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Effect of donor W and acceptor Ni codoping at Ti site on the structure and electrical properties of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ thin film

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ABSTRACT

Pure $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT), donor W^{6+} doped NBT (NBTW), acceptor Ni^{2+} doped NBT (NBTNi), as well as donor W^{6+} and acceptor Ni^{2+} codoped NBT (NBTWNI) polycrystalline films are fabricated on indium tin oxide (ITO)/glass substrates via a chemical solution deposition method. The roles of aliovalent-ion substitution on the crystallinity, ferroelectric and dielectric properties of NBT film are mainly investigated. With the introduction of aliovalent-ion, the surface of the doped film becomes more uniform and the leakage current is reduced. Well saturated polarization-electric field (*P-E*) loops can be observed in W^{6+} and Ni^{2+} codoped NBT film due to its lowest leakage currents compared to those of other films. Also, the effect of voltage and frequency on the capacitance-voltage (*C-V*) curve and the dielectric tunability for the NBTWNI film is discussed. The ferroelectric and dielectric properties are largely improved in NBTWNI film, which can be ascribed to the synergetic effect of high-valence W^{6+} and low-valence Ni^{2+} ions. The cooperation between the acceptor and donor cations can effectively eliminate the mobile oxygen vacancies in NBT films.

1. Introduction

Ferroelectric materials have been extensively studied since the subject of the material covers various fields like material science, physics, and engineering [1–3]. Recently, sodium bismuth titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, abbreviated as NBT) as a typical lead-free ferroelectric material has received considerable attention due to its excellent ferroelectric and piezoelectric properties [4–7]. However, it is often reported to have high leakage current that is problematic for its piezoelectric and ferroelectric applications, especially for thin films. The leakage problem for NBT is mainly attributed to the presence of mobile charge defects of oxygen vacancies due to the volatilization of A-site element [8–11].

So far, several attempts have been made to solve the leakage problem in NBT, such as, by doping cation at A/B site [12–17], formation of heterogeneous multilayered structure [18], and control the crystal orientations [19,20]. Among various methods, the site-engineering has been proved to be effective in enhancing the insulating properties in NBT films. Doping in NBT can be broadly separated into two categories: mono and dual substitution, such as $\text{Pr}^{3+}/\text{Sr}^{2+}$ / Nd^{3+} for A site [12–14], $\text{Fe}^{2+}/\text{Mn}^{2+}$ for B site [15,16] as well as co-doping Mn^{2+} for B site and K^+ for A site [17]. Compared to the widespread reports of A or B site individual substitution with single-element, there are relatively few literatures about codoping in NBT films, particularly for codoping

at A or B site by using two aliovalent-ions at the same time. More recently, Li et al. found that high-valence Nb^{5+} as donor incorporated on the Ti-site can significantly reduce the leakage current in NBT because donor-doping can fill up the oxygen vacancies [21]. On the other hand, Davies et al. examined the piezoelectric properties in B-site acceptor (Mn^{2+} or Fe^{2+}) substituted NBT [22]. They found that acceptor doping has a pronounced effect on the piezoelectric property, which is attributed primarily to the formation of defect dipoles, e.g. $[(\text{Mn}_{\text{Ti}^{4+}}^{2+})'-(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}]$ or $[(\text{Fe}_{\text{Ti}^{4+}}^{2+})'-(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}]$. From these works, we can conclude that acceptor or donor doping can both improve the electrical properties of NBT by eliminating the mobile oxygen vacancies. Therefore, more systematic work on the defect chemistry of donor and acceptor codoping at B-site of NBT films is expected.

In this work, high-valence W^{6+} as donor is selected to cooperate with acceptor Ni^{2+} hybrid-doping at the Ti site in NBT film. In order to contrast, undoped NBT, W^{6+} doped NBT and Ni^{2+} doped NBT films were also fabricated on indium tin oxide (ITO)/glass substrates under the same condition. The influence of aliovalent-ion doping on the microstructures and properties of NBT films was mainly investigated. We found that the leakage current density in NBTWNI film was significantly reduced by codoping the two cations compared to those of other three films, and well saturated hysteresis loop was observed in this film.

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2. Experimental procedure

Pure $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT), W (1%)-doped NBT (NBTW), Ni (3%)-doped NBT (NBTNi), as well as W (1%) and Ni (3%) codoped NBT (NBTWNI) thin films were deposited on ITO/glass substrates by a chemical solution deposition (CSD) method. The precursor solution of NBTWNI was prepared by dissolving sodium acetate, bismuth nitrate pentahydrate, tungstic acid and nickel acetate tetrahydrate according to the stoichiometric ratio in a mixture of ethylene glycol and acetic acid. Besides, the titanate isopropoxide was reacted with acetylacetone to achieve the stabilization of Ti. Then the two solutions were mixed well and polyethylene glycol was added to obtain a final precursor solution. As to the pure NBT and mono substituted NBT films, the corresponding metal salt was added independently. Each precursor solution was coated on the surface of ITO/glass substrates and annealed at 520 °C. The sequential rapid thermal annealing process was repeated until the films reached a certain thickness. Au top electrodes were deposited on the films using a sputtering system. The structure of the annealed films was examined using a Cu K α X-ray diffraction (Bruker D8). The surface and cross-sectional morphologies were imaged by a field-emission-scanning electron microscope (FeSEM, Hitachi S-4200). The ferroelectric properties of all films were measured by a standard ferroelectric tester (Radiant Technologies). The insulating behavior was conducted by a Keithley 4200 semiconductor system. The dielectric properties were measured at low frequencies (from 10 kHz to 1 MHz) using an impedance analyzer (HP4294A).

3. Results and discussion

Fig. 1 shows the XRD patterns of the NBT-based thin films on the ITO/glass substrates with different doping elements. A pure perovskite phase is evidence in all films regardless of the kind of dopant. The films present similar polycrystalline structure with a strong diffraction peak of (110). More detailed pattern in the 2θ range of 31–34° is shown in the inset of Fig. 1. The (110) peak for NBTW film shifted to the higher angle of 2θ , while it shows an opposite trend for NBTNi and NBTWNI films compared to the pure NBT. Ionic radius of Ni^{2+} (0.72 Å) is larger than both Ti^{4+} (0.68 Å) and W^{6+} (0.62 Å) which may be the possible reason for the slight structure variation of the doped NBT films [23].

Fig. 2(a-d) shows the surface morphologies of all films. The surface of doped NBT films is smoother as compared to the pure NBT film, which may result from the higher uniformity of the grain size in the doped films. Fig. 2(e-h) presents the cross-sectional images of the films. The thickness of each film is about 400 nm. From the section, we can see that the NBTWNI film has a more compacted structure than those of

other three films. In order to accurately determine the grain size distribution of all films, we select 100 sample points in the SEM image analyzed by Nano Measurer 1.2 and the data are drawn in histograms [see Fig. 2(i-l)] [24]. The particle sizes for NBTW (70 nm), NBTNi (50 nm), and NBTWNI (55 nm) films are smaller than that of pure NBT (87 nm) film. That is, by introducing aliovalent-ion, the average grain size was reduced. Similar phenomenon has been observed in Ce-doped BiFeO_3 ferroelectric films [25]. In general, the grain growth induced by the minimization of surface and grain boundary energies can occur through the motion of grain boundaries, influenced by the diffusivities of the constituent ions [26]. Hence the different diffusivities for W, Ni and Ti ions should be responsible for the variations of grain sizes. Moreover, the grain boundary is also greatly affected by the defects, which are easily concentrated on the grain boundary [6,27]. For the doped films, the presence of defects, such as $(\text{Ni}_{\text{Ti}^{4+}}^{2+})'$, $(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}$ and $(\text{W}_{\text{Ti}^{4+}}^{6+})^{\bullet\bullet}$, may restrict the motion of grain boundaries. Therefore, relatively small grain sizes are observed in NBTW, NBTNi and NBTWNI films.

The leakage current density-electric field (J - E) curve for each film is shown in Fig. 3. We can find that the leakage currents in NBTW, NBTNi and NBTWNI films are much lower than that in pure NBT film. More recently studies have shown that the high conductivity in NBT is actually the result of oxygen ion conduction due to Bi deficiency and oxygen vacancies generated during annealing processing [28,29]. In NBTW film, doping high-valence ion of W can suppress the formation of $(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}$ to a great degree because $(\text{W}_{\text{Ti}^{4+}}^{6+})^{\bullet\bullet}$ carries the same electric charge as $(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}$. As to the low-valence Ni^{2+} doped NBT film, when Ti^{4+} is replaced by the acceptor of Ni^{2+} , the mobile $(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}$ can be captured by the negative charged defects of $(\text{Ni}_{\text{Ti}^{4+}}^{2+})'$ and defect complexes are built between the acceptors $(\text{Ni}_{\text{Ti}^{4+}}^{2+})'$ and $(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}$. Therefore, the formation of defect complexes of $(\text{Ni}_{\text{Ti}^{4+}}^{2+})'(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}$ is the main reason for the reduced leakage current in NBTNi film.

For the case of donor W^{6+} and acceptor Ni^{2+} codoped NBT film, its leakage current density is several orders of magnitude lower than the other three at 400 kV/cm. The cause may fall into two aspects: on one side defect complexes can also be formed between the negative charged defects [such as $(\text{Ni}_{\text{Ti}^{4+}}^{2+})'$ and $(\text{V}_{\text{Bi}^{3+}})^{\bullet\bullet}$] and the positive charged ones [such as $(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}$ and $(\text{W}_{\text{Ti}^{4+}}^{6+})^{\bullet\bullet}$]. And the formation of $(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}$ -related defect complexes is more easily since the oxygen vacancies can move in the oxygen octahedron [30]. The other side of that is the number of the complexes is greatly reduced owing to the defect elimination effect of high-valence W^{6+} ion. Therefore, the lowest leakage current is observed in NBTWNI film. For better understanding, the microscopic mechanism before and after doping W and Ni ions is also shown in Fig. 3. In the initial stoichiometric NBT film, the oxygen vacancies may be produced during the annealing processing owing to the loss of Bi_2O_3 [$2 \text{Bi}_{\text{Bi}^{3+}} + 3 \text{O}_{\text{O}^{2-}} \rightarrow 2 (\text{V}_{\text{Bi}^{3+}})^{\bullet\bullet} + 3 (\text{V}_{\text{O}^{2-}})^{\bullet\bullet} + \text{Bi}_2\text{O}_3$]. When it hybrid-doped with acceptor Ni^{2+} and donor W^{6+} , one part of $(\text{V}_{\text{O}^{2-}})^{\bullet\bullet}$ is tied by $(\text{Ni}_{\text{Ti}^{4+}}^{2+})'$ and the other part is eliminated by $(\text{W}_{\text{Ti}^{4+}}^{6+})^{\bullet\bullet}$. It is a huge synergistic effect of high-valence W and low-valence Ni ions, which can not only suppress the formation of oxygen vacancies but also limit their movement in NBT film. When compared with the previous aliovalent-ion doped NBT-based film at the same electric field (400 kV/cm) [17,31], its leakage current ($4 \times 10^{-5} \text{ A/cm}^2$) is reduced greatly.

Hysteresis loop, as a simple and effective tool, is a most commonly used method to understand the ferroelectricity of materials. The leakage currents will directly influence the shape of the loop in ferroelectrics. To further clarify the effect of aliovalent-ion substitution on the ferroelectric property of NBT film, the polarization-electric field (P - E) loops of the undoped NBT, NBTW, NBTNi and NBTWNI films are measured and shown in Fig. 4. One can find that pure NBT film shows relatively poor P - E hysteresis loops (Fig. 4a), which is obviously due to the large contribution from its high leakage current. Nevertheless, the slim P - E loop can be observed in aliovalent-ions doped NBT films. The remanent polarization (P_r) for the NBTWNI film is about $17.6 \mu\text{C/cm}^2$.

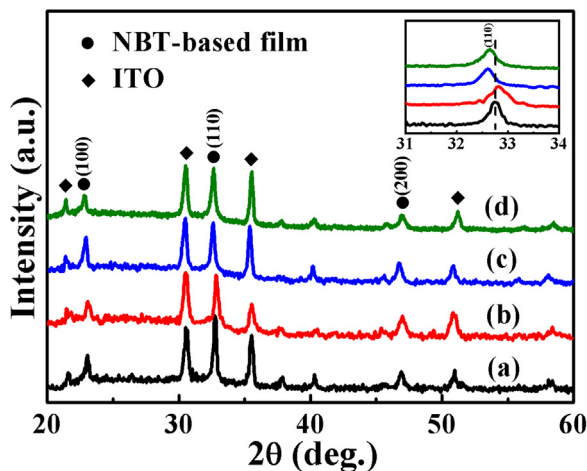


Fig. 1. XRD patterns of NBT-based films: (a) NBT thin film, (b) NBTW thin film, (c) NBTNi thin film and (d) NBTWNI thin film.

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