Pr-Fe co-doping induced room temperature multiferroic properties in SrTiO₃ films

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The structural, leakage current, ferroelectric and magnetic studies of the co-doped SPTFx (x=0.1, 0.2 and 0.3) films have been investigated. X-ray diffraction and atomic force microscopy reveal the microstructure of the samples. It is found that the dc leakage currents of the films are enhanced gradually with increasing Fe ions due to the variable valence of Fe ions and the increase of oxygen vacancies (OVs). More importantly, both the room-temperature ferroelectric and ferromagnetic properties are successfully realized in STO films, whose possible causes are discussed. This work provides an effective method for the induction of the multiferroic properties in paraelectric materials.

Keywords: Electrical properties; Ferroelectrics; Magnetic materials

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1. Introduction

In recent years, SrTiO₃ (STO) has been greatly concerned due to its variety of outstanding physical properties: (i) an insulator-metal transition [1], (ii) the formation of a two-dimensional electron gas [2], (iii) blue light emission [3], (iv) ferroelectricity [4] and (v) ferromagnetism [5]. Most of the studies on STO mainly concentrated on the induction of a certain kind of abnormal property in above researches. With the development of the multiferroics[6, 7], the coexistence of two or more than two kinds of properties in STO will be received more extensive concern in the future [8]. In 2014, the room-temperature multiferroic properties in (Fe_x, Sr_{1-x})TiO₃ thin films were reported by Kim *et al.* [9]. Meanwhile, we have studied the room-temperature *P-E* properties of Pr-doped STO at A sites [10]. In order to achieve better multiferroic in ‘Quantum paraelectric’ STO materials and further analyze their origins, in this paper, the Pr-Fe co-doped STO films were fabricated using the co-doping methods at both A and B sites.

2. Experimental procedures

Sr_{0.975}Pr_{0.025}Ti_{1-x}Fe_xO₃ (SPTFx, x=0.1, 0.2 and 0.3) films were fabricated by the metal organic deposition (MOD) method on (111) Pt/Ti/SiO₂/Si substrates [10]. The microstructure of the films was characterized by X-ray diffraction (XRD, D/Max-RB) with Cu K α radiation and atomic force microscope (AFM, Nanoscope IV). The electrical properties were evaluated with a Keithley 6517A electrometer/high-resistance meter, an Hp4194A impedance/phase analyzer and an RT66A standard ferroelectric test unit. Magnetic measurements were performed with

a vibrating sample magnetometer (VSM, EV9 ADE Technologies).

3. Results and discussion

Figure 1 shows the typical XRD patterns of SPTFx films at room temperature. The samples possess the polycrystalline structure of pure cubic perovskite phase with no additional peaks. The lattice parameters of SPTFx (x=0.1, 0.2 and 0.3) with the increase of Fe doping amount are about 3.8978 Å, 3.9007 Å and 3.9036 Å, respectively. We can see two features: (i) the lattice parameters increase with incorporation of Fe ions in STO films and this lattice distortion is obviously related with the partly substitution of larger Fe²⁺ (0.78 Å) and Fe³⁺ (0.645 Å) for Ti⁴⁺ (0.605 Å) ions. (ii) The lattice parameters of three samples are slightly smaller than that of pure STO (3.905 Å), possibly due to the substitution of smaller Pr³⁺ and Pr⁴⁺ ions for Sr²⁺ ions[10]. Insets of Fig. 1(a)–1(c) show SPTFx (x=0.1, 0.2 and 0.3) film surface, respectively. The three kinds of STO films are dense and well crystallized and their average grain sizes are about 200 nm, which are slightly larger than the results of pure STO films [11].

Figure 2 plots the *J-E* characteristics at room temperature for SPTFx films. With increasing Fe ions, the leakage current density *J* increases, which may be attributed to the hopping of the charge carriers between Fe sites similar to the hopping between Mn²⁺ and Mn³⁺ or/and Mn⁴⁺ sites in Mn-doped (Pb,Sr) TiO₃ films [12]. In addition, for above three films, with the increase of *E*, *J* first increases (region I), then jumps at a certain threshold of *E_g* (region II), followed by a gradual increase (region III). The three regions are analyzed in detail as follows: In region I, *J* increases with increasing

E . The inset of Fig. 2 shows the linear relation between $\ln J$ and $E^{1/2}$, ascribed to Schottky thermionic emission [13]. In region II, when E reaches a certain threshold E_g , J increases dramatically, and E_g decreases with the increase of Fe content. Here, we analyze that at E_g , the charge carriers (including electrons, holes and OV's, etc.) in the bulk sample obtain enough energy to move. Because of the low-valence substitution of Fe for Ti ions, the concentration of OV's increases and the correlation among the OV's strengthens, so the activation energy decreases [14], and, in turn, E_g decreases.

Fig. 3 depicts the polarization versus applied electric field P - E hysteresis loops of the SPTFx films at room temperature. An obvious hysteresis loop is presented for $x=0.1$ and 0.2 films, although its shape is different from the typical saturated ferroelectric loops and the remanent polarization is also small. To further confirm its ferroelectric properties, Fig. 3(a) shows the variation of ε with temperature at a frequency of 10 kHz. It should be noted that there is a broad peak ($250^\circ\text{C}\sim 450^\circ\text{C}$) for $x=0.3$ film, and its location moves to higher temperature with decreasing Fe ions. These behaviors are the characteristics of relaxor ferroelectric with diffuse phase transition [15], which may indicate the change of intrinsic dipoles induced by the lattice distortion, i.e., the formation of spontaneous polarization. It is consistent with the earlier analysis that the incorporation of Pr-Fe ions makes the phase of STO films more pseudocubic symmetry (see Fig.1). The phenomenon is also possibly correlated with polar nanoregions (PNRs) and the charge transfer related to Pr^{3+} and Pr^{4+} ions according with the results of Lu *et al* [10]. Table I lists the remanent polarization and

coercive field for STO films with the different doping modification. Obviously, there are two improvements as follows: (1) This Pr value is found to be greatly enhanced in comparison with that of either $(\text{Fe}_{0.1}, \text{Sr}_{0.9})\text{TiO}_3$ ($0.632 \mu\text{C}/\text{cm}^2$) or $\text{Sr}_{0.975}\text{Pr}_{0.025}\text{TiO}_3$ film (around $0.57 \mu\text{C}/\text{cm}^2$). (2) The Ec is about $35.9 \text{ kV}/\text{cm}$ in $\text{SPTF}_{0.1}$ film according to our previous results of Pr-doped STO [10], which is much less than the result of Kim *et al* [9]. However, for $x=0.3$ film (inset of Fig.3.), the hysteresis loop has been severely deformed so that the Pr and Ec cannot be read correctly. It turns out that the films are deviating from the ferroelectric materials owing to the bigger leakage behavior (see Fig.2.) that an extra conducting channel could be formed in the samples due to the coexistence of Fe^{2+} and Fe^{3+} ions with increasing Fe ions.

Magnetic measurements were carried out at room temperature. As shown in Fig. 4, the samples exhibit a well-defined magnetic hysteresis loop with a saturation magnetization for a relatively low applied magnetic field of 15 kOe and it decreases from $9.6 \text{ emu}/\text{cm}^3$ to $4.1 \text{ emu}/\text{cm}^3$ with increasing Fe ions. Inset of Fig. 4 gives the enlarged parts near zero fields. The calculated remnant magnetization ($2Mr$) and the coercive magnetic field ($2Hc$) values for the SPTF_x ($x=0.1, 0.2$ and 0.3) films are $0.21 \text{ emu}/\text{cm}^3$ and 0.10 kOe , $0.71 \text{ emu}/\text{cm}^3$ and 0.54 kOe , $0.10 \text{ emu}/\text{cm}^3$ and 0.09 kOe , respectively, at an applied magnetic field of 15 kOe . The ferromagnetism mainly originates from the interactions between neighboring Fe ions with different valence through the intermediate oxygen ions ($\text{Fe}^{2+}-\text{O}^{2-}-\text{Fe}^{3+}$), which is in accordance with the double exchange mechanism [5]. However, with increasing Fe ions, Fe^{3+} may be migrate into octahedral vacancies resulting in the improvement of

antiferromagnetic and suppressing magnetic due to superexchange interaction of $\text{Fe}^{3+}\text{--O}^{2-}\text{--Fe}^{3+}$ [8].

4. Conclusions

In summary, SPTFx ($x=0.1, 0.2$ and 0.3) films were fabricated using MOD method. The changes of Fe ions have greatly influence on the structural and electromagnetic properties of the STO samples with similar Pr content, whose ferroelectric and ferromagnetic properties could be attributed to the lattice distortion, the PNRs and the indirect double exchange interaction between Fe^{2+} and Fe^{3+} with different stations through oxygen, respectively.

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References

- [1] H. Suzuki, H. Bando, Y. Ootuka, I.H. Inoue, T.Yamamoto, K.Takahashi, et al., J. Phys. Soc. Jpn. 65 (1996) 1529-1532.
- [2] A. Ohtomo, H.Y. Hwang, Nature (London) 427 (2004) 423-426.
- [3] D. Kan, T. Terashima, R. Kanda, A. Masuno, K. Tanaka, S. Chu, et al., Nature Mater. 4 (2005) 816-819.
- [4] M. Choi, F. Oba, I. Tanaka, Phys. Rev. Lett. 103 (2009) 185502.
- [5] J. He, X.M. Lu, W.L. Zhu, Y.Y. Hou, R.X. Ti, F.Z. Huang, et al., Appl. Phys. Lett. 107 (2015) 012409.
- [6] T. Choi, Y. Horibe, H.T. Yi, Y.J. Choi, W.D. Wu, S.W. Cheong, Nature Mater. 9 (2010) 253-258.
- [7] J.F. Scott, NPG Asia Materials, 5 (2013) e72.

- [8] H.S. Kim, L. Bi, G.F. Dionne, C. A. Rossb, Appl. Phys. Lett. 93 (2008) 092506.
- [9] K.T. Kim, C. Kim, S.P. Fang, Y.K. Yoona, Appl. Phys. Lett. 105 (2014) 102903.
- [10] X.F. Wang, X.M. Lu, Y.Y. Weng, W. Cai, X.B. Wu, Y.F. Liu, et al., Solid State Commun. 150 (2010) 267-270.
- [11] X.F. Wang, X.M. Lu, H.F. Bo, Y.Y. Liu , Y.C. Shen, X.B. Wu, et al., Solid State Commun. 150 (2010) 1637-1640.
- [12] J. Yang, X.J. Meng, M.R. Shen, L.Fang, J.L. Wang, T.Lin, et al., J. Appl. Phys. 104 (2008) 104113.
- [13] W. Li, J. Ma, C.H. Song, P. Bao, X.M. Lu, J.S. Zhu, et al., Chin. Phys. Lett. 21 (2004) 544-547.
- [14] W. Li, K. Chen, Y.Y. Yao, J.S. Zhu, Y.N. Wang, Appl. Phys. Lett. 85 (2004) 4717-4149.
- [15] J.D.S. Guerra, R.G. Mendes, J.A. Eiras, I.A. Santos, E.B. Araújo, J. Appl. Phys. 103 (2008) 014102.

TABLE I. The remanent polarization (Pr) and coercive field (Ec) of STO film for different doping modes.

	Pr ($\mu\text{C}/\text{cm}^2$)	Ec (kV/cm)
$\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$	1.17	35.9
$\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_{0.8}\text{Fe}_{0.2}\text{O}_3$	1.26	71.9
$(\text{Fe}_{0.1}, \text{Sr}_{0.9})\text{TiO}_3^{\text{I}}$	0.632	72.8
$\text{Sr}_{0.975}\text{Pr}_{0.025}\text{TiO}_3^{\text{II}}$	0.57	23.8

^I the results from Refs.[9]

^{II} the results from Refs.[10]

Figure:

FIG. 1. X-ray diffraction patterns of the polycrystalline SPTFx film at room temperature. The insets (a), (b) and (c) show AFM topography images of $x=0.1$, 0.2 and 0.3, respectively.

FIG. 2. J - E characteristics of the SPTFx films at room temperature. Inset shows current density as a function of the square root of electric field ($E^{1/2}$).

FIG. 3. Polarization versus applied electric field measured at room temperature for SPTFx films. Inset (a) shows ϵ as a function of the temperature at 10 kHz.

FIG. 4. The magnetization-field ($M-H$) curves measured at room temperature for the SPTFx films. Insets give the enlarged parts near zero fields.