqueous solution in the molar ratio of 48:52 (Ti/Zr) under vigorous stirring. The mixed solution was introduced into a 0.15M ammonia solution, which resulted in the coprecipitation of Zr\textsubscript{0.52}Ti\textsubscript{0.48}O\textsubscript{3} (ZTOH). The ZTOH was filtered and lead nitrate [Pb(NO\textsubscript{3})\textsubscript{2}], potassium hydroxide (KOH), PVA, and PAA were all added to form the final hydrothermal solution with a 50 mL total volume. The concentrations of Pb(NO\textsubscript{3})\textsubscript{2}, ZTOH, and KOH were 0.1, 0.1, and 2M, respectively. The PVA and PAA concentration was 0.4 and 7.2 g/L. The TiO2 substrate and the hydrothermal solution were placed into a stainless steel autoclave with a Teflon liner, which was then placed in a vacuum oven (Fisher scientific, model 282A) at 175 °C for 12 h. After cooling the autoclave to room temperature the substrate was removed and rinsed with DI water and dried in air at 60 °C overnight.

The perovskite phase of the nanowires was verified through x-ray diffraction (XRD) performed on a PANalytical X’Pert Pro material research x-ray diffractometer with Cu K\textalpha radiation. XRD patterns of the vertically aligned PZT nanowires grown on the titanium substrate are shown in Fig. 1. All the peaks indicate the tetragonal perovskite phase of the PZT nanowires and match the diffraction data for Pb(Zr\textsubscript{0.52}Ti\textsubscript{0.48})O\textsubscript{3} (Ref. 25) well. The strong (101) peak indicates the perovskite structure of the nanowires and the sharp peaks demonstrate the aligned PZT nanowires are well crystallized. There are several minor low intensity peaks in the XRD pattern, which indicates certain impurity components in the tested sample. The impurity may be caused by the titanium substrate and the titanium oxide thin layer on the surface of the substrate.

\textsuperscript{4}Author to whom correspondence should be addressed. Tel.: 001-480-965-4317. Electronic mail: henry.sodano@asu.edu.
To study the morphology of the aligned PZT nanowires, scanning electron microscopy (SEM) images (Hitachi S-4700 FE-SEM) and high resolution transmission electron microscopy (HRTEM) analysis has been performed. The SEM images are presented in Fig. 2 and show the geometry and uniformity of the well aligned PZT nanowires. The morphology of the nanowires can be seen to exhibit a nonuniform diameter, which increases along the length. We attribute this structure to the fusing of several wires as the growth progress proceeds. The fused nanowires can be seen in Fig. 2(c) with a nonuniform diameter, while the nanowires which have not fused exhibit a uniform diameter, as shown in Fig. 2(d). It can also be seen in Fig. 2(d) that the nanowires have an octagonal cross and high aspect ratio.

High resolution transmission electron images were taken on a JEOL JEM 4000EX with acceleration voltage of 400 kV to investigate the crystallinity of the PZT nanowires. Figure 3 shows a HRTEM image of the PZT nanowire and indicates the uniformity of the crystal structure along the length of the nanowire. The electron diffraction pattern [Fig. 3(a), inset] obtained from the nanowire of Fig. 3(a) confirms the wires are single crystal. Figure 3(b) shows the HRTEM image of the nanowire crystal lattice. The lattice spacing was measured to be 2.7 Å corresponding to the [110] planes of the tetragonal perovskite structure of PZT. The nanowire dimensions vary based on the growth orientation; however the nanowire length is roughly 7 – 8 µm long. The dimensions of the nanowires can be controlled by varying the growth time or the ratio of the PVA and PAA as demonstrated by Xu et al. 21

The growth process of the aligned PZT nanowires can be divided into two steps: first the titanium oxide substrate reacts with the lead ions and $\text{Zr}_x\text{Ti}_{1-x}\text{O}_2\cdot n\text{H}_2\text{O}$ (ZTO, $x=0.52$) present in the solution to form $\text{Pb}\left(\text{Zr}_{0.52}\text{Ti}_{0.48}\right)\text{O}_3$ nucleation sites. It has been shown that the nucleation size can be used to control the crystal size. 26 Under low temperature conditions (120 °C), the nucleation rate was slow allowing the individual nuclei to grow very large, while at higher temperature (150 °C), the nucleation reaction was rapid leading to the formation of many small nuclei and smaller crystals during hydrothermal growth. This process is also seen in the crystallization of thin ferroelectric films from sol gels where higher temperatures with a slow ramp reduces the grain size.27 This result indicates that it may be possible to control the density and diameter of the aligned nanowires through control of the nucleation reaction. Because our process was carried out at 175 °C the nucleation reaction should occur rapidly leading to higher nanowire density and better alignment than a lower temperature process. Following nucleation, crystal growth occurs with the PVA and PAA acting as surfactants to restrict the nanowire growth to preferential crystal planes.28 Through analysis of the HRTEM images and XRD results it can be concluded that the nanowire growth occurs in the [110] direction. The tetragonal structure of PZT has the largest lattice spacing in the [001] direction resulting in the largest surface energy along this crystal plane. It has been found that the PVA and PAA preferentially adsorb on the crystal facets forming a polymer film minimizing the surface energy.21 The increased surface energy of the [001] plane may be responsible for the highly directional growth rate. 29 It has been demonstrated that the ratio of these surfactant polymers can be varied to control the geometry of the nanowires. 22

In conclusion, this letter has demonstrated the growth of single-crystal tetragonal perovskite vertically aligned PZT nanowires on TiO$_2$ using a hydrothermal method and polymer surfactants. The nanowires where shown to grow in the [110] direction from a nucleation site. The nanowires initially grew in random directional orientation however as the length increased only those perpendicular to the substrate were free to continue growth resulting in vertical alignment.
It was found that the nanowires would easily fuse with neighboring wires during growth resulting in a larger diameter at the tip of the nanowire. The results demonstrate the growth of single crystal vertically aligned ferroelectric nanowires with high electromechanical coupling. Because the strain coupling coefficient of PZT is up to two orders of magnitude higher than ZnO the results presented here should provide many opportunities for the creation of active nanodevices and systems.

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