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Abstract

$Nd_{0.1}Bi_{0.9}FeO_3$ /Bi_2FeMnO_6 bilayered films were deposited on Pt/Ti/SiO_2 / Si substrate by pulsed laser deposition method. $BiFeO_3$ is antiferromagnet while $BiMnO_3$ is ferromagnet, the ordering of –Mn–O–Fe–O–Mn– is expected, which will induce the ferromagnetic interation 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:$BiFeO_3$/Bi_2FeMnO_6 bilayered films

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$Nd_{0.1}Bi_{0.9}FeO_3$/Bi_2FeMnO_6 bilayered films were deposited on Pt/Ti/SiO_2/Si substrate by pulsed laser deposition method. $BiFeO_3$ is antiferromagnet while $BiMnO_3$ is ferromagnet, the ordering of –Mn–O–Fe–O–Mn– is expected, which will induce the ferromagnetic interation 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, $BiFeO_3$ 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 ABO_3 perovskite structured ferroelectric materials, they usually show antiferromagnetic order because the same B site magnetic element except $BiMnO_3$ is ferromagnet. While for the $A_2BB'O_6$ 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 $BiFeO_3$ and bismuth-based double perovskite oxides ($BiBB'O_6$), many of which have aroused great interest such as Bi_2NiMnO_6[9,10] and $BiFeO_3$–$BiCrO_3$.[11–13] But as we know, few researches are focused on Bi_2FeMnO_6. We believe it is particularly interesting to investigate the multilayered films containing Nd:$BiFeO_3$ and Bi_2FeMnO_6 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° –Fe^{3+}–O–Mn^{3+}– 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 $BiFeO_3$, and the couplings of –Fe–O–Mn–. The ferromagnetism is expected to overcome the other effects in the as-designed films.

In this study, $Nd_{0.1}Bi_{0.9}FeO_3$ (Nd:$BiFeO_3$), Bi_2FeMnO_6, and bilayered Nd:$BiFeO_3$/Bi_2FeMnO_6 films on Pt/Ti/SiO_2/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 Bi_2O_3, Fe_3O_4, Nd_2O_3, and $MnCO_3$ were weighed according to the molecular mole ratio with 10 mol % extra Bi_2O_3. 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:$BiFeO_3$ films were fabricated at 550–580 °C with 200 mTorr dynamic oxygen pressure, Bi_2FeMnO_6 films were fabricated at 550–580 °C with $\sim 10^{-5}$ Torr.

The phases of the films were determined by x-ray diffraction (XRD) using Cu $K\alpha$ radiation. The surface morphology was studied using an atomic force microscope. Pt upper electrodes with an area of 0.0314 mm^2 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:$BiFeO_3$/Bi_2FeMnO_6 and Nd:$BiFeO_3$ films are shown in Fig. 1. Both Nd:$BiFeO_3$ and Bi_2FeMnO_6 phases were observed in the bilayered film, and there are not other second phases except some peaks from

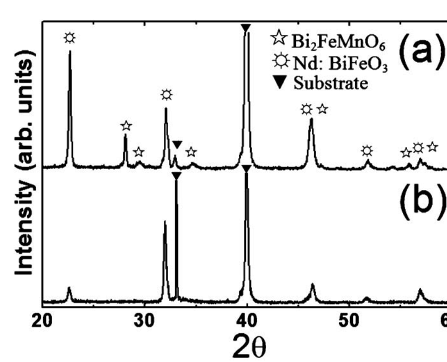

FIG. 1. XRD patterns of (a) Nd:$BiFeO_3$/Bi_2FeMnO_6 and (b) Nd:$BiFeO_3$ films.

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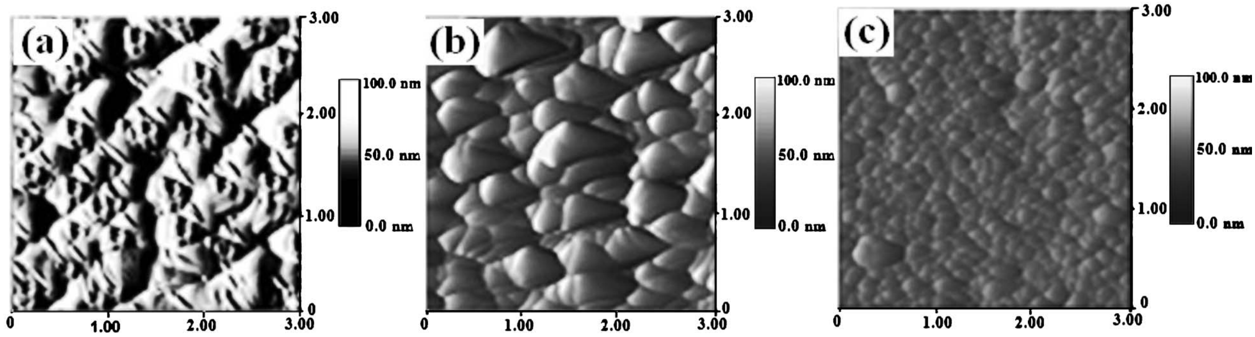

FIG. 2. Surface morphology of (a) Nd:$BiFeO_3$/Bi_2FeMnO_6, (b) Bi_2FeMnO_6, and (c) Nd:$BiFeO_3$.

the Pt/Ti/SiO_2/Si substrate. For Bi_2FeMnO_6 films, it shows complicated structure when deposited at different conditions. Bi *et al.*[14] has calculated three structures of Bi_2FeMnO_6 with the space group of $Pm\bar{3}m$, R3, and *C*2. It was observed in our experiments for Bi_2FeMnO_6 films which will be showed elsewhere.

The surface morphology of the Nd:$BiFeO_3$/Bi_2FeMnO_6 and Nd:$BiFeO_3$ 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:$BiFeO_3$), $<R_{rms}$ (Nd:$BiFeO_3$/Bi_2FeMnO_6), $<R_{rms}$ (Bi_2FeMnO_6), S (Nd:$BiFeO_3$), $<$S (Nd:$BiFeO_3$/Bi_2FeMnO_6), $<$S (Bi_2FeMnO_6). Figure 2(a) revealed the morphology of Nd:$BiFeO_3$ film on the Bi_2FeMnO_6 Pt/Ti/SiO_2/Si, which indicated that Nd:$BiFeO_3$ had a larger growth rate on Bi_2FeMnO_6 than on Pt/Ti/SiO_2/Si substrate.

Figure 3(a) shows ferroelectric hysteresis loops of the Nd:$BiFeO_3$/Bi_2FeMnO_6 film, the top inset shows the polarization fatigue as a function of switching cycles up to 10^8 and the below inset shows frequency dependence of the real part of dielectric permittivity. The remnant polarization P_r is 54 $\mu C/cm^2$ 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 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:$BiFeO_3$ and Bi_2FeMnO_6, 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).

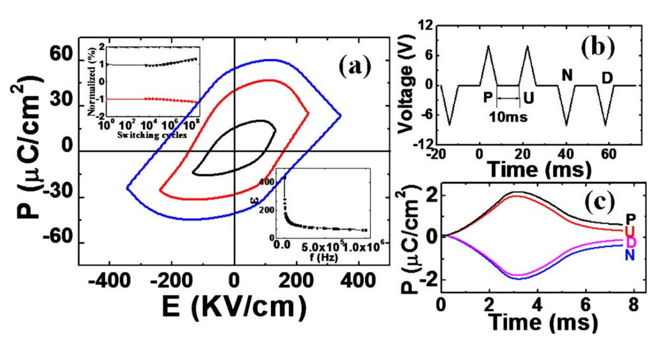

FIG. 3. (Color online) Ferroelectric characterization of Nd:$BiFeO_3$/Bi_2FeMnO_6 film. (a) Ferrroelectric hysteresis loops, the polarization fatigue as a function of switching cycles (top inset) and the frequency dependence of the real part of dielectric permittivity (below inset). (b) PUND waveform and (c) corresponding switching polarization.

Figure 4(a) shows the magnetic moment versus magnetic field loops of the Nd:$BiFeO_3$/Bi_2FeMnO_6 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 $1.02\pm0.11\times10^{-4}$ $K^{-1.6}$. This fit gives an estimated ferromagnetic transition temperature of T_c $=440$ 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 Mn^{3+} and Fe^{3+} ions. The observed ferromagnetism may be the result of a 5° canted antiferromagnetic ordering that

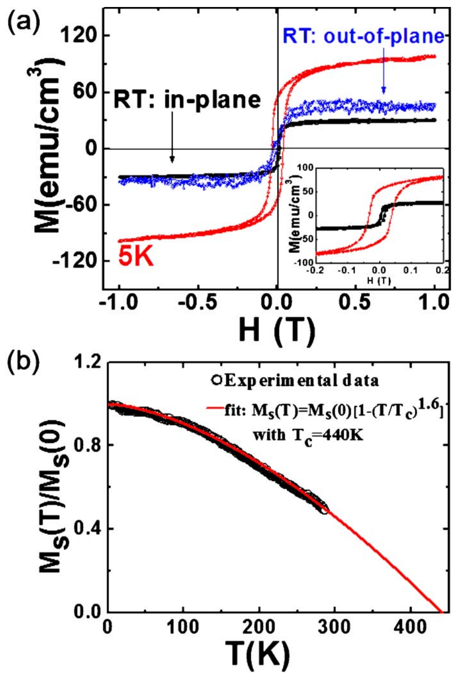

FIG. 4. (Color online) (a) Magnetization curves measured at RT and 5 K. (b) Plot of normalized magnetization $M_s(T)/M_s(0)$ against temperature (t) at 0.5 T.

leaves a small net magnetic moment and modest Curie temperature.[18,19]

In summary, we fabricated the Nd:$BiFeO_3/Bi_2FeMnO_6$ bilayered films on Pt/Ti/SiO_2/Si substrate by PLD method. The film showed good ferroelectric properties with P_r and E_c values of 54 $\mu C/cm^2$ 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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