Orientation of Bi$_{3.2}$La$_{0.8}$Ti$_3$O$_{12}$ Ferroelectric Thin Films with Different Annealing Schedules

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Abstract: Fatigue-free Bi$_{3.2}$La$_{0.8}$Ti$_3$O$_{12}$ 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 processing conditions using XRD. Experimental results indicate that increase in annealing time at 700 °C after preannealing for 10 min at 400 °C can remarkably increase (200)-orientation of the films derived from the precursor solutions with two contents of citric acid. Meanwhile, high content of citric acid increases the film thickness and is conducive to the $a$-orientation of the films with the preannealing, and low concentration of the solution is conducive to the $c$-orientation of the films without the preannealing.

Key words: Bi$_{3.2}$La$_{0.8}$Ti$_3$O$_{12}$; ferroelectric film; technologic condition; orientation

1 Introduction

Ferroelectric thin films have been widely investigated for their 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 $2P_r$ of Bi$_4$Ti$_3$O$_{12}$ 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$_4$Ti$_3$O$_{12}$)$^{[4,7]}$, but turn toward the $c$-axis, as reported in other literatures$^{[3,12]}$. Large degree of orientation 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. It is especially of interest to increase the $a$-orientation of the film the polarization due to which is polarization vector of Bi$_4$Ti$_3$O$_{12}$.

Many studies indicated that lanthanum substituted Bi$_4$Ti$_3$O$_{12}$ thin films can be fabricated by rapid thermal annealing at 550-750 °C for 3 min. With these techniques, orientation of film is mainly depended on the lattice parameters and orientation of substrate and influenced also by annealing temperature and annealing time$^{[13,14]}$. It is suggested that the La-substituted Bi$_{4-x}$La$_x$Ti$_3$O$_{12}$ thin films have the highest remanent polarization as $x=0.8$$^{[12,15]}$. The effects of annealing schedules and film thickness on the orientation of Bi$_{3.2}$La$_{0.8}$Ti$_3$O$_{12}$ film, which was prepared via metalorganic deposited process on p-Si (100) substrate, and the transformation process of orientation of film under different annealing schedules and film thickness on the XRD and AFM analysis were investigated. Rapid thermal annealing without a preannealing produced a columnar nuclei perpendicular to the substrate surface, and the $c$-oriented columnar film was formed on this columnar nuclei. Meanwhile, the preannealing produced non-columnar nuclei, restricted formation of column film, and resulted in the $a$-oriented plate-like film on good matching in lattice parameters $a$ and $b$ with substrate. We focused on the preparation of Bi$_{3.2}$La$_{0.8}$Ti$_3$O$_{12}$ thin films on p-Si(100) substrates using metalorganic deposition process at different contents of citric acid in precursor solution, and the variation of orientation degree of the 5-layers films annealed for different annealing time with preannealing and annealed at different temperatures without preannealing.

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2 Experimental

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 acetylacetone as stabilizing agent. The metalorganic precursors were formed by mixing starting materials at base composition of Bi$_{3.2}$La$_{0.8}$Ti$_3$O$_{12}$ and 5 at% excessive 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 ratios 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 0.0168 M, 0.004 M and 0.015 M for Bi$_{3+}$, La$_{3+}$ and Ti$_{4+}$ respectively.

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 0.5-2 cm/s. The as-deposited films were dried at 150°C for 1-2 min in a furnace to remove the solvent after each coating. 5-layer 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 10 min followed by insert the film to a furnace at 700°C and annealed for 3 min and 10 min; (ii) the films were inserted in to a furnace at 700°C and 800°C annealing for 3 min.

Phase indentification of the deposited lanthanum substituted Bi$_4$Ti$_3$O$_{12}$ thin films were conducted at room temperature using X-Ray diffractometer (XRD, Cu Kα, λ=0.154 06 nm, Model No: D/Max-2200PC, Rigaku, Japan). 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 and the films were characterized by XRD. At high content of citric acid, ie molar ratio of (Bi$_{3+}$+Nd$_{3+}$+Ti$_{4+}$)∶CA=1∶2, XRD patterns of Bi$_{3.2}$La$_{0.8}$Ti$_3$O$_{12}$ thin films annealed at 700°C and 800°C for 3 min without preannealing are shown in Fig.1, in which (117) peak around 30.78° is the only obvious peak for the film annealed at 700°C, and (200) peak at 32.78° and (008) peak at 21.44° are enhanced at 800°C, indicating the 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, leading to the formation of c-oriented crystalline in the film, similar to a transformation process reported in the literatures[17-19]. Meanwhile, 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, result in formation of a-oriented crystalline in the film. XRD patterns of Bi$_{3.2}$La$_{0.8}$Ti$_3$O$_{12}$ thin films preannealed at 400°C for 10 min and then annealed at 700°C for 3 min and 10 min are shown in Fig.2. (200) peak at 32.78° are remarkable, indicating obvious a-axis orientation in the texture of the film. The intensity ratio of I$_{(200)}$/I$_{(117)}$ also increases from 0.805 to 8.32 as annealing time increasing from 3 min to 10 min, which may be due to the epitaxial overgrowth process originating at