OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 3, No. 11, November 2009, p. 1243 - 1246

Orientation and Raman study of $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$ ferroelectric films prepared in condition of different annealing schedules

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Fatigue-free $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$ ferroelectric thin films were successfully prepared on p-Si(100) substrate using metalorganic precursor deposition process. The orientation and formation of five-layer thin film under different annealing schedules were studied. XRD analysis indicated that (200)-oriented films with degree of orientation of $I_{(200)}/I_{(117)}=0.574$ and 0.633 were obtained by preannealing at 400 ℃for 10 min followed by rapid thermal annealing at 700 ℃for 3 min and 10 min, respectively, (008)-oriented film with degree of orientation of $I_{(008)}/I_{(117)}=0.605$ and 1.671 were obtained by rapid thermal annealing at 700 ℃ and 800 ℃for 3 min without preannealing. AFM was used to further analysis the morphologies of the films. The mechanisms in the formation and the variation of the single *a*- and *c*-oriented textures are discussed. Raman analysis revealed that the polarization vector should be at *a*-axis direction of the film.

(Received October 17, 2009; accepted October 29, 2009)

Keywords: $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$, Ferroelectric film, Annealing schedule, Orientation

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1. Introduction

Ferroelectric thin films have been investigated widely for potential applications in nonvolatile random-access memories (NVRAM) and dynamic random-access memories (DRAM) [1]. It is important in these applications that the films have a low coercive field, high remanent polarization, low leakage current and low polarization fatigue [2]. Lead zirconium titanate (PZT) ferroelectric thin films on Pt/Si substrates suffer from serious loss of switchable polarization after 10^7 cycles although having higher remanent polarization. Barium titanate and strontium titanat thin films have better fatigue resistance but have lower remanent polarization [3，4]。Bismuth-containing layered perovskites ($SrBi_2Ta_2O_9$, $SrBi_2NbTaO_9$ and $SrBi_4Ta_4O_{15}$, *et al*)have been found to be ferroelectric properties by Smolenskii *et al* [5]. Many such materials have a very high curie temperature and good fatigue resistance, but relatively small values of 2Pr in form of a film. Many researchers started to be interest in $Bi_4Ti_3O_{12}$ with its bulk value of 2Pr about 60μC cm^{-2}, however $Bi_4Ti_3O_{12}$ as a thin film shows fatigue and has an unexpectedly low value of 2Pr of 4-8μC cm^{-2} [6]. To enhance the fatigue resistance and remanent polarization 2Pr of $Bi_4Ti_3O_{12}$ thin film, substitution of bismuth with ions such as lanthanum (La) [7-10], neodymium (Nd) [9,11-14], samarium (Sm) [9,15] or yttrium (Y) [16] were studied. Among these, neodymium substituted bismuth titanate ($Bi_{4-x}Nd_xTi_3O_{12}$) (BNT) system exhibited the most remarkable ferroelectric properties, for example Chou and co-workers [17] reported that the *c*-axis oriented BNT capacitor was characterized by a switchable remanent polarization 2Pr of over 100μC cm^{-2} and imprinting and fatigue-free. The polarization vector of the substituted bismuth titanate thin films remained at *a*-axis as bismuth titanate ($Bi_4Ti_3O_{12}$), as reported in some literatures [8,11], but turn toward to *a*-axis as reported in other literature[7,9,13-15,17]. Thus, it is necessary to investigate effects of technique conditions on texture and orientation of *a*-axis oriented and *c*-axis orientated neodymium substituted bismuth titanate thin films.

The many studies indicated that neodymium substituted $Bi_4Ti_3O_{12}$ thin films can be fabricated by rapid thermal annealingat 550-750 ℃ for 3min. With this technique, orientation of film is mainly depended on the lattice parameters and orientation of substrate and influenced also by annealing temperature and annealing time [18，19] . In this paper we reported on (i) preparation of neodymium substituted $Bi_4Ti_3O_{12}$ thin films on p-Si(100) substrates using chemical solution deposition process and (ii) effects of annealing schedules on orientation of the film.

2. Experimental procedure

2.1 Fabrication of precursor solution

The starting materials for metalorganic solution deposition process were bismuth nitrate, neodymium nitrate and titanium isopropoxide with glacial acetic acid as solvent and citrate acid (CA) as chelating agent and acetylaccetone as stabilizing agent. Bismuth nitrate and neodymium nitrate were initially dissolved in glacial acetic acid, citrate acid and glycols with molar ratio of (Bi^{3+}+Nd^{3+}+Ti^{4+}): CA=1: 2 were added to this solution with constant stirring. The titanium isopropoxide stabilized with acetylaccetone was dissolved in glacial acetic acid. 2mol% excess bismuth was additionally added to compensate the bismuth loss during firing. Two solutions were mixed together followed by adding HCl until pH=1-2 with stirring and stable for 72 h. As-mixed solution was red-colored transparent resin with the concentrations of 0.03264 M, 0.008 M and 0.03 M for Bi^{3+}, Nd^{3+} and Ti^{4+} respectively.

2.2 Coating film and annealing

The p-Si(100) substrates were cleaned by ultrasonification in acetone and ethanol. The precursor solution was dip coated on the substrate at a hoist speed of 0.8-1 cm/min. The as-deposited films were dried at 120-130 ℃ for 1-2 min in a furnace to remove the solvent. 5-layers films were achieved by repeating dip-coating and drying.

The as-dried multiple films were annealed using the following schedules: (i) the films were preannealed at 400 ℃ for 10 min followed by insert the film to a furnace at 700 ℃ and annealed for 3 min and 10 min respectively; (ii) the film were directly insert to a furnace at 700 ℃ and 800 ℃ and annealed for 3 min respectively. Stablilizing the solusion for a longer period and slower rate of hoisting the films are essential for compacting the films.

2.3 Characterization of the films

The phase identification of the deposited neodymium substituted $Bi_4Ti_3O_{12}$ thin films was conducted at room temperature using X-Ray diffractometry (XRD, CuK$_{\alpha 1}$, λ=0.15406nm, Model No: D/Max-2200PC, Rigaku, Japan).. The phases and particle sizes of the films were determined with the Jade5 analytic software carried with X-Ray diffractometry. The morphologies of the films were analyzed using atomic force microscopy (AFM, Model No: SPI3800N, Japan). Raman spectroscopy of the films was performed using a MiniRam spectrometer. The laser beam used as excitation source is of a wavelength of 785nm and a power of 300 mW. The laser beam was focused on the sample through a 50× objective (numerical aperture = 0.75).

3. Results and discussion

To investigate the effects of annealing schedules on orientation of $Bi_{3.2}Nd_{0.8}Ti_3O_1$ thin films deposited by metalorganic precursor process, annealing schedules with preannealing and without preannealing were used. As-deposited films were preannealed at 400 ℃ for 10 min followed by annealed at 700 ℃ for 3 min and 10 min respectively. Fig. 1 shows the XRD patterns of as-annealed $Bi_{3.2}Nd_{0.8}Ti_3O_1$ thin films. When annealed for 3 min, the intensity of (200) strong peak at 2θ≈32.98º was remarkable larger than that of other peaks, the degree of orientation of the film was $I_{(200)}/I_{(117)}=0.574$, indicating texture of the film was obviously a-axis orientation. Particle size of the films determined with (117) strong peak was 24.3 nm. For 10 min intensity of (200) peak at 2θ≈32.98º increased further, the degree of orientation of the film was $I_{(200)}/I_{(117)}=0.633$, indicating texture of film was also a-axis orientation. Particle size of the films determined with (117) strong peak was 25.7 nm. As-deposited films were also annealed at 700 ℃ and 800 ℃ for 3 min without preannealing. Fig. 2 shows the XRD patters of as-annealed $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$ thin films. When annealed at 700 ℃, the intensity of (008) peak at 2θ≈21.64º was remarkably larger than that of other peaks, the degree of orientation of the film was $I_{(008)}/I_{(117)}=0.605$, indicating that the texture of the film was obvious c-axis orientation. At 800 ℃ the intensity of (008) peak successively increased, indicating c-axis orientation further enhanced. Particle size of the films determined with strong peak (008) was 36.2 nm.

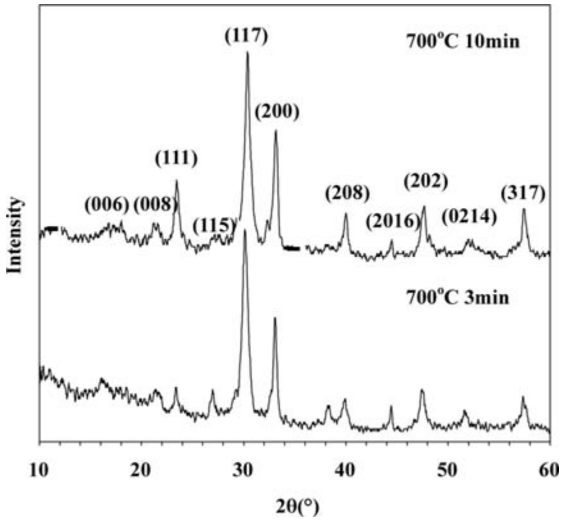

Fig. 1. XRD patterns of $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$ ferroelectric films preannealed at 400 ℃ for 10 min and annealed at 700 ℃for 3 min and 10 min, respectively.

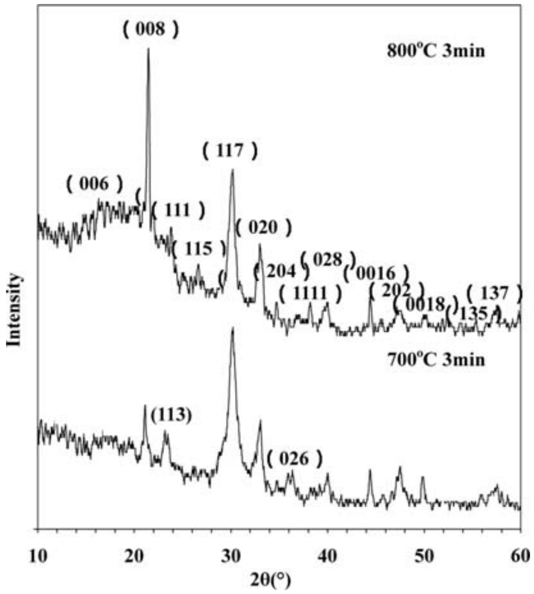

Fig. 2. XRD patterns of $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$ ferroelectric films annealed at 700 ℃ and 800 ℃ for 3 min respectively without preannealing.

Fig. 3 shows the AFM photograghs of the $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$ films rapidly annealed at 700 ℃ and 800 ℃ for 3 min respectively with and without preannealing at 400 ℃ for 10 min. Two films had respectively particle sizes about 100 nm and 40 nm. It is could deduced that the film with preannealing was of the strip grains texture that lengthwise and widthwise directions of the strip grain were respectively *b*-axis and *c*-axis direction of film parallel to *b*-axis and *c*-axis of substrate respectively and *a*-axis of film was perpendicular to substrate surface, which was formed due to good matching in lattice parameter *b* with p-Si(100) substrate. The film without preannealing consisted of columnar crystallites perpendicular to substrate surface or consisted of spherical grain.

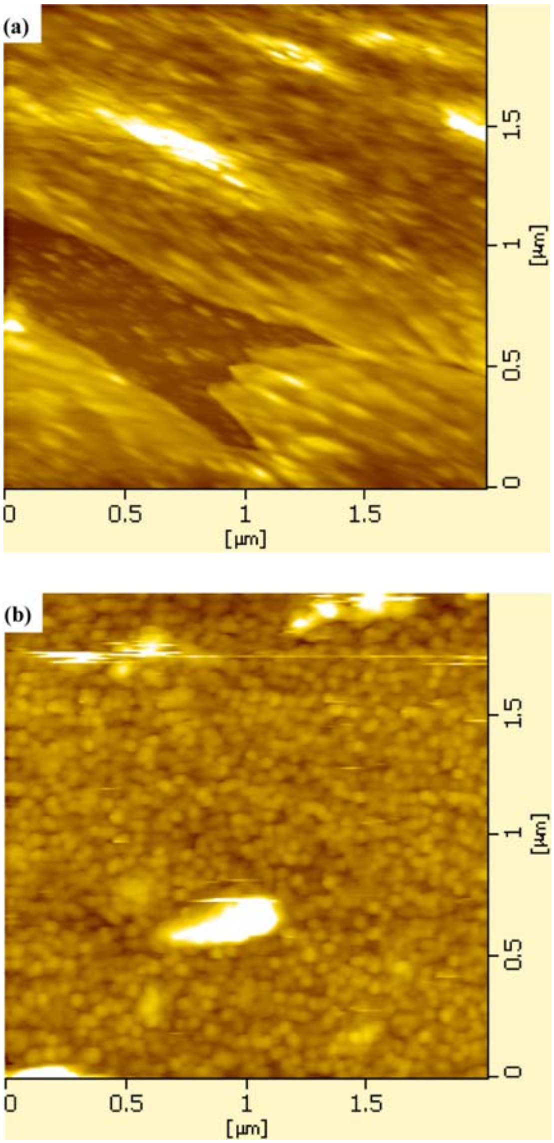

Fig. 3. AFM photograghs of $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$ ferroelectric films annealed (a) at 700 ℃ for 10 min with preannealing and (b) at 800 ℃ for 3 min without preannealing.

The formation of the c-axis oriented columnar $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$ film without preannealing was similar to the transformation process of chemical solution deposited columnar $BaTiO_3$ film at a rapid heating rate that involved the bulk nucleation throughout the film originating film surface followed by the consumption of matrix by an epitaxial overgrowth process originating at the seed layer, as reported by Schwartz et al [20]. In the nucleation process, columnar nuclei perpendicular to substrate surface was formed in the film without preannealing and became original site of epitaxial overgrowth and resulted in formation of the columnar film. At lower annealing temperature of 700 ℃ columnar nuclei and its effect were weak and resulted in less *c*-orientation degree (Fig. 2). The nuclei formed by preannealing film at 400 ℃ were not similar column and restricted formation of the columnar nuclei in rapid heating process. Substrate effect motivated in nucleation and crystallization of the strip $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$ crystallite. The preheat treatment also had the effect in the formation of *a*-axis orientation texture motivated by the substrate effect. The increase of the *a*-orientation degrees as increase in annealing time (Fig. 1) may be due to enhancement of effect of Si(100) substrate as original site of film epitaxial overgrowth with increasing annealing time.

Fig. 4 shows the Raman spectra of the films with different orientations. According to Ref. 21 and 22, we assigned the 850 cm^{-1} mode as stretching mode of TiO_6 octahedron. This mode appears at higher frequency for the *a*-oriented film, which means a less distortion and larger O_h symmetry of TiO_6 octahedron. The 970 cm^{-1} mode is very strong and do not appears in the Raman spectra of $Bi_{4-x}La_xTi_3O_{12}$ film and $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ nanorods respectively reported by Yau *et al* [21] and Hu [22]. This high frequency mode could be a characteristics mode arisen from the polarization of the films induced by surface electromagnetic wave introduced by high power laser of 300 mW. The mode appears more intense for the (200)-oriented film compared to the (800)-oriented film, which could implies the polarization vector should be at *a*-axis of the film.

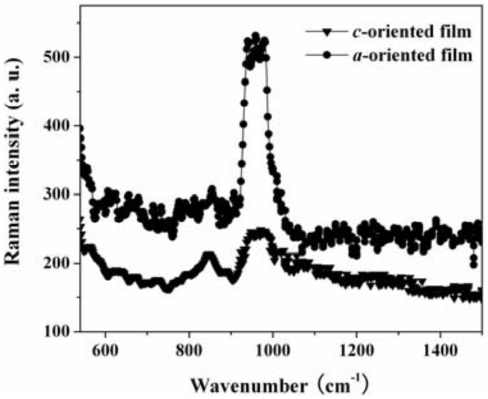

Fig. 4. Raman spectra of the films (●) annealed at 700 ℃ for 10 min after the preannealing., (▼) directly annealed at 800 ℃ for 3 min.

4. Conclusions

The ferroelectric $Bi_{3.2}Nd_{0.8}Ti_3O_{12}$ thin films were successfully prepared on p-Si(100) substrates by using metalorganic solution deposition process. The films with extremely different orientations were achieved by using different annealing schedules.

The *a*-axis and *c*-oriented films can be achieved with and without preannealing followed by rapid thermal annealing respectively. Their orientation degrees can be increased with increasing the annealing time and annealing temperature respectively. Raman analysis revealed that *a*-oriented film is of more intense polarization compared to the *c*-oriented film.

Acknowledgements

Authors gratefully thanks professor K. Q. Liu (Advanced Material Analysis and Test Center, Xi'an University of Technology) and S. N. Li (College of Chemistry and Chemical Engineering, Shaanxi Normal University) for their helps of the SEM and Raman measurement.

Authors also thank the financial assistance of the specific scientific research projects of Shaanxi Provincial Education Committee (09KJ348).

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