Effect of Pr-Fe doping on dielectric and modulus properties of SrTiO₃ films

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Pr-Fe co-doped SrTiO₃ films are prepared by the metal organic deposition method on (111) Pt/Ti/SiO₂/Si substrates. Their dielectric and electric modulus behaviors are investigated in the temperature range of 30~500°C with different measuring frequency of 10²~10⁶ Hz. A typical ferroelectric relaxation phase transition is shown and its location shifts to the low temperature with the increase of Fe content. The imaginary parts of electric modulus M'' exhibits the variable relaxation process with different Fe content, which is relation with OV_s, PNR_s and phase transition, and the possible causes of relaxation behavior dependence are analyzed in detail.

Keywords: Dielectric relaxation; Electric modulus; Metal organic deposition method

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1. Introduction

Single-phase multiferroic materials are the substances possessing simultaneously ferroelectric and ferromagnetic properties, which can be used to convert the magnetic signals to electric responses or vice versa, and become excellent candidates for new generation memory devices, spintronics, sensors etc [1]. Among the best candidates for such applications are solid solutions of a ternary perovskite $\text{PbFe}_{0.5}\text{Ta}_{0.5}\text{O}_3$, BiFeO_3 , $\text{Lu}_3\text{Fe}_5\text{O}_{12}$, BiMnO_3 , YMnO_3 and so on[2,3]. However, there remain several issues to be solved before it is practically applied in multiferroic devices operating at room temperature including inhomogeneous spin structure, small ferroelectric polarization, high leakage current and low Curie temperature [4]. Therefore, exploiting new materials that let magnetism and ferroelectricity coexist in a single phase above room temperature have become a hot spot [5].

SrTiO_3 (STO), as a quantum paraelectric material, shows many interesting properties, including ferroelectric behavior, ferromagnetism, superconductivity etc., which is related to the lattice vibration, electric polarization, and the transportation of electrons in the matrix of the STO lattice [6-8]. With the development of the multiferroics, the coexistence of two or more properties in SrTiO_3 will be received extensive concern in the future [7, 9]. Kim et al. [5] reported a room temperature multiferroic properties in $(\text{Fe}_x, \text{Sr}_{1-x})\text{TiO}_3$ thin films. Then the room temperature multiferroic properties have been further improved by Wang et al [10] using Pr-Fe co-doping methods in STO films, but its dielectric properties have not been paid sufficient attention. For STO materials, the

dielectric anomalies are attributable to the doping of impurities such as oxygen vacancies (OVs), polar nanoregions (PNRs) and defect centers [11-15], which provides people with a method to have a better understanding of the movement mechanism of charged-defects and to adjust material properties. In this work, the dielectric properties and the electric modulus of multiferroic materials Pr-Fe co-doped SrTiO_3 films are studied. The variable relaxation processes are found for different Fe content, and the possible causes of which are analyzed and discussed.

2. Experimental

$\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_{1-x}\text{Fe}_x\text{O}_3$ ($x=0.1, 0.2$ and 0.3) films were fabricated by the metal organic deposition (MOD) method on (111) Pt/Ti/SiO₂/Si substrates. Strontium acetate, tetrabutyl titanate, praseodymium oxide (Pr_6O_{11}) and iron nitrate were used as the precursors for Sr, Ti, Pr and Fe, respectively. Acetic acid, 2-methoxyethanol, and nitric acid were the solvent. The films were deposited by spin coating on (111) Pt/Ti/SiO₂/Si substrates and were crystallized at 750 °C for 1 h in O₂. The microstructure of the films was characterized by X-ray diffraction (XRD, D/Max-RB) with Cu K α radiation. Morphology and chemical composition of the samples were studied by the scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) using SEM-EDX Hitachi S-3400 N. The electrical properties were evaluated with an Hp4194A impedance/phase analyzer.

3. Results and discussion

Figure 1 shows the typical XRD patterns of $\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_{1-x}\text{Fe}_x\text{O}_3$ ($x=0.1, 0.2$ and

0.3) films at room temperature. These samples possess the polycrystalline structure of pure cubic perovskite phase with no additional peaks similar to the results of pure STO [17]. The surface morphology of Pr-Fe co-doped STO films detected by SEM is shown in the insets of Fig. 1(a)–(c). Three kinds of STO films are crystallized well and dense. The average grain sizes are about 100 nm for x=0.1 sample and they gradually decrease with increasing Fe content. According to the results of EDX analysis, the nominal Fe content from 0.1 to 0.3 in our samples is actually 0.093, 0.177, 0.277, respectively. In addition, the content of Pr ions is not detected due to the precision of the instrument.

Fig. 2(a), (b) and (c) show the variation of ϵ' and the loss $\tan\delta$ ($\tan\delta = \frac{\epsilon''}{\epsilon'}$) with temperature at different frequencies for Fe=0.1, 0.2 and 0.3 samples, respectively. Here ϵ' and ϵ'' are the real and imaginary parts of the dielectric constant, respectively. For ϵ' , its maximum value would decrease with the increase of frequency and corresponding peak temperature (T_p) shifts up to higher temperatures, showing high frequency dispersion. This above-mentioned result is a typical relaxor behavior of the ferroelectric-paraelectric transition, whose position obviously shifts to lower temperature with increasing Fe ions. The same dielectric peaks were also shown in Pr-doped STO sample at a higher temperature (240 °C) strongly, indicative of a ferroelectric-paraelectric transition, which may be the displacive character with Curie temperature of ~118 °C[16]. For $\tan\delta$, with increasing temperature its value increases stepwise and shows no obvious relaxation process. It turns out that $\tan\delta$ is deviating from the relaxation behaviors and reaches higher value (over 100 at 500 °C) due to the bigger leakage behavior that an extra

conducting channel could be formed in the samples, which is relation with the coexistence of Fe^{2+} and Fe^{3+} ions. With increasing Fe content from 0 to 0.3, the leakage current density of $\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_{1-x}\text{Fe}_x\text{O}_3$ films increased from the order of magnitude of 10^{-7} to 10^{-5} A/cm² when E increased to about 100 KV/cm [10,17].

To clarify the origin of relaxation behavior, modulus has been done for our samples. Modulus research is an important theory, formulated by Taher et al. [18], which studies charge transport processes in ion conductors and eliminates electrode polarization effect. The complex electric modulus (M^*) is calculated from the following equation and is defined as the reciprocal of the complex dielectric constant (ϵ^* , here $\epsilon^* = \epsilon' + i\epsilon''$)

$$M^* = M' + iM'' = \frac{1}{\epsilon^*} = \frac{\epsilon'}{\epsilon'^2 + \epsilon''^2} + i \frac{\epsilon''}{\epsilon'^2 + \epsilon''^2} \quad (1)$$

where M' and M'' are the real and imaginary parts of electric modulus, respectively.

Figure 3 shows the variation of the imaginary part of the electric modulus (M'') as a function of temperatures at different frequency. A M'' peak appears near 284°C in the M'' -temperature spectrum at 100 Hz and its location moves to higher temperature with the increase in frequency, which shows a typical relaxation behavior in $x=0.1$ sample (as shown in Fig.3(a)). With the Fe ions increased to 0.2, two sets of relaxation peaks begin to appear at 99.8°C and 195.1°C, respectively (as shown in Fig.3 (b)). In Fig. 3(c), one relaxation behavior is observed. These relaxation processes are labeled as regions I, II, III and IV for $x=0.1$, 0.2 and 0.3 samples, respectively. The maximum value of M'' (M''_{max}) happening is due to the interfacial polarization produced by the travelling charge carriers and pilling up at the interface of the two dielectrics. At a certain temperature, the

influence of the applied field results in a free movement of the intrinsic immobilized charge carriers. The charge carriers hopping from one localized state to another may be represented by an analogous process of associated dipolar moment reorientation, and thus a dielectric relaxation occurs. In addition, as the relaxation peak shifts towards the higher temperature with increasing frequency, we consider that the charge carrier mobility increases and free charges accumulate at the interface within the sample. As a result, the relaxation time decreases and the peak shifts towards the higher temperature with increase in frequency. To clarify the origin of carrier hopping accounting for the present relaxation process, the detailed analysis is as follows:

According to the point defect relaxation theory, the peak height is in proportion to the concentration of relaxation units [19], the temperature variation of the characteristic frequency can be described by the Arrhenius relation. The relaxation time (τ) can be written as

$$\tau = \tau_0 \exp(U / k_B T), \quad (2)$$

where T is the absolute temperature, τ_0 is the relaxation time at an infinite temperature, U is the activation energy, and k_B is the Boltzmann constant. Using the extreme value condition,

$$\omega_{\max} \tau = 1, \quad (3)$$

where angular frequency $\omega_{\max} = 2 \pi f_{\max}$ ($f_{\max}$ is the frequency at which the maximum M'' occurs). The relationship between the measuring temperature and peak frequency can be given by

$$\ln (2\pi f_{\max}) = -U/k_B T + \ln \tau_0, \quad (4)$$

according to Eq. (4), the peak frequency of M'' at different temperature for $x=0.1$, 0.2 and 0.3 films are well fitted as shown in Fig. 4. These activation energies are listed in Fig.4 from the slope of the fitted straight line. In region I, the value is about 1.192 eV, which is close to the typical value (1.0 eV) of activation energy for OV_s in the perovskites or related oxide structures [20]. Paladino et al.[21] measured the activation energy for diffusion OV_s in STO crystal to be 0.98–1.13 eV. Therefore, the relaxation peaks may be associated with the migration of OV_s inside $\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_{0.9}\text{Fe}_{0.1}\text{O}_3$ film. Lu et al.[22] reported a broad relaxation peak of the dielectric loss above room temperature for pure STO ceramics, in which the activation energy was about 0.84 eV. Also the $\text{Sr}_{0.975}\text{Pr}_{0.025}\text{TiO}_3$ ceramics showed a relaxation behavior which originated from the migration of OV_s and the activation energy was about 0.85 eV [23]. The activation energy for $x=0.1$ sample at high temperature is slightly bigger than the ceramics mentioned above due to the relaxation parameters strongly affected by thermal history and grain boundaries [24, 25]

With increasing Fe ions, in region II, the activation energy is about 1.441 eV that is larger than the value of $x=0.1$ sample. We consider that the relaxation peaks may not be associated with the migration of OV_s inside films because of the low-valence substitution of $\text{Fe}^{2+}/\text{Fe}^{3+}$ for Ti^{4+} ions, resulting in the increase of OV_s. With the increase in OV_s concentration and the formation of OV_s clusters, the correlation among the OV_s strengthens, and thus the movement of OV_s becomes easier and the activation energy

decreases [22], which is in contradiction with the change of activation energy from $x=0.1$ to 0.2 . It has been reported in the literature [23] that polar distortion may give rise to the relaxor ferroelectric behavior of Pr-doped STO due to the variable valence of Pr ions. Similarly, there should be more PNRs in $x=0.2$ film as a result of the variable valence of Pr and Fe ions; the main contributors for this relaxation process (region II) may not be OV's, but PNRs.

In addition, the Arrhenius relation for the region III is not a straight line and the distinct deviation is very obvious. Grubbs et al.[26] ascribed the deviation to two Arrhenius segments, and the linear regions with different slopes suggested the different relaxation mechanisms in the corresponding regions. If the reduced electric modulus is plotted, $M''/M''_{\max}$ as a function of T_p/T , as shown in Fig. 5, we can see that the curves for the region III cannot merge into one master peak and the widened peaks at high frequencies, imply that there may be a different mechanism with the components from both long range and localized relaxation[27]. On second thoughts, similar to the results of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ by Zhang and Tang [28], the relaxation is possible to be related to polaron relaxation. According to the fitted curves by applying the following Mott's variable range hopping (VRH) relation

$$f_{\max} = f_0 \exp \left[-\left(\frac{T_0}{T_p} \right)^{1/4} \right] \quad (5)$$

where f_0 is the eigenfrequency which has a meaning of the inverse minimum relaxation time, or is the frequency at infinite temperature and T_0 is a constant relation to the

activation energy. From Fig. 6, the plot of $\ln f_{\max}$ vs $T_p^{-1/4}$, actually produces nonlinear behavior, which cannot be qualitatively explained in the frame of the polaronic model. In Fig.4. the activation energies from the slope of the theoretical fitting of the Arrhenius relation are $U_{\text{III}} = 1.159$ eV above T_c and $U_{\text{III}} = 1.909$ eV below T_c . These values from 1.159 to 1.909 eV are found to have a dielectric transition at about 264 °C corresponding to the results of Figure 2(b). Capacitance dispersion is significant in the temperature range in which the contributions of the two conduction mechanisms are comparable to each other. The higher frequency region may be due to the grain-grain boundary, meanwhile the lower frequency region is interpreted as the formation and migration of ions at the surface or electrode/crystal interfacial polarization [29]. To further confirm the results, Figure 7 shows the electric modulus spectrum (M' vs M'') of the $\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_{0.8}\text{Fe}_{0.2}\text{O}_3$ at different temperature. The deformed semi-circles with their centers lying over the real axis indicate the distributions of relaxation time which support the non-Debye type of relaxation in the materials [30]. Due to the limitation of the experimental set-up, the electric modulus properties with higher or lower frequency cannot be obtained at present in our sample. Although the Cole-Cole figure shows only 1/4 circles, it can be seen that the low frequency shrinkage is changed into high frequency. This further proves that there are two kinds of relaxation mechanisms in the vicinity of the phase transition.

Finally, in region IV, the activation energies are $U_{\text{IV}} = 1.567$ eV above T_c and $U_{\text{IV}} = 1.199$ eV below T_c , which show the similar relaxation behavior to region III. In short,

with the increase of Fe ions, the numbers of the relaxation behaviors increase and decrease alternatively. We consider that when Fe content is 0.1, the relaxation process mainly caused by OV's begins to appear (region I). With the increase of Fe ions from 0.1 to 0.3, the relaxation process near the phase transition gradually moves towards the low temperature, and covers one by one the relaxation process caused by OV's (region I) and PRNs (region II). This work can regulate the electrical property STO films by Pr-Fe co-doping methods and then facilitate practical applications.

4. Conclusions

In summary, $\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_{1-x}\text{Fe}_x\text{O}_3$ ($x=0.1, 0.2$ and 0.3) films are fabricated by MOD method. The location of the typical ferroelectric relaxation phase transition shifts to low temperature with the increase of Fe content. The variation of imaginary part of M^* with temperatures at different frequencies exhibits the different relaxation process for Pr-Fe co-doped STO samples, which are related with OV's, phase transition and PNRs. The process is analyzed in detail by Arrhenius diagram, Cole-Cole relation, modulus master curve and VRH relation. The fact that the incorporation of Fe ions leading to the changes of the internal defects of the films has a great influence on the dielectric properties of the films, which could be beneficial for understanding the movement mechanism of charged-defects and thus get a little closer to actual applications in microwave devices.

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Figure captions

FIG. 1. X-ray diffraction patterns of the polycrystalline $\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_x\text{Fe}_{1-x}\text{O}_3$ film at room temperature. The insets (a), (b) and (c) show SEM topography images of $x=0.1$, 0.2 and 0.3 , respectively.

FIG. 2. Temperature dependence of ϵ' and $\tan\delta$ at various frequencies of 10^2 , $10^{2.5}$, 10^3 , $10^{3.5}$, 10^4 , $10^{4.5}$, 10^5 , $10^{5.5}$, and 10^6 Hz for $\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_x\text{Fe}_{1-x}\text{O}_3$ films (a) $x=0.1$; (b) $x=0.2$; and (c) $x=0.3$.

FIG. 3. M'' as a function of temperature at various frequencies of 10^2 , $10^{2.5}$, 10^3 , $10^{3.5}$, 10^4 , $10^{4.5}$, 10^5 , $10^{5.5}$, and 10^6 Hz for Pr-Fe co-doped SrTiO_3 films with different Fe content.

FIG. 4. The plot between $\ln(2\pi f_{\max})$ and $1/k_B T$ of Pr-Fe co-doped SrTiO_3 films ($x=0.1$, 0.2 and 0.3) samples according to the Arrhenius law. The solid line is the Arrhenius fitting.

FIG. 5. $M''/M''_{\max}$ vs T_p/T curve of $\text{Sr}_{0.975}\text{Pr}_{0.025}\text{Ti}_{0.8}\text{Fe}_{0.2}\text{O}_3$ at various frequencies.

FIG. 6. Peak frequency of M'' as a function of $100/T_p^{1/4}$ for region III and IV.

FIG. 7. The imaginary parts as a function of real parts of the electric modulus.

Figure 1

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Figure 2

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Figure 6

Figure 10 is a plot of the loss modulus M'' versus the storage modulus M' for the epoxy/PPG-400 system at various temperatures. The plot shows seven curves for temperatures: 100.1°C (dark blue diamonds), 150.1°C (cyan left-pointing triangles), 200.1°C (blue downward-pointing triangles), 240.2°C (black squares), 300°C (red circles), 340°C (green upward-pointing triangles), and 380.1°C (magenta right-pointing triangles). The curves generally show a peak in M'' at intermediate M' values, with the peak height increasing with temperature. Arrows indicate 'High frequency' at low M' and 'Low frequency' at high M' .

Figure 7