Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Tunable performance of $BaZr_{0.2}Ti_{0.8}O_3$ thin films prepared by pulsed laser deposition

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ARTICLE INFO

Keywords:
$BaZr_xTi_{1-x}O_3$
Oxygen pressure
Dielectric properties
Thin films

ABSTRACT

$BaZr_{0.2}Ti_{0.8}O_3$ (BZT) thin films were deposited at various oxygen pressures (0–60 Pa) on $Pt/TiO_x/SiO_2/Si$ substrates by using pulsed laser deposition. The crystallinity of the thin films initially improves but subsequently deteriorates with increasing oxygen pressure. The tunable performance of BZT thin films is associated with crystal structure and oxygen vacancies. The theoretical mechanisms for the relative permittivity and dielectric loss as a function of electric field are proposed. The frequency response of dielectric properties is also investigated and the variation mechanisms are supposed. Eventually, BZT thin films fabricated under 15 Pa have the highest tunability (70.3% at 400 kV/cm) with the largest relative permittivity of 486, the lowest loss tangent of 0.021 and the maximum commutation quality factor of 7744.8. The results imply that BZT thin films are potential candidates for tunable device applications.

1. Introduction

Recently, tunable dielectric materials are attracting much attention for the applications in phase shifters, filters, oscillators, varactors, due to their dielectric nonlinearity, simple structure and high-speed operation [1–5]. In order to realize miniaturization and integration with silicon technology, materials with large tunability and low dielectric loss are in urgent demand [6,7]. Although lead-based thin films have been widely investigated for their excellent properties, the intrinsic volatility and toxicity limit their further practical utilizations [8,9]. Therefore, many researchers focus their attention on alternative materials with comparable properties. Lead-free $BaZr_xTi_{1-x}O_3$ (BZT) solid solutions have attracted much interest due to their field dependent tunable relative permittivity [10–12]. In addition, Ti^{4+} is substituted by chemically more stable Zr^{4+}, which not only suppresses the conduction by electron hopping between $Ti^{4+}$and Ti^{3+}, but also reduces dielectric loss [13,14]. Since BZT with Zr/Ti ratio of 0.2/0.8 has very good dielectric nonlinearity at room temperature [15], we choose to investigate $BaZr_{0.2}Ti_{0.8}O_3$ composition in this work.

BZT thin films have been grown by several techniques, such as pulsed laser deposition (PLD) [16,17], sol-gel processing [18,19] and magnetron sputtering [20,21]. Among them, PLD is an effective technique to control the composition of multi-component thin films, quite close to the stoichiometry of the target [22]. Besides, the deposition surroundings are cleaner due to the absence of energy source of evaporation in the chamber, and the thin films grown by PLD are more smooth, which is advantage for the fabrication of microwave devices [23]. Generally, substrate temperature and oxygen pressure play a major role in the deposition process of thin films [24]. When grown at the same temperature, the crystalline quality and dielectric properties of the thin films are dramatically influenced by the oxygen pressure. In this paper, $BaZr_{0.2}Ti_{0.8}O_3$ thin films were prepared on $Pt/TiO_x/SiO_2/Si$ substrates by pulsed laser deposition. The effects of oxygen pressure on the crystal structure and dielectric properties of BZT thin films were systematically investigated.

2. Experimental details

The $BaZr_{0.2}Ti_{0.8}O_3$ (BZT) ceramic target was fabricated by a solid state reaction route with reagent-grade barium carbonate ($BaCO_3$), zirconium dioxide (ZrO_2) and titanium dioxide (TiO_2) as raw materials. Powdered carbonate and oxides were weighted in stoichiometry, and ball milled in deionized water for 6 h. After being mixed with 0.8 wt% polyvinyl binder, the powders were pressed into a disk of 50 mm in diameter and 4 mm in thickness, and then sintered at 1200 °C for 5 h in air. Sintered BZT disk was used as a target for laser ablation by pulse laser deposition using a KrF excimer laser with a laser beam of 248 nm wavelength, 30 ns pulse width and 5 Hz repetition rate. The Pt-coated Si substrates were cleaned in an ultrasonic bath with alcohol for 30 min, and the distance between target and substrates was fixed at

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http://dx.doi.org/10.1016/j.ceramint.2017.07.008
Received 14 June 2017; Received in revised form 1 July 2017; Accepted 1 July 2017

60 mm. Before deposition, the chamber was evacuated down to 3 × 10^{-4} Pa as base pressure. The BZT thin films were deposited at the substrate temperature of 700 °C under different oxygen pressures of 0 Pa, 0.8 Pa, 15 Pa and 60 Pa, respectively. The thickness of BZT thin films was controlled by the deposition rate and deposition time. After preparation, the thin films were cooled to room temperature at the same oxygen pressure.

The thin films had a typical thickness of about 250 nm measured by Alpha Step D-100 profilometer (KLA-Tencor, California, USA). The phase and crystal structure of the films were characterized by X-ray diffraction (Rigaku D/MAX-RB, Akishima, Tokyo, Japan) using Cu Kα radiation (λ = 0.1542 nm). Au top electrodes having 0.2 mm in diameter were prepared on the samples with a shadow mask for electrical measurement. The precision impedance analyzer (Agilent 4294A, California, USA) was adopted to measure the dielectric properties and tunability of BZT thin films. The ε_r-E curves are obtained by measuring the capacitance-voltage (*C-V*) characteristics at 100 kHz with a small oscillation voltage of 5 mV, and the dc voltage is swept from negative bias (− 10 V) to positive bias (+ 10 V).

3. Results and discussion

The XRD patterns of BZT thin films deposited under various oxygen pressures are shown in Fig. 1. It can be seen that the crystal structure is strongly affected by oxygen pressure during the deposition process. There are no BZT characteristic peaks below 0.8 Pa, indicating that the thin films are amorphous structures. At the higher oxygen pressure (0.8–60 Pa), BZT thin films exhibit a pure perovskite structure with three peaks identified as the (0 1 1), (1 1 1) and (1 1 2) diffraction planes, and no secondary phases are detected except for the peaks of substrates. Furthermore, the (0 1 1) plane is observed to be the strongest peak among the three characteristic peaks, which suggests that it is the preferential orientation of $BaZr_{0.2}Ti_{0.8}O_3$ thin films. With the increase of oxygen pressure, the reflection intensities of BZT diffraction peaks initially increase and become strongest at 15 Pa, but subsequently decrease with further increasing the oxygen pressure. These imply that the thin films fabricated under 15 Pa have the better crystalline quality than others.

It is known that the full-width at half-maximum (FWHM) values can be used to evaluate the crystallinity of thin films [25]. Thus, the FWHM of (0 1 1) peak is discussed and extracted from Fig. 2. It is found that the value of FWHM for BZT thin films decreases from 0.29 to 0.22 with the oxygen pressure increasing from 0.8 to 15 Pa, and slightly rises to 0.24 at a higher oxygen pressure of 60 Pa. The decrease of FWHM means larger grain size and better crystallinity [26]. Generally, the Scherrer's formula is adopted to calculate the average grain size of thin films [27,28].

$$D = 0.9\lambda/\beta cos\theta \quad (1)$$

where D, λ, β and θ represent the mean grain size, the wave length of Cu-Kα radiation (1.5418 Å), the FWHM value of (0 1 1) peak and the Bragg diffraction angle, respectively. As shown in Fig. 2, the obtained grain size according to Eq. (1) initially increases from 28 to 38 nm, and then decreases to 34 nm with the change of oxygen pressure. These indicate that 15 Pa is the optimum oxygen pressure, which is consistent with the XRD results.

In general, the degree of defects in the thin films can be determined by dislocation density, which is defined as the length of dislocation lines per unit volume [29]. Williamson and Smallman have proposed a simple approach to calculate the dislocation density from the following equation [30]:

$$\delta = \frac{1}{D^2} \quad (2)$$

where δ and D are the dislocation density and the mean grain size, respectively. Fig. 3 shows the variation of δ values for BZT thin films prepared under different oxygen pressures. It is found that the dislocation density first decreases, reaches the minimum value at 15 Pa, and then increases. These reveal that appropriate oxygen pressure can effectively suppress defects (e.g., oxygen vacancies) and enhance the crystalline quality of BZT thin films.

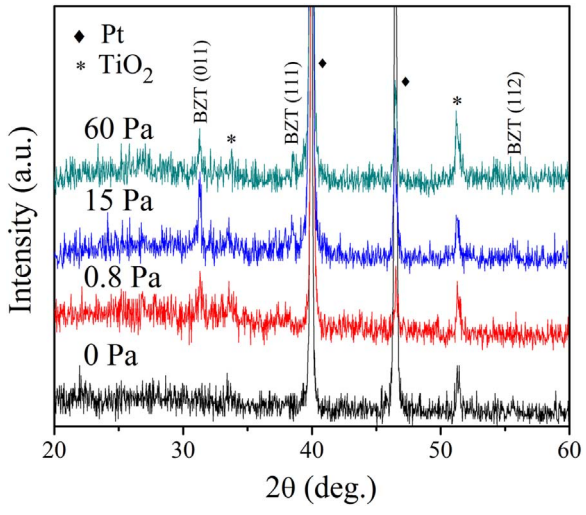

Fig. 1. X-ray diffraction patterns of BZT thin films deposited under various oxygen pressures.

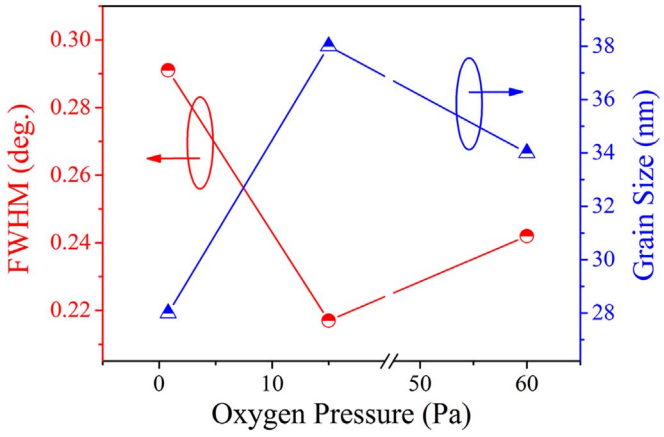

Fig. 2. FWHM of the (0 1 1) peak and obtained grain size under various oxygen pressures.

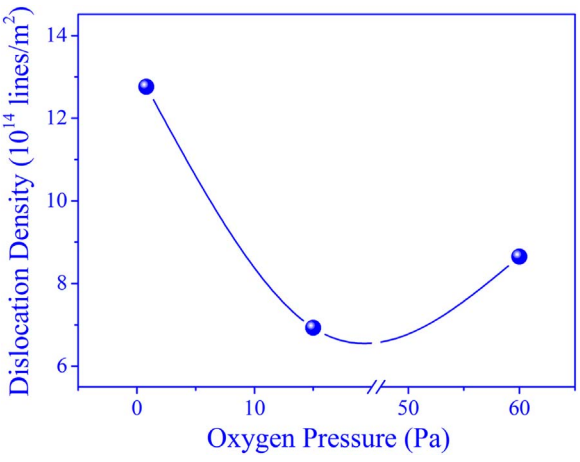

Fig. 3. Dislocation density of BZT thin films deposited under various oxygen pressures.