

A modified sol-gel process for multiferroic nanocomposite films

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Multiferroic CoFe_2O_4 – $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (CFO-PZT) composite films with nanoscale mixture of the two phases were prepared by a modified sol-gel process, in which a mixed precursor solution of both CFO and PZT was used. X-ray diffraction and transmission electron microscopy examinations revealed the coexistence of perovskite PZT and spinel CFO that were mixed in nanoscale with mean grain sizes of 5–10 nm. Magnetic properties of the CFO-PZT nanocomposite were examined, which were consistent with their microstructures. The magnetoelectric coupling between CFO and PZT was demonstrated by an external magnetic field induced electric polarization change. This modified sol-gel processing provides an alternative for multiferroic composite films, which is simpler and easier to control compared to the conventional layer-layer sol-gel process for multiferroic composite films. © 2007 American Institute of Physics. [DOI: [10.1063/1.2800804](https://doi.org/10.1063/1.2800804)]

I. INTRODUCTION

Multiferroic composite materials consisting of both ferro/ferrimagnetic and ferroelectric phases have drawn an increasing amount of interest due to their capability of efficient energy transfer between electric energy and magnetic energy, and their potential applications in many multifunctional devices.^{1–8} Such materials can display the magnetoelectric (ME) effect, a dielectric polarization variation as a response to an applied magnetic field, or an induced magnetization by an external electric field. Several synthesis methods have been developed for multiferroic composite materials in the bulk form, such as eutectic unidirectional solidification,⁹ ceramic sintering,¹⁰ glue bonded laminates,¹¹ tape casting,¹² and hot molding,¹³ while pulsed laser deposition (PLD),^{4,7,14–18} physical vapor deposition,¹⁹ and sol-gel processing have been used for synthesizing multiferroic composite film materials.^{20–23}

Achieving strong magnetoelectric coupling in multiferroic composite films has been challenging. Zavaliche *et al.*^{7,14} reported that multiferroic composite films with self-assembled CoFe_2O_4 spinel nanopillars in a BaTiO_3 perovskite matrix on single crystalline SrTiO_3 substrate was synthesized by pulsed laser deposition, and the magnetoelectric coupling was demonstrated by observing magnetization change at the ferroelectric Curie temperature⁷ and magnetization reversal induced by applying electric field.¹⁴ Wan *et al.*²⁴ reported CoFe_2O_4 – $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (CFO-PZT) multiferroic composite films with a ME voltage coefficient of 220 mV/cm Oe at magnetic frequency of 1 kHz, in which the CFO and PZT phases were spin coated sequentially by

sol-gel process. Zhou *et al.* also reported layer by layer CoFe_2O_4 – $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ and $\text{Co}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4$ – $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ multiferroic films, which were grown by PLD (Ref. 15) and sol-gel,²⁵ respectively. For reported sol-gel processes for multiferroic composite films, the two phases (ferrimagnetic and ferroelectric phases) were typically deposited from different sources, and the nanocomposite multiferroic films were formed by a spontaneous phase separation process that occurred during the deposition or annealing process.^{7,14,15,26–28} It was found that spontaneous phase separation could occur in the sol-gel processed CFO-PZT nanocomposite film during the annealing step, leading to 0-3-type nanocomposite film structure with the less-resistive CFO phase embedded in PZT matrix. This 0-3-type microstructure with less leakage is critical in achieving magnetoelectric coupling in sol-gel processed ME composite films.

In this work, we report a modified sol-gel synthesis method for nanocomposite multiferroic thin film with nanoscale mixed CFO and PZT phase, in which the precursors of both the ferrimagnetic and ferroelectric phases were mixed before spin coating. The spin coating of the mixed precursor solution of the ferrimagnetic and ferroelectric phases allows for nanoscale mixing of the subsequent multiferroic composite phases which leads to a strong ME coupling.

II. EXPERIMENT

The nanocomposite thin films studied here were prepared by a sol-gel process and spin-coating technique. A 0.2M PZT precursor with the molar ratio of 1:0.52:0.48 was prepared by dissolving lead acetate $\text{Pb}(\text{CH}_3\text{CO}_2)_2\text{H}_2\text{O}$, zirconium propoxide $\text{Zr}(\text{CH}_2\text{CH}_2\text{CH}_3\text{O})_4$, and titanium butoxide $\text{Ti}(\text{C}_4\text{H}_9\text{O})_4$ into 2-methoxyethanol. Also, cobalt acetate

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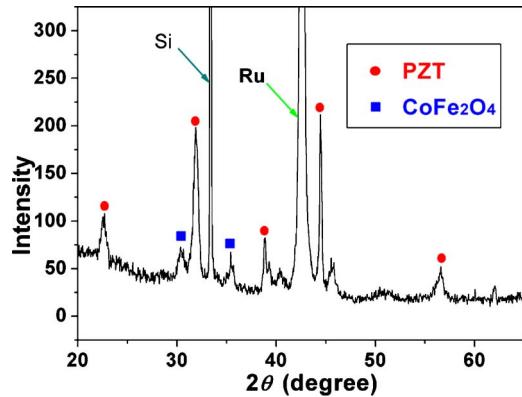


FIG. 1. (Color online) X-ray diffraction pattern of multiferroic CFO-PZT nanocomposite thin film.

$\text{Co}(\text{CH}_3\text{CO}_2)_2$ and iron acetate $\text{Fe}(\text{CH}_3\text{CO}_2)_2\text{H}_2\text{O}$ were dissolved into 2-methoxyethanol to derive 0.1M CFO precursor with molar ratio of 1:2. Then, both of precursor solutions for PZT and CFO were mixed together with volume ratio of 1:2 and stirred continuously to form a mixed PZT-CFO precursor solution. The mixed solution was spin coated onto Ru/SiO₂/Si substrate with a thickness of 0.5 mm at 2000 rpm for 20 s and subsequently baked at 90 °C for 5 min and 300 °C for 5 min. This spinning coating and baking procedures were repeated twice. After being calcined at 800 °C for 10 min in air, nanocomposite PZT-CFO films with a thickness of 100 nm were obtained. It is expected that the volumetric ratio between the CFO phase and PZT phase is 0.52:0.48 in the final nanocomposite films.

III. RESULTS AND DISCUSSIONS

Phase structure characterization of the nanocomposite thin films was performed with x-ray diffraction (XRD) using Cu $K\alpha$ radiation. Figure 1 shows the typical XRD pattern of nanocomposite thin film. Perovskite PZT phase and the spinel CFO phase can be identified without obvious preferential crystallographic orientations. Clearly, mixing the precursor solutions of the CFO phase and the PZT phase before spin coating does not lead to obvious adverse effect on the resultant CFO phase and the PZT phase. High-resolution transmission electron microscopy (TEM) examination on these multiferroic films was performed to obtain further microstructure information. Figure 2(a) shows the cross section image of nanocomposite thin film in which a well-defined interface between substrate and PZT-CFO layer with a thickness of

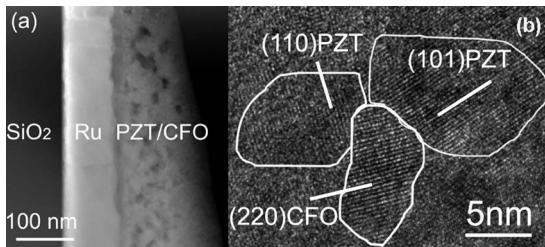


FIG. 2. Cross-section scanning electron microscopy (STEM) image (a) and HRTEM image (b) of multiferroic CFO-PZT nanocomposite thin film.

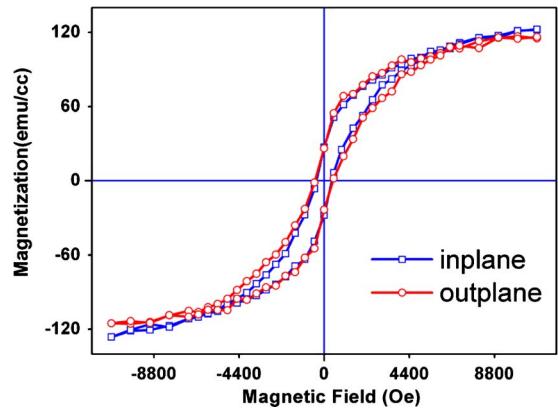


FIG. 3. (Color online) Magnetic hysteresis loops of CFO-PZT nanocomposite thin film.

~100 nm was observed. Both the PZT phase and CFO phase can be identified, together with some amorphous phase(s), as shown in Fig. 2(b), which is an indication of insufficient annealing. The presence of the amorphous phase(s) could lead to reduced magnetoelectric coupling between ferroelectric and magnetic phases. In addition, the PZT and CFO phases show well-defined grains with their grain sizes in the range of 5–10 nm with CFO nanograins nearly surrounded by PZT nanograins, which indicates nanoscale mixture of the CFO phase and PZT phase. This 5–10 nm scale mixture of the magnetic phase and the ferroelectric phase, which was not reported before, could be due to the spontaneous phase separation in the spin-coated mixed CFO and PZT precursor layer during the short annealing process. This nanoscale mixing of the CFO and PZT phases could lead to significantly reduced eddy current loss and lowered leakage current path in multiferroic films and, therefore, an enhanced magnetoelectric coupling.

Magnetic properties of the multiferroic nanocomposite thin films were characterized with vibrating sample magnetometer with the applied magnetic fields perpendicular and parallel to the thickness of the film at room temperature, as shown in Fig. 3. The CFO-PZT multiferroic nanocomposite films show very similar magnetic hysteresis loops for both in-plane and out-plane orientations with an overall saturation magnetization of 118 emu/cm³ for the whole film. This magnetization is relatively low even after considering the volume fraction effect of CFO phase, which could be due to the small particle sizes of the CFO phase within the PZT matrix, as well as due to the existence of amorphous phase in the film. The similarity in the magnetic hysteresis loops for both in-plane and out-plane orientations is consistent with the TEM observations that the CFO nanograins are dispersed in the PZT phase to form isolated CFO nanograin islands with a 0-3 connection.

The ferroelectric properties of the nanocomposite thin films were also measured using a Radiant Precision LC test system. Figure 4 shows the polarization versus electric field (P - E) hysteresis loops of a PZT-CFO nanocomposite film (at zero magnetic field) and a pure PZT film which was obtained by sol-gel process under similar conditions. The saturation polarization (P_s) and remanent polarization (P_r) of the PZT-CFO film are 18.5 and 8.3 $\mu\text{C}/\text{cm}^2$, respectively, compared

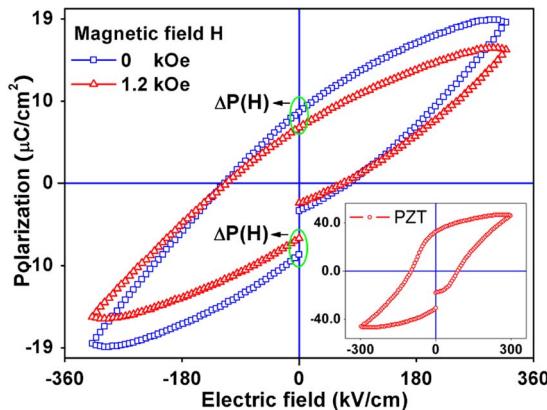


FIG. 4. (Color online) Polarization-electric field hysteresis loops of the multiferroic CFO-PZT nanocomposite film and pure PZT film.

to a P_s of $45 \mu\text{C}/\text{cm}^2$ and P_r of $32.8 \mu\text{C}/\text{cm}^2$ for the pure PZT film. The reduction of the P_r and P_s values of CFO-PZT nanocomposite thin film is expected to be due to the presence of nonferroelectric and less-resistive CFO phase.

The magnetoelectric coupling in these CFO-PZT films was demonstrated through the measurement of magnetic field induced change of the electric polarization by measuring the P - E hysteresis under different magnetic fields, similar to what was done in Refs. 14 and 16. As shown in Fig. 4, the P - E hysteresis loops were changed with the application of a 1200 Oe magnetic field perpendicular to the film surface. The remnant polarization values were reduced by 22%, with the presence of a 1200 Oe magnetic field applied perpendicular to the thin film. This remnant polarization reduction of 22% is much larger than the polarization measurement error of $<2\%$ for the P - E hysteresis loop.

In summary, multiferroic CFO-PZT nanocomposite thin film with the average grain size of 5–10 nm has been synthesized with a modified sol-gel process in which a mixed precursor solution of the CFO phase and the PZT phase was used. Strong magnetoelectric coupling was observed in this nanoscale mixed CFO and PZT nanocomposite film. This modified sol-gel processing method provides a simpler alternative for synthesizing multiferroic composite films which is easier to control compared to the conventional layer-layer sol-gel process for multiferroic composite films.

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