Magnetoelectric $CoFe_2O_4$–Pb(Zr,Ti)O_3 composite thin films derived by a sol-gel process

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Magnetoelectric (ME) $CoFe_2O_4$–Pb(Zr,Ti)O_3 composite thin films have been prepared by a sol-gel process and spin-coating technique. X-ray diffraction and scanning electron microscopy reveal that there exists local aggregation or phase separation of the $CoFe_2O_4$ and Pb(Zr,Ti)O_3 phases in the films. Vibrating sample magnetometer, ferroelectric test unit, and magnetoelectric measuring device were used to characterize the magnetic and ferroelectric properties, as well as the ME effect of the films. It is shown that the films exhibit both good magnetic and ferroelectric properties, as well as a ME effect. A high initial magnetoelectric voltage coefficient for the film is observed. The ME effect of the film strongly depends on the magnetic bias and magnetic field frequency. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1889237]

In the past decades, there has been a continually increasing interest in magnetoelectric (ME) materials due to their attractive physical properties and wide applications in the fields of sensors, data storage, and transducers for magnetic-electric energy conversion.[1,2] Such materials can display a spontaneous dielectric polarization as a response to an applied magnetic field, or an induced magnetization by an external electric field.[3] The primary requirement for the observation of the ME effect is the coexistence of magnetic and electric dipoles. Based on this outline, the ME effect could be realized in a composite consisting of both ferroelectric phase and ferromagnetic phase by using the product property, which is first proposed by Van Suchetelene.[4] Up to now, various ME composites have been developed. Most of them are bulk materials, e.g., the sintered composites of Ni(Co,Mn)Fe_2O_4–$BaTiO_3$, and $CoFe_2O_4$-Pb(Zr,Ti)O_3 (PZT),[5–7] and multilayer composites of $NiFe_2O_4$-PZT and Terfenol-D-PZT,[8,9] etc.

Recently, attention to ME materials has been gradually drawn toward composite thin films. Compared to bulk composites, ME composite thin films exhibit unique advantages. Their composition and connectivity could be modulated at the microscopic scale, and the artificial thin film heterostructures can thus be achieved, which have potential applications in all kinds of microdevices and integrated units such as microsensors, MEMS devices, and high density information storage devices. So far few investigations on ME composite thin films have been carried out except for the $CoFe_2O_4$–$BaTiO_3$ thin-film heterostructures recently developed by Zheng *et al.*[10,11] and Chang *et al.*[12] Such thin-film heterostructures were achieved by pulsed laser deposition and composition spread methods. However, the correlative investigations on the ME effect for these heterostructures were absent. In this letter, we report a self-assembled ME composite thin film of $CoFe_2O_4$–PZT that shows a well-defined microstructure and exhibits a ME effect.

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In the present composite thin films, the ferroelectric and ferromagnetic phases are, respectively, perovskite lead zirconate titanate $Pb(Zr_{0.52}Ti_{0.48})O_3$ (lattice parameter: $a=b=4.03$ Å and $c=4.14$ Å) and spinel cobalt ferrite $CoFe_2O_4$ (lattice parameter: $a=8.39$ Å). The lattice mismatch between the two phases is less than 4%, which brings about their better compatibility. The composite thin films were prepared by a sol-gel process and spin-coating technique. A 0.3 M 2-methoxyethanol solution of $CoFe_2O_4$ (with a molar ratio of $Co^{2+}:Fe^{3+}=1:2$) and 0.3 M 2-methoxyethanol solution of PZT (with a molar ratio of Zr:Ti=52:48) were used for the sol solutions. Both sol solutions were alternately spin coated onto the Pt/Ti/SiO_2/Si substrate to form a multilayer precursor composite film. The prepared precursor film consisted of four-layer PZT and two-layer $CoFe_2O_4$. After calcined at 650 °C for 6 min under the oxygen atmosphere by the rapid annealing process, the final composite thin film was formed with a thickness of ~400 nm, accompanying with the deep diffusion between the PZT layers and $CoFe_2O_4$ layers.

The phase structure characterization of the composite thin films was carried out by x-ray diffraction (XRD) on a D/MAX-RA diffractometer using Cu $K\alpha$ radiation. Figure 1(a) shows the typical XRD pattern of the composite thin film. All peaks can be identified. Two evident sets of well-defined peaks are observed and there are no additional or intermediate phase peaks apart from $CoFe_2O_4$ and PZT. In addition, the pattern indicates that both $CoFe_2O_4$ and PZT phases are polycrystalline structures and have no evident preferential crystallographic orientations.

The morphology examination for the film, as shown in Fig. 1(b), was made using a scanning electron microscopy (SEM, LEO-1530VP) connected to an energy dispersive x-ray microanalysis (EDX). The random-distributed particles with an average diameter of ~150 nm are observed in the film. The volume fraction of the particles calculated using the SEM image is about 0.31. The elemental composition analyses using EDX confirm that the main metal elements in the particles are Co and Fe, whereas they are Pb, Ti, and Zr in the matrix. That is to say, the $CoFe_2O_4$ and PZT phase

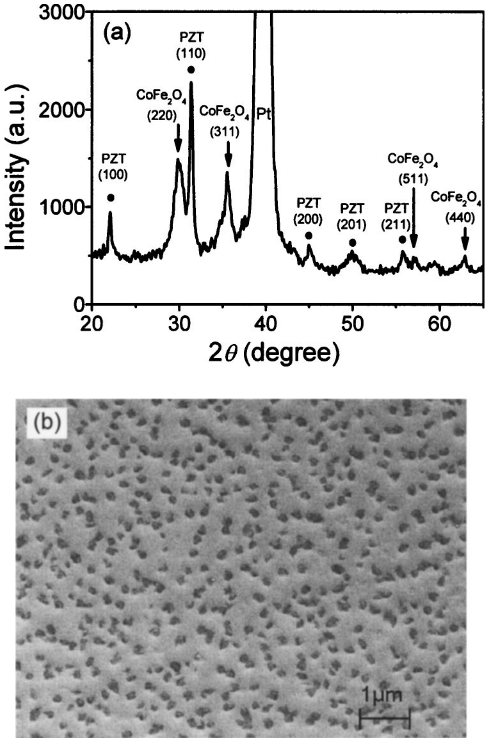

FIG. 1. (a) XRD pattern and (b) SEM image of the $CoFe_2O_4$–PZT composite thin film.

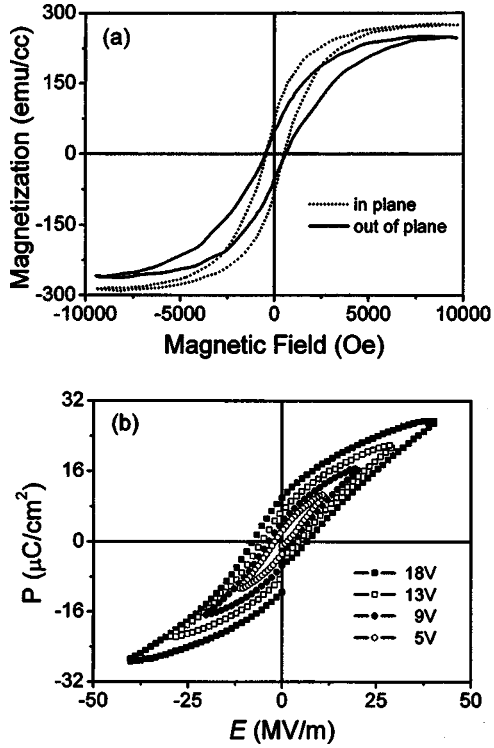

FIG. 2. (a) Magnetic hysteresis loops and (b) $P-E$ hysteresis loops of the $CoFe_2O_4$–PZT composite thin film.

spontaneously separated into two individual phases, indicating that local aggregation or phase separation occurred during the film growth. This can be explained by the thermodynamic equilibrium and kinetic diffusion. Indeed, there is very little solid solubility between the perovskite and spinel phases.[11,13] The spontaneous phase separation will appear in the perovskite-spinel heterostructure during growth due to the thermodynamic instability of the phases at the growth temperature.[14,15] In this work, the annealing process at 650 °C is adequate to drive the $CoFe_2O_4$ and PZT phases to separate and aggregate into individual phases. We did not observe phase separation in the composite thin films when the annealing temperature was below 650 °C.

In order to characterize the magnetic properties of the films, a vibrating sample magnetometer (VSM, Lakeshore, Model 7300 series) was used. We measured the field-dependent magnetizations at room temperature by applying magnetic fields perpendicular or parallel to the plane of the films. The magnetic hysteresis loops for the films are presented in Fig. 2(a). Both the in-plane and out-of-plane loops have similar shapes, and the saturation magnetizations of the in-plane and out-of-plane loops show 280 and 250 emu/cm^3, respectively, which are comparable to that of the $CoFe_2O_4$ films.[16] This illustrates that the magnetic anisotropy in the composite thin film is not evident, which should be ascribed to the polycrystalline structures and the absence of the preferential crystallographic orientations in the $CoFe_2O_4$ phase. On the other hand, however, the coercivity H_c of the composite thin film is only ~0.6 kOe for both the in-plane and out-of-plane loops, much lower than that of the $CoFe_2O_4$ films.[16] This easy-magnetization characteristic should contribute to the increase of the total magnetocrystalline anisotropy energy related to the magnetoelastic coupling due to the compressive stress in the $CoFe_2O_4$ phase caused by the lattice mismatch between the $CoFe_2O_4$ and PZT phases.[17]

For ferroelectric measurement, Pt electrodes were deposited on the composite thin films by using a pulsed laser deposition method. Electric measurement shows that the film has a high resistivity value of $\sim 5\times 10^9 \Omega$ cm at zero bias. The polarization versus electric field ($P-E$) hysteresis loops under the applied voltage in the range of 3–18 V, as shown in Fig. 2(b), were tested by an RT66 ferroelectric testing unit. The well-defined ferroelectric loops are observed. The maximum saturation polarization (P_s) and remanent polarization (P_r) reach 28 and 11.0 μC/cm^2 at $E=40$ MV/m, respectively.

The coexistence of the ferromagnetic $CoFe_2O_4$ and ferroelectric PZT phases in the present composite thin films gives rise to a ME effect, which is characterized by the magnetoelectric voltage coefficient $\alpha_E = dE/dH$. The small alternating magnetic field H (10 Oe) was generated by a solenoid that was superimposed onto a magnetic bias H_{bias} up to 6 kOe. The electric field E induced by H and H_{bias} was measured using a lock-in amplifier (SRS Inc., SR830). The variations of α_E with H_{bias} at various magnetic frequency f are shown in Fig. 3. At $H_{\text{bias}}=0$, the film exhibits an initial high α_E value (e.g., 220 mV/cm Oe at $f=1$ kHz), much larger than that of the bulk ferroelectric–ferromagnetic composite which is nearly close to zero.[5,6] With increasing H_{bias} from zero, one observes the strong H_{bias} dependence of α_E (i.e., high α_E value and saturation at lower H_{bias} below ~2 kOe, and a sharp decrease at higher H_{bias} above ~2 kOe). Moreover, an optimized H_{bias} at which α_E reaches the maximum value appears in the α_E saturation region. In addition, an overall α_E increase with increasing f from 1 to 50 kHz is observed. We obtained the maximum α_E value of 317 mV/cm Oe at $f \sim 50$ kHz.

The reason that causes the ME effect of the present composite thin film will now be discussed. In the magnetostrictive-ferroelectric composite system (e.g., the

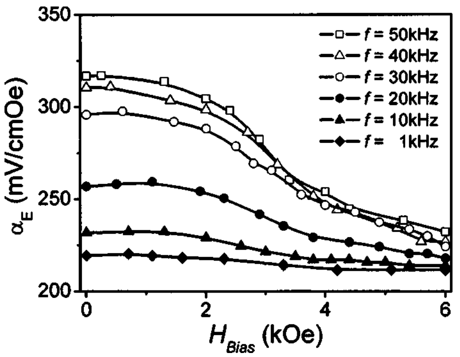

FIG. 3. Variations of α_E with $H_{\rm Bias}$ at various magnetic frequency f for the $CoFe_2O_4$–PZT composite thin film.

$CoFe_2O_4$–PZT composite), ME coupling mainly arises from the magnetic–mechanical–electric transform through the stress-mediated transfer in the interface. The dynamic magnetoelastic coupling, which is caused by the magnetostriction of the $CoFe_2O_4$ phase, due to the domain-wall motion and domain rotation, is involved in the ME effect. Therefore, the low coercivity and high magnetostriction are advantageous for a strong ME effect.[9] For general bulk $CoFe_2O_4$ material, the domain rotation is greatly limited due to the fact that $CoFe_2O_4$ is magnetically hard with a large coercivity beyond ~2 kOe.[16] In the present $CoFe_2O_4$–PZT composite thin film, however, the coercivity H_c of the $CoFe_2O_4$ phase is quite low. The film exhibits an easy-magnetization characteristic, which is very helpful for the magnetic domain rotation and results in a larger magnetostriction λ under a very low magnetic field, consequently leading to a strong ME coupling by interface coupling.

As for the $H_{\rm bias}$ dependence of α_E, it essentially tracks the $H_{\rm bias}$ dependence of the piezomagnetic coupling coefficient $q=\delta\lambda/\delta H_{\rm bias}$.[9,18] For most ferrites (including $CoFe_2O_4$), once the magnetostriction attains the saturation value, the q decreases and the piezomagnetic coupling gradually becomes weak, resulting in a decrease of the ME effect. With respect to the variation of α_E with f, it is most likely due to the frequency dependence of the dielectric constant for the individual phases and the piezoelectric coefficient for PZT.[9] Since the ME coupling originates in the interface, one should also consider the influence of other factors such as interface defects, grain boundaries, and domain direction, all of which affect the interface coupling. Further microstructural investigations for understanding these influences on the ME effect are now underway.

In summary, the magnetoelectric $CoFe_2O_4$–PZT composite thin films have been successfully prepared by using a simple sol-gel process and spin-coating technique. Local aggregation or phase separation of the PZT and $CoFe_2O_4$ phase have been observed in the films. The films exhibit both good magnetic and electric properties, as well as magnetoelectric effect.

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