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Ni doping dependent dielectric, leakage, ferroelectric and magnetic properties in $Bi_7Fe_{3-x}Ni_xTi_3O_{21}$ thin films

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ABSTRACT

$Bi_7Fe_{3-x}Ni_xTi_3O_{21}$ thin films were prepared by chemical solution deposition on $Pt/Ti/SiO_2/Si$ substrates. The Ni doping effects on the dielectric, leakage, ferroelectric and magnetic properties were investigated. Coexistence of ferroelectric and ferromagnetic properties at room-temperature was observed in the $Bi_7Fe_2NiTi_3O_{21}$ thin film with a remnant polarization $2P_r$ of 36.4 μC/cm^2 and a remnant magnetization $2M_r$ of 3.9 emu/cm^3. The dielectric and leakage properties were discussed in detailed. The results will provide important information to explore single-phase multiferroic materials.

1. Introduction

Multiferroic materials, which simultaneously exhibit the coexistence of at least two primary ferroic properties, for example ferroelectricity and ferromagnetism, have been widely investigated due to the potential applications in upcoming electronics technologies, such as non-volatile memories, multi-state storage and quantum controlling devices [1–4]. In recent years, as one type of multiferroic materials, the Aurivillius phase compounds [5,6] with the general formula $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$ consisting of perovskite-like blocks $(A_{n-1}B_nO_{3n+1})^{2-}$ layers intergrowths along the *c*-axis between the fluorite-like $(Bi_2O_2)^{2-}$ layers, where n is the number of the BO_6 octahedra, have roused wide investigations due to the encouraging characteristics. For example, the $SrBi_2Ta_2O_9$-based compounds show excellent fatigue endurance and low leakage current [7,8]. The rare-earth ions doped $Bi_4Ti_3O_{12}$ compounds exhibit good fatigue endurance and ferroelectric properties [1,9,10]. Recently, the Aurivillius compounds with higher n ($n \geq 4$) have attracted much more attention because of their potential applications as room-temperature multiferroics [11,12]. Zhao et al. reported the room-temperature multiferroic characteristics in Aurivillius single crystals with n = 4, 5, 6 and 8 [13]. On the other hand, lots of investigations about magnetic ions doping in Aurivillius compounds to improve the multiferroic properties have been also reported. Sun et al. reported that the Co-doped $Bi_5FeTi_3O_{15}$ thin films show a coexistence of ferroelectric and ferromagnetic properties with the remnant polarization of $2P_r$ = 31.7 μC/cm^2 and the saturate magnetization of M_s = 2.6 emu/cm^3 [14]. Liu and Keeney at al. reported the enhanced multiferroic properties in Co and Mn doped $Bi_6Fe_2Ti_3O_{18}$ thin films [15,16]. These results indicate that doping is an effective route to improve multiferroic properties. As for the multiferroic Aurivillius compounds, the magnetization is still weak for applications and the samples usually show large leakage current resulting in poor ferroelectric properties. It has been reported that increasing the n in Aurivillius compounds can enhance magnetic responses and reduce leakage current, which are desirable for multiferroic properties [17]. On the other hand, it is difficult to obtain phase-pure Aurivillius phases with high n value [18,19].

$Bi_7Fe_3Ti_3O_{21}$ (BFTO) with n = 6 has been investigated in recent years due to its interesting properties. The $Bi_7Fe_3Ti_3O_{21}$ bulk ceramics show coexistence of ferroelectric and weak magnetic properties. The magnetization can be obviously improved by doping of magnetic ions. For an example, La and Co co-doped $Bi_7Fe_3Ti_3O_{21}$ ceramics show a coexistence of ferroelectric and

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ferromagnetism with $2P_r = 4.02$ μC/cm^2 and $2M_r = 2.58$ emu/g at room-temperature [20]. The Ni-substituted $Bi_7Fe_3Ti_3O_{21}$ ceramics exhibit an enhanced ferromagnetic property with a $2M_r = 1.32$ emu/g at room-temperature [21]. The Co-doped $Bi_7Fe_{3-x}Co_xTi_3O_{21}$ nanoplates have been reported with improved room-temperature ferromagnetism of $2M_s = 9$ emu/g [22]. These doped BFTO bulk ceramics show coexistence of ferroelectric and magnetic properties at room-temperature, however, the magnetism is still needed to improve. Besides, these compounds often exhibit poor polarization (P)-electric field (E) hysteresis loops due to large leakage current. Compared to the bulk ceramics, multiferroic thin films usually show improved ferroelectric and magnetic properties because of the reduced leakage current [23,24]. Raghavan et al. reported W-doped $Bi_7Fe_3Ti_3O_{21}$ thin films show good ferroelectric properties, reduced leakage current and weak ferromagnetic [24], which maybe related with the doping of W ions. Song et al. studied the multiferroic properties of Co-doped $Bi_7Fe_2CoTi_3O_{21}$ thin films with $P_r = 19.2$ μC/cm^2 and $M_r = 2.67$ emu/cm^3 [25].

In this work, $Bi_7Fe_{3-x}Ni_xTi_3O_{21}$ thin films were fabricated on the Pt/Ti/SiO_2/Si substrates by chemical solution deposition. Room-temperature multiferroic properties were obtained due to Ni doping. Besides, the dielectric and leakage properties were discussed in detailed.

2. Experimental process

The $Bi_7Fe_{3-x}Ni_xTi_3O_{21}$ (x = 0.0, 0.5, 1.0 and 1.5) thin films were deposited on Pt/Ti/SiO_2/Si substrates by chemical solution deposition (CSD). The raw materials of high-purity bismuth (III) acetate with 5 mol% excess amounts to compensate the volatilization of Bi in processing, iron (II) acetate, nickel (II) acetate and tetrabutyl titanate were dissolved into propionic acid to form the precursor solutions. The ethanolamine was added to stabilize the solutions. The used precursor solution concentration was adjusted to 0.1 mol/L. The thin films were spin-coated with a rotation speed of 6000 rpm for 20 s, and then baked in a 400 °C-preheated tube furnace for 10 min in air. The processing of the spin-coating and baking were repeated for several times in order to enhance the thin film thickness. Finally, the baked thin films were crystallized at 750 °C for 30 min in air. For the sake of simplicity, the $Bi_7Fe_{3-x}Ni_xTi_3O_{21}$ thin films with x = 0.0, 0.5, 1.0 and 1.5 are defined as BFNT0, BFNT5, BFNT10 and BFNT15, respectively.

The crystal structures were analyzed by a Philips X'Pert PRO X-ray diffractometer (XRD) with Cu-K_α radiation at room-temperature. The microstructures were measured by a high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) (JEM-2010, JEOL Ltd., Japan). The cross-sectional and surface morphologies were detected by a field-emission scanning electron microscopy (FE-SEM; FEI Sirion 200 type, FEI, Hillsboro, OR). To measure the electric properties, Au top electrodes with a diameter of 0.1 mm were deposited on the surfaces of the derived thin films by using a shadow mask using sputtering with Miriam small-ion sputtering system (SCB-12). A precision LCR meter (TH2828/A/S, Tonghui Electronic Co., Ltd., Changzhou, China) was used to measure the dielectric properties in the frequency range of 10 kHz–1 MHz with a driving voltage of 100 mV. A Sawyer-Tower circuit attached to a computer controlled standardized ferroelectric test system (Precision Premier II; Radiant Technologies, Albuquerque, NM) was applied to test the ferroelectric and leakage properties. The element valence states were determined by the X-ray photoelectron spectroscopy (XPS, ESCALAB250, Thermo, USA) with an Al-K_α radiation. Magnetic properties were measured by quantum designed superconducting quantum interference device (SQUID) magnetic property measurement system (MPMS) system ($2 \leq T \leq 400$ K, $0 \leq H \leq 5$ T).

3. Results and discussions

Fig. 1 shows the room-temperature XRD patterns for all the derived thin films. It confirms that all thin films are polycrystalline and phase-pure without detectable impure phases which can be indexed into $Bi_7Fe_3Ti_3O_{21}$ phase (JCPDS No. 00-054-1044) with orthorhombic crystal structure. With increasing the Ni concentration, the diffraction intensity corresponding to the (*00l*) diffraction peaks such as (00 14), (00 18) and (00 28) is enhanced, which means an enhanced *c*-axis grain growth. The inset of Fig. 1 shows the variation of lattice constant *a*, *b* and *c* as a function of Ni content. It is seen that Ni doping leads to the increase in *a* and the decrease in *b* and *c*. Moreover, the difference between *a* and *b* is increased with Ni doping content, suggesting the enhanced structural distortions due to the different ion radius of Ni and Fe.

To further visualize the microscopic stacked structure and crystal structure, the out-of and in-plane HRTEM were carried out for the undoped BFNT0 thin film and the results are shown in Fig. 2 (a) and (b). As shown in Fig. (a), the periodically-stacked layered-structure between two fluorite-like $(Bi_2O_2)^{2+}$ layers is formed along *c*-axis direction, which is analogous to the atomic schematic structure in Fig. 2(c). It is similar to the results from other investigations on Aurivillius compounds [17,21,26]. The lattice constant *c* is measured as ~5.72 nm, which is close to the value from XRD result of ~5.73 nm. The inset of Fig. 2(a) shows the selected area electron diffraction (SAED) result, which confirms the orthorhombic crystal structure. The in-plane lattice structure is shown in Fig. 2(b), suggesting that the in-plane lattice constant is 0.547 and 0.549 nm, respectively, which are close to the values from XRD results of *a* ~ 0.546 and *b* ~ 0.548 nm.

Fig. 3 shows the FE-SEM surface images for all the derived thin films. It is observed that all the thin films have dense and crack-free surface morphologies. With increasing the Ni content, the grain size increases and the grain shape changes from grain-like to thin plate-like. It has been reported that the plate-like grains are easy to form in Aurivillius phase ceramics because of the preferential growth along the *ab* crystalline plane [22,27]. As for the BFNT0 thin film, grain-like grains are observed due to the lower annealing temperature as compared to that of the ceramics. The enhanced plate-like grains with Ni doping may stem from the decreased crystallization temperature by Ni doping [25,28]. The corresponding insets of Fig. 3 display the cross-sectional FE-SEM images, from which the thickness is determined as 470, 470, 480

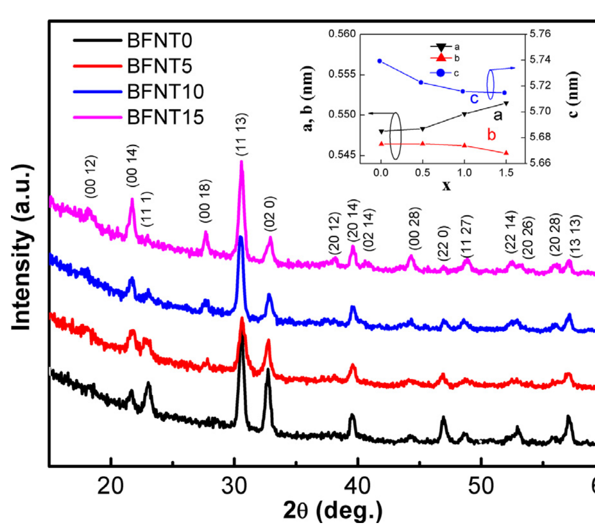

Fig. 1. XRD patterns for all the derived thin films and the inset exhibits the lattice constant with Ni content.