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

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Abstract
Nd$_{0.1}$Bi$_{0.9}$FeO$_3$ /Bi$_2$FeMnO$_6$ 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

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

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Nd₀.₁Bi₀.₉FeO₃/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 ferroelectric properties with the transition temperature of Tc 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).³–⁸ 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⁺–Fe³⁺–O–Mn³⁺– bonds is quasistatic, partly because the ordering of –Mn–O–Fe–O–Mn– is expected, which will induce the ferromagnetic interaction in the film. The film shows typical ferroelectric properties with the transition temperature of Tc of 440 K. The room temperature (RT) ferroelectric polarization was also observed, suggesting that the film is a promising RT multiferroism.

The phases of the films were determined by x-ray diffraction (XRD) using Cu Kα 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

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the Pt/Ti/SiO2/Si substrate. For Bi2FeMnO6 films, it shows complicated structure when deposited at different conditions. Bi et al. has calculated three structures of Bi2FeMnO6 with the space group of Pm3m, 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 (Rrms) and grain size (S) are different: Rrms (Nd:BiFeO3), <Rrms (Nd:BiFeO3)/Bi2FeMnO6), <Rrms (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 is 54 μC/cm² and Ec 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:BiFeO3 and Bi2FeMnO6, which will affect the ferroelectric properties. As the definition of ferroelectricity is strict, we have also measured the so-called positive-up-negative-down test. 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∥) and “out-of-plane” (H⊥) magnetization are also compared. The two loops show clearly magnetic anisotropy. The results suggest that the sample has magnetoelectric 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/cm³ at RT and 83 emu/cm³ 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 T⁴ dependence below RT. The temperature dependence of magnetization in saturation could be described by M∥(T)=M∥(0)[1−b(T/T_c)³] with the best fit for b value of 1.02±0.11×10⁻⁴ K⁻¹. 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 4.49μB. 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
leaves a small net magnetic moment and modest Curie temperature.\textsuperscript{18,19}

In summary, we fabricated the Nd:BiFeO$_3$/Bi$_2$FeMnO$_6$ 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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