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C-axis-oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ferroelectric thin film fabricated by chemical solution deposition

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Abstract

C-axis-oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) ferroelectric thin films were successfully prepared by chemical solution deposition. According to X-ray diffraction, it is found that the orientation degree increases with the increase of sintering temperature, and at the same time the grain morphology changes from equiaxed to plate-like. Due to the dense morphology and $[Bi_2O_2]^{2+}$ layer of *c*-preferred orientation of BLT film sintered at 650 °C, it exhibits the lowest leakage current density at room temperature. Additionally, a linear relation between $V^{0.5}$ and $\log(J/T^2)$ is found, suggesting the behavior of leakage current of BLT films obeys the Schottky emission model. *P–E* loops show that the *c*-axis-oriented BLT ferroelectric film exhibits low polarization and small coercive field.

Keywords: Ferroelectrics; Thin films; Orientation; Bismuth titanate

1. Introduction

$Bi_4Ti_3O_{12}$ (BiT) belongs to Aurivillius phases, a family of layered bismuth compounds, which consist of $[Bi_2O_2]^{2+}$ and perovskite-like $[A_{n-1}B_nO_{3n+1}]^{2-}$ layers [1,2]. The symmetry of BiT has been reported to be monoclinic with β very close to 90° [3]. Recently, Hervoches and Lightfood [4] refined the structure by neutron diffraction, and claimed that it is orthorhombic with the lattice parameter: $a=5.4444$ Å, $b=5.4086$ Å, and $c=32.8425$ Å. The Curie temperature of BiT was reported to be 676 °C, and spontaneous polarizations along the *a* and *c* axes are 50 ± 5 μC/cm^2 and 4 ± 0.1 μC/cm^2 respectively [5,6]. Recently, *c*-axis-oriented BiT-based ferroelectric film attracts extensively interests for application in metal–ferroelectric–metal–insulator–semiconductor (MFMIS), due to a low remnant spontaneous polarization (P_r), a low dielectric constant, and a low processing temperature [7,8]. However, pure BiT ferroelectric film always exhibits a large leakage current as well as a rough surface due to evaporation of bismuth [9]. As known, substituting La in BiT suppresses the evaporation of bismuth and the extensive grain growth, therefore it is expected that La-substitute BiT film may be a promising candidate for MFMIS application. In this paper, the structure characteristics and electrical properties of *c*-axis-oriented $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) films fabricated by chemical solution deposition are investigated.

2. Experiment procedure

Thin films were fabricated by chemical solution deposition (CSD). $Bi(NO_3)_3\cdot5H_2O$, $Ti(O_nC_4H_9)_4$ and $La(NO_3)_3\cdot6H_2O$ were selected as starting materials. The details of the precursor solution preparation were similar to Wu et al. [10]. After spin coating, the deposited film was dried at 260 °C for 10 min. To crystallize films, a 2-step Rapid Thermal Annealing (RTA) was employed. The dried films were heated at 500 °C for 60 s, and then heated at a higher annealing temperature (600 °C, 650 °C, 700 °C or 750 °C) for 60 s (abbreviated as BLT600, BLT650, BLT700 and BLT700, respectively). The crystallinity and morphology of the BLT film were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscope (AFM). The *P–E* hysteresis loop measurement was carried out at room temperature using TF analyzer 2000 (aixACCT).

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3. Results and discussion

Fig. 1 shows that the thickness of BLT films was about 300 nm. X-ray diffraction patterns of BLT/Pt/Si films are shown in Fig. 2, and almost all of the diffraction peaks are indexed according to the standard powder diffraction data of $Bi_4Ti_3O_{12}$ (PDF#73-2181). Only a weak peak responding to $Bi_2Ti_2O_7$ is found in BLT750, which is attributed to the extensive evaporation of bismuth at high temperature. When the sintering temperature increases to 650 °C, 700 °C, or 750 °C, strong *c*-axis-orientation reflection peaks dominate X-ray diffraction pattern. It demonstrates that BLT650, BLT700 and BLT750 show the preferred *c*-orientation, and the intensity of *00l* reflections increases with sintering temperature. Simplified approximation of the Lotgering degree of orientation (*f*) was evaluated according to the following equation [11]:

$$f = \frac{I_{006}}{I_{006} + I_{117}} \tag{1}$$

where I_{006} and I_{117} are 006 and 117 peak intensities.

The *c*-orientation degrees (f) of BLT650, BLT700 and BLT750 are estimated to be 72.4%, 95.4% and 97.9% respectively, suggesting that the degree of orientation increases with the increase of sintering temperature, which agrees with Xiang et al. [12]. It is believed that the development of *c*-orientation closely relates to the anisotropic growth of $Bi_4Ti_3O_{12}$ grain. Similar to the growth of $Bi_4Ti_3O_{12}$ film on amorphous fused quartz [13], there is no lattice matching between the $Bi_{3.25}La_{0.75}Ti_3O_{12}$ films and the Pt substrate in the current work. Therefore, the growth of films is mainly determined by the balance of the interfacial energy of the $Bi_{3.25}La_{0.75}Ti_3O_{12}$ films and the Pt substrate. As known, the higher the atomic plane density, the lower the interfacial energy, thus *c*-plane of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ film exhibits the lowest interfacial energy, which contributes to the *c*-preferred orientation of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ in the current work [13,14].

Fig. 3 shows the surface morphology of BLT films by an AFM. As shown, grain size increases with the sintering temperature. The equiaxed grains are found in BLT600 and BLT650, whereas the plate-like grains appear in BLT700, and dominate in BLT750. As known, the formation of plate-like grain is attributed to anisotropic growth of BLT. $Bi_4Ti_3O_{12}$-based ferroelectric exhibits much lower interfacial energy of *c*-plane than that of *a*/*b*-plane, resulting in a higher growth speed of *c*-plane. At high sintering temperature, the extensive grain growth by consuming the equiaxed small grains results in the formation of plate-like grain [15]. Together with the X-ray diffraction results, the growth of plate-like grain might correspond to *c*-axis preferred orientation, which is similar to previous reports. [12,16].

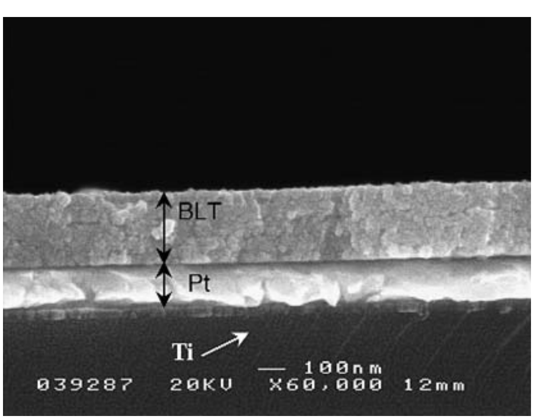

Fig. 1. SEM image of cross section view of BLT600/Pt/Ti/SiO_2/Si.

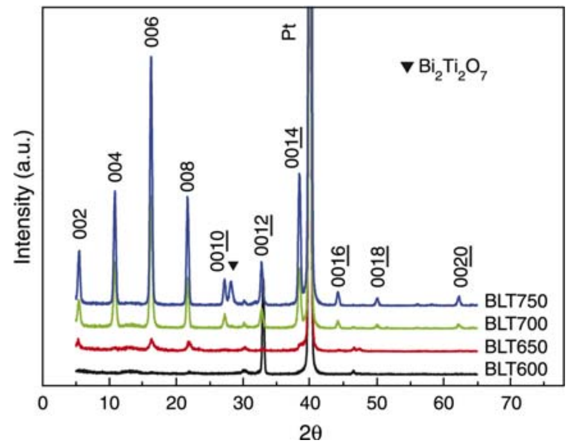

Fig. 2. X-ray diffraction patterns of BLT/Pt thin films.

The dependence of leakage current density on applied voltage for BLT films is shown in Fig. 4. Leakage current density increases gradually with applied voltage when electric field is lower than 200 kV/cm, and it is generally in the order of 10^{-9}–10^{-6} A/cm^2. Wu et al. has reported that when electric field is lower than 100 kV/cm, leakage current density is in the order of 10^{-7}–10^{-6} A/cm^2, and when the electric field is higher than 100 kV/cm leakage current density jumps to $\sim 10^{-2}$ A/cm^2 in $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ thin film [17]. Moreover, leakage current density firstly decreases with the increase of sintering temperature from 600 °C to 650 °C, and then increases with the increase of sintering temperature from 650 °C to 750 °C. As shown in Fig. 4(a, b), BLT600 and BLT650 exhibit dense morphology, while a porous morphology is found in BLT700 and BLT750 (pores are signed by arrows, as shown in Fig. 4(c, d)). It is believed that the appearance of pores due to extensive growth of plate-like grains leads to the low quality of thin film, resulting in higher leakage current density. For BLT600 and BLT650, even though they show similar dense morphology, BLT650 exhibits preferred *c*-axis-orientation (Fig. 2). As known, $(Bi_2O_2)^{2+}$ layers in BLT act as an insulator [18], therefore it is expected that the *c*-axis-oriented BLT films exhibit low leakage current, which well agrees with our results, and it can also explain the lower leakage current density in the current work than that in Wu et al.'s report [17]. At high sintering temperature, the extensive evaporation of bismuth results in the formation of several kinds of defects such as bismuth vacancies and oxygen vacancies [19,20], which is attributed to the increase of leakage current density. So far the dominant reason of the increase of leakage current density with sintering temperature is still ambiguous.

The behavior of leakage current density is fitted by the Schottky emission, as given by [21]

$$J = AT^2 e^{-\frac{\Phi_b}{kT}} e^{\frac{q}{kT}\sqrt{qV/4\pi d\varepsilon_0\varepsilon_r}} \tag{2}$$

Where A is the effective Richardson's constant; T is the temperature; Φ_b is the potential height on the surface; k is Boltzmann's constant; d is the film thickness; q is the magnitude of electronic charge; V is the applied voltage; ε_0 is the dielectric permittivity of vacuum; and ε_r is the dielectric constant of BLT.

If the current obeys the Schottky emission model, linear relation between $\log(J/T^2)$ and $V^{0.5}$ should be found. The dependence of log (J/T^2) on the applied voltage (V) ($1.0 < V^{0.5} < 2.2$) is shown in Fig. 4. As shown in the insert of Fig. 3, the linear relation between $V^{0.5}$ and $\log(J/T^2)$ suggests the validity of the Schottky emission current in