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Thickness dependence of microstructure, dielectric and leakage properties of $BaSn_{0.15}Ti_{0.85}O_3$ thin films

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ABSTRACT

The $BaSn_{0.15}Ti_{0.85}O_3$ (BTS) thin films are prepared on Pt-Si substrates with thickness ranging from ~ 60 nm to ~ 380 nm by radio frequency magnetron sputtering. The effects of thickness on microstructure, surface morphologies and dielectric properties of thin films are investigated. The thickness dependence of dielectric constant is explained based on the series capacitor model that the BTS thin film is consisted by a BTS bulk layer and an interfacial layer (dead layer) between the BTS and bottom electrode. The thin films with thickness of 260 nm give the largest figure of merit of 76.9@100 kHz, while the tunability and leakage current density are 64.6% and 7.46 × 10^{-7} A/cm^2 at 400 kV/cm, respectively.

1. Introduction

Lead free barium titanate based tunable thin films are being investigated for applications in electrical tunable devices such as tunable capacitors, phase shifters, resonators, antennas, tunable filters, electrical controlled oscillators and so on [1–4]. Barium strontium titanate ($Ba_xSr_{1-x}TiO_3$, BST) and barium zirconate titanate ($BaZr_xTi_{1-x}O_3$, BZT) thin films have been most extensively investigated because of their large tunability and moderate dielectric constant. However, the high dielectric loss (~ 0.02) strongly inhibits further practical application in tunable devices [5–7]. Alternative tunable thin films are therefore of great scientific and technological interest. Among various alternatives, barium tin titanium ($BaSn_{0.15}Ti_{0.85}O_3$, BTS) thin films have been paid much attention due to the large tunability and relatively low loss tangent [8–10]. In previous study, under an applied bias field of 400 kV/cm and a frequency of 100 kHz, the loss tangent of ~ 0.01 was achieved for the BTS thin films [9]. However, the loss tangent still cannot meet the requirement of application, more studies need to be done to further decrease the loss tangent [11].

The determinateness of dielectric properties is a collective phenomenon, associating with a critical correlation volume [12,13]. However, some other factors should be taken into account in the monitoring of the dielectric properties [14–17]. A low-dielectric and high-loss interfacial layer exists at the electrode/film interface, such an interfacial layer deteriorates the dielectric properties of thin films [18,19]. This interfacial layer acts as a parasitic capacitor in series with the "bulk-like" dielectric layer [20]. Therefore, the analysis of the thickness dependence on dielectric properties of the BTS thin films is very decisive for the performance optimization. In this paper, the $BaSn_{0.15}Ti_{0.85}O_3$ thin films with thickness ranging from 60 to 380 nm are grown on Pt-Si substrates by radio frequency (RF) magnetron sputtering. The effects of thickness on the microstructure and dielectric tunable properties as well as leakage current density are systematically investigated.

2. Experimental procedures

The BTS ceramic target was obtained by conventional solid state reaction method. $BaCO_3$ (99.9%), SnO_2 (99.9%) and TiO_2 (99.9%) powders were utilized for the preparation of target. The BTS was made from the chemical reaction as follow:

$$20BaCO_3 + 3SnO_2 + 17TiO_2 \rightarrow 20BaSn_{0.15}Ti_{0.85}O_3 + 20CO_2 \quad (1)$$

The raw powders were mixed in stoichiometric quantities and ball milled through ZrO_2 balls (diameter: 5.0 mm) in deionized water for 6 h. The obtained powder was calcined under air at 1100 °C for 2 h, and then mixed uniformly with polyvinyl alcohol (PVA) solution and uniaxial pressed into disk sample of around 60 mm of diameter and 3 mm of thickness. After removal of the binder, the disk was sintered in air at 1300 °C for 10 h. The diameter, thickness and density of the obtained BTS ceramic target were 51 mm, 2.9 mm and 95%, respectively. Before the deposition of BTS thin films, the distance from target to substrate was fixed at 8.0 cm and the base pressure of deposition chamber was evacuated to 3 × 10^{-4} Pa. BTS thin films were deposited on Pt-Si

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substrates by RF magnetron sputtering at the substrate temperature of 700 °C. The O_2 (15%) and Ar (85%) mixture gas was used as sputtering gas, the sputtering total pressure is 1 Pa. The deposition rate was ~ 6.0 nm/min, the sputtering power was 80 W. The thickness of BTS thin films was varied from 60 nm to 380 mm and estimated by control of deposition rate and time. At last, the as-deposited BTS thin films were in-situ annealed at 700 °C for 20 min in oxygen pressure of 1000 Pa.

X-ray diffraction (XRD) measurements of BTS thin films were carried out by a Bruker diffractometer (D8–Focus; Bruker AXS GmbH, Karlsruhe, German) with CuKα radiation. The density of the BTS ceramic target was measured by density meter (Alfamirage SD-200L). The thickness of BTS thin films was determined by Alpha–Step D–100 profilometer (KLA–Tencor, California, USA). The surface morphologies and roughness were characterized by the atomic force microscopy (AFM, Bruker, Santa Barbara, CA, USA) using a Nanoscope Multimode 8. For the electrical measurement, the Au electrodes with a thickness of 200 nm and a diameter of 200 μm was deposited by thermal evaporation using a shadow metal mask. The loss tangent and dielectric constant were measured by an Agilent 4294A LCR meter (Santa Clara, California, USA). The leakage current density was measured by ferroelectric test system (Radiant Technologies, Inc. of Albuquerque, New Mexico, USA.).

3. Results and discussion

Fig. 1 shows the XRD patterns of BTS thin films with various thicknesses. It can be seen that all the BTS thin films show single perovskite phase and exhibit four growth directions that are (1 1 0), (1 1 1), (2 1 0) and (2 1 1) phases. The intensity of main (1 1 0) peak in XRD patterns increases evidently as the increase in thickness, indicating that the crystallinity is improved. The full-width at half-maximum (FWHM) values of (1 1 0) peak for the BTS thin films with different thicknesses are shown in inset of Fig. 1. As the thickness of BTS thin films increases from 60 nm to 380 nm, the FWHM decreases from 0.75 to 0.24, which is generally related to the improvement of the crystallinity and enlargement of the crystallite size with increasing the thickness. Since both the microstructures and dielectric properties of thin films may be influenced by crystallite size [21,22], the average crystallite size can be calculated by using Scherrer's formula [23], the average crystallite sizes are 10.90, 16.03, 25.56 and 32.72 nm for the 60, 150, 160 and 380 nm thick BTS thin films, respectively. The increase of the average crystallite size with thickness is explained on the basis of Zener pinning effect (induced defects created in the system) [24]. The outward movement of grain boundaries is restricted by the retarding force generated by the

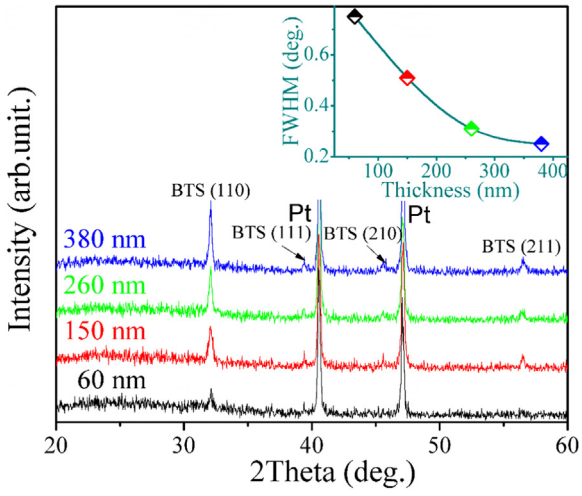

Fig. 1. XRD patterns of BTS thin films with various thicknesses. Inset shows thickness dependence of FWHM values of (1 1 0) peak for BTS thin films.

defects like vacancies and dislocation. For the 60 nm thick BTS thin films, a large number of defects exist in the thin films due the poor crystal quality. These defects suppress the grain growth owing to the Zener pinning effect. As the increase in thickness, the crystal quality is improved, the defects in BTS thin films are greatly reduced, the restriction of growth of the crystallites is greatly weakened. As a result, the crystallite size increases. In addition, the dislocation density can be used to estimate the amount of defects in a crystal, and it can be calculated as $\delta = 1/D^2$, where D is the crystallite size and δ is the length of dislocation [25]. As the dislocation density means the length of dislocation lines per unit volume of the crystal. Thus, the dislocation densities are 8.42×10^{15}, 3.89×10^{15}, 1.55×10^{15}, and 0.93×10^{15} lin/m^2 for the 60, 150, 160 and 380 nm thick BTS thin films, respectively. As the increase of thickness, the dislocation density decreases, which indicates the thick thickness can prevent defects generated in the BTS lattice.

Fig. 2a-e shows the AFM surface morphologies and roughness of the BTS thin films with various thicknesses. As shown in Fig. 2a, the surface is very harsh, many visible defects were observed on the surface. This special surface morphology can be due to the poor crystal quality for the thin thickness of 60 nm. For the BTS thin films whose thickness is greater than 60 nm (as shown in Fig. 2b-d), the surfaces are relatively smooth, uniform, continuous and crack-free. Moreover, the surface grain size increases from ~ 15 nm to 35 nm with the thickness increases from 150 nm to 380 nm, which is in good agreement with the crystallite size calculated by Scherrer's formula. As shown in Fig. 2e, with increasing thicknesses from 60 nm to 380 nm, the surface roughness initially decreases from 18.5 nm to 3.2 nm, and then increases to 7.6 nm. The large surface roughness for the BTS thin films with thickness of 60 nm is because of bad crystallinity. As the thickness increases to 150 nm, the crystallization is enhanced (as shown in Fig. 1), and the surface roughness decreases to 3.2 nm. However, with the thickness further increases to 380 nm, the increase of surface roughness can be ascribed to the increase of surface grain size.

Fig. 3 shows the loss tangents and dielectric constants of BTS thin films with various thicknesses as a function of frequency. These measurements without dc bias field were performed at a small ac oscillation of 20 mV. As shown in Fig. 3, the loss tangents of all the BST thin films exhibit a frequency independent characteristic in the range of 1 kHz to 1 MHz. However, the dielectric constants slightly decrease with increasing the frequency. Such frequency dispersion is related to the dielectric relaxation. In the low frequency region (≤ 1 MHz), the dielectric relaxation occurring is due to the influences of the space charges in the thin films, electrode polarization at the interface and interfacial polarization at the grain boundaries [26,27]. Consequently, dielectric constant (ε) changes as function of frequency (f) changes, which complies with the following relation [28]:

$$\varepsilon = \alpha + \beta f^{n-1} \quad (2)$$

where α and β are associated with temperature (set the appropriate values of α and β to plot a fitting curve at the same time), n is the dispersion parameter, $1 > n > 0$. The values of n are set as 0.989, 0.984, 0.978 and 0.971 for the 60, 150, 260 and 380 nm thick BTS thin films, respectively. As indicated by the solid line in Fig. 3, Eq. (2) agrees well with the experimental data, and the n values decrease as the thickness of BTS thin films increases. These results show the thicker the BTS thin films, the larger the frequency dispersion. The frequency dispersion of BTS thin films with various thicknesses is different may be owing to the presence of the interface region. As the thickness of BTS thin films increases, the influence of interface layer decreases owing to the reduction of the ratio of interface and "bulk-like" layers. The dielectric constant of interface layer is independent of frequency [29], hence, dispersion parameter decreases with the increase of thickness for the BTS thin films.

Fig. 4a shows the loss tangents and dielectric constants of BTS thin films with various thicknesses at a measuring frequency of 100 kHz. The