Tunable multiferroic properties in nanocomposite PbTiO₃–CoFe₂O₄ epitaxial thin films

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We report on the synthesis of PbTiO₃–CoFe₂O₄ multiferroic nanocomposites and continuous tuning of their ferroelectric and magnetic properties as a function of the average composition on thin-film composition spreads. The highest dielectric constant and nonlinear dielectric signal was observed at (PbTiO₃)ₓ(−(CoFe₂O₄))₁, where robust magnetism was also observed. Transmission electron microscopy revealed a pancake-shaped epitaxial nanostructure of PbTiO₃ on the order of 30 nm embedded in the matrix of CoFe₂O₄ at this composition. Composition dependent ferroics properties observed here indicate that there is considerable interdiffusion of cations into each other. © 2005 American Institute of Physics. [DOI: 10.1063/1.2041825]

Multiferroic materials are of significant scientific and technological interests. In particular, composite multiferroics can exhibit sizable magnetoelectric (ME) coupling at room temperature, and therefore they have the potential for novel device applications such as sensitive magnetic field sensors. In such systems, the ME effect arises from the elastic coupling between the piezoproperties of the ferromagnetic and ferroelectric components. There have been a number of reports on BaTiO₃–CoFe₂O₄ multiferroic composites and related materials. In these composite systems, eutectic separation of CFO and BTO give rise to the segregation of the two phases. Pursuing such materials in thin film structures is desirable because they offer the possibility to create compositions where the component materials are modulated and coupled at the nanometer level.

Previously, we have reported on investigation of thin film multiferroic compounds in BTO–CFO composition spreads where we identified a composition region which was ferromagnetic and displayed a relatively high dielectric constant at room temperature. In this letter, we report on the microstructure and tunable multiferroic properties of CFO–PbTiO₃(PTO) thin film composition spreads.

In order to create composition spread structures modulated at the nanometer level, we deposited CFO and PTO by laser ablation in the “superlattice spread” geometry where the wedge thickness of each layer equals multiples of the lattice constants of CFO and PTO (Fig. 1). The resulting average composition of the spread varies continuously form pure PTO at one end to pure CFO at the other. The detail of the spread synthesis is described in Ref. 10. (100) MgO substrates were used. The deposition substrate temperature was 600 °C and the oxygen partial pressure was 65 mTorr. The ablation energy was approximately 2 J/cm², and the total thickness at each position on the spread was 300 nm. The sample was approximately 6 mm long in the spread direction.

We have found that by varying the layering configuration and the deposition condition, a variety of different nanocomposite configurations can be obtained. Cross-sectional high-resolution transmission electron microscopy (TEM) was performed at different compositions on various spreads. Figure 2(a) was taken from a spot on a spread where the average composition was approximately 80% PTO and 20% CFO (PTO₀₈₀–CFO₂₀). The wedge thickness of each depos-

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itted layer for this particular spread was 12.6 nm which correspond to roughly 15 unit cells of CFO and 30 units cells of PTO. Pancake-shaped nanostructures of PTO on the order of 30 nm are seen as embedded in the matrix of CFO. In other samples, we have observed structures where one component has formed an ordered array of nanopillars in the matrix of the other component as well as structures where the superlattice configurations have maintained. It is interesting to note that even though we fabricated our samples in a layered manner, the resulting structures have revealed very a different microstructure.

The lattice constants of the end compounds are \( a = 0.839 \) nm for CFO (cubic spinel, \( Fd\bar{3}m \)) and \( a = 0.390 \) nm and \( c = 0.415 \) nm for PTO (low-temperature pseudocubic perovskite, tetragonal \( P4mm \)), and they are expected to grow heteroepitaxially with the MgO substrate (cubic rocksalt, \( Fm\bar{3}m \), \( a = 0.421 \) nm). Figure 2(b) shows the electron diffraction of the same sample as Fig. 2(a) taken along the (100) direction of MgO. Cubic-like PTO and CFO are clearly observed to have an epitaxial relationship \((100)_{\text{MgO}}|(100)_{\text{PTO}}|(100)_{\text{CFO}}\). Although the phase diagram for PTO–CFO is not known, by analogy with BaTiO\(_3\) we expect pseudobinary eutectic separation. The nonequilibrium laser deposition process used here together with the nucleation of phases and the eutectic separation is expected to give rise to complex nanostructures. Details of the dependence of the microstructure on various parameters will be published elsewhere.

Figure 3 shows the mapping of ferromagnetic and ferroelectric properties of a CFO–PTO spread with the same layering scheme as the one used to make the sample shown in Fig. 2. The out-of-plane and in-plane remanent magnetization were used as measures of ferromagnetism and determined as a function of average composition using a room-temperature scanning superconducting quantum interference device (SQUID) microscope [Fig. 3(a)]. The magnetization value is defined here as the magnetic moment per film volume. At the pure CFO end, the film is out-of-plane magnetized. As a small amount of PTO is introduced in the structure, there is a sudden increase in in-plane magnetization indicating a dramatic change in anisotropy. We attribute this to the diffusion of Pb and Ti ions into CFO leading to a metastable solid solution and the subsequent change in magnetocrystalline anisotropy as well as the microstructure of the material. TEM of this region showed CFO layers to be nanocrystalline anisotropy as well as the microstructure of the device temperature scanning superconducting quantum interference device. For the present measurement, the amplitude of this ac voltage was 16 V. The nonlinear signal here represents the tunability of the dielectric constant \( \varepsilon \) which is measured as \( \delta E / \varepsilon E \), where \( \delta E \) is the change in the resonant frequency of the microwave microcrowave microscopy cavity due to the applied electric field \( E \) in the vertical direction due to a voltage \( V_{\text{tip-substrate}} \) applied between the microscope tip and an electrode on the back of the sample substrate. For the present measurement, the amplitude of this ac voltage was 16 V. Overall, both the linear dielectric constant and the nonlinear dielectric signal show a decreasing trend toward the low PTO concentration as expected. However, they display an unexpected peak at approximately PTO\(_{85}\)–CFO\(_{15}\). To understand this behavior, we performed scanning x-ray microdiffraction (using a D8 DISCOVER with GADDS for combinatorial screening by Bruker-AXS). Figure 3(a) shows the x-ray diffraction spectra taken at room temperature with a 500 \( \mu m \) diameter beam in the 2\( \theta \) range which includes the PTO (200) and (002) peaks in the composition range of PTO to PTO\(_{90}\)–CFO\(_{10}\). Continuous shifts in the peaks are observed as a function of the average composition, and the peaks appear to merge at the composition of PTO\(_{85}\)–CFO\(_{15}\) indicating the occurrence of a structural transition. The linear dielectric constant \( \varepsilon \) and the nonlinear dielectric signal were measured across the spread using a scanning microwave microscope operating at 1 GHz [Fig. 3(b)]. The nonlinear signal here represents the tunability of the dielectric constant \( \delta \varepsilon / \varepsilon E \), which is measured as \( \delta \varepsilon / \varepsilon E \), where \( \delta \varepsilon / \varepsilon E \) is the change in the resonant frequency of the microwave microcavity due to the applied electric field \( E \). For the present measurement, the amplitude of this ac voltage was 16 V.
has revealed a trace of CFO with shifts in the PTO peaks. Because of the complex nonequilibrium nature of our nano-composite growth process, it is not unreasonable to expect a continuous cation substitution between PTO and CFO across the spread well into the region where the separated CFO matrix is clearly also present. We found this shift in the transition temperature to be highly reproducible from sample to sample.

Further investigation of the interdiffusion near the CFO/PTO interfaces is currently underway. The result of the ME effect measurement will be published elsewhere.25

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FIG. 4. Structural changes across the spread. (a) X-ray microdiffraction of the PbTiO₃-rich side of the spread sample. Upon introducing CoFe₂O₄, the (200) and (002) reflections of the twinned tetragonal PbTiO₃ are seen to continuously shift and eventually merge at $2\theta=45.8^\circ$. Inset shows the continuous shift in this phase transition temperature as a function of the composition across the spread.

tice constant of this composition is in good agreement with the lattice constant of the cubic phase of pure PTO. Thus, the peaks in the room temperature dielectric properties can be identified as the composition where the PTO phase is undergoing a cubic to tetragonal transition at room temperature. We have also performed variable temperature scanning microdiffraction to confirm that the transition temperature (defined to be the temperature at which the tetragonal peaks merge) shifts continuously across the spread in this composition region [Fig. 3(b)]. Based on the fact that we see enhanced dielectric properties and the structural change, we associate this transition to be the ferroelectric Curie temperature. Thus, composition near PTO₈₅–CFO₁₅ has optimum biferroic properties: it shows substantial magnetism, while displaying the onset of ferroelectricity and peaking of the piezoelectric coefficient.²⁰

There are several factors that could give rise to the continuous shift in the transition temperature as a function of the composition. In epitaxial nanocomposite geometries, the mechanical interaction between the components is known to introduce stress in each other, resulting in a shift in the Curie temperature.²¹ But the observed shift from $T_C$ (pure PTO) $\sim$ 500 °C down to near room temperature is substantial, and stress itself cannot be used to explain such a large shift (Fig. 4). Another possibility is the ferroelectric size effect in our nanometer-sized PTO grains.²² However, the TEM micrograph of the PTO₈₀–CFO₂₀ (where the Curie temperature approximately equals room temperature) region seen in Fig. 2(a) clearly shows the grain size to be of the order of 30 nm. According to the literature, one would not expect to see a significantly reduced $T_C$ until the grain size decreases down to about 20 nm.²³ This is in clear contrast to the microstructure in our nanocomposite.

We believe the dominant effect giving rise to the shift in $T_C$ is the diffusion of Fe and Co ions into PTO leading to a metastable solid solution. In such a solid solution system, $T_C$ can be dramatically affected by even small additions of solute atoms.²⁴ TEM of a PTO₈₅–CFO₅ thin film from the spread has shown it to be a single tetragonal phase, although x-ray diffraction of a bulk PTO₈₅–CFO₅ sample we made