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Magnetostatic Coupling in $Ba_{0.8}Sr_{0.2}TiO_3/CoFe_2O_4$ Magnetoelectric Composite Thin Films of 2-2-Type Structure *

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$Ba_{0.8}Sr_{0.2}TiO_3/CoFe_2O_4$ (BST/CFO) magnetoelectric composite thin films of 2-2-type structures are prepared onto Pt/Ti/SiO_2/Si substrates by a sol-gel process and spin coating technique. The structure of the prepared thin film is substrate/BST/CFO/.../CFO/BST. Three CFO ferromagnetic layers are separated from each other by a thin BST layer. The upper CFO layer is magnetostatically coupled with the lower CFO layer. Subsequent scanning electron microscopy investigations show that the prepared thin films exhibit good morphologies and have a compact structure, and the cross-sectional micrographs clearly display a multilayered nanostructure of multilayered thin films. The composite thin films exhibit good magnetic and ferroelectric properties. The spacing between ferromagnetic layers can be varied by adjusting the thickness of intermediate BST layer. It is found that the strength of magnetostatic coupling has a great impact on magnetoelectric properties of composite thin film; that is, the magnetoelectric voltage coefficient of the composite thin film tends to increase with the decrease of pacing between two neighboring CFO ferromagnetic layers as a result of magnetostatic coupling effect.

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Magnetoelectric (ME) multiferroic materials, which simultaneously exhibit ferroelectricity and ferromagnetism, have recently stimulated considerable interest because of their significant potential applications in next-generation, novel, multi-functional devices.[1,2] It has been predicted that fluctuations in P (polarization) or M (magnetization) can be activated upon external magnetic field H or electric field E being applied, respectively. The development of magnetoelectric thin films has become the subject of considerable attention due to their potential applications in microelectromechanical systems.[3,4] Because of the large magnetostrictive coefficient of $CoFe_2O_4$ (CFO) and the good piezoelectric coefficient of $Ba_{0.8}Sr_{0.2}TiO_3$ (BST), BST/CFO composite thin films have stimulated extensive interest.[5−8] ME thin films have three different nanostructures, which are: 0-3 type, 2-2 type, and 1-3 type. In comparison, it is easier to take control of the growth of horizontal heterostructured (the so-called 2-2-type structure) thin films. On the other hand, 2-2-type structure can significantly reduce the leakage current by isolating the low resistive magnetic layers with insulating ferroelectric layers.[9] Therefore, 2-2-type composite thin films have been seen as potential candidates for ME coupling applications.

As the lateral size of layers is reduced, the magnetostatic coupling between ferromagnetic layers, which are usually neglected in the case of continuous macroscopic multilayer, can become relevant and change the overall magnetic behavior.[10] As the distance between layers is increased, the magnetostatic coupling strength is reduced and, hence, at a large layer separation the magnetic properties of films would be identical with that of a single film.[11] Therefore, magnetostatic coupling is an important parameter in the design of magnetic devices. However, there have been few reports on how the magnetoelectric properties of composite thin films can be affected due to the magnetostatic coupling between ferromagnetic layers.

In this Letter, BST/CFO magnetoelectric composite thin films of 2-2-type heterostructure have been prepared onto Pt/Ti/SiO_2/Si substrates by a sol-gel process and spin coating technique. The structure is substrate/BST/CFO/.../CFO/BST. Composite thin films with good morphologies exhibit good magnetic and ferroelectric properties. In principle, the strength of magnetostatic coupling in composite thin films can be controlled by varying the thickness of the middle BST layer. The magnetoelectric voltage coefficient is then measured under different magnetostatic coupling conditions.

The precursor solutions for the BST were prepared by the sol-gel method, in which barium acetate ($Ba(C_2H_3O_2)_2$), strontium acetate ($Sr(C_2H_3O_2)_2{\cdot}1/2H_2O$) and tetrabutyl titanate ($Ti(OC_4H_9)_4$) were used as raw materials. Glacial acetic acid (CH_3COOH) and acetylacetone ($CH_3COCH_2COCH_3$) were used as the solvent and stabilizer. Afterwards, the solution was stirred for 3 h at 75℃ to obtain the BST precursor solution with a concentration of 0.30 mol/L.

Iron nitrate ($Fe(NO_3)_3{\cdot}9H_2O$), cobalt nitrate ($Co(NO_3)_2{\cdot}6H_2O$), and citric acid ($C_6H_8O_7{\cdot}H_2O$)

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were first dissolved into anhydrous alcohol to form a mixed solution. After the solution was stirred for 5 h at 70℃, a CFO precursor solution (0.20 mol/L) was obtained by adding anhydrous alcohol.

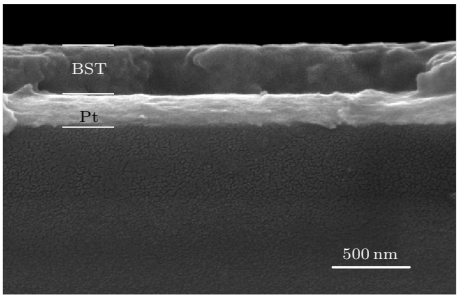


Fig. 1. SEM images of the cross-sectional micrographs of pure BST thin films.

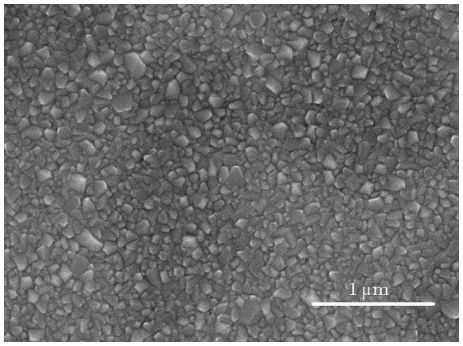


Fig. 2. SEM image of the surface of pure BST thin films.

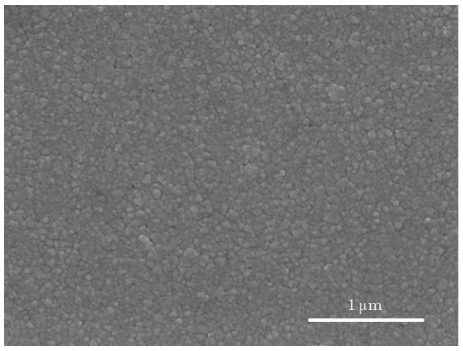


Fig. 3. SEM image of the surface of CFO thin films.

Si has a certain electrical conductivity: direct contacting with the bottom electrode will adversely affect the result of the electrical measurement. SiO_2 as the Si natural oxide layer can act as a passivation and isolation layer. Pt is a proper electrode material; however, Pt's adhesion strength is weak and it is easily striped with the Si substrate. TiO_2 has strong adhesion, and when used as a buffer layer it can improve the adhesion of Pt. Following oxidation of the Si(100) wafer sputtering Ti and Pt in proper order by magnetron sputtering, the multilayer structure $Pt/Ti/SiO_2/Si$ was obtained as a substrate.

The BST starting precursor solution was spin coated onto the $Pt/Ti/SiO_2/Si$ substrate at a spinning rate of 4000 r/min for 30 s. Then, the gel film was successively dried at 150℃ for 2 min and pre-annealed at 350℃ for 2 min. This spin-coating/drying procedure was repeated several times until the required thickness of the films was reached. Finally, the film was annealed at 700℃ for 10 min by a rapid annealing process.

After that, the CFO starting precursor solution was spin coated onto the BST films and annealed at 700℃ for 10 min by a rapid annealing process. The composite thin films were prepared by repeating the above process, with structure of substrate/ BST /CFO/.../CFO/ BST. By varying the concentration of the BST starting precursor solution (0.1, 0.15, 0.2, and 0.25 mol/L), the thickness of the intermediate BST layer which separates the CFO ferromagnetic layers can be changed. Composite thin films prepared with different thicknesses of intermediate BST layer were used to probe into the influence of magnetostatic coupling on magnetoelectric properties.

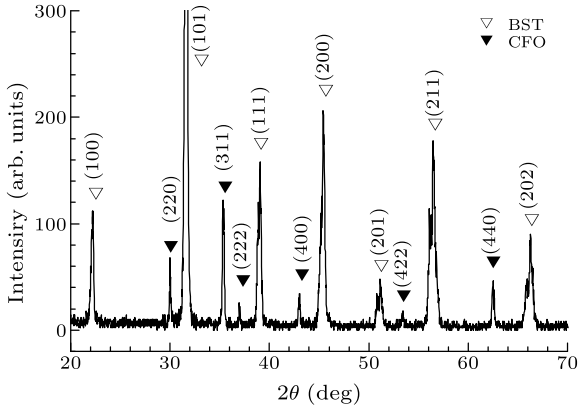


Fig. 4. X-ray diffraction (XRD) results of BST/CFO composite thin films annealed at 700℃.

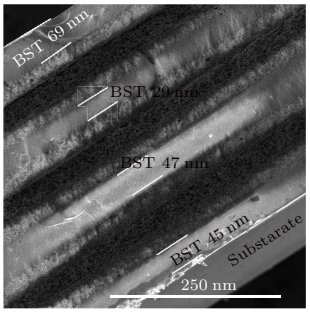


Fig. 5. SEM cross-sectional micrograph of composite thin films, and the concentration of intermediate BST solution is 0.1 mol/L.

XRD (X'Pert PRO, PANalytical B.V.) with Cu K_α radiation ($\lambda = 1.5406$ Å) was used for phase analysis of the films. The cross-sectional and surface morphologies of the films were observed by a scanning electron microscope (SEM, Quanta 200). Magnetic behavior was detected at room temperature by a vibration sample magnetometer (VSM, LakeShore 7404). The ferroelectric measurements were performed by using a radiant technologies precision workstation ferroelectric

test system. The ME effects of the films were measured by using an ME measuring device.

Figure 1 shows the SEM cross-sectional micrographs of BST thin films, the concentration of BST starting precursor solution is 0.25 mol/L. Figure 2 shows the SEM image of the surface of above-mentioned BST films. The results reveal that the films are crack-free and have a compact structure without any pores. Figure 3 shows the SEM images of surfaces of CFO thin films. Based on the SEM results, it can be seen that the CFO film is crack-free and has a compact structure. Figure 4 shows the XRD results of BST/CFO composite thin films annealed at 700℃. All of the peaks can be identified and there are no additional or intermediate phase peaks, apart from BST and CFO.

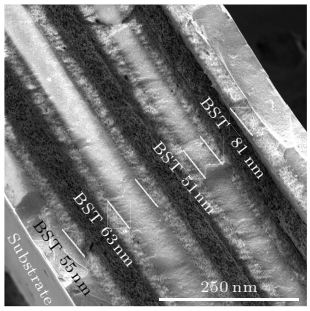


Fig. 6. SEM cross-sectional micrograph of composite thin films at the concentration of intermediate BST solution to be 0.25 mol/L.

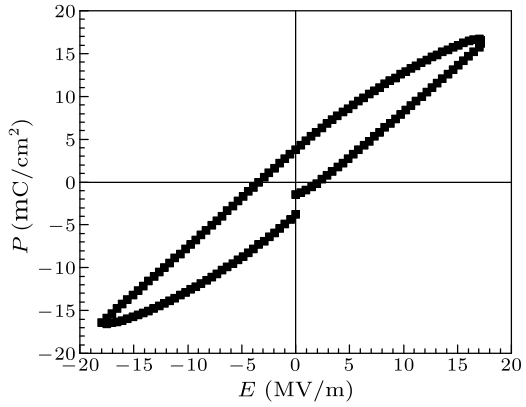


Fig. 7. P–E hysteresis loops of the composite thin films.

Figures 5 and 6 show the SEM cross-sectional micrographs of composite thin films prepared by using different concentrations of BST solution (0.1 and 0.25 mol/L), in which the top BST layer (the fifth layer) is added to facilitate the occurrence of magnetoelectric coupling and subsequent magnetoelectric measurements. It is shown that there is a clear multilayer structure for the prepared composite thin films. A flat cross section and a uniform distribution of thickness of composite films are observed. Based on the SEM images, the thickness of the intermediate BST layer is increased from about the smallest 29 nm to the largest 51 nm, as the concentration of BST solution changes from 0.1 mol/L to 0.25 mol/L. The thickness of the other layers does not change significantly. It is seen from the morphology that grains with a thickness of ∼10 nm exist and cross each other at the interface. This is quite different from the interfacial microstructure of multilayered PZNT-NCZF composites.[11] The presence of the grains can be attributed to the residual stresses resulted from the lattice mismatch[12] and the thermal expansion coefficient (TEC) difference between BST and CFO phases.[13]

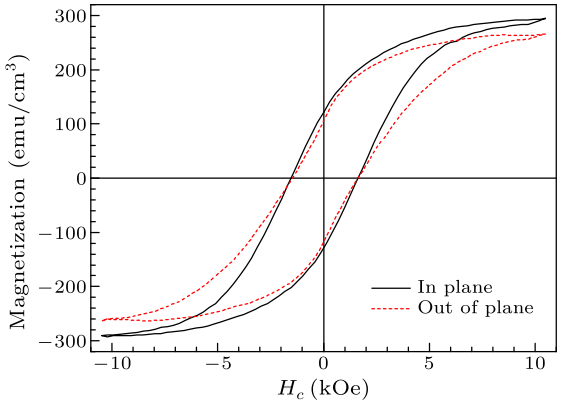


Fig. 8. Magnetic hysteresis loops of the composite thin films.

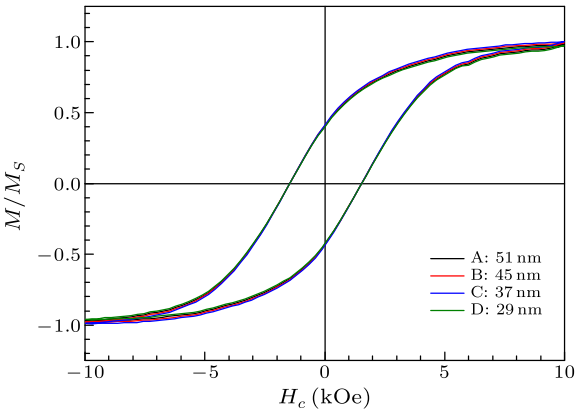


Fig. 9. Magnetic hysteresis loops of different composite thin films after magnetization data normalized.

Table 1. The ferromagnetic parameters of the films with different concentrations of intermediate BST solution.

Lable	C^{a} (mol/L)	d^{b} (nm)	H_c (kOe)	M_r/M_s (10^3)
A	0.25	51	1.07	437.72
B	0.20	45	1.05	431.63
C	0.15	37	1.02	429.87
D	0.10	29	1.01	427.69

[a]The concentration of the intermediate BST solution.
[b]The real thickness of the intermedia BST layer.

Pt electrodes were deposited on the composite thin films by a pulsed laser deposition method for ferroelectric measurement. Figure 7 shows the ferroelectric P–E curves of films under the applied voltage of 8 V. Well-defined ferroelectric loops are observed, and the maximum saturation polarization (P_s) and remanent polarization (P_r) reach 16.7 and 5.6 μC/cm² at

$E = 17\,\mathrm{MV/m}$.

A vibrating sample magnetometer was used to characterize the magnetic properties of films. The field-dependent magnetizations were measured at room temperature by applying magnetic fields perpendicular or parallel to the plane of the films. The magnetic hysteresis loops for the films are shown in Fig. 8. The saturation magnetizations of the in-plane and out-of-plane loops are 298 and 272 emu/cm^3, and the composite films show relatively large values when compared with some of the other corresponding results. The results also show that the coercivity H_c of the composite thin film is the same for both loops. Both the in-plane and out-of-plane loops have similar shapes, showing that the magnetic anisotropy in the composite thin film is not evident, which can be ascribed to the polycrystalline structures of films.

Figure 9 shows the in-plane magnetic hysteresis loops of different films after magnetization data normalized. The real thickness of intermediate BST layer, H_c and remanence ratio (M_r/M_s) of each films are shown in Table 1. As the spacing between ferromagnetic layers is decreased, the strength of magnetostatic coupling is larger, and the date of coercivity and remanence ratio are both reduced. This means that the composite films are more easily magnetized, which can be ascribed to the magnetostatic coupling in films. The reason for this might be that a ferromagnetic layer can be seen in a magnetostatically coupled film, which is the sum of the applied field and the highly nonuniform field of the neighbouring layers constituting the films.[14]

The magnetoelectric voltage coefficient $\alpha_E = dE/dH$, which is characterized by the induced electric field E under an applied ac magnetic field H (9 V) generated by a pair of Helmholtz coils, was then measured as function of dc magnetic bias H_{bias} for the composite thin films. Both the ac magnetic field and the dc magnetic field were superimposed and parallel to the film plane. The frequency of the voltage signal applied on Helmholtz coils was 50 kHz.

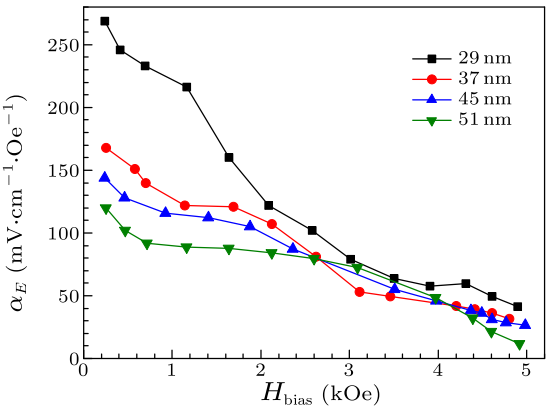


Fig. 10. Variations of α_E with H_{bias} for the composite thin films.

Figure 10 shows the variation of α_E with H_{bias} at an ac magnetic frequency of 50 kHz. It is clear that the composite thin film exhibits a significant magnetoelectric effect, which depends on H_{bias} and the spacing between ferromagnetic layers. At $H_{\mathrm{bias}} = 0$, each composite film exhibits an initial high α_E value, much larger than that of the bulk ferroelectric-ferromagnetic composite, which is close to zero,[15,16] and an optimized H_{bias} of each film can be found to reach the maximum value. In a large dc magnetic field, α_E is quite similar in different films. The value of initial α_E is much larger when the spacing is at the minimum. This can be ascribed to the magnetostatic coupling in films. In addition, the magnetoelectric voltage coefficient α_E of the composite thin film tends to increase with the decrease of BST pacing between two neighboring CFO ferromagnetic layers from 29 nm to 51 nm. Because of this spacing, the magnetostatic coupling strength is at the maximum. When the spacing between layers was increased, the magnetostatic coupling strength was reduced and, finally, the effect can be ignored.

In summary, $Ba_{0.8}Sr_{0.2}TiO_3/CoFe_2O_4$ (BST/CFO) magnetoelectric composite thin films of 2-2-type heterostructure have been prepared onto $Pt/Ti/SiO_2/Si$ substrates by a sol-gel process and spin coating technique. The structure of composite thin films is substrate/BST/CFO/.../CFO/BST. The finally prepared composite thin films have good surface and a compact structure without any pore. The composite thin films also exhibit good magnetic and ferroelectric properties. The strength of magnetostatic coupling has a great impact on magnetic and magnetoelectric properties of composite thin films by adjusting the thickness of the BST layer to vary the spacing between ferromagnetic layers. As the magnetostatic coupling strength is increased, the composite films show a better magnetoelectric effect. These observations show that magnetostatic coupling can be an important parameter in the design of magnetoelectric devices.

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