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Abstract

Nd_{0.1}Bi_{0.9}FeO₃ / Bi₂FeMnO₆ bilayered films were deposited on Pt/Ti/SiO₂ / Si substrate by pulsed laser deposition method. BiFeO₃ is antiferromagnet while BiMnO₃ is ferromagnet, the ordering of –Mn–O–Fe–O–Mn– is expected, which will induce the ferromagnetic interaction in the film. The film shows typical ferromagnetic properties with the transition temperature of T_c of 440 K. The room temperature (RT) ferroelectric polarization was also observed, suggesting that the film is a promising RT multiferroism.

Keywords

Room, temperature, multiferroic, properties, BiFeO₃, Bi₂FeMnO₆, bilayered, films

Disciplines

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Room temperature multiferroic properties of Nd:BiFeO₃/Bi₂FeMnO₆ bilayered films

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Nd_{0.1}Bi_{0.9}FeO₃/Bi₂FeMnO₆ bilayered films were deposited on Pt/Ti/SiO₂/Si substrate by pulsed laser deposition method. BiFeO₃ is antiferromagnet while BiMnO₃ is ferromagnet, the ordering of –Mn–O–Fe–O–Mn– is expected, which will induce the ferromagnetic interaction in the film. The film shows typical ferromagnetic properties with the transition temperature of T_c of 440 K. The room temperature (RT) ferroelectric polarization was also observed, suggesting that the film is a promising RT multiferroism. © 2009 American Institute of Physics. [doi:10.1063/1.3271032]

Recently, multiferroic materials with the magnetoelectric coupling of ferroelectric (or antiferroelectric) properties and ferromagnetic (or antiferromagnetic) properties have attracted a lot of attention.^{1–4} Among them, BiFeO₃ has been studied intensively because it is one of the very few materials that exhibit multiferroic properties at room temperature (RT).^{5–8} For such ABO₃ perovskite structured ferroelectric materials, they usually show antiferromagnetic order because the same B site magnetic element except BiMnO₃ is ferromagnet. While for the A₂BB'O₆ double perovskite oxides, the combination between B and B' give rise to a ferromagnetic coupling. They are also expected to be multiferroic materials. The ferroelectric polarization is induced by the distortion, which usually cause a lower symmetry. For device application, a large magnetoelectric effect is expected in the BiFeO₃ and bismuth-based double perovskite oxides (BiBB'O₆), many of which have aroused great interest such as Bi₂NiMnO₆^{9,10} and BiFeO₃–BiCrO₃.^{11–13} But as we know, few researches are focused on Bi₂FeMnO₆. We believe it is particularly interesting to investigate the multilayered films containing Nd:BiFeO₃ and Bi₂FeMnO₆ nanolayers. In the former research, the doping of Nd was proven to further improve the ferroelectricity so the Nd is chosen. According to Goodenough–Kanamori rules, the 180° –Fe³⁺–O–Mn³⁺– bonds is quasistatic, partly because the strong Jahn–Teller uniaxial strain in an octahedral site. In the as-grown film, it includes the diamagnetic contribution of substrate, the paramagnetic contribution of Nd, the antiferromagnetic contribution of BiFeO₃, and the couplings of –Fe–O–Mn–. The ferromagnetism is expected to overcome the other effects in the as-designed films.

In this study, Nd_{0.1}Bi_{0.9}FeO₃ (Nd:BiFeO₃), Bi₂FeMnO₆, and bilayered Nd:BiFeO₃/Bi₂FeMnO₆ films on Pt/Ti/SiO₂/Si substrate were fabricated. The films were deposited using a pulsed laser deposition (PLD) system. Third harmonic generation of neodymium doped yttrium aluminum garnet laser with a wavelength of 355 nm and a repetition

rate of 10 Hz was used as the laser source. The ceramic targets were fabricated by a traditional solid state reaction. The starting materials of Bi₂O₃, Fe₃O₄, Nd₂O₃, and MnCO₃ were weighed according to the molecular mole ratio with 10 mol % extra Bi₂O₃. They were mixed, pressed into pellets, and sintered at 800 °C for 3 h. Then the ceramics were crushed, ground, pressed into pellets, and sintered again at 880 °C for 1 h. Nd:BiFeO₃ films were fabricated at 550–580 °C with 200 mTorr dynamic oxygen pressure, Bi₂FeMnO₆ films were fabricated at 550–580 °C with ~10^{–5} Torr.

The phases of the films were determined by x-ray diffraction (XRD) using Cu K α radiation. The surface morphology was studied using an atomic force microscope. Pt upper electrodes with an area of 0.0314 mm² were deposited by magnetron sputtering through a metal shadow mask. The ferroelectric properties were measured at RT by an aixACCT EASY CHECK 300 ferroelectric tester. The dielectric properties were measured using a HP4248 LCR meter. Magnetic properties were investigated using a vibrating sample magnetometer.

The XRD patterns of the Nd:BiFeO₃/Bi₂FeMnO₆ and Nd:BiFeO₃ films are shown in Fig. 1. Both Nd:BiFeO₃ and Bi₂FeMnO₆ phases were observed in the bilayered film, and there are not other second phases except some peaks from

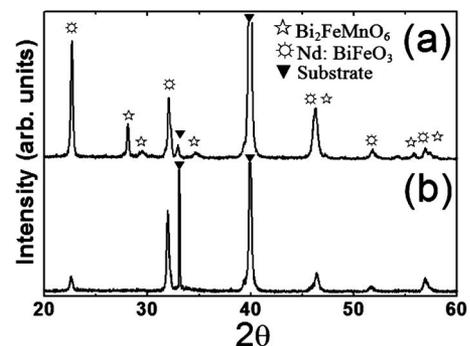


FIG. 1. XRD patterns of (a) Nd:BiFeO₃/Bi₂FeMnO₆ and (b) Nd:BiFeO₃ films.

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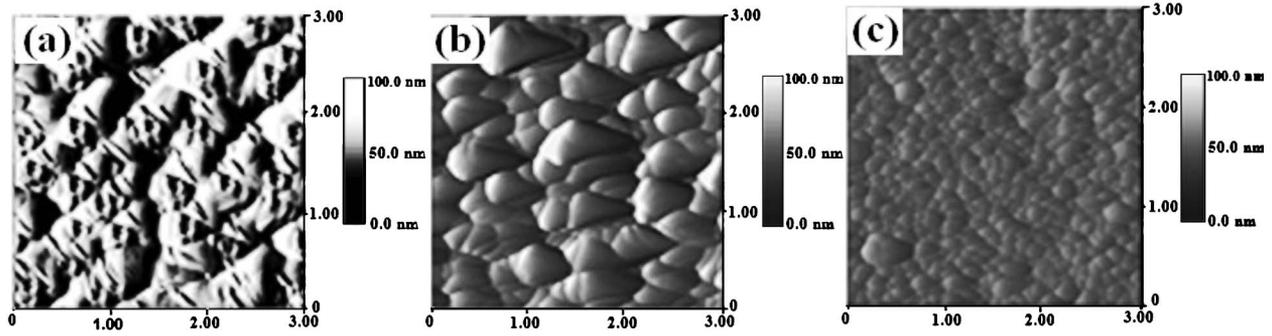


FIG. 2. Surface morphology of (a) Nd:BiFeO₃/Bi₂FeMnO₆, (b) Bi₂FeMnO₆, and (c) Nd:BiFeO₃.

the Pt/Ti/SiO₂/Si substrate. For Bi₂FeMnO₆ films, it shows complicated structure when deposited at different conditions. Bi *et al.*¹⁴ has calculated three structures of Bi₂FeMnO₆ with the space group of Pm $\bar{3}$ m, R3, and C2. It was observed in our experiments for Bi₂FeMnO₆ films which will be showed elsewhere.

The surface morphology of the Nd:BiFeO₃/Bi₂FeMnO₆ and Nd:BiFeO₃ films were studied, as shown in Fig. 2. It can be found that root-mean-square roughness (R_{rms}) and grain size (S) are different: R_{rms} (Nd:BiFeO₃), $<R_{\text{rms}}$ (Nd:BiFeO₃/Bi₂FeMnO₆), $<R_{\text{rms}}$ (Bi₂FeMnO₆), S (Nd:BiFeO₃), $<S$ (Nd:BiFeO₃/Bi₂FeMnO₆), $<S$ (Bi₂FeMnO₆). Figure 2(a) revealed the morphology of Nd:BiFeO₃ film on the Bi₂FeMnO₆ Pt/Ti/SiO₂/Si, which indicated that Nd:BiFeO₃ had a larger growth rate on Bi₂FeMnO₆ than on Pt/Ti/SiO₂/Si substrate.

Figure 3(a) shows ferroelectric hysteresis loops of the Nd:BiFeO₃/Bi₂FeMnO₆ film, the top inset shows the polarization fatigue as a function of switching cycles up to 10⁸ and the below inset shows frequency dependence of the real part of dielectric permittivity. The remnant polarization P_r is 54 $\mu\text{C}/\text{cm}^2$ and E_c is 237 kV/cm. Some anomalies were observed in the P-E loop. The loop is asymmetry and the polarization decreased as the increasing of the electric field, which was also observed in Ref. 15 in the case of low frequency. It can be caused by many effects but some of them can be neglected like the macroscopic electrode influence and nonuniform polarization on the surface of the film. We consider that there are two main reasons. The film is insulating so there is no movable carriers to balance the bound charge. Therefore, the polarization gradient will be arisen in

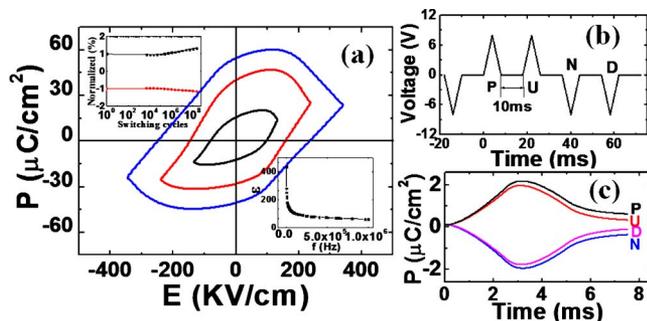


FIG. 3. (Color online) Ferroelectric characterization of Nd:BiFeO₃/Bi₂FeMnO₆ film. (a) Ferroelectric hysteresis loops, the polarization fatigue as a function of switching cycles (top inset) and the frequency dependence of the real part of dielectric permittivity (below inset). (b) PUND waveform and (c) corresponding switching polarization.

the film and induced the depolarization field. In addition, there are inhomogeneous domains with different coercivity in the film, some of which are difficult to switch with applied field. Evidence can also be seen in the fatigue results, which showed that the polarization increased with the increasing of the switching cycles. The fatigue can be caused by domain nucleation, domain wall pinning due to space charges or oxygen vacancies, interface between electrode and film, thermodynamic history of the sample, and so on. For the unusual profile of fatigue (polarization increased with the increasing of switching cycles), we consider the different domain wall played important roles during the polarization reversal. Frequency dependence of the real part of the permittivity was measured at RT. There is a notable increase at low frequencies [as shown in bottom of Fig. 3(a)]. In such bilayered films, it is believed that there are space charges at the interface between the two layers of Nd:BiFeO₃ and Bi₂FeMnO₆, which will affect the ferroelectric properties.¹⁶ As the definition of ferroelectricity is strict, we have also measured the so-called positive-up-negative-down test.¹⁷ The applied voltage waveform is shown in Fig. 3(b). The switching polarization was observed using the triangle waveform as a function of time, as shown in Fig. 3(c).

Figure 4(a) shows the magnetic moment versus magnetic field loops of the Nd:BiFeO₃/Bi₂FeMnO₆ film measured at RT and 5 K. The RT magnetic field dependence of “in-plane” (H_{\parallel}) and “out-of-plane” (H_{\perp}) magnetization are also compared. The two loops show clearly magnetic anisotropy. The results suggest that the sample has magnetoelastic effects. The hysteresis was observed both in RT and 5 K loop. The film shows typical ferromagnetic properties and a high saturated magnetization (25 emu/cm^3 at RT and 83 emu/cm^3 at 5 K). The profiles especially the RT loop were affected by the substrate, which has strong diamagnetic signals. All the data presented here were collected by subtracting the background of the substrate from the raw data. The saturation magnetization $M_s(T)/M_s(0)$ as a function of temperature (T) was measured below RT at 0.5 T, as shown in Fig. 4(b). The magnetization shows $T^{1.6}$ dependence below RT. The temperature dependence of magnetization in saturation could be described by $M_s(T) = M_s(0)[1 - b(T/T_c)^{1.6}]$ with the best fit for b value of $1.02 \pm 0.11 \times 10^{-4} \text{ K}^{-1.6}$. This fit gives an estimated ferromagnetic transition temperature of $T_c = 440 \text{ K}$. Based on the hysteresis loop measured at 5 K, the average magnetons per B-site cation are $4.49\mu_B$. This value is consistent with those anticipated for high-spin states of Mn³⁺ and Fe³⁺ ions. The observed ferromagnetism may be the result of a 5° canted antiferromagnetic ordering that

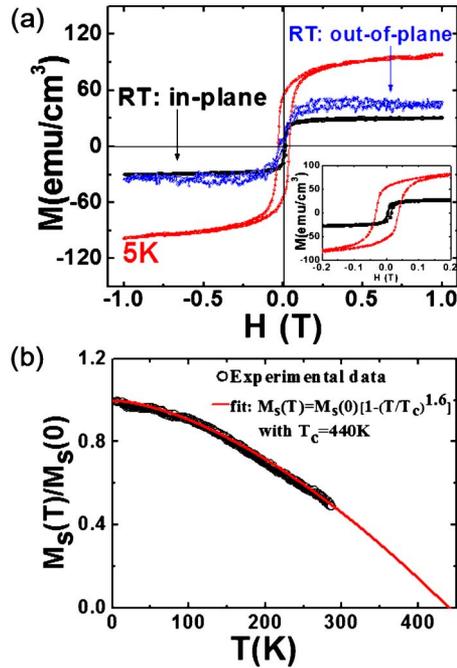


FIG. 4. (Color online) (a) Magnetization curves measured at RT and 5 K. (b) Plot of normalized magnetization $M_s(T)/M_s(0)$ against temperature (t) at 0.5 T.

leaves a small net magnetic moment and modest Curie temperature.^{18,19}

In summary, we fabricated the Nd:BiFeO₃/Bi₂FeMnO₆ bilayered films on Pt/Ti/SiO₂/Si substrate by PLD method. The film showed good ferroelectric properties with P_r and E_c values of 54 $\mu\text{C}/\text{cm}^2$ and 237 kV/cm, respectively. The magnetic measurement revealed ferromagnetic properties of the bilayered film. The ferromagnetic transition temperature of T_c was estimated to be 440 K. The hysteresis in P-E loop and M-H loop revealed that the coexist of ferroelectric and ferromagnetic properties at RT. There are some anomalies observed in P-E loop and fatigue measurement which are still to be investigated thoroughly.

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