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Magnetoelectric coupling of multilayered Pb(Zr0.52Ti0.48)O3-CoFe2O4 film by piezoresponse force microscopy under magnetic field

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Multiferroic Pb(Zr0.52Ti0.48)O3-CoFe2O4-Pb(Zr0.52Ti0.48)O3 (PCP) laminated film has been synthesized by sol-gel process and spin coating, with the spinel structure of CoFe2O4 and perovskite structure of Pb(Zr0.52Ti0.48)O3 verified by x-ray diffraction. The good multiferroic properties of PCP film have been confirmed by ferroelectric and magnetic hysteresis loops, with leakage current substantially reduced. The local magnetoelectric coupling has been verified using piezoresponse force microscopy under external magnetic field, showing magnetically induced evolution of piezoresponse and ferroelectric switching characteristics, with piezoresponse amplitude reduced and coercive voltage increased. Such technique will be useful in characterizing local magnetoelectric (ME) couplings for a wide range of multiferroic materials. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4757621]

I. INTRODUCTION

Multiferroic materials possess two or more types of orders simultaneously that couple the electric and magnetic fields,1,2 making it promising for a wide range of applications.3–6 It is well known that the magnetoelectric (ME) coupling in single-phase multiferroics is extremely small, and in order to enhance the ME coupling for practical applications, hybrid multiferroic composites consisting of ferroelectric and ferromagnetic phases have been widely explored,7 wherein the magnetoelectric effect is induced through the so-call product property8 via mechanical interactions arising from magnetostrictive and piezoelectric effects in individual phases. Among various multiferroic composites developed, laminated multiferroic materials often exhibit higher ME response owing to the tight interactions between individual layers and the reduction of leakage current. Indeed, ME couplings in a variety of laminated composites have been reported, with ferromagnetic constituents including TbDyFe,9,10 CoFe2O4 (CFO),11,12 NiFe2O4,13 La1.2Sr1.8 Mn2O7,14 and Metglas15 and piezoelectric constituents including BaTiO3,16 lead zirconate titanate (PZT),17–19 and Pb(Mg,Nb)O3-PbTiO3,20 resulting in ME coefficient for example as high as 470 V/cm·Oe in metglas/piezofiber laminate composite.9

In recent years, there are also tremendous progresses made in laminated multiferroic thin films, assisted by improved thin film deposition and advanced theoretical predications.21 However, the local characterization of ME couplings in multiferroic thin films is rather challenging, and majority of the works focused on the macroscopic ME effects in the composites,18,19,22–24 with little attention paid to its microstructural evolution under either electric or magnetic fields.25,26 Such microstructural evolution is important, for example, for multiferroic data storage, which relies on localized instead of macroscopic ME couplings. In order to overcome this shortcoming and enable the characterization of ME couplings at nanoscale, we have recently developed novel scanning probe microscope (SPM) techniques to examine the local ME effects in multiferroic materials, where the evolution of ferroelectric domains and switching characteristics of CFO-PZT core-shell nanofiber induced by an external magnetic field have been observed.27 In this work, we apply such technique to characterize the ME couplings of multilayered multiferroic thin films. In particular, evolution of ferroelectric domains under an applied magnetic field is probed using piezoresponse force microscopy (PFM), and local ferroelectric hysteresis and butterfly loops are observed to be affected by the applied magnetic field as well, confirming the ME coupling in the multiferroic composite thin film at nanoscale.

II. EXPERIMENTAL PROCEDURES

Multiferroic Pb(Zr0.52Ti0.48)O3-CoFe2O4-Pb(Zr0.52Ti0.48)O3 (PCP) laminated film has been synthesized by sol-gel process and spin coating. The preparations of PZT and CFO precursors with concentration of 0.2 M were described in our early work.28 The first layer of PZT was spin coated on Pt/Ti/SiO2/Si(100) substrate at a rate of 500 rpm for 6 s and 4000 rpm for 30 s, followed by a drying process at 180 °C for 5 min and a pyrolysis process at 400 °C for 10 min. These processes were repeated one time for CFO layer and another time for PZT layer, resulting in a multilayered PCP film. The film was then annealed at 750 °C for 10 min under the oxygen atmosphere by a rapid thermal annealing process.

The crystalline structure of the film was examined by x-ray diffraction (XRD, Bruker D8 Focus) with Cu Kα.
radiation ($\lambda = 0.15406$ nm), and its morphology and thickness were examined by scanning electron microscope (SEM, FEI Sirion). The macroscopic ferroelectric hysteresis loops at various applied voltage were measured by ferroelectric test system (Radiant Technologies Precision Workstation) along with its leakage current, and the ferromagnetic hysteresis loop was measured by Lakeshore vibrating sample magnetometer (VSM). For localized characterizations at nanoscale, PFM was carried out using an Asylum Research MFP-3D atomic force microscope (AFM), as described in our earlier paper. To confirm the local ME coupling of PCP thin film at nanoscale, PFM and switching spectroscopy piezoresponse force microscopy (SSPFM) were carried out under an in-plane magnetic field up to 2000 Oe, applied using an Asylum research variable field module (VFM). This allows us to examine the evolution of ferroelectric domains and polarization switching characteristics induced by the external magnetic field. The topography image was used to ensure that PFM images from the same area are compared under different magnetic fields.

### III. RESULTS AND DISCUSSION

The crystalline structure of PCP film was examined by XRD, as shown in Fig. 1, where two sets of diffraction peaks are observed, corresponding to perovskite PZT and spinel CFO phases, respectively, with [110] being the preferential orientation. It is also observed that the crystallinity of PZT is higher than that of CFO, since the PZT concentration is higher, and its crystallization temperature is lower. The SEM morphology of PCP film is shown in Fig. 2, and it is observed that the film surface is relatively smooth with some voids, and the grain size is in the range of 10-30 nm. The multilayered structure is evident in the cross section SEM image in Fig. 2(b), where it is observed that the thickness of PCP film is about 400 nm, consisting of approximately 140 nm PZT at bottom, 130 nm CFO in the middle, and 130 nm PZT on the top.

The ferroelectric hysteresis loops of PCP film at various applied voltage are shown in Fig. 3(a), confirming ferroelectric characteristics of the film. The ferroelectric hysteresis appears to be asymmetric with a horizontal shift toward negative electric field, which indicates the presence of internal field. From the major loop measured under 56 V, the remnant polarization and coercive electric field are estimated to be 28.8 $\mu$C/cm$^2$ and 100.0 kV/cm, respectively. Compared to pure PZT film, the remnant polarization of PCP film is lower, while its coercive field is higher, due to the existence of an intermediate CFO layer. On the other hand, the typical leakage current density of PCP thin film is shown in Fig. 3(b), which is smaller than $7 \times 10^{-9}$ A/cm$^2$ and is substantially lower than $10^{-8}$ A/cm$^2$ that was reported in PZT-CFO bilayered thin film, suggesting better insulating property of PCP film due to one extra PZT layer.
Furthermore, the room temperature ferromagnetism of PCP film is confirmed by magnetic hysteresis loop, as shown in Fig. 3(c). The saturation and remnant magnetization are measured to be 36.1 and 11.2 emu/cm³, respectively, and the corresponding coercive magnetic field is 540 Oe. Both the remnant magnetization and coercive field are less than that of PZT-CFO thin film due to lower CFO concentration.24

An in-plane magnetic field is applied to the PCP thin film using VFM, as schematically shown in Fig. 4(a), and the induced changes in PFM is examined to verify the ME coupling in the multilayered film. The topography images in Figs. 4(b) and 4(d) confirm that the same area is compared under different magnetic fields, and the corresponding lateral PFM amplitude mapping without and with the in-plane magnetic field are shown in Figs. 4(c) and 4(e), representing distribution of in-plane polarization parallel to the applied magnetic field. In the absence of external magnetic field, the average lateral PFM amplitude is 3.80 nm in Fig. 4(c). After the application of external magnetic field of 2000 Oe, substantial decrease of lateral PFM amplitude is observed, with the average amplitude reduced to 939 pm. Such reduction can be understood from negative magnetostrictive coefficient of CFO,33 which leads to a compressive strain along the direction of applied magnetic field in CFO and thus a corresponding compressive stress in PZT layers, which reduces the polarization along the magnetic field direction and thus a reduced lateral PFM amplitude.34–36 This confirms local ME couplings in PCP film induced indirectly through the mechanical interactions between magnetostrictive and piezoelectric effects.

The piezoelectricity and ME coupling of the PCP film is also confirmed by vertical PFM. Dual frequency resonance tracking technique is used for quantitative analysis,37,38 with the intrinsic vertical piezoresponse of the film determined by correcting the quality factor $Q$,39 as shown in Figs. 5(a)–5(h). The resulting vertical PFM phase and amplitude mappings before and after the application of magnetic field confirm the ME coupling in PCP thin film. In the absence of external magnetic field, the average intrinsic vertical PFM amplitude is 55 pm (Fig. 5(a)). After the application of external magnetic field of 2000 Oe, the corresponding vertical amplitude decreases to 29 pm (Fig. 5(e)), due to polarization rotation toward direction perpendicular to the applied magnetic field in-plane, as we discussed earlier, though the reduction is smaller than lateral PFM amplitude.35,40 The changes in PFM phase mappings are also observed (Figs. 5(b) and 5(f)), with some initially disconnected domains connected together, and some small domain disappear, further confirming ferroelectric domain evolution in PCP thin film induced by external magnetic field. The corresponding mappings of quality factor before and after the application of external magnetic field (Figs. 5(c) and 5(g)) indicate that the quality factor is increased by magnetic field, especially in areas where disconnected domains become
connected. Furthermore, upward shift in resonant frequency mapping is observed (Figs. 5(d) and 5(h)), where the average resonant frequency is about 330 kHz in the absence of magnetic field, which is increased to around 336 kHz under 2000 Oe. This can be understood from the fact that magnetic field tend to increase the stiffness of magnetic materials.41

Finally, we study local ferroelectric switching behavior of PCP thin film before and after the application of magnetic field using SSPFM, where ferroelectric hysteresis loops are measured on 5 × 40 grid points. Representative loops at two different locations are shown in Figs. 6(a) and 6(b), where the amplitude-voltage butterfly loop and phase-voltage hysteresis loop are combined together via \( A \cos \phi \), with \( A \) being the PFM amplitude and \( \phi \) being the phase. It is observed that in addition to PFM amplitude reduction as discussed earlier, the coercive field is increased by the applied magnetic field. Such trend is evident in the mappings of coercive voltage before and after the application of magnetic field, as shown in Figs. 6(c) and 6(d), where it is observed that the average coercive voltage is around 12.5 V in the absence of magnetic field, which increases to 13.6 V under 2000 Oe. This again can be understood from vertical compressive stress that makes it harder for ferroelectric polarization to switch, as we discussed earlier.40,42 The strength of local magnetoelectric interaction thus can be estimated from \( \Delta E_c/\Delta H = 13.75 \text{ V/cmOe} \), where \( \Delta E_c \) is the increased coercive field induced by applied magnetic field \( \Delta H \), although it is cautioned that this local measure cannot be compared with macroscopic magnetoelectric coefficient directly.

IV. CONCLUSIONS

In summary, multilayered PCP composite thin film has been synthesized by sol-gel process and spinning coating with smooth surface and good crystallinity. Good multiferroic properties of PCP thin film have been demonstrated, with ferroelectricity of the composite film confirmed by ferroelectric and magnetic hysteresis loops. The evolution of ferroelectric domains under a magnetic field has been observed using novel SPM techniques we developed,
confirming the ME couplings of PCP thin film at nanoscale. The technique will be useful in characterizing local ME couplings for a wide range of multiferroic materials.

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