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Influence of annealing on the structure and ferroelectric properties of $Sr_{0.13}Na_{0.37}Bi_{0.50}TiO_3$ thin films prepared by metalorganic solution deposition

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ABSTRACT

$Sr_{0.13}Na_{0.37}Bi_{0.50}TiO_3$ thin films were prepared by metalorganic solution deposition, and annealed at temperatures from 550 to 700 °C for 1–15 min. The influence of annealing on the morphology, phase and ferroelectric properties was studied by scanning electron microscopy, X-ray diffraction and ferroelectric analyzer. The doping of $Na_{0.50}Bi_{0.50}TiO_3$ films with Sr results in the existence of two phases, i. e., $Na_{0.5}Bi_{0.5}TiO_3$-like *(matrix)* phase and $BiTiO_3$-like *(second)* phase, the relative contents of which depend on the annealing conditions. With the increase of annealing temperature and prolongation of annealing time, the phase content of the $BiTiO_3$-like second phase increases and a phenocryst structure was formed, which leads to the decrease of remnant polarization of $Sr_{0.13}Na_{0.37}Bi_{0.50}TiO_3$ thin films.

1. Introduction

Sodium bismuth titanate ($Na_{0.5}Bi_{0.5}TiO_3$, NBT) crystals and ceramics are an attractive candidate for lead-free electronic materials for their good piezoelectric and ferroelectric properties [1–6]. In recent years, there have been lots of researches focusing on NBT thin films. For example, high quality NBT thin films were prepared by radio-frequency magnetron sputtering, pulsed laser deposition, sol–gel and chemical solution deposition [7–15]. The structures and properties of the thin films were also studied. In order to achieve better electric properties of NBT thin films, many complex systems have been explored, such as K^+-doped NBT thin films [16–18], K^+ and Li^+ co-doped NBT films [19,20], Ba^{2+}-doped NBT films [21–23], and Ca^{2+}-doped NBT films [24]. Fu et al. [25] prepared Sr^{2+}-doped NBT thin films by sol–gel method and found that the films had good dielectric tenability and the doping of Sr in NBT films could greatly reduce the dielectric loss. In our previous work [26], we prepared $(1-x)Bi_{0.5}Na_{0.5}TiO_3$–$xSrTiO_3$ (SNBT) ferroelectric thin films by metalorganic solution deposition (MOSD), and found that the films have higher remnant polarizations (P_r) and better resistance against imprinting failure with doping content of $x = 0.13$. Beside the NBT-like phase, there is a second phase, which can significantly affect the electric properties of the films. In the present work, the influence of annealing on the morphology, phase structure and ferroelectric properties of SNBT films was systematically studied.

2. Experimental

2.1. Preparation of films

Sodium acetate, calcium acetate, bismuth acetate and tetrabutyl titanate in stoichiometric proportion (Na:Sr:Bi:Ti = 0.37:0.13:0.50:1.00) were dissolved in the solvent of glacial acetic acid. 2-methoxyethanol and acetylacetone were used to adjust the viscosity and stabilize the precursor solution. The precursor solution was deposited on *p*-type Si (1 1 1) substrates by spin coating at 4000 rpm to make a wet film. Then the wet film was heated at 350 °C for 15 min to remove organic solvent and other volatile materials. The above procedure was repeated till an expected thickness (about 300 nm) was achieved. The obtained SNBT films were annealed at 550–700 °C for 1–15 min using PTP-300 short annealing furnace.

2.2. Characterization

The surface and cross-section morphology of the SNBT films were observed by field-emission scanning electron microscope (SEM, JSM 6700F). Phase structure was determined by X-ray diffractometer (XRD, XRD-6100X). Ferroelectric hysteresis loops were obtained by ferroelectric analyzer (TF Analyzer 2000).

3. Results and discussion

3.1. Films morphology

Fig. 1 shows the SEM micrographs of the SNBT films annealed at different temperatures for different time. It was found that the grain sizes of the films increased obviously with the increase of annealing temperature and the prolongation of annealing time. With the annealing time of 15 min, some large crystallized grains with sizes of several hundreds of nanometers (defined as *phenocryst* herein) were formed, which will be discussed in Section 3.2.

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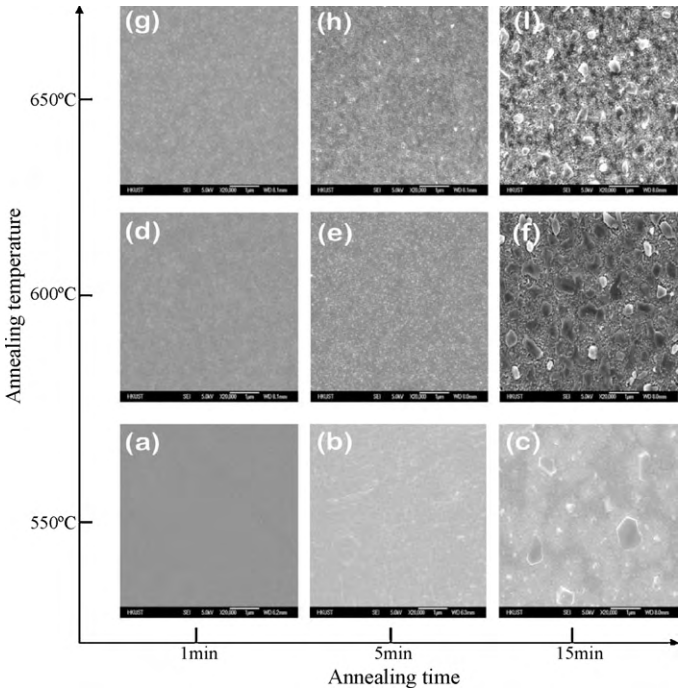

Fig. 1. SEM micrographs of SNBT films annealed at different temperatures for different time. (a) 550 °C, 1 min; (b) 550 °C, 5 min; (c) 550 °C, 15 min; (d) 600 °C, 1 min; (e) 600 °C, 5 min; (f) 600 °C, 15 min; (g) 650 °C, 1 min; (h) 650 °C, 5 min; (i) 650 °C, 15 min. Scale bar: 1 μm.

When the films were annealed at 550 °C for 1 min, there were only a few crystallized nano-grains, as shown in Fig. 1a. With the prolonged annealing time of 5 min, the films were fully crystallized although the crystalline quality was not good yet, as shown in Fig. 1b. The average grain size is about several tens of nanometers. The phenocryst grains with size ranging from 100 nm to 1 μm appeared when the films were annealed at 550 °C for 15 min. At higher annealing temperature of 600 °C, apparent crystallizing could be found with annealing time as short as 1 min. The average grain size increased slightly from tens of nanometers to about 100 nm with the prolongation of annealing time to 5 min. Compared with the sample annealed at 550 °C for 5 min, the crystallinity was greatly improved as observed by SEM. The phenocryst grains were formed with the annealing time of 15 min at 600 °C, and the density of phenocryst grains increased dramatically at higher annealing temperature. High quality polycrystalline films could be obtained with annealing temperature of 650 °C for only 1 min. With prolonged annealing time of 5 min, the grain sizes increased significantly, as shown in Fig. 1h. Fig. 1i shows the surface morphology of the films annealed at 650 °C for 15 min, and microcracks are observed besides the existence of large amount of phenocrysts.

Figs. 2a and c show the high magnification SEM images of the SNBT films annealed at 600 °C for 5 min and at 650 °C for 1 min, respectively. It was shown that uniform grains with average size of about 100 nm could be obtained at annealing temperatures of both 600 and 650 °C for a short period. It should be noted that some intergrain microcracks could be formed when the films were annealed at 600 °C for 5 min, while the films annealed at 650 °C for 1 min were more compact. Figs. 2b and d are the cross-section SEM images of the SNBT films annealed at 600 °C for 5 min and at 650 °C for 1 min, respectively. The thickness of the annealed films is about 200 nm, which is evidently lower than that of the pristine films due to the contraction of the as-prepared films during high temperature annealing. Although the film thickness is reduced, the surface of the annealed films is flat. The interface between the annealed films and Si substrate can be clearly seen.

3.2. Phase component analysis

Fig. 3 shows the XRD patterns of the SNBT thin films annealed at different temperatures for 5 min. The crystallinility of the films annealed at 550 °C for 5 min is low, which is consistent with that observed by SEM. When the annealing temperature is higher than

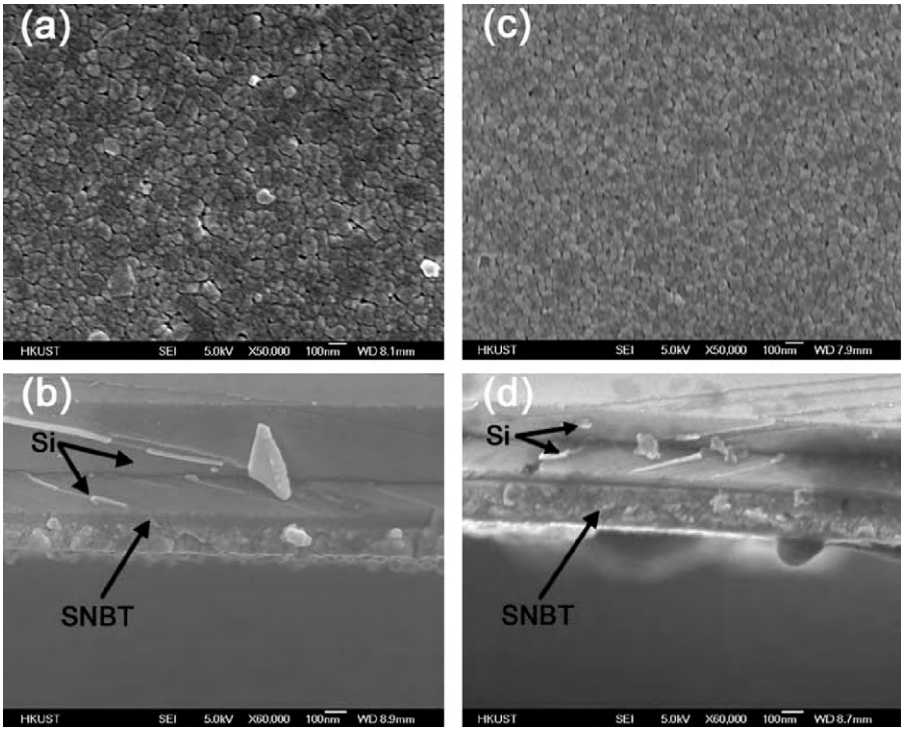

Fig. 2. Surface and cross-section SEM images of SNBT thin films annealed at 600 °C for 5 min and 650 °C for 1 min. (a, c) 600 °C, 5 min; (b, d) 650 °C, 1 min.

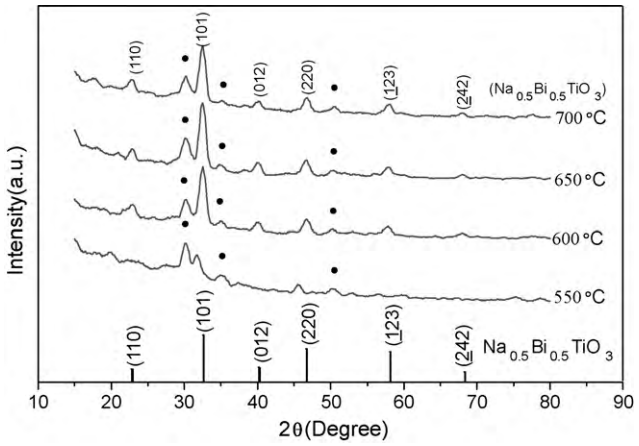

Fig. 3. XRD patterns of SNBT films annealed at different temperatures for 5 min.

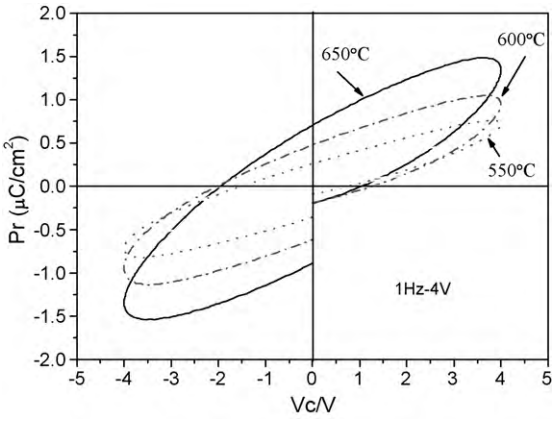

Fig. 5. *P–E* hysteresis loops of SNBT thin films annealed at different temperatures for 5 min.

600 °C, the SNBT thin films are well crystallinzed with major phase component of $Na_{0.5}Bi_{0.5}TiO_3$-like phase accompanied with a second phase marked with ● in the figure. This indicates that Sr-doping would not result in the change of crystal structure of the SNBT as compared with the matrix NBT phase when annealed at 600 to 700 °C for a short duration of 5 min.

Fig. 4 is the XRD patterns of the SNBT thin films annealed at different temperatures for 15 min. When the annealing time increased to 15 min, the content of second phase increased dramatically. The crystallinility of the films annealed at 550 °C was improved with longer annealing time, and the major phase was still $Na_{0.5}Bi_{0.5}TiO_3$-like phase although the intensity of the second phase was also high. The second phase became the major phase when the annealing temperature increased to 600 °C. When the annealing temperature was 650 °C, $Na_{0.5}Bi_{0.5}TiO_3$-like phase disappeared and the phase component was almost all second phase. The diffraction lines of the second phase fit well with that of $Bi_{0.87}TiO_{3.12}$ (PDF No. 89-4732), the standard angles of which are shown in the lower part of Fig. 4. The crystal structure of $Bi_{0.87}TiO_{3.12}$ is similar to that of $BiTiO_3$ (BiTO).

Comparing Fig. 4 with Fig. 1, it can be seen that the variation of second phase content is similar to that of second phase quantity as observed by SEM. Well-crystallized SNBT films with similar crystal structure of NBT could be obtained at suitable annealing conditions. When the annealing time is long (≥15 min), the phase content of NBT-like phase decreases and the content of BiTO-like increases, and with the annealing temperature increase, the content of BiTO-like phase increased *(the content of BiTO-like phase did not vary evidently with the increase of annealing temperature as shown in Fig. 3)*. Especially, when the films were annealed at 650–700 °C for 15 min, the annealed films only consisted of BiTO-like phase. The formation of BiTO-like phase might be attributed to the following aspects: first, the evaporation of Na and Bi under the condition of high annealing temperature or long annealing time results in the collapse of NBT structure. Second, NBT is a *harder* crystal than BiTO-like phase for its larger bulk modulus [27], thus BiTO crystals can grow faster to form the phenocryst, and Na^+ and Sr^{2+} are excluded during its lattice rearrangement.

3.3. Ferroelectric properties

Fig. 5 shows the *P–E* hysteresis loops of SNBT thin films annealed at different temperatures for 5 min. The remnant polarization of SNBT films increases with the increase of annealing temperature, while the coercive field seems to be independent with annealing temperature. This is favorable for the practical application of SNBT thin films as ferroelectric materials. The enhancement of remnant polarization should be due to the better crystallinility of SNBT with the increase of annealing temperature.

The remnant polarization of SNBT films decreases significantly when the annealing time increases from 5 to 15 min, as shown in Fig. 6. This is due to the formation of more BiTO-like phase with the increasing annealing time. With the increase of annealing temperature, the remnant polarization decreases although the crystalline quality becomes better, which is also due to the formation of more BiTO-like phase.

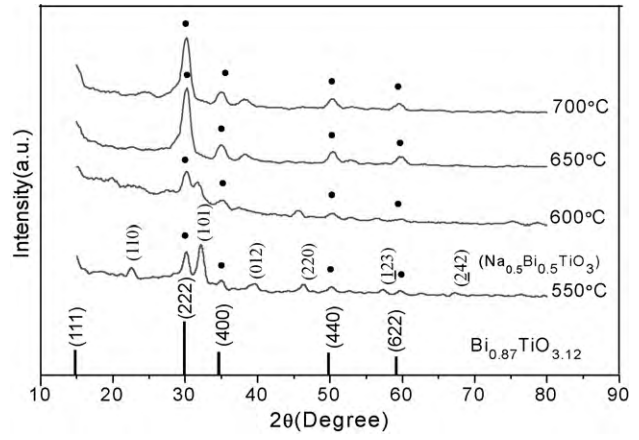

Fig. 4. XRD patterns of SNBT films annealed at different temperatures for 15 min.

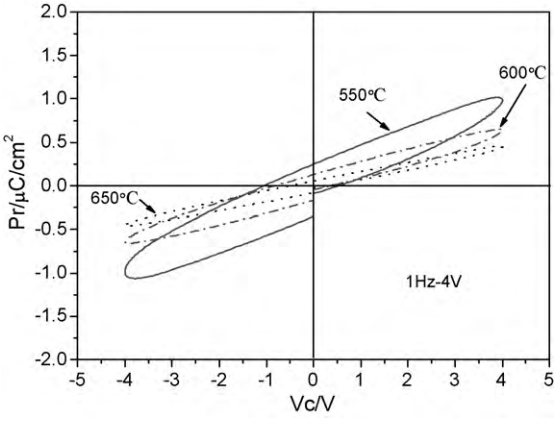

Fig. 6. *P–E* hysteresis loops of SNBT thin films annealed at different temperatures for 15 min.

4. Conclusions

In summary, we have prepared Sr-doped NBT thin films by metalorganic solution deposition. High quality polycrystalline SNBT films with dominant NBT-like structure could be obtained at suitable annealing conditions, i.e., annealing temperature of 600–650 °C for less than 5 min. Higher annealing temperature and prolonged annealing time lead to the formation of more unfavorable BiTO-like phase, resulting in the deterioration of ferroelectric properties.

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