Magnetoelectric coupling in $CoFe_2O_4/SrRuO_3/Pb(Zr_{0.52}Ti_{0.48})O_3$ heteroepitaxial thin film structure

J. X. Zhang, J. Y. Dai,[a] C. K. Chow, C. L. Sun, V. C. Lo, and H. L. W. Chan
Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, People's Republic of China

(Received 3 October 2007; accepted 11 December 2007; published online 14 January 2008)

Epitaxial magnetoelectric $Pb(Zr_{0.52}Ti_{0.48})O_3/SrRuO_3/CoFe_2O_4$ composite thin films are fabricated on $SrTiO_3$ single crystal substrate by pulsed-laser deposition. x-ray diffraction study reveals their crystalline structure and epitaxial relationship, which is cubic on cubic without in-plane rotation. The good dielectric, ferroelectric, and magnetic properties for the heteroepitaxial films are obtained simultaneously under room temperature, and the magnetoelectric coupling effect is manifested by the magnetic-field-dependent ferroelectric characteristics and spectroscopic dielectric constant. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2830813]

In recent years, magnetoelectric (ME) composite materials, consisting of ferroelectric and magnetic phases, have attracted a great deal of attention owing to their coexistence of simultaneous magnetic and electric ordering and also the conversion between magnetic energy and electric energy. These characteristics make the ME composite material a good candidate in its potential applications in many multifunctional devices such as electromagnetic sensor, nonvolatile memory, and microwave devices.[1] The ME coupling effect can be manifested by the magnetic field induced electric polarization and dielectric constant change due to the mechanical coupling between magnetostrictive and piezoelectric materials. Since the observation of ME coupling in the self-assembled multiferroic $BaTiO_3-CoFe_2O_4$(CFO) nanostructures,[2] there have been several reports concerning thin film ME composites such as the sol-gel prepared $Pb(Zr_{1-x},Ti_x)O_3$ (PZT)-CFO thick films,[3] epitaxial $La_{1-x}Sr_xMnO_3$ (LSMO)-PZT composite thin films,[4] and the PZT–$Co_{1-x}Zn_xFe_2O_4$ multilayer thin films.[5] In particular, ME response can still be detected directly in double layered polycrystalline PZT–CFO composites regardless of the large substrate clamping effect.[6] In the epitaxial LSMO–PZT system, however, although the LSMO can be chosen as the bottom electrode during electric property measurement, it has negligible magnetostrictive coefficient compared to CFO (magnetostrictive coefficient $\lambda_s=-110\times10^{-6}$ at 300 K) in oxide-based magnetostrictive materials. In the reported PZT–CFO system, the ferroelectric property is relatively poor in polycrystalline PZT thin film without preferential orientation. In this letter, we report the magnetic modulated ferroelectric and dielectric properties of the PZT/$SrRuO_3$ (SRO)/CFO heteroepitaxial structure. The ME effect is enhanced in the epitaxial heterostructure system due to its strong anisotropy and the perfect lattice matching between ferromagnetic and piezoelectric phases.

$Pb(Zr_{0.52}Ti_{0.48})O_3$ (500 nm)/$SrRuO_3$(100 nm)/$CoFe_2O_4$(150 nm) trilayers were sequentially deposited on 0.5-mm-thick (100)-oriented $SrTiO_3$ (STO) single crystal substrate by pulsed-laser deposition (PLD) using a KrF exciter laser of 248 nm in wavelength, 5 Hz in repetition rate, and 2.50 J/cm^2 in laser energy density. The oxygen pressures used for depositing different materials in the PZT/SRO/CFO trilayers were 27, 27, and 20 Pa and substrate temperatures were 620, 700, and 800 °C, respectively, for each layer's deposition. The stoichiometric targets of $CoFe_2O_4$, $SrRuO_3$, and $Pb(Zr_{0.52}Ti_{0.48})O_3$ were prepared through a standard solid reaction sintering processing. In the PZT target, over 10% of Pb was added to avoid Pb deficiency due to its volatilization during sintering and depositing.

The structural characterization of the composite thin films was carried out by x-ray diffraction (XRD) pattern using a Bruker D8 discover XRD system equipped with copper radiation. As shown in Fig. 1, only (l00) diffraction peaks for CFO and PZT were observed in the diffraction pattern, following those of the single crystal STO substrate. θ-2θ scan confirms the c-axis orientation of the PZT/SRO/CFO multilayered film without any contribution from a-axis oriented domains and impurity phases. The cubic-on-cubic epitaxial relationship between PZT and CFO layers, and even between CFO layer and STO substrate with fourfold symmetry has been confirmed by XRD Φ scan. The scan data were recorded around the CFO (404), PZT (202), and STO (202) reflections, which show a set of four distinct peaks with 90° of separation. The inserted thin SRO electrode benefits the epitaxial growth of the following PZT film. From the θ-2θ scan XRD pattern, the CFO and PZT peaks shift 0.35° and −0.1° from their respective bulk materials, indicating that the lattice constant of CFO and PZT are highly dependent on

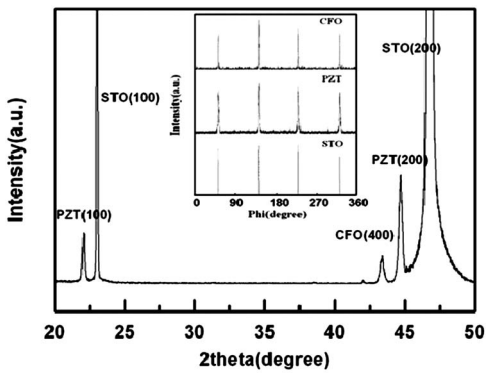

FIG. 1. θ-2θ scan and Φ scan of {101} diffraction of epitaxial PZT/SRO/CFO thin film.

[a]Author to whom correspondence should be addressed. Electronic mail: apdaijy@inet.polyu.edu.hk.

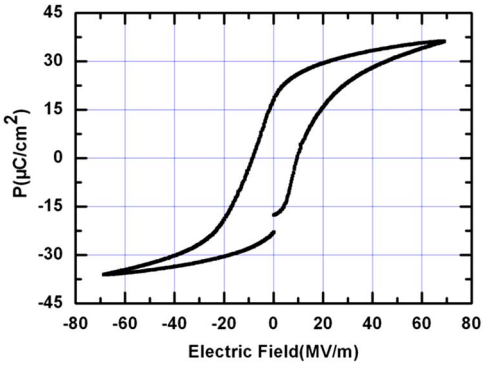

FIG. 2. (Color online) Ferroelectric hysteresis loop of the PZT/SRO/CFO epitaxial composite films at 1000 Hz.

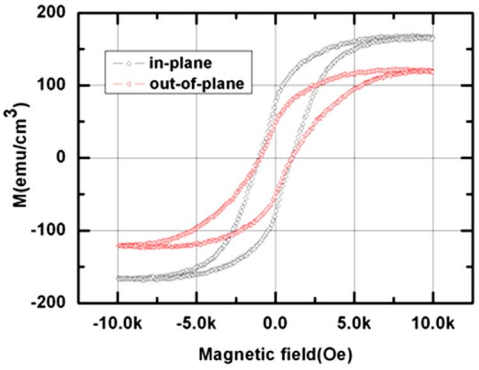

FIG. 3. (Color online) Magnetization hysteresis loops of the PZT/SRO/CFO epitaxial composite thin films under room temperature.

their substrates. The *c*-axis lattice parameters of CFO and PZT thin films were determined to be 0.842 nm (0.839 nm for bulk) and 0.409 nm (0.411 nm for bulk), respectively. This result further suggests that the CFO and PZT films suffer the compressive and tensile strains, respectively. This tensile strains existed in PZT layer originates mainly from the CFO and SRO layer but not the STO (lattice constant a =0.391 nm) substrate. The influence of STO substrate on the PZT film is reduced and the restriction originated from the substrate is relaxed, to some extent, after the growth of CFO thin film and SRO electrode. This suggests that the substrate clamping effect in PZT layer may be reduced with the growth of CFO thin film and SRO buffer layer.

In order to carry out the ferroelectric property measurement, Pt dot electrode with 0.2 mm diameter was deposited on the top surface of PZT thin film by PLD. Spectroscopic dielectric property of the composite film was measured by an impedance analyzer (Agilent 4294A). The dielectric constant measured for the composite film at 1 kHz was around 1270, which is in good agreement with the theoretical value[7] and the experimental value[8] obtained from single epitaxial PZT thin film. The ferroelectric hysteresis loops of the PZT/SRO/CFO trilayered thin film were measured using a ferroelectric tester (TF Analyzer 2000, aixACCT) at 1 kHz. We can measure the dielectric and ferroelectric properties along the thickness direction (ε_{33} and P_3) with a SRO bottom electrode. As shown in Fig. 2. Tested under a field with a maximum strength of 70 MV/m, the sample is found to exhibit a saturated hysteresis loop with a remnant polarization (P_r) of 20 μC/cm^2 and coercive field (E_c) of 9 MV/m. The ferroelectric property is much better than the polycrystalline CFO/PZT double layer film[6] prepared by PLD. This may be attributed to the good epitaxial growth of PZT film. Moreover, PZT films on Pt/Si substrate may carry relatively large amounts of lattice and thermal strain, which may lower the remnant polarization.[9] The coercive field is much lower than that of the single epitaxial PZT film[10] and PZT/LSMO double layered film[4] reported elsewhere, which will lower the power consumption during magnetic induced electric domain rotation and electric field induced magnetic domain rotation.

The magnetic property of the PZT/SRO/CFO trilayer film was characterized by a vibrating sample magnetometer (Lakeshore, Model 7300 series). Field-dependent magnetization at room temperature was measured by applying the magnetic field perpendicular or parallel to the plane of the films with the measurement up to a field of 10 kOe. The typical saturated magnetic hysteresis loops from the in-plane and out-of-plane directions are shown in Fig. 3. The saturation magnetizations of the in-plane and out-of-plane loops are 170 and 120 emu/cm^3, respectively, which are comparable to that of the single $CoFe_2O_4$ epitaxial films.[11] This magnetic anisotropy may be attributed to the residual in-plane compressive strain induced by the lattice mismatch between the CFO film and substrate. The in-plane and out-of-plane measurements show that the coercive fields exhibit almost the same value in the two directions (1 kOe). The coercive field is lower than that of CFO epitaxial film with a thickness of 80 nm,[11] which may indicate that the restriction of domain movement and rotation originated from the compressive strain between CFO and STO is reduced with the increase of CFO film thickness.

The ME effect in the PZT/SRO/CFO trilayered structure was studied by measuring the magnetic-field-dependent polarization and spectroscopic dielectric constant at room temperature. The dc magnetic field with 5 kOe was applied parallel to the film. As shown in Fig. 4(a), with the application

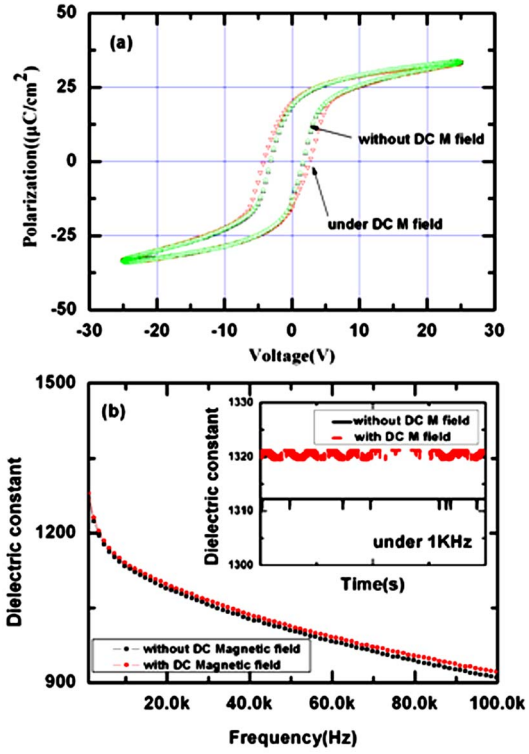

FIG. 4. (Color online) (a) Magnetic field dependence of the ferroelectric hysteresis loops and (b) magnetic field dependence of dielectric constant under room temperature.

of a dc magnetic field, the remnant polarization of the film increases slightly from 18.6 to 19.7 $\mu C/cm^2$. The coercive field of the film increases from 4.8 to 6.6 MV/m after the dc magnetic field has been applied. The magnetic-field-dependent dielectric constant from 1 to 100 kHz is depicted in Fig. 4(b), where the inset shows that the dielectric constant at 1 kHz changes from 1270 to 1279 when the dc magnetic field is applied. The percentage change increases with the raise of frequency from 0.71% at 1 kHz to 3.92% at 100 kHz. A similar phenomenon has also been reported by another group.[12] At higher frequency, the charge polarization, which is strongly dependent on the lattice structure, plays a leading role in PZT unit cell to the dielectric constant; similar change in lattice constant gives rise to larger charge distribution in the unit cell. Therefore, the magnetic field effect on the dielectric constant is expected to be stronger at higher frequency. The remnant polarization and dielectric constant return to the original values when we remove the dc magnetic field. The enhancement of coercive field, remnant polarization, and dielectric constant with the external dc magnetic field can be explained as a result of the strain induced lattice deformation in ferroelectric layer.

In the present PZT/SRO/CFO epitaxial film, the PZT layer suffers the tensile strain due to the residual stress originated from the lattice mismatch and different thermal expansion coefficients between PZT and the SRO/CFO layers. Once a dc magnetic field is applied parallel to the film plane, the magnetostrictive CFO film will contract along 1 or 2 directions due to the large negative magnetostrictive coefficient. The tensile strain suffered by PZT layer will be reduced due to its mechanical coupling with CFO layer. Namely, the external stress on PZT layer will be reduced with the constriction of CFO film along one or two directions. On the other hand, the coercive field increases with the in-plane dc magnetic field. When the in-plane constriction happens in the CFO layer due to the applied magnetic field, an in-plane stress will be applied on the upper PZT layer along the one or two directions. It is easy to understand that the in-plane ferroelectric domain in PZT epitaxial film will rotate, to some extent, to the out-of-plane direction. Therefore, the switching electric field along the normal direction (the coercive field) during ferroelectric hysteresis loop measurement will be increased.

In order to obtain a qualitative understanding on the ME coupling, we have simulated the polarization response of a single crystal PZT material under tensile stress by a time dependent Landau Khalatnikov model.[13] The simulation results suggest that the ferroelectric hysteresis loop of PZT under a transverse tensile stress will be suppressed; while reducing the external tensile stress, the hysteresis loop area of the PE loop increases. The increased remnant polarization and coercive field is due to the reduction of dipolar clamping effect in PZT epitaxial film. It has been shown that the application of tensile stress will oblige the dipoles to undergo rotations, particularly near the domain walls, such that the *c* axis will become parallel to the stress direction. As a result, the polarization strength will be reduced along the direction perpendicular to the applied stress. In our experiment, the application of magnetic field results in the generation of an in-plane compressive stress to the ferromagnetic film, which can relax the tensile stress in the PZT layer due to mechanical coupling. Therefore, more dipoles can undergo switching along the out-of-plane direction, resulting in increased remnant polarization, coercive field, and hysteresis loop area as our simulation result predicts.

In addition, magnetic-field-dependent dielectric constant has been analyzed based on the work of Kanno *et al.*,[14] where the stress-induced film dielectric constant (ε_{33}) of *c*-axis-oriented epitaxial thin films is expressed as a function of the external stress (σ) on the PZT film along 1 or 2 directions, i.e.,

$$\varepsilon_{33} = (2\alpha_1 + 2\alpha_{11}P_3^2 + 30\alpha_{111}P_3^4 - 2Q_{12}\sigma)^{-1}, \quad (1)$$

where $\alpha_1, \alpha_{11}, \alpha_{111}$ are the dielectric stiffness coefficients and Q_{12} represents the electrostrictive coefficient of PZT epitaxial film.[14] It is obvious from formula (1) that the ε_{33} in PZT film increases with the decrease of external stress arise from the magnetic-field-induced constriction in CFO layer, which is consistent with our measurement.

The authors would like to thank the financial support from the collaboration project grant between the Hong Kong Polytechnic University and Beijing Institute of Technology (No. 1-BB84).

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