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Improved dielectric and ferroelectric properties in Ti-doped $BiFeO_3$–$PbTiO_3$ thin films prepared by pulsed laser deposition

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ABSTRACT

Ti-modified thin films of multiferroic $0.72Bi(Fe_{1-x}Ti_x)O_3$–$0.28PbTiO_3$ (BFPT, $x=0$ and 0.02) solid solution were prepared by pulsed laser deposition. The BFPT ($x=0$ and 0.02) films possess a tetragonal structure with highly preferential (001) orientation. The effects of the ionic substitution on the properties of BFPT ($x=0$ and 0.02) films have been investigated. The leakage current of the BFPT ($x=0.02$) thin film is significantly reduced, and the dielectric and ferroelectric properties greatly improved by the aliovalent ionic substitution of Ti^{4+} for Fe^{3+}. The BFPT ($x=0.02$) thin film exhibits a reasonably high remnant polarization P_r with $2P_r$ up to 90 μC/cm^2 at 312 kV/cm and a switchable polarization up to 92 μC/cm^2 at 417 kV/cm.

1. Introduction

Thin films of multiferroic materials have become the renewed focus of attention recently because of their potential applications for micro-/integrated electronic and spintronic devices [1]. Various deposition methods including chemical solution deposition, RF sputtering and pulsed laser deposition (PLD) were used to prepare heteroepitaxial or polycrystalline multiferroic thin films [2–5]. Multiferroic $BiFeO_3$, with a space group $R3c$, has a high ferroelectric Curie temperature ($T_C=820$–850 °C) and a high Néel temperature ($T_N=310$–370 °C), accordingly possessing simultaneous ferroelectric and antiferromagnetic orderings below T_N [6–8]. As a promising candidate of room temperature multiferroic materials, $BiFeO_3$ and its solid solutions have attracted much attention recently. $BiFeO_3$ thin films prepared on $Pt/TiO_2/SiO_2/Si$ substrates showed good ferroelectric performance with a remnant polarization $2P_r$ of 71.3 μC/cm^2 at room temperature [9]. Epitaxial $(Bi_{0.9}La_{0.1})FeO_3$ films on (001)$SrTiO_3$/(001)Si substrates exhibited well-saturated ferroelectric hysteresis loops with a remnant polarization of 45 μC/cm [2,10]. Introduction of $PbTiO_3$ into $BiFeO_3$ can form continuous solid solution, which helps to stabilize the perovskite phase and also to decrease the coercive field E_c [11]. In addition, a morphotropic phase boundary (MPB) is formed in which rhombohedral, tetragonal and orthorhombic phases are found to coexist [12]. Recently, $(1-x)BiFeO_3$–$xPbTiO_3$ ($0.3\le x\le 0.5$) films deposited on Pt/Si substrates by PLD were reported [13]. The films with $x=0.4$ exhibit a remnant polarization $2P_r$ up to 100 μC/cm^2 at −10 °C. It was suggested that the enhanced polarization arises from the decrease of leakage current when cooled down to −10 °C. However, for practical applications, low electric conduction and good ferroelectric properties at room temperature are desired. Previous results on $(1-x)BiFeO_3$–$xPbTiO_3$ (BFPT) bulk ceramics suggested that the electric conduction wherein, which arises from the hopping of electrons from Fe^{2+} to Fe^{3+} through oxygen vacancies, can be effectively decreased by aliovalent ionic substitutions, namely Ti^{4+} for Fe^{3+} on the B site [14].

In the present work, we have deposited the thin films of $0.72Bi(Fe_{1-x}Ti_x)O_3$–$0.28PbTiO_3$ (BFPT, $x=0$ and 0.02) on $Pt/TiO_2/SiO_2/Si$ substrates by PLD, and investigated the effects of the ionic substitution of Ti^{4+} for Fe^{3+} on the structures and dielectric and ferroelectric properties of the BFPT ($x=0$ and 0.02) thin films.

For the PLD deposition of BFPT ($x=0$ and 0.02) thin films, the ceramic targets of $0.72BiFeO_3$–$0.28PbTiO_3$ (BFPT) and $0.72Bi(Fe_{0.98}Ti_{0.02})O_3$–$0.28PbTiO_3$ (BFPT, $x=0.02$) were prepared by conventional ceramic processing. The powders were pressed into green

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pellets at 15 kN/cm^2 and sintered at 1000 °C for 5 h. The shrinkage rate and relative density of both kinds of ceramic disks reached 15% and 95%~97%, respectively.

The PLD process was performed using a 248 nm KrF excimer laser system (Lambda Compex Pro205, Germany). A laser beam with a power density of 3.5 J/cm^2 and a repetition rate of 3 Hz was focused on the BFPT ($x=0$ and 0.02) targets. The distance between the target and the substrate was set at 4 cm. The films were deposited at a substrate temperature of 680 °C, followed by post-deposition annealing at 700 °C for 30 min in a rapid thermal annealing furnace. The oxygen pressure was set at 2 Pa for $x=0$ and 10 Pa for $x=0.02$, respectively. The thickness of both BFPT and BFPT ($x=0.02$) films was 480 nm. For electrical measurements, gold top electrodes with a diameter of 0.5 mm were sputtered through a shadow mask.

The phase analysis of the BFPT ($x=0$ and 0.02) films was performed by a x-ray diffraction (XRD) system (Rigaku D/max-2400, Japan) using Cu Kα radiation. The microstructures and surface morphologies were examined by a field-emission scanning electronic microscope (FESEM, JEOL, JSM-7000F, Japan). The current–field (J–E) curves were measured by a semiconductor characterization system (Keithley 4200-SCS, USA). The dielectric measurements were carried out using an HP4294 precision *LCR* meter (Hewlett-Packard, USA). The ferroelectric P–E hysteresis loops and the positive-up-negative-down (PUND) measurements were performed using a standardized ferroelectric test system (TF Analyzer 2000 Systems, Aix ACCT, Germany) and a Standard Ferroelectric Testing System (RT66A, Radiant Tech., USA), respectively.

Fig. 1 shows the XRD patterns (on a log scale) of the BFPT ($x=0$ and 0.02) thin films grown on Pt/TiO_2/SiO_2/Si substrates. All the films exhibit pure phase and a tetragonal perovskite structure with preferential (001) orientation. Besides some dominating peaks in the films, some weak peaks, such as the (100), (200) peaks, also appear near 23° and 46°, respectively in both undoped and doped BFPT films. The degree of preferential (001) orientation can be calculated according to the formula $\alpha_{001}=I(001)/\{I(001)+I(011)+I(111)\}$ by using the integrated intensity (I) of the corresponding diffraction peaks. Both films show a highly preferential (100) orientation with the values of α_{001} reaching 76.5% and 80.4%, for the BFPT and BFPT ($x=0.02$) films, respectively. Based on the XRD pattern of the undoped thin film, the 2-theta value of the T(001) peak is 19.48° and the 2-theta value of the T(011) peak is 30.52° (with a Cu Kα source). The lattice parameters of the tetragonal phase are calculated to be: $c=4.5530$ Å and $a=3.8204$ Å, which give rise to the ratio $c/a=1.1917$, defined as tetragonality. This value of tetragonality (c/a) is higher than that in the ceramics and single crystals (1.1675 [12] and 1.18 [15]) of the BFPT solid solution on the tetragonal side of the MPB. This is because of the crystal aberrance caused by the stress effect in the films. The dielectric constant (ε_{33}) would be further enhanced when the film is of (001) preferential orientation with a large tetragonality. This structure with (001) preferential orientation and a large tetragonality certainly contributes to the enhancement of the dielectric and ferroelectric properties in the films deposited.

In order to further study the surface and inner structure, we employed FESEM to observe the microstructure and morphologies of the BFPT ($x=0$ and 0.02) films. The surface morphologies revealed in

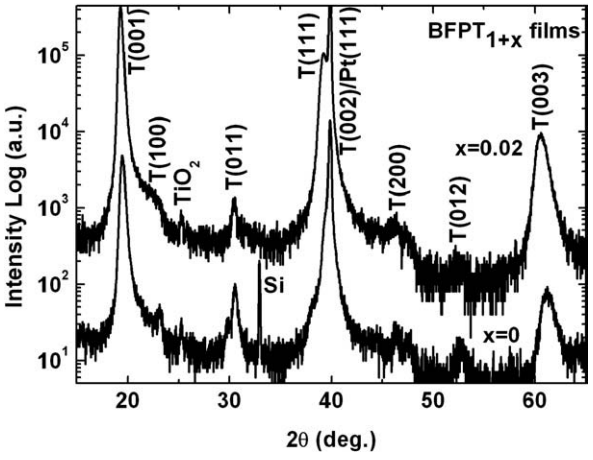

Fig. 1. XRD patterns (on a log scale) of the thin films of BFPT ($x=0$ and 0.02).

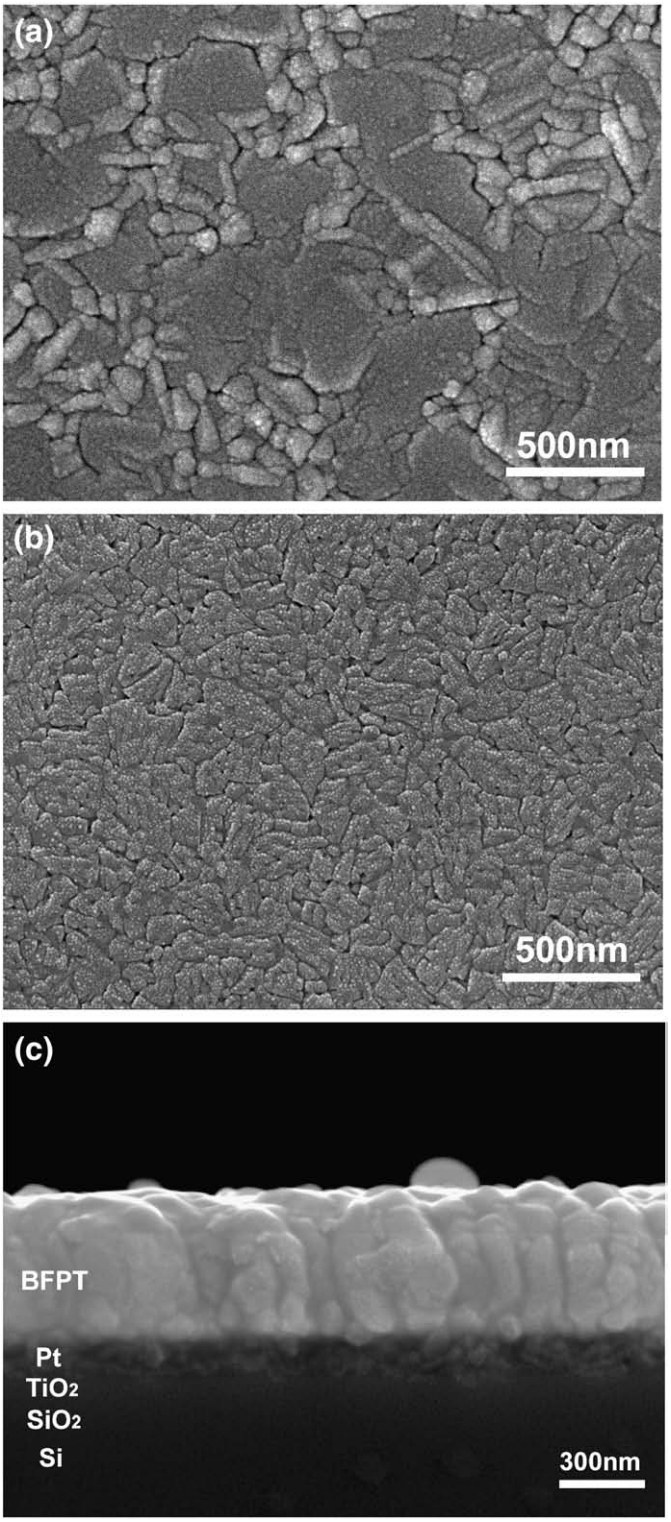

Fig. 2. FE-SEM image of surface morphologies for (a) BFPT film, (b) BFPT ($x=0.02$) film and (c) cross-sectional morphology for BFPT film.