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Infrared optical properties of $Ba(Zr_{0.20}Ti_{0.80})O_3$ and $Ba(Zr_{0.30}Ti_{0.70})O_3$ thin films prepared by sol–gel method

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ABSTRACT

$Ba(Zr_xTi_{1-x})O_3$ (BZT) ($x = 0.20$ and 0.30) thin films are deposited on Pt(1 1 1)/Ti/SiO_2/Si(1 0 0) substrate by sol–gel method. X-ray diffraction patterns show that the thin films have a good crystallinity. Optical properties of the films in the wavelength range of 2.5–12 μm are studied by infrared spectroscopic ellipsometry (IRSE). The optical constants of the BZT thin films are determined by fitting the IRSE data using a classical dispersion formula. As the wavelength increases, the refractive index decreases, while the extinction coefficients increase. The effective static ionic charges are derived, which are smaller than that in a purely ionic material for the BZT thin films.

1. Introduction

Lead-free $BaTiO_3$ based materials have attracted much attention because of their environmental friendliness, which have a lot of potential application such as capacitive and nonvolatile random memory cell, electro-optic integrated circuits and pyroelectric device [1–3]. Barium zirconium titanate $BaZr_xTi_{1-x}O_3$ (BZT) ($x = 0.2$ and 0.3), substitution of Ti by Zr in $BaTiO_3$, has better characteristics than $BaTiO_3$ [4–6], The Zr^{4+} ion (atomic radius of 86 pm) is chemically more stable than the Ti^{4+} ions (atomic radius of 74.5 pm) and has a larger ionic size to expand the perovskite lattice [7]. It has many merits, like high dielectric constants and low leakage current, controlled Curie temperature. So it will be a very promising ferroelectric material. Recently, BZT thin films with good dielectric characteristics has been prepared by sol–gel method [8,9]. However, some few studies of optical properties in BZT films has been reported in literature [10–13]. Thus, the investigation of infrared optical of BZT thin films is very important to optimize the design and understood of devices based on the pyroelectric and electric-optical properties of BZT thin films.

Spectroscopic ellipsometry is a nondestructive and powerful technique to investigate the optical characteristics of materials. It is able to measure the thickness and the dielectric function of a multilayer system simultaneously.

In this paper, we report the optical properties of $Ba(Zr_xTi_{1-x})O_3$ thin films, with $x = 0.20$ and 0.30 on platinized silicon Pt(1 1 1)/Ti/SiO_2/Si(1 0 0) substrates by infrared spectroscopic ellipsometry (IRSE) in the wavelength range of 2.5–12 μm. We assume a three-layer model (ambient/BZT/Pt) for obtention of data of IRSE.

2. Experimental procedure

The $Ba(Zr_xTi_{1-x})O_3$ thin films with $x = 0.20$ and 0.30 on Pt(1 1 1)/Ti/SiO_2(1 0 0)/Si(1 0 0) substrates were fabricated by sol–gel method. The starting materials were barium acetate [$Ba(CH_3COO)_2$, 99% (Aldrich)], zirconium isopropoxide [$Zr(OC_3H_7)_4$, 99.9% (Aldrich)] and titanium isopropoxide [$Ti(OC_3H_7)_4$, 97% (Aldrich)]. Glacial acetic acid [CH_3COOH, 99.5% (SUZHOU SANJIE in China)], 2-methoxyethanol [$C_3H_8O_2$, 99% (Aldrich)] and ethylene glycol [$C_2H_6O_2$, 99% (Aldrich)] were used as the solvents and polymerizing agents, respectively. [$Ba(CH_3COO)_2$] was dissolved into heated [CH_3COOH]. This was followed by an addition of [$Ti(OC_3H_7)_4$] and [$Zr(OC_3H_7)_4$] under constant stirring. The mixture was added with [$C_2H_6O_2$] to form a stock solution. The spin-on solution was prepared by diluting the stock solution with equi-volume amounts

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of glacial acetic acid and 2-methoxyethanol to become 0.3 M in concentration. After aging the hydrolyzed solution for 24 h, thin films deposition was carried out on Pt(1 1 1)/Ti/SiO_2/Si(1 0 0) substrates by spin coating three layers at 3000 rpm for 30 s. the wet films were dried and annealed on a hot plate for 5 min at 500 °C. The crystalline structure of thin films was identified by X-ray diffraction using a SIMENS D-5000 Power Diffractometer. The ellipsometric measurements were carried out by a variable-angle infrared spectroscopic ellipsometer by synchronously rotating the polarized and analyzer with a speed ratio of 1:1. The accuracy was better than 1% for $\tan \Psi$ and $\cos \Delta$ in the measurements. The incident angle was 70° for the samples.

We describe the dielectric function of BZT thin films in the 2.5–12.5 μm wavelength range. This energy is higher than the phonon frequencies, but much lower than the band gap energy of BZT thin film. Complex dielectric function is described as follows [14]:

$$\varepsilon_1 = \varepsilon_\infty - \frac{Nq^2}{M^*\varepsilon_0}\frac{\tau^2}{1+\omega^2\tau^2}, \qquad \varepsilon_2 = \frac{Nq^2}{M^*\varepsilon_0}\frac{\tau}{\omega(1+\omega^2\tau^2)} \tag{1}$$

where N is the cell number per unit volume, q is the ionic average effective charge, $1/M^* = 1/M_+ + 1/M_-$ is the reduced mass of cations M_+ and anions M_- in a unit cell, τ is an energy-independent relaxation time, and ω is the light frequency. ε_0 and ε_∞ are the dielectric constants in vacuum and the high-frequency dielectric constant, respectively.

The root mean square fractional error is defined by

$$\sigma^2 = \frac{1}{2J-K}\sum_{i=1}^{J}\left[\left(\frac{\Psi_i^{\mathrm{mod}} - \Psi_i^{\mathrm{exp}}}{\sigma_{\Psi,i}^{\mathrm{exp}}}\right)^2 + \left(\frac{\Delta_i^{\mathrm{mod}} - \Delta_i^{\mathrm{exp}}}{\sigma_{\Delta,i}^{\mathrm{exp}}}\right)^2\right], \tag{2}$$

is used to judge the quality of the fit between the experimental and model data, where J is the number of measured Ψ and Δ pairs in the fitting, and K is the number of fit parameters. This equation has $2J$ in the prefactor because there are two measured values included in the calculation for each Ψ and Δ pair. The standard deviations were calculated from the known error bars on the calibration parameters and the fluctuations of the measured data over averaged cycles of the rotation polarizer and analyzer.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $Ba(Zr_xTi_{1-x}O)_3$ (x = 0.2 and x = 0.3) (BZT20, BZT30) thin films on platinized silicon substrates. The obvious peaks indicate the BZT thin films have good crystallinity with typical perovskite structure. The nature of the ferroelectric phase transition at the transition temperature (T_m) of BTZ bulk ceramics is known to change strongly with zirconium (Zr) content. For Zr contents $x > 0.08$, the $Ba(Ti_{1-x}Zr_x)O_3$ bulk ceramics show a broad dielectric constant-temperature ($\varepsilon \sim T$) curve near T_m, which is caused by the inhomogeneous distribution of Zr^{4+} ions on Ti^{4+} ions sites and mechanical stress in the grain [15]. As the Zr content increases, the phase transition temperatures approach each other until at a Zr content of $x \sim 0.20$, only one phase transition exists [16]. Ravez and Simon [17] have reported that BTZ shows typical relaxor-like behavior when x = 0.25. So the samples of BZT thin films have a cubic lattice. The calculated lattice constants of BZT20 and BZT30 are 4.028 and 4.079 Å, respectively. Pontes et al. [18] reported that this substitution promote an expansion in the unit cell and that the Zr addition at around 25 at.%, making the BZT thin films to crystallize in the cubic structure. Tang et al. [19] showed that BTZ with a high Zr content (with x = 0.30 and 0.35) has a slim hysteresis behavior, which is typical of a relaxor ferroelectric owing to the existence of micropolar regions.

The measured IRSE data, Ψ and Δ of BZT thin films on Pt(1 1 1)/Ti/SiO2/Si(1 1 1) substrates with x = 0.2 and 0.3 in the wavelength range 2.5–12.5 μm are shown in Figs. 2 and 3, respectively. We analyzed these experimental data using a three-phase model [20], as the Pt layer was thick enough and the infrared light could not

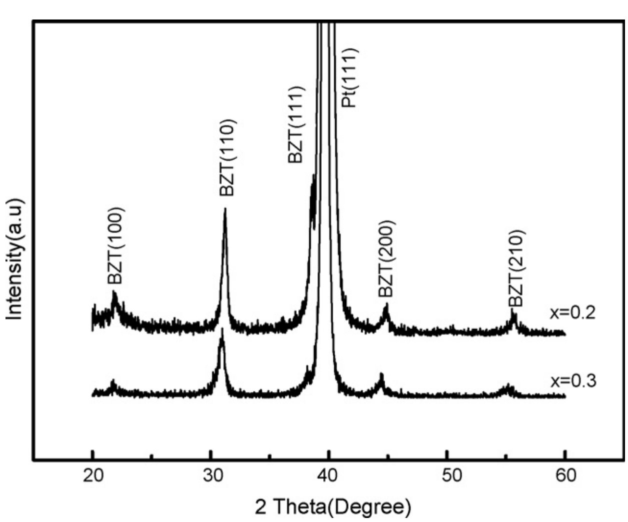

Fig. 1. XRD patterns of BZT thin films on platinized silicon substrates with x = 0.2 and 0.3.

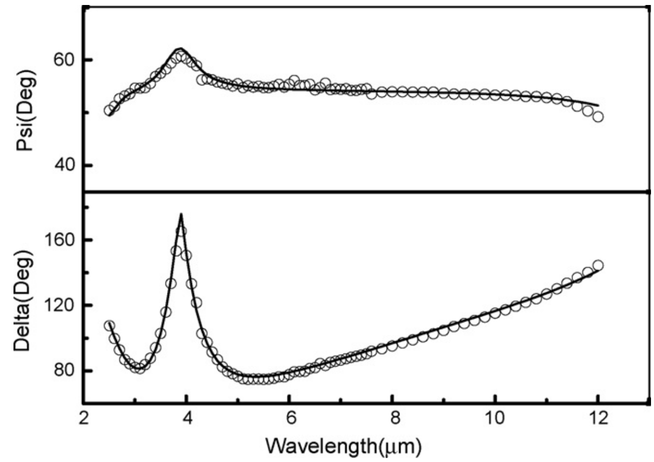

Fig. 2. Experimental (circle dot) and calculated (solid line) IRSE data for BZT20 on a platinized silicon substrate.

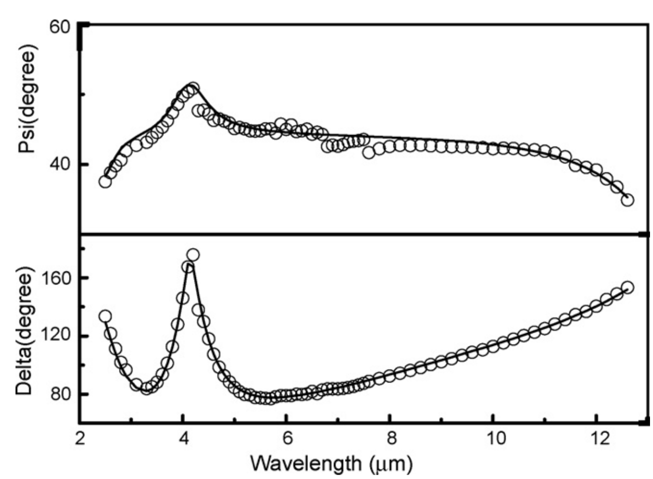

Fig. 3. Experimental (circle dot) and calculated (solid line) IRSE data for BZT30 on a platinized silicon substrate.