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Leakage current and breakdown behavior of bismuth-doped amorphous strontium titanate thin film

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HIGHLIGHTS

- Bi-doped amorphous $SrTiO_3$ thin film is prepared first time via sol-gel.
- The absorbed water in the dielectrics is critical to the durability of the films.
- Decrease in leakage current is observed by increasing the source doping concentration of Bi.
- The breakdown strength of 412 MV/m is obtained for Bi content of 5% tested in a vacuum.

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ABSTRACT

In this paper, the leakage current and breakdown behavior of amorphous $Sr_{1-1.5x}Bi_xTiO_3$ (x = 0, 2, 5, 10 and 15 mol %) thin films in ambient air and a vacuum were studied firstly. The results showed that the leakage current and breakdown strength could be effectively affected by Bi doping. The leakage current decreased with the increase of Bi doping. The breakdown strength of all doped samples in air was close to that of the $SrTiO_3$ film (189 MV/m). However, the breakdown strength was significantly enhanced in a vacuum. Typically, the breakdown strength of 5% Bi doped sample was up to 412 MV/m, about 2 times as high as that of the $SrTiO_3$ sample (215 MV/m). It was explained in terms of the absorbed water, which was critical to the durability of the films. The effect of bismuth on the electric properties was validated by experimental *J*–*E* curves acquired for a broad range of applied electric field, where the suppression of ionic conduction and the additional traps-filling consecutively dominated in the low field (0–100 MV/m) and high field (100–400 MV/m) regions. These results indicate the potential of Bi-doped $SrTiO_3$ thin film as high-energy density dielectric capacitors.

1. Introduction

As an important and widely used electronic material, perovskite strontium titanate (STO) exhibits excellent nonlinear optical properties, ultra-wide tunable range of dielectric constant, high thermal stability and photocatalytic properties [1–5]. Particularly, the outstanding characteristics of high dielectric constant and capability of ultrafast charging-discharging enable STO to be a promising candidate for high power density capacitor [6,7].

However, a high leakage current and low breakdown strength of STO thin films hinder their practical application in the microelectronic industry and MIM capacitor (metal-insulator-metal capacitor). The electrical properties of STO have been significantly enhanced by the means of tailoring the material structure according to previous studies. Among all the means of improvement, chemical element substitution with transition metal provides a practical and effective method to realize high performance STO thin film. For instance, Tang et al. [8] found that the resistive switching properties of vanadium-doped STO films were superior to those of unhoped ones due to their formative defects. Morito et al. [9] reported that the gradual reduction of the leakage current in the high electric Field region was observed with the increasing Mn concentration. The study of Hofman et al. [10] showed that La, as donor-type substituent, gives rise to the increase of the leakage while it reduces the resistance degradation of STO thin films. For perovskite dielectric, the major intrinsic defect is oxygen vacancy which supplies the carrier for the leakage current with applied field. Thus, the formation of oxygen vacancy is effectively suppressed by doping high valence cation [11].

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Inspired by its altered properties, Bi-doped strontium titanate, $Sr_{1-1.5x}Bi_xTiO_3$ has been widely studied in theory as well as in experiment [12,13]. Trivalent Bi^{3+} ions that substitute for Sr^{2+} act as donors, and at the same time, strontium vacancies are induced for valence compensation. According to defect chemistry, Bi doping in STO films can be described as follows.

$$Bi_2O_3 \rightarrow 2Bi^{\cdot}_{Sr} + 3O_O + V''_{Sr}$$

It is obvious that 2 Bi^{3+} ions are substituted for 2 Sr^{2+} sites with the creation of 1 Sr vacancy. According to previous studies on the systematic tailoring of the structure of polycrystalline $Sr_{1-1.5x}Bi_xTiO_3$ ceramics, a large portion of the electrons can be trapped by ionized Sr vacancies [14–16]. Related report of Chen et al. [17] showed that a “giant” dielectric constant was achieved at the cost of substantially increased dielectric loss by Bi-doping STO polycrystalline ceramic, which is primarily ascribed to the adverse effect of electron conduction. As is known, high temperature sintered polycrystalline ceramics leads to the volatilization of bismuth. This creates a drawback for further deep analysis. Extensive experimental results show that amorphous dielectrics possess high breakdown strength and low leakage current compared with polycrystalline dielectrics. McKenna et al. [18] demonstrated that grain boundaries act as preferential paths for atomic diffusion, current leakage and dielectric breakdown, and can therefore compromise device reliability and endurance. Ezhilvalavan et al. [19] found that the leakage current density dramatically raises from 10^{-10} to 10^{-7} A/cm^2 with the increase of the crystallinity in Ta_2O_5 film. Besides, the breakdown strength of polycrystalline STO (~20 MV/m) is at least one order of magnitude lower than that of the amorphous STO (~180 MV/m) for the thin films [20,21]. In order to further improve the electrical property of STO film on the basis of predecessors, amorphous STO film with different Bi doping levels were investigated to achieve lower leakage current and higher breakdown in this work.

2. Experimental

2.1. Sample preparation

$Sr_{1-1.5x}Bi_xTiO_3$ (x = 0, 2, 5, 10, and 15 mol %) thin films were deposited on Pt (100)/Ti/SiO_2/Si substrates using a sol-gel process combined with spin-coating, as seen in Fig. 1. Bismuth nitrate pentahydrate and semi-hydrate strontium acetate were dissolved in heated acetic acid to form solutions A and B, respectively. Then, polyvinyl pyrrolidone (PVP) acetic acid solutions were added to the above solutions. Different amounts of titanium isopropoxide were dissolved into ethylene glycol monomethyl ether to form solutions C and D. Then acetylacetone, which controls the rate of hydrolysis, was added to solutions C and D. Afterwards, solutions C and D were added dropwise to solutions A and B, respectively. Next, ethylene glycol was added to the above 2 mixtures to adjust the viscosity and prevent the films from cracking. Solution A was then added to solution B. Finally, the mixture was constantly stirred for 3 h to react completely. A clear and transparent yellow sol was obtained.

Subsequently, the films were deposited on Pt (100)/Ti/SiO_2/Si substrates, with a spin-coating speed of 3000 rpm for 20 s. The as-deposited films were dried at 200 °C, 350 °C, and 500 °C for 5 min in a tube furnace to evaporate the solvents and organic addenda. The spin-coating and preheating processes were repeated 7 times to obtain films with a thickness of about 300 nm. Finally, the prepared films were annealed at 500 °C for 3 h. To measure the electrical properties, 100-nm-thick Au topped electrodes with the diameter of 1 mm were coated onto the $Sr_{1-1.5x}Bi_xTiO_3$ thin films. The $Sr_{1-1.5x}Bi_xTiO_3$ films with the Au topped electrodes were annealed at 200 °C for 2 h after the fabrication of the topped electrodes.

2.2. Material characterizations

The roughness of the thin films was investigated by the atomic force microscope (AFM, SPA 400, SPI3800N, Seiko, Japan), and the thickness was measured by the cross-sectional field emission scanning electron microscope (FESEM, S-4700, HITACHI). The phase structure was examined using glancing-angle X-ray diffraction with an incident angle of 1° to the film surface (XRD, Rigaku D/max-2550). An infrared spectrometer (FT-IR, EQUINOX 55) was utilized for the Fourier transform infrared spectroscopy. The binding states were identified with an Escalab 250Xi X-ray photoelectron spectrometer (XPS, Thermo Scientific). Electrical characteristics were measured by a computer-controlled Keithley 2400 source meter unit interfaced with a computer to perform the measurements and record the experimental data. 10 breakdown trials were tested to estimate the breakdown strength through the Weibull distribution function due to the randomness of the dielectric breakdown voltage.

3. Results and discussion

3.1. Morphology and binding structure

Fig. 2 depicts the surface morphology and XRD patterns of the $Sr_{1-1.5x}Bi_xTiO_3$ thin films. All films presented a smooth and uniform surface with the r.m.s. roughness (RMS) value of 1 nm estimated from AFM images. The XRD patterns of all thin films have the broad peak around 30°without any $Sr_{1-1.5x}Bi_xTiO_3$ crystallization peaks. The only crystallization peak is associated with Pt substrate. This suggests that the amorphous films had formed. According to the above results, both the phase composition and surface morphology of films annealed at 500 °C were almost not influenced by the Bi doping. The thickness of the thin films measured by the cross-sectional SEM images in Fig. 3 are 261, 264, 288, 276 and 285 nm for x = 0, 2, 5, 10, and 15 mol %, respectively.

FT-IR spectroscopy was employed to further study the structure of the Bi-doped strontium titanate films. The FT-IR spectra in Fig. 4 shows the main bonds are distributed around 3400, 2934, 1418, and 633 cm^{-1}, which correspond to the O-H, C-H, C-O, and Ti-O stretching vibrations, respectively [22–24]. The FT-IR investigation confirmed that all of the films had the surface OH groups due to the absorbed water. It was remarkable that the intensity of the O-H stretching vibration bonds becomes weaker as $x \geq 10\%$, because bismuth doping may reduce the formation of the surface oxygen vacancies, thereby inhibiting the existence of absorbed water [25].

X-ray photoelectron spectroscopy (XPS) was used for the compositional and chemical state analyses. Fig. 5 shows the XPS data of the $Sr_{1-1.5x}Bi_xTiO_3$ thin films. The binding energy was calibrated by locating the C 1s level at 285.0 eV. As shown in Fig. 5a, Bi was found from the XPS survey spectra of the Bi-doped samples and in the state with a +3 valence. The Ti 2p spectra of the Bi-doped samples are presented in Fig. 5b. The peaks of Ti $2p_{3/2}$ occurred at 458.32 eV −457.64 eV, suggesting that the titanium atoms existed in the form of a +4 valence in the $Sr_{1-1.5x}Bi_xTiO_3$ thin films [26]. However, the decrease in the binding energy of Ti $2p_{3/2}$ indicates that the Ti atoms were off-center due to the incorporation of Bi into STO. The ionic radius of the cation Bi and its charge affect the percentage of the ionic characteristics of the Ti-O bonds [27]. Fig. 5c displays the XPS narrow scan spectrum of O1s core-level for the all thin films. The O1s high-resolution XPS can be fitted into 2 Gaussian peaks denoted in the text as O1s(1) and O1s(2). The main O1s(1) peak at 529.36 eV was ascribed to the oxygen of the titanate species [28]. The O1s(2) peak, located at 530.92 eV, was ascribed to