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Characterization of $Ba(Zr_{0.05}\ Ti_{0.95})O_3$ thin film prepared by sol-gel process

W. X. Cheng · A. L. Ding · X. Y. He · X. S. Zheng · P. S. Qiu

Abstract $Ba(Zr_{0.05}Ti_{0.95})O_3$ (BZT) thin film (∼330 nm) was grown on $Pt/Ti/SiO_2/Si(100)$ substrate by a simple sol-gel process. The microstructure and the surface morphology of BZT thin film were studied by X-ray diffraction and atomic force microscopy. The optical properties of BZT thin film were obtained by spectroscopic ellipsometry. The optical bandgap was found to be 3.74 eV of direct-transition type. Ferroelectric and dielectric properties of BZT thin film were also discussed. The electrical measurements were conducted on BZT films in metal-ferroelectric-metal (MFM) capacitor configuration. The results showed the film exhibited good ferroelectrity with remanent polarization and coercive electric field of 3.54 $\mu C/cm^2$ and 95.5 kV/cm, respectively. At 10 kHz, the dielectric constant and dielectric loss of the film are 201 and 0.029, respectively.

Keywords $Ba(Zr_{0.05}Ti_{0.95})O_3$ (BZT) thin film · Sol-gel · Optical properties · Dielectric properties

1 Introduction

Ferroelectric thin films are very promising for wide range of applications such as high dielectric constant capacitors, non-volatile memories with low switching voltage, infrared sensors and electro-optic devices [1]. Among these materials, $Ba_xSr_{1-x}TiO_3$ (BST) is paid more attention because of its unique combination of large dielectric constant, large electro-optical coefficient, low optical losses [2–4]. There have been some investigations on these electrical and optical properties of $BaTiO_3$, $SrTiO_3$, and BST thin films [5–7]. Recently, $Ba(Zr_x\ Ti_{1-x})O$ (BZT) has been suggested as an alternative to BST in the fabrication of ceramic capacitors because Zr^{4+} is chemically more stable than Ti^{4+} [8–10]. There are a few papers that reported on the preparation and properties of BZT thin films. Hofer et al. reported the electrical properties of $Ba(Zr,Ti)O_3$ thin films prepared by chemical solution deposition [11]. Kamehara et al. and Choi et al. reported on preparation of $Ba(Zr,Ti)O_3$ thin films by sputtering [12]. Halder et al. reported on electrical characterization of $Ba(Zr,Ti)O_3$ thin films by pulsed laser deposition (PLD) [13]. In this work, we prepared $Ba(Zr,Ti)O_3$ thin film on Pt coated Si(100) substrates by sol-gel deposition and studied the optical properties and the dielectric, ferroelectric properties of the thin film.

2 Experimental procedure

$Ba(Zr_x,Ti_{1-x})O_3$ (with $x = 0.05$, denoted as BZT) thin films were prepared by a chemical solution route with a spin-coating process. Barium acetate $Ba(CH_3COO)_2$, zirconium-*n*-propoxide $Zr(O(CH_2)_2CH_3)_4$, tetrabutyl titanate $Ti(OC_4H_9)_4$ were used as starting materials. 2-methoxyethanol $C_3H_8O_2$ was selected as solvents, acetylacetone $C_5H_8O_2$ was selected as a reagent to stabilize the tetrabutyl titanate. The barium acetate was initially dissolved into acetic acid and stirred for 30 min at 70°C; the zirconium-*n*propoxide and the tetrabutyl titanate were mixed, then dissolved in 2-methoxyethanol and stirred for 30 min at 70°C, appropriate amounts of acetylacetone were added to stabilize the solution. After cooling to room temperature, the barium acetate solution was added to the Zr-Ti-solution and mixed

W. X. Cheng (✉) · A. L. Ding · X. Y. He · X. S. Zheng · P. S. Qiu
State Key Lab of High Performance Ceramics and Superfine Microstructure. Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People's Republic of China
e-mail: chwx_99@yahoo.com

in the flask at 70°C. Then the solution was stirred for 30 min, without a reflux and high temperature distillation of water. The whole process of the preparation of the precursor solution is performed in an ambient atmosphere. The solution is stable and no precipitates form for six months.

Before spin coating on the substrates, the solution is filtered with filter paper to avoid particulate contamination. The thermal treatment process for the samples was completed with a hot plate and a rapid thermal annealing (RTA) furnace. The BZT coating solution was deposited onto Pt(111)/Ti/SiO_2/Si(100) substrates by spin coating at 3600 rpm for 30s. After each spin coating process, the sample was heat-treated at 350°C on a hot plate for 10 min in air. This step was repeated four to five times to obtain the desired thickness of the films. The BTZ film was annealed at 650°C for 10 min by RTA in an oxygen atmosphere.

The microstructure of BZT/Pt/Ti/SiO_2/Si(100) was analyzed by a D/Max2550V(Raguku, Japan) rotating X-ray diffractometer (XRD) with Cu Kα radiation in the angle range from 20 to 60 degree. The surface morphology of thin film was examined by an SPA400 (Seiko. Inc, Japan) atomic force microscopy (AFM). The grain size and surface roughness of the thin film were obtained from AFM images.

A spectroellipsometer (VASE^{TM}, J. A. Wollam Co., Inc., USA) was used to measure the ellipsometric parameters ($\tan\psi$ and $\cos\Delta$) as a function of the photon energy from 0.7 to 3.5 eV.

To investigate the electric properties of prepared BZT thin film, the top electrode of gold (Au) with diameter of 0.4 mm was prepared on the surface of BZT film through a shadow mask by evaporation. The capacitance and dielectric loss ($\tan\delta$) were measured using a HP 4294A LCR impedance analyzer in the frequency range from 1 to 100 kHz. The ferroelectric hysteresis loops were tested by a Radiant Technologies RT66 ferroelectrics instrument.

3 Result and discussion

3.1 Structure and morphology

Figure 1 shows the x-ray diffraction pattern of BZT thin film deposited on Pt(111)/Ti/SiO_2/Si(100) substrates annealed at 650°C for 10 min in oxygen atmosphere by RTA. According to the XRD pattern shown in Fig.1, it can be found that film show highly polycrystalline perovskite BZT peaks at (110) directions.

Figure 2 show the AFM images of BZT thin film on Pt coated Si (100) substrate. It is obvious that the surface is smooth, and the root mean square (rms) roughness of the surface is 1.32 nm. The average grain size is about 50–100 nm.

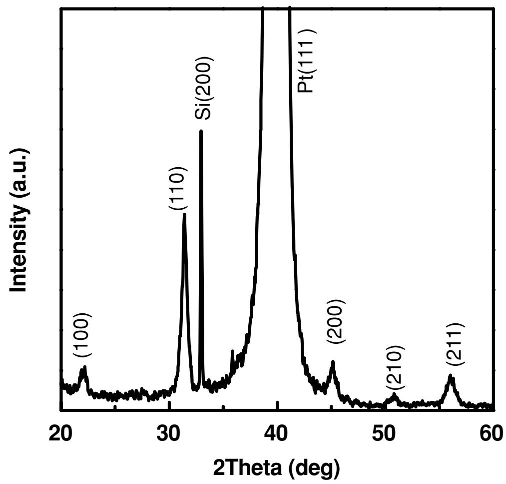

Fig. 1 The XRD pattern of BZT thin film annealed at 650°C for 10 min in oxygen atmosphere by RTA

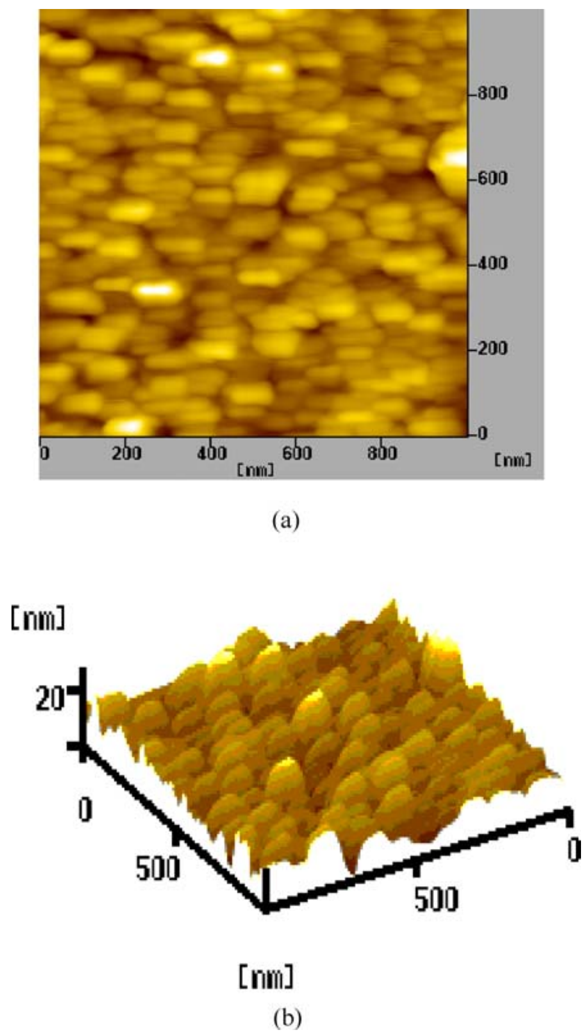

Fig. 2 The AFM images of BZT thin film on Pt coated Si(100) substrate annealed at 650°C by RTA, (a) plane-view, (b) 3-D view

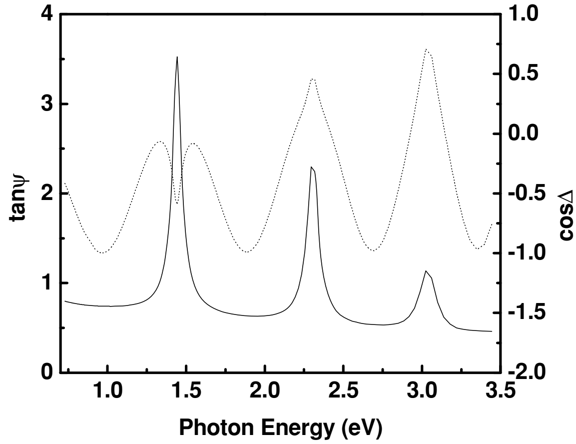

Fig. 3 Spectra of the ellipometric parameter tan ψ(solid lines) and cos Δ (dotted lines) for BZT film deposited on Pt coated Si(100) substrate

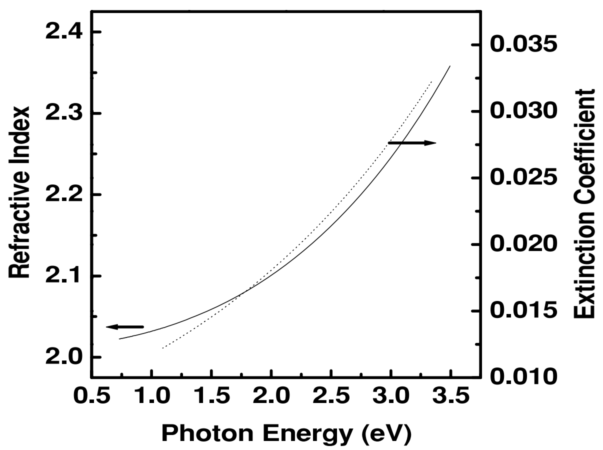

Fig. 4 Refractive index n and extinction coefficient k of BZT thin film on Pt coated Si(100) substrate

3.2 Optical properties

Figure 3 shows the spectra of tan Ψ and cos Δ of BZT film as a function of photon energy from 0.7 to 3.5 eV. In the lower energy range, the spectra exhibit oscillations due to the interference among multiple reflected beams within the film, which correspond to the "transparent" range of the film.

We analyzed these experimental data using a three-layer model (ambient/BZT/Pt) as the Pt layers were thick enough that light could not propagate thought the Pt layer. The reflective index n and extinction coefficient k as functions of photon energy, as well as the thickness of the film, were determined by an optimization process. The experimental data were fitted using a Cauchy dispersion relationship.

$$n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4} \quad (1)$$

$$k(\lambda) = A_k \exp\left[B_k\left(1.24\left(\frac{1}{\lambda} - \frac{1}{C_k}\right)\right)\right] \quad (2)$$

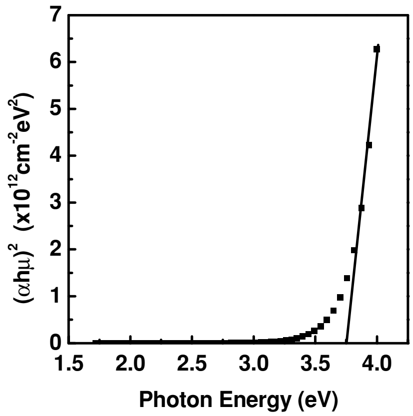

Fig. 5 The $(\alpha h\nu)^2$ versus $h\nu$ curves of BZT thin film on Pt coated Si(100) substrate

where A_n, B_n, C_n, A_k, B_k, and C_k, are constants, and λ is the wavelength of light in micrometers.

The refractive index n and extinction coefficient k of BZT film on Pt-coated Si substrate as a function of photon energy were shown in Fig. 4, which is derived from model fitting the experiment spectrospic ellipsometric data. As shown in Fig. 4, the refractive index of BZT thin film increases as the photon energy increase in the range of 0.7 to 3.5 eV (normal dispersion). The extinction coefficient k increase as photon energy increases and it is very small at low energy part, where the film is transparent.

The absorption data for thin film was analysed based on the well known relations:

$$(\alpha h\nu)^2 = C(h\nu - Eg) \quad (3)$$

Figure 5 shows $(\alpha h\nu)^2$ versus $h\nu$ plotted for BZT film. The band gap Eg can be obtained by extrapolating the linear portion of plot relation $(\alpha h\nu)^2$ versus $h\nu$ to $(\alpha h\nu)^2 = 0$. The bandgap energy is 3.74 eV for BZT thin film.

3.3 Electric properties

Figure 6 shows the *P-E* loop of BZT thin film on pt coated Si(100) substrate annealed at 650°C for 10 min by RTA in an oxygen atmosphere. The remnant polarization (*Pr*) and coercive field (*Ec*) of BZT thin film were 3.54 μC/cm^2 and 95.5 kV/cm, respectively. The value of *Pr* obtained is similar to that obtained in bulk ceramics, and is about a third lower than in single crystals [10]. Typically, values of *Pr* are lower in thin films than in their bulk counterparts, on account of several effects such as the clamping effect of the substrate on the films and strains, etc.

The dielectric constant and dissipation factor measurements were made at room temperature as a function of frequency in the range of 1–100 kHz. Figure 7 shows the dielec-

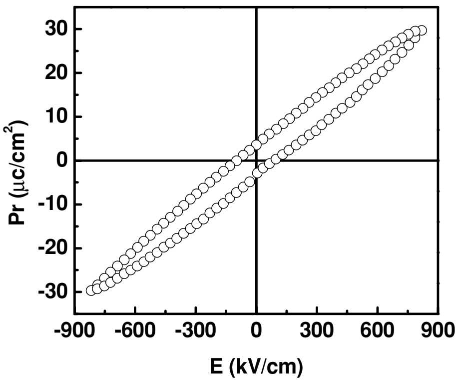

Fig. 6 The P-E loop for BZT thin film deposited on Pt coated Si(100) substrates

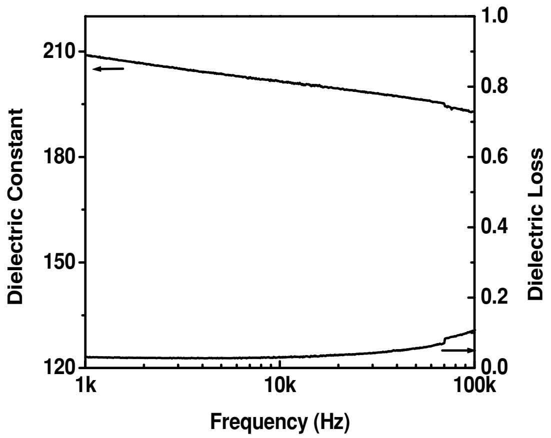

Fig. 7 Dielectric constant and dielectric loss for BZT thin film as a function of frequency

tric constant and dissipation factor as a function of frequency for the BTZ film deposited on Pt coated Si(100) substrate was annealed at 650°C for 10 min by a RTA process in oxygen atmosphere. The dielectric constant of BZT film decreased from 208 to 193 with increasing frequency from 1 to 100 KHz. At 10 kHz, the dielectric constant and dissipation factor were 201 and 0.029, respectively. A dielectric constant (ε) of 150 was reported by Kamehara et al. [12], for a BZT (80/20) thin film on a Pt-coated Si substrate prepared by sputtering. A series of ε values of 100, 150 and 250 have been reported for BZT (80/20) films on Pt-coated Si substrates with various deposition temperatures prepared by sputtering [14] A ε value of 452 has been reported for BZT (90/10) thin film on Pt coated Si substrate prepared by the PLD technique [13].

4 Conclusion

Polycrystalline BZT thin film with thickness of 330 nm have been prepared on Pt-coated Si(100) and substrate sol-gel process. Atomic force micoscope reveals that the film on Pt coated Si substrate is smooth, the grain size and the root mean roughness (rms) are 50–100 nm and 1.32 nm respectively. The refractive index and extinction coefficient of BZT thin film were obtained by spectroscopy ellipsometry. The band gap energy is found to be 3.74 eV of direct-transition type. BZT thin film have good ferroelectric properties, the remnant polarization is similar to that of bulk ceramics. The dielectric constant and dissipation factor of BZT at 100 kHz are 201 and 0.029.

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