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Infrared optical properties of ferroelectric $0.5BaZr_{0.2}Ti_{0.8}O_3$–$0.5Ba_{0.7}Ca_{0.3}TiO_3$ thin films

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Abstract

$0.5BaZr_{0.2}Ti_{0.8}O_3$–$0.5Ba_{0.7}Ca_{0.3}TiO_3$ (BCZT50) thin films have been prepared on platinized silicon substrates by a modified sol–gel technique and proved to be well-crystallized perovskite ferroelectrics at room temperature. Optical properties of these films in the 2.5–12.5 μm wavelength range have been investigated by infrared spectroscopic ellipsometry (IRSE) at room temperature. The measured ellipsometry parameters are well fitted by Brendel oscillator dispersion formula. The optical functions and thickness of films have been uniquely extracted. As the wavelength increases, the refractive index decreases while its extinction coefficient increases. The calculated infrared absorption coefficient increases with increasing wavelength in measured wavelength range. It is greater than 1000 cm^{-1} for the wavelength over 11.3 μm. And it is very small and less than 100 cm^{-1} for the wavelength under 7.5 μm. The relatively large of the thin films reveals that it is a promising material for infrared pyroelectric detectors and arrays.

Keywords: Ferroelectric; Infrared spectroscopic ellipsometry; Refractive index; Extinction coefficient

1. Introduction

Ferroelectric materials, which are necessarily pyroelectric, have found significant and irreplaceable applications in infrared detectors [1–3]. As is well known, infrared sensors made of ferroelectric materials exhibit great advantages of uncooled operation, high sensitivity, broad spectral response range and low cost compared with photon detectors and are widely used in alarms, thermal imaging and intruder imaging [4–6]. Thin film ferroelectric infrared detectors and focal plan arrays are expected to yield better sensitivities and faster response than equivalent ceramics and bulk single crystals, and can be deposited directly on silicon readout integrated circuitry [7,8]. Therefore, thin-film optical devices are especially attractive for monolithic integration with optoelectronic devices and systems. Among these materials, $PbZr_{1-x}Ti_xO_3$ (PZT) and doped-PZT films are the most promising compounds for the pyroelectric infrared imaging sensors, which have been successfully applied in manufacturing monolithic pyroelectric film IRFPA [9,10]. However, the application restricts from toxicity of lead based materials stimulate the research for environmentally friendly alternatives with excellent pyroelectric properties. Some ferroelectric thin films, such as barium titanate, bismuth sodium titanate and potassium sodium niobate films etc., have been intensively investigated these years [11–15]. However, their performances are far from being satisfactory enough to replace PZT. Recently, Yao et al. [6] reported high pyroelectricity of $17.17 \times 10^{-4}\ C\ m^{-2}\ K^{-1}$ at 300 K in lead-free $0.5BaZr_{0.2}Ti_{0.8}O_3$–$0.5Ba_{0.7}Ca_{0.3}TiO_3$ (abbreviated as BCZT50), which is comparable to those of PZT-based ceramics and higher than many other lead-free

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pyroelectric materials, making it a promising material for pyroelectric detector applications. The understanding of the optical properties of BCZT thin films in infrared region is significant to optimize the device fabrication and improve the potential performance of thin-film infrared pyroelectric detectors.

In this paper, we deposited $0.5BaZr_{0.2}Ti_{0.8}O_3$–$0.5Ba_{0.7}Ca_{0.3}TiO_3$ thin films on platinized silicon substrates by a modified sol–gel technique. Then the optical properties were investigated in the wavelength range of 2.5–12.5 μm by infrared spectroscopic ellipsometry (IRSE) using a three layers model (ambient/BCZT/Pt). A good fit of the model to the measured Ψ and Δ of IRSE has been obtained.

2. Experiment procedure

The BCZT50 films were fabricated on commercial Pt/Ti/SiO_2/Si substrates by a modified sol–gel technique with starting materials: barium acetate [$Ba(CH_3COO)_2$], calcium acetate monohydrate [$(CH_3COO)_2Ca\cdot H_2O$], tetrabutyl zirconate solution [$Zr(OC_4H_9)_4$], and tetrabutyl titanate [$C_{16}H_{36}O_4Ti$]. Acetic acid and 2-methoxyethanol were used as co-solvents, and acetylacetone as a chelating reagent to reduce the vigorous hydrolysis of tetrabutyl titanate and tetrabutyl zirconate solution. Initially, barium acetate and calcium acetate monohydrate were dissolved in acetic acid and 2-methoxyethanol co-solvents and stirred for 30 min at 120 °C, then cooled down to room temperature. The tetrabutyl titanate and tetrabutyl zirconate solution were mixed at the desired ratios with an appropriate amount of acetylacetone as the chelating reagent. Then the two solutions prepared above were mixed together and stirred for 2 h at room temperature. The concentration of obtained sol is about 0.2 M. Spin-coating of the solutions was performed at 3000 rpm for 30 s on Pt/Ti/SiO_2/Si substrates. Each spin coated BCZT50 layer was subsequently heat-treated in air at 350 °C for 10 min. The above coating and heat-treatment procedures were repeated 10 times and annealed at 950 °C for 1 h.

Phase identification of BCZT50 thin films were done using an X-ray diffractometer (BRUKE D8 ADVANCE, Germany) with Cu $K\alpha$ radiation ($\lambda = 0.15406$ nm) with a working voltage of 40 kV and a current of 40 mA at a step of 0.02 in the range $2\theta = 20^\circ$ to 60°. The topography was illustrated by an Asylum Research MFP-3DTM atomic force microscope (AFM). The measurement of optical responses of BCZT50 was carried out by spectroscopic ellipsometry (SENDIRA from SENTECH). The wavelength region was 2.5–12.5 μm and incident angle was 70° for measurement using a three-layer model (ambient/BCZT50/Pt). All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1a shows that the BCZT50 films are well-developed perovskite structure. There exist no obvious peaks of impurity and secondary phases. It suggests that Ca and Zr diffuse into the $BaTiO_3$ lattice to form a homogeneous solid solution. The

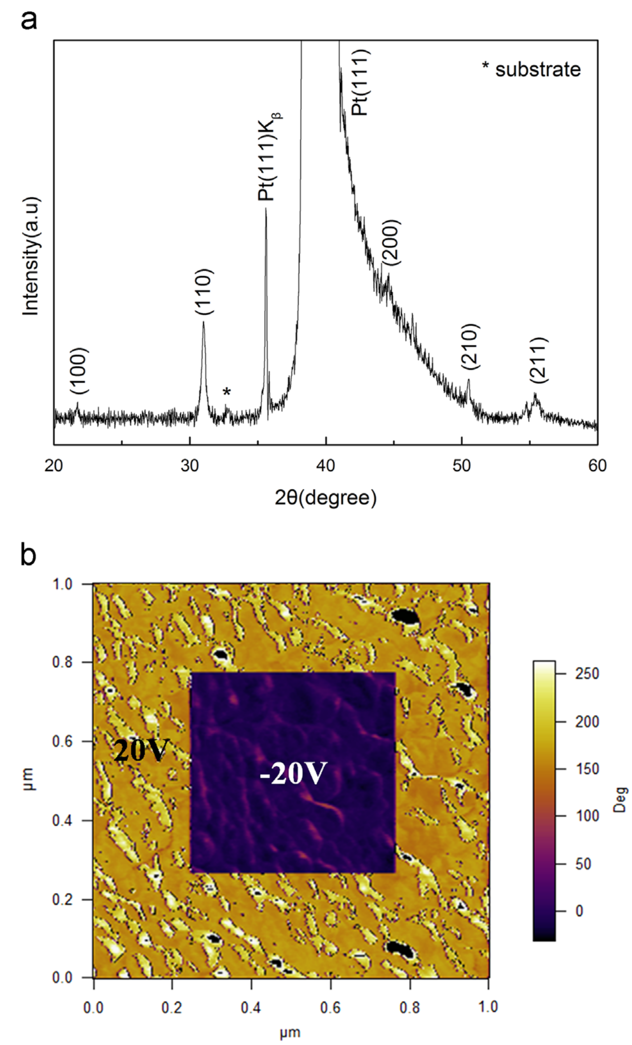

Fig. 1. (a) XRD and (b) phase pattern of BCZT50 thin films.

phase pattern for $1\times 1\ \mu m^2$ area in BCZT50 thin film measured as a function of applied DC voltage by Piezoelectric Atomic Force Microscope (PFM) are shown in Fig. 1b. The phase changes almost from 0° to 180°, which implies a nearly complete polarization switching behavior. The polarization switching shows clearly that as the deposited BCZT50 thin film is ferroelectric at room temperature.

Spectroscopic ellipsometry deals with the relative changes in the amplitude and the phase of a linearly polarized incident light upon an oblique reflection from the sample surface [16]. The experimental parameters measured by ellipsometry are the angles Psi (Ψ) and Delta (Δ), which are related to the optical and structural properties of the samples and defined by

$$\rho = \frac{R_p}{R_s} = \tan \Psi \exp(i\Delta) \tag{1}$$

where R_p and R_s are the complex reflection coefficients of the light polarized parallel and perpendicular to the plane of incidence, respectively. The ellipsometry parameters Ψ and Δ are ellipsometry angles. The tan Ψ gives the ratio between the absolute values of these two electric field components and Δ represents the phase difference between them. The schematic