Orientation of $Bi_{3.2}La_{0.8}Ti_3O_{12}$ Ferroelectric Thin Films with Different Annealing schedules

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Abstract: Fatigue-free $Bi_{3.2}La_{0.8}Ti_3O_{12}$ Ferroelectric thin films were successfully prepared on p-Si(100) substrates using metalorganic solution deposition process. The orientation and formation of 5-layers thin films were studied under different technologic condition using XRD. Experiment results indicated that increase in annealing time at 700°C after preannealing for 10min at 400°C can remarkably increased (200)-orientation of the films either at high content of citric acid or at low content of citric acid in the precursor solution, and high content of citric acid increased the film thickness and was conducive to the a-orientation of the films with the preannealing, low concentration of the solution was conducive to the c-orientation of the films without the preannealing.

Key words: $Bi_{3.2}La_{0.8}Ti_3O_{12}$, ferroelectric film, technologic condition, orientation

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]. To enhance the fatigue resistance and remanent polarization 2Pr of $Bi_4Ti_3O_{12}$ thin film, substitution of bismuth ion (Bi^{3+}) with ions such as lanthanum (La^{3+}) [3-6], neodymium (Nd^{3+}) [5,7-10], samarium (Sm^{3+}) [5,11] or yttrium (Y^{3+}) [12] were studied. The polarization vector of substituted bismuth titanate thin films remained at a-axis as bismuth titanate ($Bi_4Ti_3O_{12}$)[4, 7], but turn toward the c-axis, as reported in other literatures [3,12]. Large orientation degrees of films in a polarization vector can result in a large remanent polarization. Thus, it is necessary to investigate the technique conditions of fabricating a-axis oriented and c-axis oriented substituted bismuth titanate thin films and enhancing orientation of thin films. To increase the a-orientation of the film is especially of interesting to polarization due to which is polarization vector of $Bi_4Ti_3O_{12}$.

Many studies indicated that lanthanum substituted $Bi_4Ti_3O_{12}$ thin films can be fabricated by rapid thermal annealing at 550-750°C for 3min. With these technique, orientation of film is mainly depended on the lattice parameters and orientation of substrate and influenced also by annealing temperature and annealing time [13□14]. Author and co-workers[15] studied the effects of annealing schedules and film thickness on the orientation of $Bi_{3.2}La_{0.8}Ti_3O_{12}$ film prepared via metalorganic deposited process on p-Si(100) substrate and deduced further transformation process of orientation of film under different annealing schedules and film thickness on the XRD and AFM analysis, that is, rapid thermal annealing without preannealing produced columnar nuclei perpendicular to the substrate surface on which the c-oriented columnar film was formed and preannealing produced non-columnar nuclei and restricted formation of column film and resulted in the a-oriented platelike film on good matching in lattice parameter a and b with substrate. In present paper we focus on (i) preparation of lanthanum substituted $Bi_4Ti_3O_{12}$ thin films on p-Si(100) substrates using metalorganic deposition process at different content of citric acid in precursor solution and (ii) variation of orientation degree of the 5-layers films annealed for different annealing time with preannealing and annealed at different temperature without prerannealing.

2. Experimental Procedure

2.1. Fabrication of Precursor Solution

The starting materials for metalorganic deposition process were bismuth nitrite, lanthanum chloride and titanium isopropoxide with glacial acetic acid as solvent and citrate acid as chelating agent and acetylaccetone as stabilizing agent. The metalorganic precursors were formed by mixing starting materials at base composition of $Bi_{3.2}La_{0.8}Ti_3O_{12}$ and 5mol% excess bismuth to compensate the bismuth loss during firing followed by added HCl aqueous until pH=1-2 with constant stirring. Citrate acid (CA) and ethylene glycols (EG) with molar ratio of (Bi^{3+}+Nd^{3+}+Ti^{4+}): EG: CA=1: 1: 1 and 1: 1: 2 were then added to two portions of the precursors, respectively. The resultant solution precursors were rose red-colored transparent resin with the concentrations of 0.0168M, 0.004M and 0.015M for Bi^{3+}, La^{3+} and Ti^{4+} respectively.

2.2 Coating Film and Annealing

The p-Si(111) and (100) substrates were cleaned by ultrasonification in ethanol. The precursors containing two citric acid contents were respectively dip coated on the substrates at a withdrawal speed of 0.5-2cm/s. The as-deposited films were dried at 150°C for 1-2min in a furnace to remove the solvent after each coating. 5 layers films were achieved by repeating dip-coating and drying.

The as-dried multiple films were annealed using the following two schedules: (i) the films were preannealed at 400°C for 10min followed by insert the film to a furnace at 700°C and annealed for 3min and 10min; (ii) the films were insert to a furnace at 700°C and 800°C and annealed for 3min.

2.3 Characterization of the Films

The phase indentification of the deposited lanthanum substituted $Bi_4Ti_3O_{12}$ thin films were conducted at room temperature using X-Ray diffractometer (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 diffractometer.

3. Results and Discussion

To investigate the effects of citric acid content in the precursor solution and annealing schedule on the orientation and formation of the films, the precursors containing two contents of citric acid and two annealing schedules were used in this study and the films were characterized with XRD. At high content of citric acid, i.e. molar ratio of (Bi^{3+}+Nd^{3+}+Ti^{4+}): CA=1: 2, the XRD patterns of $Bi_{3.2}La_{0.8}Ti_3O_{12}$ thin films annealed at 700°C and 800°C for 3min without preannealing were shown in figure2, the (117) peak at 2θ≈30.78° was only obvious peak for the film annealed at 700°C, and (200) peak at 2θ≈32.78°and (008) peak at 2θ≈21.44° were enhanced at 800°C which indicated formation of multi-crystalline. These can be contributed to the bulk nucleation throughout the film originating at film surface followed by the consumption of matrix by an epitaxial overgrowth process originating at the columnar nuclei which result in formation of c-oriented crystalline in the film, similar to a transformation process reported in the literature[16-18], and the epitaxial overgrowth process originating at Si(100) substrate in processes of nucleation and crystallization on matching in lattice parameter a and b with Si(100) substrate, which result in formation of a-oriented crystalline in the film. The XRD patterns of $Bi_{3.2}La_{0.8}Ti_3O_1$ thin films with high citric acid content preannealed at 400°C10min and then annealed at 700°C for 3min and 10min were shown in figure3, the (200) peak at 2θ≈32.78°in these figures were remarkable, indicating texture of the film was also obvious a-axis orientation. The orientation degree of $I_{(200)}/I_{(117)}$ was also increased from 0.805 to 8.32 as increasing annealing time from 3min to 10min.

At low content of citric acid, i.e. molar ratio of (Bi^{3+}+Nd^{3+}+Ti^{4+}): CA=1: 1, the XRD patterns of $Bi_{3.2}La_{0.8}Ti_3O_1$ thin films preannealed at 400°C10min and annealed at 700°C for 3min and 10min were shown in figure 1, the (200) peak at 2θ≈32.78°in these figures were remarkable, indicating the texture of the film was obvious a-axis orientation. The orientation degree of $I_{(200)}/I_{(117)}$ was increased from 0.589 to 2.933 as increasing annealing time from 3min to 10min. These may was due to the epitaxial overgrowth process originating at Si(100) substrate in processes of nucleation and crystallization was absolute superior during annealing time of 10min and good matching in lattice parameter a and b of film with Si(100) substrate as reported in the literature[15].

By comparison, high content of citric acid was conducive to enhancement of the a-orientation of the films. These may be due to high content of citric acid in the precursor solution produced a high viscosity of the solution which resulted in increase in thickness of films, and thicker film provided more matrix from which the a-oriented films can further grew because the a-axis of the film was perpendicular to the p-Si (100) substrate surface on the good matching in lattice parameter a and b of film with Si(100) substrate.

To investigate variation of the film prepared with different concentration of precursor solution, in this work we deposited the films at lower concentration than reported by author and co-workers[15] with same other deposition process. For comparing table1 summarize the orientation degrees of 5-layer films prepared under various technique conditions. The high concentration of the precursor solution obviously resulted in enhancement of a-orientation of the film, which is due to high concentration of the precursor solution resulted in increase in thickness of the films. However, low concentration of the precursor solution resulted in c-orientation of the film without preannealing, similar to enhancement of c-orientation of $BaTiO_3$ film resulted from low concentration of solution that produced small individual layer thickness as reported by Cheng and co-workers[19].

4. Conclusions

The fatigue-free ferroelectric $Bi_{3.2}La_{0.8}Ti_3O_{12}$ thin films were successfully prepared on p-Si(100) substrates using metalorganic solution deposition process. The films with extremely different orientations and orientation degree were achieved by using two annealing schedules and different annealing time respectively.

The obviously a-axis oriented film were achieved by preannealing films at 400°C for 10 min followed by inserting the films to a furnace at 700°C and annealing for 3min and 10min. Increase of annealing time after preannealing can further enhanced the a-orientation of the films. High content of citric acid increased film thickness and was conductive to enhancement of a-orientation of the films.

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5. References

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Figure Captions Legend:

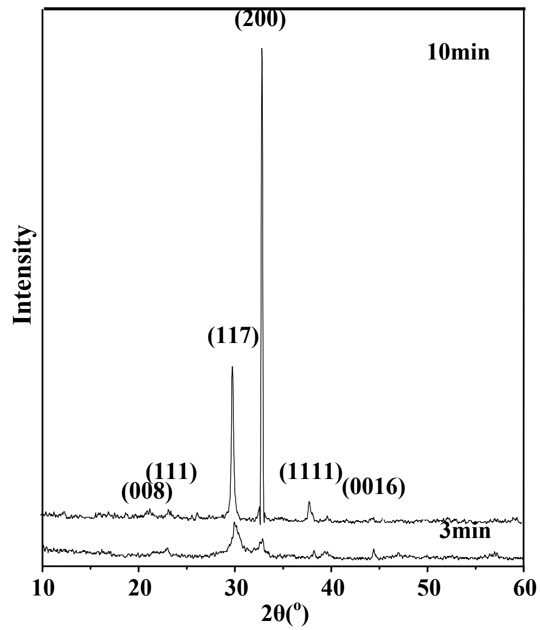

Figure 1: XRD patterns of $Bi_{3.2}La_{0.8}Ti_3O_{12}$ films preannealed at 400°C for 10 min and then annealed at 700°C for 3min and 10min, $(Bi^{3+}+Nd^{3+}+Ti^{4+})$: CA=1: 1

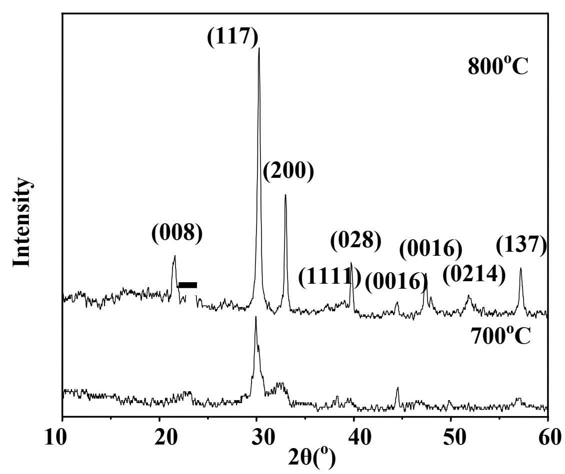

Figure 2: XRD patterns of $Bi_{3.2}La_{0.8}Ti_3O_{12}$ films annealed at 700°C and 800°C for 3min without preannealing, $(Bi^{3+}+Nd^{3+}+Ti^{4+})$: CA=1: 2

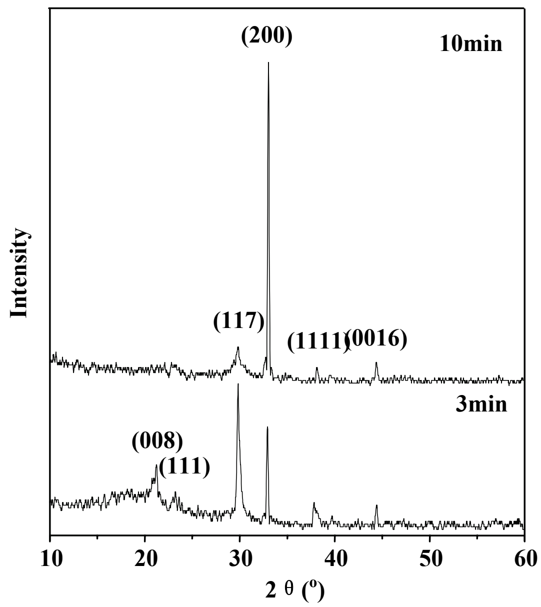

Figure 3: XRD patterns of $Bi_{3.2}La_{0.8}Ti_3O_{12}$ films preannealed at 400°C for 10 min and then annealed at 700°Cfor 3min and 10min, $(Bi^{3+}+Nd^{3+}+Ti^{4+})$: CA=1: 2

Table Captions Legend:

Table1. orientation degrees of $Bi_{3.2}La_{0.8}Ti_3O_{12}$ films prepared under different conditions, concentration of Ti^{4+} cation(M_{Ti4+}), Me: CA, annealing schedule

Technique condition			Orientation degree		Particle size
M_{Ti4+}	Me□CA	annealing schedule	$I_{(200)}/I_{(117)}$	$I_{(008)}/I_{(117)}$	(nm)
0.03M	1□2	700°C 3min,	2.849		45.6
0.03M	1□2	400°C 10 min+ 700°C 3min	5.700		67.3
0.015M	1□1	400°C10 min+700°C 3min	0.589		11.0
0.015M	1□1	400°C10 min+700°C 10min	2.933		72.9
0.015M	1□2	700°C 3min	0.066	10.4	
0.015M	1□2	800°C 3min	0.246	24.0	
0.015M	1□2	400°C10 min+700°C 3min	0.805		22.5
0.015M	1□2	400°C10 min+700°C 0min	8.320		55.0