Magnetoelectric $CoFe_2O_4/Pb(Zr_{0.52}Ti_{0.48})O_3$ double-layer thin film prepared by pulsed-laser deposition

Jian-ping Zhou
State Key Lab of New Ceramics and Fine Processing, and Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China and Key Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, P.O. Box 912, Beijing 100083, People's Republic of China

Hongcai He, Zhan Shi, and Ce-Wen Nan[a)]
State Key Lab of New Ceramics and Fine Processing, and Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

(Received 13 September 2005; accepted 24 November 2005; published online 5 January 2006)

Double-layer magnetoelectric $CoFe_2O_4$ (CFO)/$Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) nanocomposite thin film was prepared via a pulsed-laser deposition. X-ray diffraction showed that there are no other phases but PZT and CFO phases in the film. The smooth film surface was obtained after depositing the CFO and PZT layers. The double-layer thin film exhibits both good ferromagnetic and electric properties, as well as a magnetoelectric coupling effect. The magnetic-field-induced polarization in the thin film is zero below the dc magnetic field of 800 Oe and keeps constant above 800 Oe, and is strongly dependent on the ac magnetic field frequency which drives the magnetic domain rotation and then the electric polarization in the PZT layer. © *2006 American Institute of Physics*.
[DOI: 10.1063/1.2162262]

Multiferroic materials have drawn a continually increasing interest due to their attractive multifunctional features and potential applications in the multifuntional devices such as transducers, actuators and sensors.[1] Such materials can display a spontaneous dielectric polarization induced by an external magnetic field, or a magnetization induced by an applied electric field, i.e., magnetoelectric (ME) effect. The basic requirement for observation of the ME effect is the coexistence of ferromagnetic and ferroelectric subsystem. A large ME effect, resulting from the coupling magnetic-mechanical-electric interaction, has been observed in the bulk composite ceramics such as $CoFe_2O_4/BaTiO_3$ composites.[2] Most recently, much attention has been paid to composite films.[3–5] In comparison to bulk composites,[6] ME composite thin films present some unique advantages. Their phase composition could be modified or controlled at nanoscale, offering a technical way to study the ME physical mechanism in nanoscale and potential applications in microelectronic devices. The ME effect in the multilayer thin film deposited on the stiff substrate would be negligible due to the clamping effect of the substrate,[7,8] since the ME coupling in such a composite system is through elastic interactions. Recently, the ME coupling has been observed in a self-assembled epitaxial multiferroic $BaTiO_3$-$CoFe_2O_4$ film with vertically aligned nanostructure by an indirect way.[2] But the direct ME measurement of such a column structure is difficult because of low resistance of $CoFe_2O_4$ (CFO) pillars penetrating through the film, though there exists a potentially giant ME effect in the column structure.[8] By comparison, the ME coupling has been measured directly in the thin film with $CoFe_2O_4$ nanoparticles embedded in $Pb(Zr,Ti)O_3$ (PZT) matrix due to the high resistance of the PZT matrix.[9] In this letter, we report a double-layer ME composite thin film of $CoFe_2O_4/PbZr_{0.52}Ti_{0.48}O_3$ (CFO/PZT) that shows a well microstructure and ME effect.

Double-layer CFO/PZT thin film was grown on Si (100) via a pulsed-laser deposition (PLD) technique. The stoichiometric targets of $CoFe_2O_4$ and $PbZr_{0.52}Ti_{0.48}O_3$, in which Pb was over 10% to avoid Pb vacancy for its volatilization during sintering and depositing, were prepared through a standard solid reaction sintering processing. The PLD experiment was performed by using a KrF exciter laser of 248 nm in wavelength, and 5 Hz in repetition rate. A laser fluency of 200 mJ with an energy density of $\sim 2.0\ J/cm^2$ was employed. The CFO layer was first deposited on silicon substrate at 560 °C and oxygen pressure of 1 Pa, and then the PZT layer was deposited at 650 °C and 22 Pa. Both layers were deposited for 30 min. The total film thickness was about 30 nm determined by a SOPRAGES5 type of ellipsometer.

The prepared thin film is checked by x-ray diffraction (XRD) and atomic force microscopy (AFM) for crystallite. Figure 1(a) shows the XRD pattern of the double-layer thin film. All peaks can be identified by reference to the PZT or CFO phase apart from the substrate. Figure 1(b) shows a typical AFM image of the film surface. The root-means-square of the surface roughness is about 3.7 nm. The smooth surface and good structure of the film are obtained after depositing the two layers.

For ferroelectric measurement, a conductive layer is commonly deposited on the substrate as the bottom electrode. However, the additional conductive layer would decrease the smoothness of the substrate. Semiconductor silicon has a higher conductivity in comparison with CFO and PZT and is set approximately as the bottom electrode. Pt electrode dots with 100 μm in diameter are deposited on the composite film surface. The electric properties are measured between two Pt electrode dots, equivalently measuring two capacitors in series. A TFAnalyzer 2000 ferroelectric testing

[a)]Author to whom correspondence should be addressed; electronic mail: cwnan@tsinghua.edu.cn

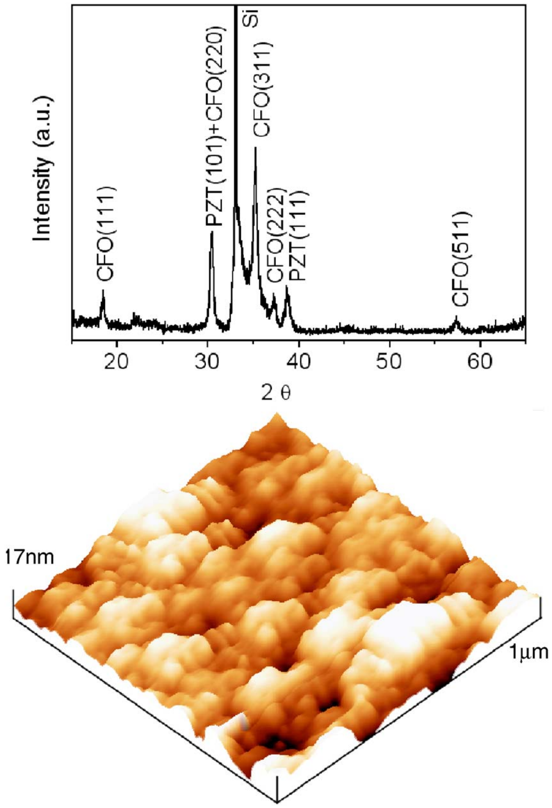

FIG. 1. (a) XRD pattern and (b) AFM image of the CFO/PZT double-layer thin film.

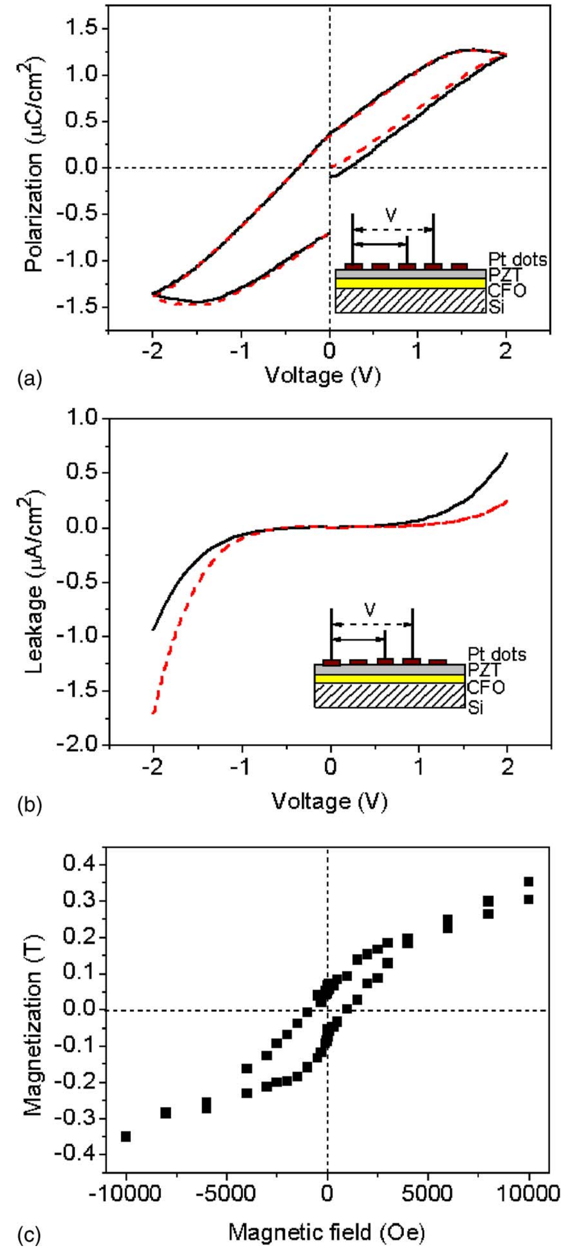

FIG. 2. (a) Polarization-electric field hysteresis loops (in-plane) and (b) leakage current as a function of voltage measured between two Pt electrode dots at different distances. (c) Magnetic hysteresis loop. The insets show the schematic of the two measurements for the solid and dashed curves.

unit is employed to investigate the polarization-electric field hysteresis loops and the leakage current. Figure 2(a) shows the ferroelectric loops (in-plane) measured between two Pt electrode dots at different distances at 100 Hz. There is an evident ferroelectric characteristic in the composite film. The low saturation polarization of PZT is caused by the effect of the paraelectric CFO layer.[10] The two close loops indicate that the silicon can perform a good conductor relative to the CFO/PZT composite film. But there is a little difference for the leakage current measurement [Fig. 2(b)] because the polarization measurement mainly occurs at the surface of the film while the leakage current is relative to the whole film as well as the semiconductive substrate. The leakage current between two electrode dots is equivalent to that of two metal-oxide-semiconductors (MOSs) in series. Figure 2(b) shows the leakage current variation with the voltage measured between two electrode dots at different distances, where a very low leakage indicates that there are no any holes in the PZT layer. The dash curve moves about 0.4 V relative to the solid curve. This is caused by the inhomogeneous intrinsic electric field in the MOS structures.

A vibrating sample magnetometer (VSM) is employed to characterize the magnetic properties of the film. The magnetization dependence on the magnetic field is measured at room temperature by applying a magnetic field up to 10 kOe. As shown in Fig. 2(c), the saturation magnetization of the composite film is 0.35 T, which is about half of that for the bulk CFO (i.e., 0.65 T). The coercivity of the composite film is about 1 kOe, lower than that of the pure CFO film.[11,12] This easy-magnetization enhances the sensitivity of CFO.

The coexistence of the ferroelectric PZT and ferromagnetic CFO phases in the composite thin film could generate a ME effect, which is measured in terms of the variation in the electric polarization, ΔP_3, as a function of dc magnetic field H_{dc}. The sample is put into the dc magnetic field up to 5.5 kOe superimposed a small AC parallel disturbed magnetic field dH. A signal generator drives the Helmholtz coil to generate the ac magnetic field in the frequency range from 10 Hz to 100 kHz. The ac magnetic field amplitude generated at a constant voltage of 20 V reduces with increasing frequency because of the coil impendence, for instance, dH =12 Oe at the frequency of 1 kHz and dH=3.1 Oe at 10 kHz. The magnetic filed is applied parallel to the plane of the thin film. The in-plane charge induced by the in-plane magnetic field is collected with a charge amplifier (DSC3062, Beijing, China).

As shown in Fig. 3(a), at H_{dc}=0, the composite film does not show the ME effect. As H_{dc} is over 800 Oe, the electric polarization almost keeps constant and nearly independent

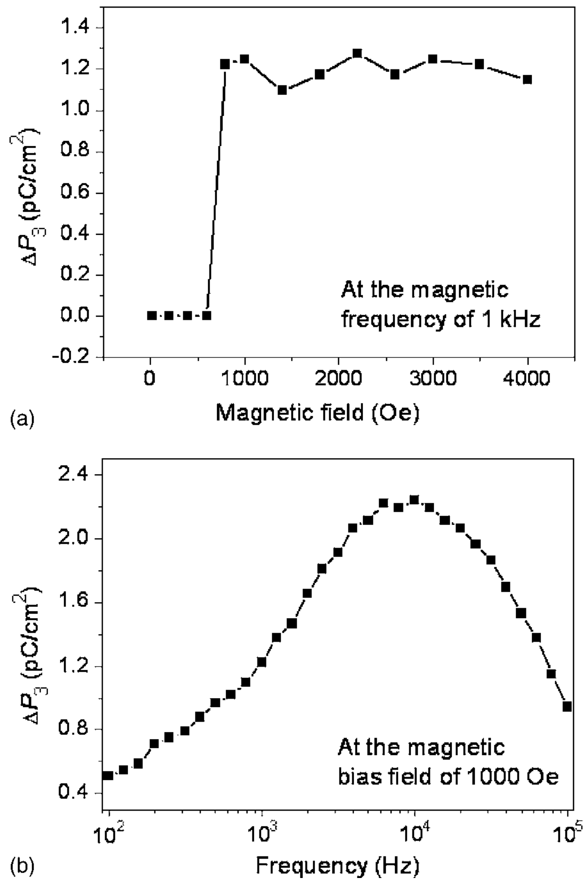

FIG. 3. Magnetic-field-induced electric polarization as a function of (a) the magnetic bias field and (b) frequency.

on the magnetic bias H_{dc}. This observation is different from that on the composite films obtained by the sol-gel processing,[9] but similar to the Green's function prediction on $BaTiO_3/CoFe_2O_4$ laminated film.[8] In the multiferroic composites, the ME coupling mainly arises from the magnetic-mechanical-electric interaction through the stress/strain transforming from one subsystem to another. In the magnetic field, the driving force of the ME coupling comes from the magnetostriction of the CFO phase, involving the domain-wall motion and domain rotation. The in-plane domain-wall motion is ignored due to the clamping effect of the substrate. The out-of-plane domain-wall motion, if any under the condition of the in-plane magnetic field, cannot bring the strain to the PZT phase, since the boundary condition of the film surface is considered as end free in the direction perpendicular to the film surface in the measurement. As a result, both the domain-wall motions have no contribution to the ME effect. The domain rotation in the CFO phase is limited due to its hard magnetic feature.[11,12] In the present CFO/PZT double-layer thin film, the coercivity of the CFO phase is as low as 1 kOe. The domain rotations could occur near the coercivity of the CFO, and thus the composite film does not show the obvious ME effect below 800 Oe but exhibits the magnetic-field-induced electric polarization over 800 Oe, as shown in Fig. 3(a). The static domains before and after rotating cannot bring lattice distortion to the PZT layer. Only the dynamic domain rotation processing under the ac magnetic field *dH* disturbs the PZT to induce a change in the electric polarization, which could happen near the coercivity and remains almost constant over the coercivity (e.g., about 800 Oe as observed).

The dependence of the magnetic-field-induced polarization ΔP_3 on the frequency is shown in Fig. 3(b). With increasing frequency, ΔP_3 increases to reach a maximum at about 10 kHz, and then decreases. As discussed above, the domain rotation processing is the dominant factor to affect the ME coupling. With increasing frequency, the domains rotate more frequently so as to induce an increasing change in the electric polarization in the PZT layer. Dielectric loss of the films usually decreases with frequency in this frequency range, especially for the ferrites.[13,14] This may be another factor of increasing ΔP_3 with the frequency. But on the other hand, the amplitude of the AC magnetic field *dH* decreases with increasing frequency, e.g., lower than 3.1 Oe above 10 kHz, resulting in a decrease in ΔP_3. The ac disturbed magnetic field *dH* is the main driving factor for the ME coupling variation as the dc magnetic field is over the coercivity. These cause such a frequency-dependent ΔP_3 behavior as shown in Fig. 3(b).

In summary, a double-layer CFO/PZT multiferroic nanocomposite film has been obtained by a PLD method. The double-layer thin film contains PZT and CFO phases and shows good magnetic-electric properties. The dynamic ME coupling is attributed to the magnetic domain rotation in CFO layer, which disturbs PZT to induce a change in the electric polarization in the PZT layer. The electric polarization in the films is strongly dependent on the applied magnetic field. The magnetic-field-induced polarization in the double-layer CFO/PZT composite thin films is small due to the clamping effect of the substrate as recently predicted.[8]

This work was supported by the State Key Project of Fundamental Research of China (Grant No. 2002CB613303) and the National Natural Science Foundation of China (Grant Nos. 50232030, 50318002, 50328203, and 10574078).

[1] N. A. Spaldin and M. Fiebig, Science **309**, 391 (2005).
[2] C. W. Nan, Phys. Rev. B **50**, 6082 (1994).
[3] H. Zheng, J. Wang, S. E. Lofland, Z. Ma, L. Mohaddes-Ardabili, T. Zhao, L. Salamanca-Riba, S. R. Shinde, S. B. Ogale, F. Bai, D. Viehland, Y. Jia, D. G. Schlomm, M. Wuttig, A. Roytburd, and R. Ramesh, Science **303**, 661 (2004).
[4] J.-H. Li, I. Levin, J. Slutsker, V. Provenzano, P. K. Schenck, R. Ramesh, J. Ouyang, and A. L. Roytburd, Appl. Phys. Lett. **87**, 072909 (2005).
[5] K.-S. Chang, M. A. Aronova, C.-L. Lin, M. Murakami, M.-H. Yu, J. Hattrick-Simpers, O. O. Famodu, S. Y. Lee, R. Ramesh, M. Wuttig, I. Takeuchi, C. Gao, and L. A. Bendersky, Appl. Phys. Lett. **84**, 3091 (2004).
[6] C. W. Nan, N. Cai, Z. Shi, J. Zhai, G. Liu, and Y. Lin, Phys. Rev. B **71**, 014102 (2005).
[7] K. Lefki and G. J. M. Dormans, J. Appl. Phys. **76**, 1764 (1994).
[8] C. W. Nan, G. Liu, Y.-H. Lin, and H. Chen, Phys. Rev. Lett. **94**, 197203 (2005).
[9] J. G. Wan, X. W. Wang, Y. J. Wu, M. Zeng, Y. Wang, H. Jiang, W. Q. Zhou, G. H. Wang, and J.-M. Liu, Appl. Phys. Lett. **86**, 122501 (2005).
[10] A. L. Royturd, S. Zhong, and S. P. Alpay, Appl. Phys. Lett. **87**, 092902 (2005).
[11] S. D. Sathaye, K. R. Patil, S. D. Kulkarni, P. P. Bakre, S. D. Pradhan, B. D. Sarwade, and S. N. Shintre, J. Mater. Sci. **38**, 29 (2003).
[12] M. C. Terzzoli, S. Cuhalde, S. Jacobo, L. Steren, and C. Moina, J. Alloys Compd. **369**, 209 (2004).
[13] Z. Yue, J. Zhou, Z. Gui, and L. Li, J. Magn. Magn. Mater. **264**, 258 (2003).
[14] S. A. Mazen and H. M. Zaki, Phys. Status Solidi A **199**, 305 (2003).