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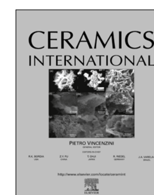

Effect of substrate temperature on structural and electrical properties of $BaZr_{0.2}Ti_{0.8}O_3$ lead-free thin films by pulsed laser deposition

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ABSTRACT

Barium zirconate titanate ($BaZr_{0.2}Ti_{0.8}O_3$, BZT) 250 nm thick thin films were fabricated by pulsed laser deposition and the influence of the substrate temperature on their preferred orientation, microstructure, morphology and dielectric properties was investigated. Dielectric measurements indicated the (1 1 0)-oriented BZT thin films deposited at 750 °C to show good dielectric properties with high dielectric constant (~500 at 100 kHz), low loss tangent (<0.01 at 100 kHz), and superior tunability (>70% at 400 kV/cm), while the largest figure of merit was 78.8. The possible microstructural background responsible for the high dielectric constant and tenability is discussed. In addition, thin films deposited at 750 °C with device quality factor of 8738 and dielectric nonlinearity coefficient of 1.66×10^{-10} J/C^{4}m^5 were demonstrated.

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1. Introduction

In recent years, electric-field tunable ferroelectric thin films have attracted considerable interest for applications in microwave tunable devices such as frequency-agile filters, resonators, voltage-controlled oscillators and phase shifters [1–4]. Barium strontium titanate ($Ba_xSr_{1-x}TiO_3$, BST) thin films have been intensively investigated for its large tunability [5–7]. However, BST thin films have the essential problem of high dielectric loss due to the oxidation state of titanium being easily reduced from Ti^{4+} to Ti^{3+} [8,9], the high dielectric loss (generally $\geq 2\times10^{-2}$) is a crucial limitation for practical utilizations [10,11]. As a consequence, alternative tunable materials are therefore of great technological and scientific interest. The barium zirconium titanate ($BaZr_xTi_{1-x}O_3$, BZT) lead-free ferroelectric thin films have been paid much attention because of their field dependent tunability and high dielectric constant, the substitution of Zr^{4+} for Ti^{4+} is a benefit to the reduction of dielectric loss [12,13]. In addition, the poor stoichiometry control and defects from energetic deposition are also important factors leading to high dielectric losses for the ferroelectric thin films [14]. Among preparation methods of ferroelectric thin films, pulsed laser deposition (PLD) provides several advantages for the growth of multi-component oxide thin films. The composition of films grown by PLD is quite close to that of the target, and it is true even for a multi-component target [15]. And, PLD allows for low defect densities, because it is a high-purity, low energetic deposition technique [16].

In our previous work, we found that the dielectric constant and loss tangent of bismuth magnesium niobate thin films papered by pulsed laser deposition were influenced by growth orientation [17]. Recently, several groups have investigated the relationship between electric properties (dielectric constant, loss tangent, leakage current and pyroelectric coefficients) and orientation in several ferroelectric thin films, such as $Ba_{0.6}Sr_{0.4}TiO_3$ [18], $PbZr_{0.6}Ti_{0.4}O_3$ [19], $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ [20] and $(Na_{0.85}K_{0.15})_{0.5}Bi_{0.5}TiO_3$ [21] thin films. These results indicate that the electrical properties could be improved by controlling the preferential orientations of the thin films. In this paper, we prepared the preferential (1 1 0)-oriented $BaZr_{0.2}Ti_{0.8}O_3$ thin films on Pt–coated Si substrates by pulsed laser deposition. The dependence of the texture of BZT thin films prepared at different substrate temperature is experimentally investigated by X–ray diffraction (XRD) measurements. The high tunability of preferential (1 1 0)-oriented thin films is reported. The substrate temperature dependent dielectric properties of the prepared BZT thin films are systematically investigated as well.

2. Experimental section

The $BaZr_{0.2}Ti_{0.8}O_3$ (BZT) thin films were grown on $Pt/TiO_2/SiO_2/Si$ by pulsed laser deposition using a KrF eximer laser (248 nm, 300 mJ, 5 Hz) and BZT ceramic target. The BZT ceramic

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targets were prepared by a conventional solid-state reaction process using raw materials $BaCO_3$ (99.99%), ZrO_2 (99.99%) and TiO_2 (99.99%). The starting materials were weighed and mixed according to the stoichiometric mole ratio of the BZT, then milled in an agate mortar for 4 h, pressed into 50 mm diameter and 4 mm thickness pellet at 20 t. The target was sintered at 1250 °C for 10 h in air. The substrates were cleaned in an ultrasonic bath with alcohol for 30 min The substrates are fixed at an on–axis distance of 6 cm from the target. The laser radiation is impinged on the target at 45° with respect to normal in a dynamic flow of oxygen. Before irradiations, the deposition chamber is evacuated down to a base pressure of 3×10^{-4} Pa. The thin films were deposited for 60 min at the substrate temperature of 350–750 °C and under an oxygen pressure of 15 Pa. The substrate temperature was measured using a thermocouple gauge and a hot cathode gauge. The variation of substrate temperature during deposition was maintained within ± 1 °C. After deposition, the thin films are cooled to room temperature at the same oxygen pressure. All of the thin films with a typical thickness of about 250 nm obtained from the step height measurement instrument.

The phase and crystal structure were examined using X-ray diffraction using a (XRD DX-2700, Fangyuan) system equipped with a Cu-Kα radiation source (1.542 Å) in the diffraction angle range of 20–60° (increment 0.02°). Surface morphologies were characterized by the atomic force microscopy (AFM) using a Nanoscope Multimode 8 (Bruker, Santa Barbara, CA, USA). The thickness of the thin films was measured by Alpha-Step D-100 profilometer (KLA-Tencor, California, USA). For electrical measurement, Au top electrodes with 0.2 mm in diameter were patterned by lift-off process to form the metal-insulator-metal type capacitors. The dielectric properties were investigated by using a precision impedance analyzer (Agilent 4294A, Santa Clara, California, USA). The polarization versus electric field loops (P-E loops) were carried out with a ferroelectric testing system (Precision Workstation, RADIANT, USA) at room temperature.

3. Results and discussions

Fig. 1 shows the X-ray diffraction patterns of the BZT thin films prepared on $Pt/TiO_2/SiO_2/Si$ substrates at different substrate temperatures. The absence of characteristic peaks for the BZT thin films deposited at below 550 °C indicates that the thin films are amorphous in nature. In the substrate temperature range of 550–750 °C, it can be seen that the thin films exhibit an orthorhombic phase structure [22] and without the formation of secondary phases. Two pronounced diffraction peaks correspond to the (1 1 0) and (1 1 1) peaks are observed. The peak intensity of the BZT thin films increases as increasing the substrate temperature, indicating the crystallinity is improved. And, the $I(110)/\sum I(hkl)$ was found to be 0.60, 0.62, and 0.67 for the BZT thin films prepared at 550 °C, 650 °C and 750 °C, indicating a preferential (1 1 0) grain orientation. The (1 1 0) plane has the lowest surface energy and hence the (1 1 0) plane of the BZT thin films has a preferential orientation perpendicular to the substrate surface.

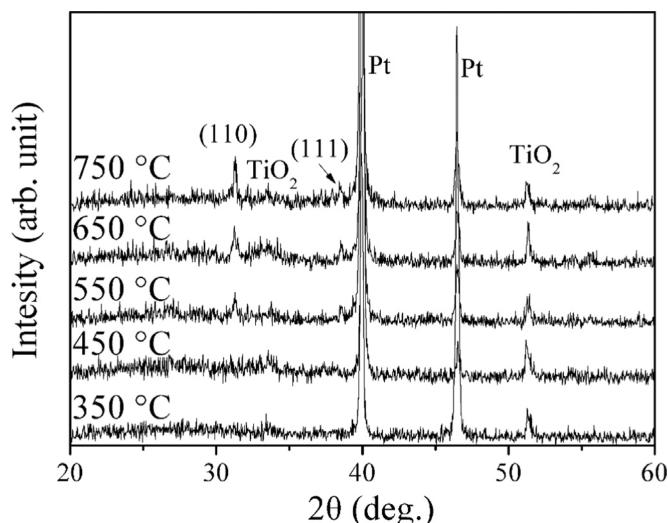

Fig. 1. The XRD patterns of the BZT thin films deposited on $Pt/TiO_2/SiO_2/Si$ substrates at various substrate temperatures.

The crystalline quality of crystallized BZT thin films can be evaluated by the full width at half–maximum (FWHM) of (1 1 0) peak. The FWHM decreases from 0.37 to 0.22 as the substrate temperature increases from 550 °C to 750 °C. It is well known that the FWHM values are related with the crystallization of the thin films. That decrease of FWHM is generally related to an improvement of the crystal quality of the BZT thin films and to an enlargement of the grain size [23]. These results indicate that the high substrate temperature can improve the crystallinity of the BZT thin films due to small crystallites coalesce together to make larger crystallites in the thin films [24]. Based on the results, 750 °C is determined to be the optimum substrate temperature, at which the BZT thin films possesses an orthorhombic structure.

The atomic force microscopy (AFM) micrographs of the BZT thin films grown at different substrate temperatures are shown in Fig. 2. The dense and crack–free BZT thin films are obtained without droplets from the laser ablation. However, the surface morphologies of the BZT thin films are altered when deposited at different substrate temperatures. As shown in Fig. 2(a) and (b), the surface morphology of multilayer films deposited at below 550 °C is an incompact structure, which indicating the amorphous nature of thin films. As the substrate temperature rises to 550 °C, the thin films begin to crystallize, the surface morphology transforms to a compact and smooth structure. In the substrate temperature regime of 550 °C to 750 °C, we observe increases in average particle size with increasing the substrate temperature, which attributes to the increase of the diffusion coefficient of deposited particles and the enhancement of kinetic energy with the substrate temperature.

The frequency dependent room temperature relative dielectric constant and dielectric loss of the BZT thin films prepared at different substrate temperatures have been measured and the results are exhibited in Fig. 3. The amplitude of the ac signal used for these measurements is 10 mV, which is considerably less than the coercive field of the material so that the ac field does not address the polarization state. The dielectric constant does not show obvious dispersion behavior, although there is a slight decrease with increasing frequency due to the space charges at the interface between BZT thin film and metal electrode. As we know, the frequency dependence of dielectric constant can be attributed to the dielectric relaxation [25]. There occurs a formation of a Schottky junction at the interface after the BZT contact with Au. The depletion layer width is modulated with electrons charging or discharging at oxygen vacancies in the depletion layer, when an oscillation voltage is applied in the dielectric measurement. The migration of electrons in this process may results in dielectric relaxation [26]. However, the dielectric loss tangent for all the BZT thin films except that papered at 350 °C is almost independent of frequency. The dielectric constant and loss tangent at microwave frequencies should be further explored for potential microwave applications.

Fig. 4 shows the effects of substrate temperature on dielectric constant and loss tangent of BZT thin films under a measurement frequency of 100 kHz. The BZT thin films show a low dielectric constant of below 30, and exhibit relatively large dielectric losses,

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