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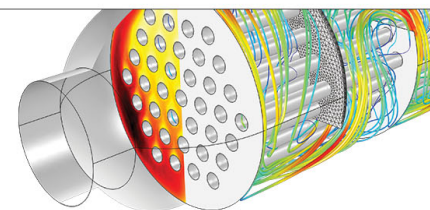
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Direct measurement of magnetoelectric exchange in self-assembled epitaxial BiFeO₃–CoFe₂O₄ nanocomposite thin films

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We report the direct measurement of a magnetoelectric (ME) exchange between magnetostrictive CoFe₂O₄ nanopillars in a piezoelectric BiFeO₃ matrix for single-layer nanocomposite epitaxial thin films grown on (001) SrTiO₃ substrates with SrRuO₃ bottom electrodes. The ME coefficient was measured by a magnetic cantilever method and had a maximum value of ~ 20 mV/cm Oe. The films possessed saturation polarization ($60 \mu\text{C}/\text{cm}^2$) and magnetization (410 emu/cc) properties equivalent to bulk values, with typical hysteresis loops. © 2009 American Institute of Physics. [DOI: 10.1063/1.3138138]

Magnetoelectricity is a physical property that results from an exchange between polar and spin subsystem, i.e., a change in polarization (P) with application of magnetic field (H), or a change in magnetization (M) with applied electric field (E).^{1,2} Magnetoelectric (ME) properties have been reported in ferroelectric-ferromagnetic two-phase composite systems, consisting of piezoelectric and magnetostrictive phases.^{3–8} These two phases were elastically coupled to each other at the interfaces through their strictions.

Two-phase bulk composites have been studied with regards to ME effects. Layered sandwich structures are known to have the highest ME coefficients, with values up to 10 V/cm Oe at quasistatic frequencies.⁸ Zheng *et al.*⁹ deposited epitaxial two phase films that self-assembled into nanopillars of CoFe₂O₄ (CFO) in a BaTiO₃ (BTO) matrix. For two-phase multiferroic thin films, not only have such (1–3) and (3–1) structures (i.e., nanopillars in a second phase matrix) been reported,^{9–17} but many other types of structures with different phase interconnectives have also, such as (0–3) nanoparticles dispersed in a matrix^{18–22} and (2–2) multilayer two-phase composite thin films.^{23,24} Theoretically, the (1–3) structure should be the best type for ME coupling in epitaxial films.²⁵ This is because the constraint stress from the substrate will clamp the CFO layer along the in-plane orientation, making it hard to respond to magnetic fields applied along that direction; whereas, CFO nanopillars oriented out-of-plane have only a small constraint imposed by the substrate, and thus should respond readily to magnetic field.

After self-assembled BTO-CFO nanostructured epitaxial thin films were reported, significant research efforts were expended to determine their ME coupling. In the original work of 2004, a kink was observed in the temperature dependent magnetization at the ferroelectric Curie temperature.⁹ Such a kink was not observed for multilayered heteroepitaxial ferroelectric/ferromagnetic thin films. This was the first in direct observation of ME coupling in two-phase nanocomposite films. Later in 2007,²⁶ the spin of CFO nanopillars in a BiFeO₃ (BFO) matrix was reported to be rotated under modest magnetic fields of $H=700$ Oe, when superimposed with a dc electrical bias. However, direct mea-

surement of the ME coefficient has not yet been reported, probably because of two primary obstacles. First, the resistivities of the self-assembled nanocomposite thin films are low, resulting in a difficulty to pole the ferroelectric matrix. Second the sensitivity of ME composites has a scale effect.²⁷ When a composite thin film has a thickness of $<1 \mu\text{m}$, the ME signal will be $<1 \mu\text{V}$. Thus, if a conventional ME measurement method is used, such as for bulk composites, then the signal will be difficult to separate from the noise induced from the cables and environment, even when using a phase reference.

Here, in this letter, we report self-assembled nanocomposite BFO-CFO epitaxial thin films, which has good polarization and magnetization properties. Then, by using a special method, (i.e., the vibration of a permanent magnet), the ME voltage coefficient of BFO-CFO thin films at 20 mV/cm Oe was directly measured.

We deposited 0.65BiFeO₃–0.35CoFe₂O₄ composite epitaxial thin films by pulsed laser deposition on (001) oriented SrTiO₃ (STO). The thickness of the films was varied from 150 to 2400 nm. The deposition temperature was 700 °C. The films were deposited using a Lambda 305i KrF laser with wavelength of 248 nm, focused to a spot size of 2 mm², and incident on the surface of a target using an energy density of 3 J/cm². The distance between the substrate and target was 6 cm, and the base vacuum of the chamber was $<10^{-5}$ Torr. During film deposition, the oxygen pressure was 90 mTorr. The surface topology of BFO-CFO thin films was studied by atomic force microscopy (AFM) (Veeco 3100). The crystal structure of the films was measured using a Philips X'pert high resolution x-ray diffractometer equipped with a two bounce hybrid monochromator, and an open three-circle Eulerian cradle. The magnetic properties of the CFO layers were measured at 250 K using a superconducting quantum interference device (SQUID) (Quantum Design MPMS magnetometer).

Epitaxy of the BFO-CFO layers on SRO/STO substrates was confirmed by x-ray diffraction (XRD), as shown in Fig. 1(a). From these XRD data, only (0 0 1) peaks can be seen. The peaks from left to right in the inset of Fig. 1(a) were indexed as (004) CFO, (002) BFO, (002) SRO, and (002) STO, respectively. However, the (002) SRO and (002) BFO were quite close, consequently the (002) SRO peak appeared

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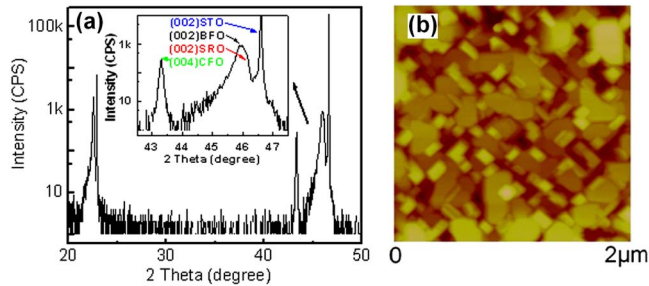


FIG. 1. (Color online) XRD scan and AFM image for a (001) BFO-CFO thin film. (a) XRD line scan over a wide range of angles, demonstrating phase purity and good epitaxy, where the inset is a line scan over a smaller range of angles used to index the peaks and (b) AFM image demonstrating the nanostructures of the films, which consisted of pyramidal CFO nanopillars embedded in a BFO matrix.

as a small hump to the right of the (002) BFO one. The surface topography of the BFO-CFO nanocomposite was measured by AFM, as shown in Fig. 1(b). The CFO phase can be seen to form as pyramidal shaped nanopillars embedded in a BFO matrix. The edges of the CFO nanopillars were oriented along the [110] directions.

The nanocomposite films were found to exhibit both ferroelectric and ferromagnetic properties which were close to bulk value.^{28,29} The polarization hysteresis loop is shown in Fig. 2(a). Please note that the center of the P - E hysteresis loop was shifted positively (i.e., to the right), along the E axis. This might be due to the development of built-in charges between the film and substrate, resulting from interface defects. Such built-in charges between film and substrate are known to make the remnant polarization asymmetric.³⁰ The coercive field was 15 kV/mm, the remnant polarization was 44 $\mu\text{C}/\text{cm}^2$, and the saturation polarization was 60 $\mu\text{C}/\text{cm}^2$. The in-plane and out-of-plane magnetization hysteresis loops are shown in Fig. 2(b), which were measured at 250 K by SQUID. The saturation magnetization was 410 emu/cc, when normalized to the volume fraction of CFO (35%). This number is slightly smaller than bulk CFO, which is 530 emu/cc.²⁹ Along the out-of-plane direction, the coercive field was 3 kOe, which means it is relatively hard to rotate the spin in the out-of-plane direction. Once the spins rotate, they saturate quite readily with increasing H , with a remnant magnetization of 310 emu/cc. However, along the in-plane direction, the coercive field was 1.8 kOe. This means the spins in-plane rotate relatively easily but are harder to saturate. The in-plane remnant magnetization was only 80 emu/cc. This anisotropy of the magnetic

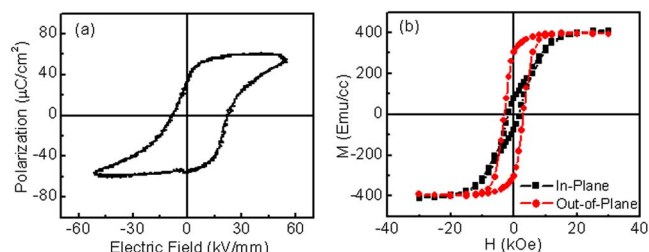


FIG. 2. (Color online) Multiferroic properties of BFO-CFO nanocomposite thin films. (a) Polarization or P - E hysteresis loops, and (b) magnetization or M - H hysteresis loops. The saturation polarization and magnetization were 60 $\mu\text{C}/\text{cm}^2$ and 410 emu/cc, respectively. The magnetization was normalized to the volume fraction of the CFO phase (35%).

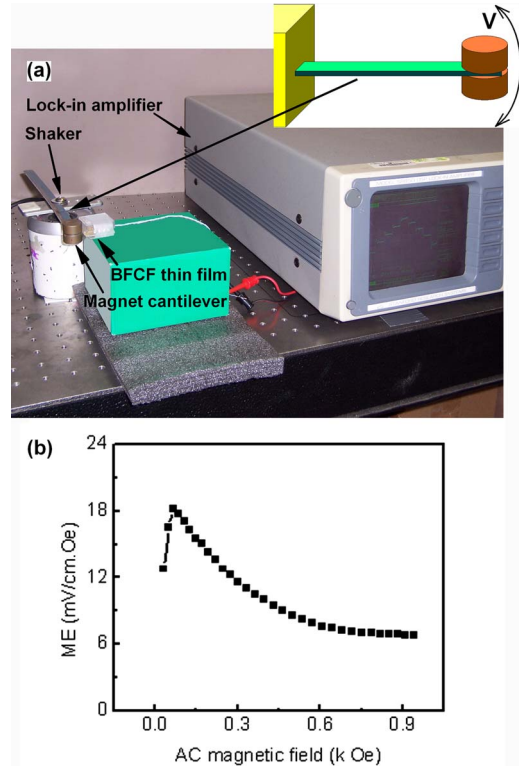


FIG. 3. (Color online) (a) Photograph of our magnetic cantilever ME measurement method, where the inset is a schematic structure of the magnetic cantilever; and (b) the ME coefficient for a self-assembled BFO-CFO single-layered nanocomposite thin film as a function of ac magnetic field amplitude. The maximum value was 18 mV/cm Oe.

behavior is undoubtedly related to the nanopillar structure that is oriented along in out-of-plane directions.

Our method for directly measuring the ME voltage of BFO-CFO thin films is illustrated in Fig. 3. A photograph is given in Fig. 3(a). A shaker was used to generate a vibration at a constant frequency and amplitude, which was then used to excite the vibration of a magnet cantilever. The detailed structure of the magnetic cantilever is illustrated in the inset of Fig. 3(a). Permanent magnets were fixed to both end of a steel slither. By adjusting the input voltage signal to that of the drive of the shaker, the vibration amplitude of the magnetic cantilever was controlled; the larger the vibration amplitude, the larger the ac magnetic field. The relationship between the vibration amplitude of the magnetic cantilever and the value of the induced ac magnetic field was calibrated using a Gauss meter. The BFO-CFO nanocomposite thin film was placed in the center of the two magnets at a distance of 3.5 mm from each of them. The polarization was measured in the out-of-plane direction, and the ac magnetic field was applied along the in-plane one. The ME voltage signal was read by a lock-in amplifier. Using this magnetic cantilever ME measurement method, it was found possible to generate large ac magnetic fields of up to $H_{ac} = 10^3$ Oe. This then made it possible to induce ME voltage responses of larger than 1 mV. By this method, we found it possible to avoid near-field electric coupling to the wires bonded to the sample, which following conventional ME measurement methods have inductive coupling to the ac magnetic field, resulting in enhanced noise.

The ME coefficient of our BFO-CFO nanocomposite thin films is shown as a function of H_{ac} in Fig. 3(b). The ME

coefficient increased quickly with increasing H_{ac} , reaching a maximum value of 18 mV/cm Oe under 100 Oe. With further increment of H_{ac} , the ME coefficient decreased notably. The ME coefficient of bulk PZT-CFO materials has been reported to have a maximum value of 100 mV/cm Oe.⁴ Because of the constraints of the film by the substrate, the piezoelectric and effective piezomagnetic coefficients of the ferroelectric and ferromagnetic phases are known to be lower than the corresponding value for bulk materials,³¹ for example, the d_{33} of commercial PZT ceramic can reach 700 pm/V, but that of BiFeO₃ thin films is only 70 pm/V.³² Accordingly, the ME coefficient of our BFO-CFO nanocomposite thin films is quite reasonable.

In summary, we have deposited epitaxial self-assembled BFO-CFO nanocomposite thin films on (001) SRO/STO. Our results demonstrate that the films were ferroelectric with a saturation polarization of 60 $\mu\text{C}/\text{cm}^2$ and a coercive field of 15 kV/mm, and ferromagnetic with a saturation magnetization of 410 emu/cc. By using a magnetic cantilever ME measurement method, the direct ME coefficient of the BFO-CFO two-phase single-layer nanocomposite thin films was measured and determined to have a maximum value of $V_{ME}=18$ mV/cm Oe.

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