Synthesis of ordered arrays of multiferroic $NiFe_2O_4$-$Pb(Zr_{0.52}Ti_{0.48})O_3$ core-shell nanowires

Ming Liu, Xin Li, Hassan Imrane, and Yajie Chen
Center for Microwave Magnetic Materials and Integrated Circuits (CM3IC), Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115

Trevor Goodrich, Zhuhua Cai, and Katherine S. Ziemer
Department of Chemical Engineering, Northeastern University, Boston, Massachusetts 02115

Jian Y. Huang
Center for Integrated Nanotechnology (CINT), Sandia National Laboratories, Albuquerque, New Mexico 87185

Nian X. Sun[a)]
Center for Microwave Magnetic Materials and Integrated Circuits (CM3IC), Department of Electrical and Computer Engineering, Northeastern University, Boston, Massachusetts 02115

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A synthesis method was developed for producing core-shell nanowire arrays, which involved a combination of a modified sol-gel process, electrochemical deposition, and subsequent oxidization in anodized nanoporous alumina membranes. This method was applied to generate ordered arrays of one dimensional multiferroic $NiFe_2O_4$ core and $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) shell nanostructures. Extensive microstructural, magnetic, and ferroelectric characterizations confirmed that the regular arrays of core-shell multiferroic nanostructures were composed of a spinel $NiFe_2O_4$ core and perovskite PZT shell. This synthesis method can be readily extended to prepare different core-shell nanowire arrays and is expected to pave the way for one dimensional core-shell nanowire arrays.
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One dimensional materials, such as nanotubes and nanowires, have attracted great attention because they exhibit different physical properties from their bulk and thin film counterparts due to their high aspect ratio. A less expensive, fast, and productive method for preparing different types of one dimensional nanostructure materials is electrochemical deposition[1–4] based on porous anodic aluminum oxide (AAO) templates, such as $CoFe_2O_4$ nanowire arrays and Cu-CoNi composite nanotubes which were fabricated by electroplating.[3,4] Sol-gel processing has also recently evolved as a powerful approach for synthesizing one dimensional nanostructures of ceramic materials based on AAO templates.[5–7] For example, $BaTiO_3$ and $PbTiO_3$ ceramic nanotubes were synthesized by wetting ordered nanoporous AAO templates with a sol-gel precursor solution.[7]

Multiferroic materials have drawn an increasing amount of interest due to their capability of efficient energy transfer between electric energy and magnetic energy and their potential applications in many multifunctional devices.[8–13] Several synthesis methods have been developed for multiferroic composite materials in the bulk form, such as eutectic unidirectional solidification,[14] ceramic sintering,[15] glue bonded laminates,[16–20] tape casting,[21] and hot molding;[22] and in the film form, such as pulsed laser deposition,[11,23,24] physical vapor deposition,[25] and sol-gel process.[5–7] However, the preparation of one dimensional composite multiferroic nanostructures with both magnetic and ferroelectric phases, for example, magnetic core and ferroelectric shell nanowires, remains an open challenge. This work demonstrates a synthesis method for core-shell nanowire arrays with a $NiFe_2O_4$ core and $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) shell using a modified sol-gel process and electrochemical deposition technique.

The synthesis of $NiFe_2O_4$-PZT core-shell nanowire arrays consists of three steps, which are (1) PZT nanotube fabrication in AAO templates by a sol-gel process, (2) filling of the PZT nanotubes with $Ni_{33}Fe_{67}$ alloys to form core-shell structure by electroplating, and (3) annealing in air (oxidization) to obtain $NiFe_2O_4$ core–PZT shell nanowire arrays. The process flow is schematically shown in Fig. 1. Considering lead loss in the annealing processes, 0.3*M* PZT precursor with 10% excess Pb composition was prepared by dissolving lead (II) acetate trihydrate $[Pb(CH_3CO_2)_2 \cdot 3H_2O]$, zirconium (IV) propoxide $[Zr(OCH_2CH_2CH_3)_4]$, and titanium (IV) butoxide $[Ti(OC_4H_9)_4]$ with a molar ratio of 1.1:0.52:0.48 into 2-methoxyethanol. An AAO template with pore diameter of ~200 nm was masked on one side and immersed into the PZT precursor solution for 10 min to ensure a full wetting of

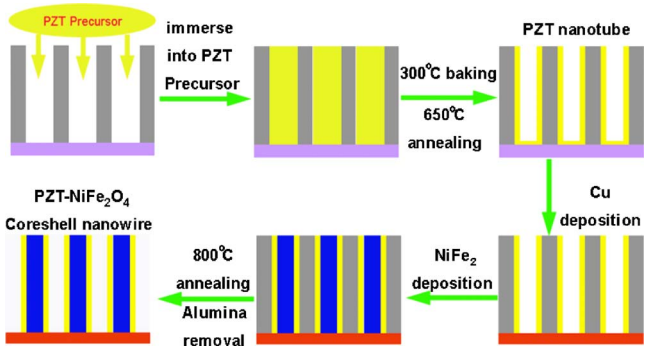

FIG. 1. (Color online) Schematic of the process flow for fabricating the ferrite core–PZT shell nanowire arrays.

[a)]Electronic mail: nian@ece.neu.edu

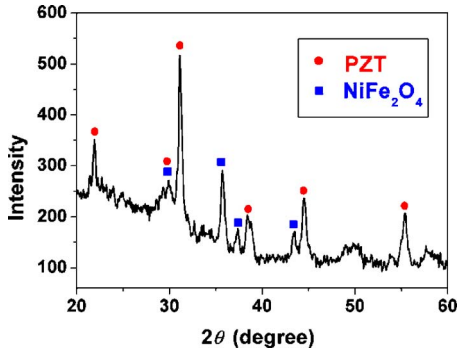

FIG. 2. (Color online) X-ray diffraction pattern of PZT-$NiFe_2O_4$ core-shell nanowire arrays in AAO template.

the inner walls of the nanopores. Then, the wet template was baked in air at 300 °C for solvent removal. A PZT precursor layer was coated onto the inner walls of the nanopores in the AAO template to minimize the surface energy of the system. The template was subsequently annealed in air at 650 °C for 30 min to obtain the PZT nanotubes.

A copper layer was sputtered onto the template containing PZT nanotubes to act as the working electrode for the electrodeposition process of $Ni_{33}Fe_{67}$ alloy nanowires. Aqueous solutions of iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and nickel (II) sulfamate $[Ni(SO_3NH_2)_2]$ were used as electrolyte. Electroplating $Ni_{33}Fe_{67}$ alloy into PZT nanotube was carried out under a galvanostatic condition with a constant current of 15 mA. This filled template was then annealed in air at 800 °C for 24 h to achieve the $NiFe_2O_4$-PZT core-shell nanowire arrays. A NaOH solution can be used to dissolve the AAO template and release the core-shell nanowire arrays.

X-ray diffraction pattern of the core-shell nanowire arrays in the amorphous AAO template is shown in Fig. 2. Polycrystalline perovskite PZT phase and the spinel $NiFe_2O_4$ phase (Ni ferrite) are clearly identified, which do not show obvious preferential crystallographic orientations. PZT nanotubes were released from the AAO template by dissolving the AAO template into NaOH solution, and their scanning electron microscopy (SEM) image is shown in Fig. 3(a). These PZT nanotubes show open ends with a thin shell thickness. In addition, from the stable constant-current electrochemical deposition process of $Ni_{33}Fe_{67}$ alloy nanowires in the PZT nanotubes, we can deduce that the PZT nanotubes are hollow with a nearly constant cross-section area throughout their entire length. Fig. 3(b) shows the image of $NiFe_2O_4$-PZT core-shell nanowire arrays with a length of $\sim 30\ \mu m$, indicating straight nanowires with a high aspect ratio.

Transmission electron microscope (TEM) images of the cross section of $NiFe_2O_4$-PZT core-shell nanowires in alumina template are shown in Fig. 4(a). Clearly, the AAO template was completely filled with nanowires which were evenly distributed in an amorphous alumina matrix with a mean outer diameter of ~200 nm. Distinct phase boundaries can be observed between $NiFe_2O_4$ core and PZT shell, as well as PZT shell and alumina template. Each of the nanowires consists of a core with an average diameter of ~140 nm and a circular shell with a mean thickness of ~30 nm. Interestingly, most of the core parts of the nanowires consist of an equal area of white region and black region, which are separated by a distinct boundary. This is believed to be the Lorentz image of two magnetic domains with a 180° Bloch domain wall, which are formed in the ferrite core when the nanowires are thinned to be in the disk shape for TEM observations. In addition, the separated phases of spinel $NiFe_2O_4$ ferrite and perovskite PZT were identified and twin boundary in the ferrite phase was observed by high-resolution transmission electron microscopy (HRTEM) image as shown in Fig. 4(b).

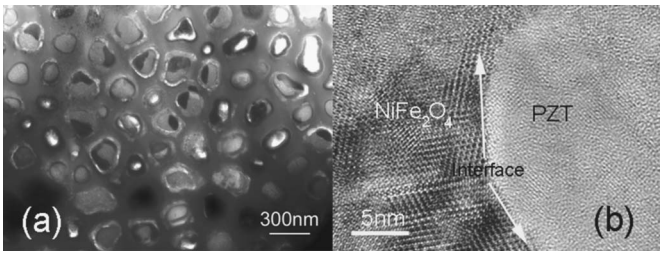

FIG. 4. (a) Cross-section TEM image of core-shell PZT-$NiFe_2O_4$ nanowire in AAO template and (b) cross-section HRTEM image of core-shell PZT-$NiFe_2O_4$ interface area.

Anisotropic magnetic hysteresis loops of multiferroic core-shell nanowire were characterized using a vibrating sample magnetometer with the applied magnetic fields perpendicular and parallel to the nanowire length direction as shown in Fig. 5(a). Well-defined magnetic hysteresis loops were observed with a coercivity of 103 Oe along the length direction and 86 Oe perpendicular to the length direction. When the magnetic field is applied perpendicular to the nanowires, the saturation magnetic field corresponds to the nanowire demagnetization field ($2\pi M_s$) for soft ferrites such as $NiFe_2O_4$. Saturation magnetization of the $NiFe_2O_4$ nanowires was thus deduced to be 245 emu/cm^3 (or a $4\pi M_s$ of 3100 G). The ferroelectric hysteresis loops of the core-shell nanowire arrays in AAO templates were measured along the wires' length direction, i.e., perpendicular to the AAO membrane, using a Radiant Precision *LC* test system as shown in Fig. 5(b). The saturated polarization (P_s) is 4 μC/cm^2 at a maximum applied voltage of 100 V, which is much lower than that of bulk PZT. This could be explained by the uncer-

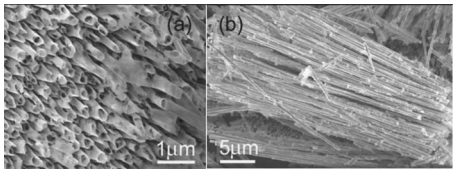

FIG. 3. SEM images of (a) open ends of PZT nanotubes with AAO template removed and (b) core-shell PZT-$NiFe_2O_4$ nanowires released from AAO template.

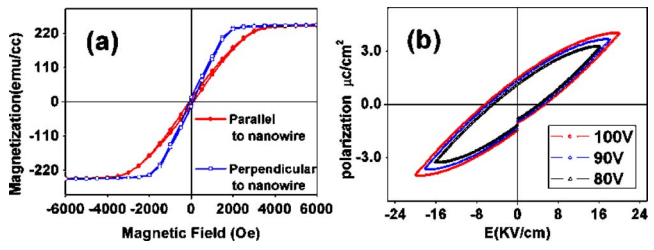

FIG. 5. (Color online) (a) Typical magnetic hysteresis loop for $NiFe_2O_4$-PZT core-shell nanowire arrays; (b) polarization–electric field hysteresis loops of the $NiFe_2O_4$-PZT core-shell nanowire arrays.

tainty involved in accurately evaluating the surface area of the PZT shells in the core-shell nanocomposites and unsaturated polarization process due to the limited maximum voltage of *P-E* hysteresis tester.

It is notable that this synthesis method for the core-shell nanowire arrays in AAO templates by using a combination of nanotube formation and nanotube filling is very versatile due to the following reasons. First, this method can be used to synthesize one dimensional core-shell nanostructure arrays with different core-shell materials, so long as these materials can be obtained by wet chemical processing. For example, ferrite shell–PZT core nanowire arrays can be synthesized using similar process steps as what we used for the PZT shell–ferrite core nanowire arrays. That is, sol-gel precursor ferrites can be used to wet the AAO templates to form the ferrite nanotubes (shell), which will be filled with PZT core by soaking the ferrite nanotubes in a PZT sol-gel precursor solution for a long enough time. Second, the dimension of the nanowire can be readily tuned. Outer diameters of the nanowires are equal to the nanopores diameter of the AAO templates, which can be adjusted with AAO templates with different nanopore dimensions. AAO templates are available with a large range of pore diameters ranging from 10 to 1000 nm. Once the outer diameter of the nanowires is determined, the thickness of the PZT shell, and therefore the ferrite core diameter, can be tuned by the concentration of PZT precursor solution as well as by the time when the AAO templates are immersed in the PZT precursor solution. The length of the core-shell nanowires can be controlled by the electrodeposition process easily.

In summary, one dimensional ordered multiferroic $NiFe_2O_4$-PZT core-shell nanowire arrays have been synthesized by a modified sol-gel process and electrochemical deposition technique. This synthesis method for one dimensional core-shell nanostructure arrays is very versatile and expected to pave the way for one dimensional core-shell nanowire arrays.

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