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Electric and magnetic properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$–$CoFe_2O_4$ particle composite thin film on the $SrTiO_3$ substrate

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Abstract

We deposited a thin epitaxial $Pb(Zr_{0.52}Ti_{0.48})O_3$ (PZT) layer on the (0 0 1) $SrTiO_3$ (STO) substrate doped with Nb (0.5 wt.%), then grew composite thin film of $CoFe_2O_4$ (CFO) and PZT phases on it. X-ray diffraction and high resolution transmission electron microscopy showed that the PZT and CFO phases in the film had perfect epitaxial structures. CFO nanoparticles were embedded in PZT matrix randomly, which was useful to enhance the insulativity of the composite film. The composite thin film exhibited good ferromagnetic and ferroelectric properties. The dielectric constants of the composite thin film kept unchangeable in a wide bias electric field, but increased in a magnetic field, namely, magnetodielectric effect. The possible reasons for the magnetodielectric effect were discussed.

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1. Introduction

Multiferroic materials, which display simultaneous electric and magnetic orders, have attracted tremendous attention due to their fundamental physics background and large potential applications in the multifunctional devices such as transducers, sensors and multistate storage. Such materials can exhibit a spontaneous dielectric polarization induced by an external magnetic field, or a magnetization induced by an applied electric field, i.e., magnetoelectric (ME) effect [1,2]. The ME effect in all currently known single-phase materials is weak and/or appears at low temperature [1,2]. In comparison, multiphase artificial composites of piezoelectric and magnetostrictive phases exhibit relative high ME responses with the product of the each phases [3,4]. Recently, much attention has been paid to nanostructured materials for their significant promise in microelectronic devices and integrated units [5–14]. Different nanostructures of the thin films have been demonstrated. Particle composite thin films were prepared by a sol–gel process and spin-coating method [6] or chemical solution deposition technique [7]. Double-layered and multi-layered

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thin films composed of piezoelectric and piezomagnetic components were obtained by a pulsed-laser deposition [9,10]. These films showed magnetic and ferroelectric properties as well as ME coupling. Other nanostructures of the composite thin films were formed by ferrite nanopillars embedded in a ferroelectric matrix [11–13]. Different surface and column features were obtained in the magnetoelectric composite thin films at different experimental conditions. By self-assembly process, rectangular shaped $CoFe_2O_4$ (CFO) nanopillars formed in $BiFeO_3$ matrix on (0 0 1) $SrTiO_3$ (STO) substrate, while on (1 1 1) STO substrate, $BiFeO_3$ formed triangular-shaped nanopillars embedded in CFO matrix [12]. But in the $PbTiO_3$–CFO composites, rod-like CFO nanopillars, triangular-shaped $PbTiO_3$ columns and even labyrinth-like morphology were observed on the different substrates [13]. However, when the ME coupling is purely through elastic interactions, the ME effect in the layered composite structures is weak due to the clamping effect of the substrate [9,10]. In the structures of CFO nanopillars in the ferroelectric matrix, there exists much larger ME coupling than in the layered composite films calculated by the Green's function method [15]. But electric polarizing becomes difficult and direct ME measurement of such a column structure would be a trouble thing because of the poorly insulating CFO pillars penetrating through the film.

At room temperature, $Pb(Zr,Ti)O_3$ (PZT) has a perovskite structure with lattice parameters $a_1 = 0.403$ nm and $c_1 = 0.415$ nm, while CFO has a spinel structure with a lattice parameter $a_2 = 0.839$ nm, approximate twice that of PZT. $SrTiO_3$ (STO) is commonly selected as a substrate [11–14] for its similar structure and lattice parameter of $a_s = 0.3905$ nm. It is possible to grow epitaxial composite thin film on the STO substrate. But the elastic interactions arise in the composite films due to epitaxy, resulting in the strain corresponding to a pure dilatation, $\varepsilon_1 = (a_1 - a_s)/a_s = 0.025$ for PZT and $\varepsilon_2 = (a_2/2 - a_s)/a_s = 0.067$ for CFO.

In the present work, we firstly grew the epitaxial PZT thin film on the STO substrate in consideration of its high resistivity, small lattice mismatch with STO, low {1 0 0} surface energy and good wettability on STO [12,16]. Then we deposited multiferroic layer from the composite ceramic target to form the PZT–CFO nanoparticle composite thin film. We analyzed the magnetic and electric properties of ME PZT–CFO composite thin films. The possible reasons for the magnetodielectric effect were discussed.

2. Experiment

The stoichiometric targets of $0.35CoFe_2O_4$-$0.65PbZr_{0.52}Ti_{0.48}O_3$ and $PbZr_{0.52}Ti_{0.48}O_3$ (PZT), in which Pb was over 10% to avoid Pb vacancies for its volatilizing during sintering and depositing, were calcined by a conventional solid reaction sintering processing. The films were prepared in a pulsed-laser deposition system with a KrF ($\lambda = 248$ nm) exciter laser. The experiment was performed with an energy density of $\sim$2.0 J/cm^2 and repetition rate of 13 Hz (0 0 1)-STO doped with Nb (0.5 wt.%) was used as substrate as well as the bottom electrode. The substrate rotated while depositing to avoid the inhomegeneity of the thickness and element stoichiometry. The deposition chamber was pumped to 6×10^{-5} Pa before preparing the thin films and high pure oxygen was used to keep the pressure 15 Pa in the chamber while depositing. We first deposited a thin PZT layer on the STO substrate for the low {0 0 1} surface energy of the perovskites [12] and the low lattice mismatch between PZT and STO, then deposited the multiferroic layer from the composite ceramic target. The substrate temperature was kept 630 °C. After deposition, the samples were cooled to room temperature at a rate of 6–7 °C/min in 200 Pa oxygen ambient.

The crystallographic properties of the prepared thin films were checked by X-ray diffraction (XRD). The film morphology was investigated by scanning electron micrography (SEM, Hitachi S-5500). And the structure was checked by a transmission electron microscopy (TEM, FEI TECNAI F30). Magnetization measurements were performed on a superconducting quantum interference device (SQUID) (MPMS-7 Quantum Design) magnetometer. The electric properties were measured between two Pt electrode dots [10], equivalently measuring two capacitors connected in series. A TFAnalyzer 2000 ferroelectric testing unit was employed to investigate the polarization-electric field hysteresis loops and dielectric constants.

3. Results and discussion

Fig. 1 shows typical X-ray diffraction spectra of the films. The diffraction peaks were assigned to (0 0 1)-oriented spinel CFO and perovskite PZT besides (0 0 1) peaks from the STO substrate, indicating preferred (0 0 l) crystallographic growth in the film. The CFO (0 0 4) and PZT (0 0 2) peaks almost overlap for their close diffraction lines and low intensity of CFO, while CFO (0 0 8) and PZT (0 0 4) peaks clearly separate from each other for their