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Structure, dielectric, ferroelectric, and optical properties of $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3-x(Ba_{0.7}Ca_{0.3})TiO_3$ thin films prepared by sol–gel method

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ABSTRACT

We report high dielectric tunabilities of $(1-x)Ba(Zr_{0.2}Ti_{0.8})O_3-x(Ba_{0.7}Ca_{0.3})TiO_3$ (BZT–xBCT) (x = 0.15, 0.30, 0.40, 0.45, 0.50, and 0.55) thin films prepared by a sol–gel method. The films show a pure perovskite structure with random orientation. They have moderate dielectric constant ranging from 350 to 500 and low dielectric loss near 3.0% at 1 kHz with 0 V bias at room temperature. The dielectric tunability of the BZT–0.55BCT thin films is up to 65% at 400 kV/cm and 100 kHz. The films exhibit a high optical transmission in the range of 420 nm–1500 nm. Their optical band gap energies are about 3.90 eV.

1. Introduction

Ferroelectric materials with large electrical field dependent dielectric constant have been extensively studied due to their potential for substantial miniaturization of tunable microwave components, such as phase shifters, tunable oscillators, and tunable filters. In such applications, it is desirable for the materials to possess relatively high tunability, moderate dielectric constant, and low dielectric loss [1–4]. Commonly, the studies in this field are mainly focused on barium strontium titanate (BST) system due to their strong electric field dependence of dielectric constant and low microwave loss. Moreover, their dielectric properties (such as tunabilities) can be tailored by adjusting the composition of BST. Much work has been devoted to improve the dielectric properties of BST ceramics and thin films in the last decade, including stoichiometry, doping, buffer layer, thickness variation, stress modification [5–11]. It has been reported that graded multilayered BST thin films exhibit good temperature stability over the temperature range of −10 °C to 90 °C [10]. Recently, $Ba(Zr_xTi_{1-x})O_3$ (BZT) has been chosen as a promising candidate in the fabrication of ceramic capacitors because Zr^{4+} ions are chemically more stable than Ti^{4+}, leading to a suppression of the conduction by electron hopping between Ti^{3+} and Ti^{4+}, thus reducing the dielectric loss [12–14]. The related system of $(Ba_{1-x}Ca_x)(Zr_yTi_{1-y})O_3$ (BCZT) ceramics has been reported to exhibit broad dielectric maxima near critical temperature T_c, with peak values as high as $\varepsilon_{max} \approx 18000$. The ceramics have been used in the fabrication of multilayer ceramic capacitors that can meet the Y5V specification, which has a wide temperature characteristic of +22% to −82% capacitance change over the operating temperature range of −30 °C to +85 °C [15,16]. Variation of the Ca and Zr concentrations has been used to broaden and shift the dielectric maximum at the Curie point to room temperature [17,18]. The diffusive character of their paraelectric-to-ferroelectric transition makes the materials promising for designing devices working in a large temperature range. The dielectric properties of BCZT ceramics and thin films have been reported in recent years. The $Ba_{0.90}Ca_{0.10}Ti_{0.75}Zr_{0.25}O_3$ ceramics show a tunability of 60% with a dielectric loss of about 0.003 and the thin films deposited on Pt substrates by pulsed laser deposition with and without $CaRuO_3$ buffer layer possess a tunability of near 50%. The Mg-doped $Ba_{0.96}Ca_{0.04}Ti_{0.84}Zr_{0.16}O_3$ thin films fabricated by metalorganic deposition method have also turned out to be a promising candidate as a high dielectric material [19–22]. Recently, a very high piezoelectric coefficient of 620 pC/N has been found in BZT–xBCT ceramics at morphotropic phase boundary (MPB) [23]. The BZT–0.50BCT thin film shows a high $d_{33,f}$ value of 80 pm/V [24]. According to the phase diagram of BZT–xBCT ceramics, the T_c of the BZT–xBCT solid solutions can be adjusted via changing the x in a wide temperature range (about 0 °C to 80 °C), There are three typical compositions in BZT–xBCT solid solutions, which are x = 0.14, 0.32, and 0.50, respectively, corresponding to cubic phase at room temperature, cubic–

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rhombohedral–tetragonal (C–R–T) triple point near 57 °C, and tetragonal phase at room temperature with a very high piezoelectric coefficient [23].

In this work, BZT–xBCT (x = 0.15, 0.30, 0.40, 0.45, 0.50, and 0.55) thin films have been prepared by a sol–gel method. The structure, dielectric constant, and dielectric tunability of BZT–xBCT thin films with different phase structures have been reported. Their hysteresis loops as well as optical transmission and band gap energies have also been investigated.

2. Experimental procedure

The BZT–xBCT (x = 0.15, 0.30, 0.40, 0.45, 0.50, and 0.55) precursor solutions were synthesized using barium acetate, calcium acetate monohydrate, titanium tetra-*n*-butoxide and zirconium-*n*-propoxide as starting materials. Acetic acid and 2-methoxyethanol were used as co-solvents, and acetylacetone as a chelating reagent to reduce the vigorous hydrolysis of titanium tetra-*n*-butoxide and zirconium-*n*-propoxide. Barium acetate and calcium acetate monohydrate were initially dissolved in acetic acid and 2-methoxyethanol co-solvents according to the predetermined ratios and stirred for 2 h, then cooled down to room temperature. The titanium tetra-*n*-butoxide and zirconium-*n*-propoxide 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 final solutions obtained were adjusted to 0.2 M. Spin-coating of the solutions was performed at 3000 rpm for 30 s on Pt/Ti/SiO_2/Si (111) and fused silica substrates. Each spin-coated BZT–xBCT layer was subsequently heat-treated in air at 600 °C for 10 min. The above coating and heat-treatment procedures were repeated until reaching the desired thickness of about 400 nm. The resulting films were heated at 700 °C for 1 h for crystallization.

The crystallography of BZT–xBCT thin films was analyzed by an X-ray diffractometer (XRD, Rigaku, D/MAX 2200 VPC) in the mode of θ–2θ scan with Cu K_α radiation ($\lambda = 0.154$ nm) with working current and voltage of 30 mA and 40 kV, respectively. The dielectric properties and capacitance–voltage curves were measured on the films in a metal–insulator–metal configuration using a 4284A LCR meter (Agilent) with the applied ac signal amplitude of 100 mV, and the hysteresis loops were measured using a TF 2000 ferroelectric analyzer with FE module (aixACCT). To measure the electrical properties, Pt dot electrodes of 0.3 mm diameter were deposited on the surfaces of the films as top electrodes through a shadow mask. The optical transmittance of the thin films on fused silica substrates was measured with a UV–vis–NIR spectrophotometer (Shimadzu UV-3500) in the wavelength range from 300 nm to 1500 nm.

3. Results and discussion

The XRD patterns of the BZT–xBCT (x = 0.15, 0.30, 0.40, 0.45, 0.50, and 0.55) thin films are shown in Fig. 1. All the films show a well-developed perovskite structure with random orientation and can be characterized by the appearance of (100), (110), (200), and (210) peaks in Fig. 1a, and no peaks from impurity phase or secondary phase can be found. A careful examination of the XRD patterns reveals that with increasing x the diffraction peaks shift to larger 2θ values, evidenced by the (210) diffraction peak at 54–58° as observed in Fig. 1 b. In BZT–xBCT system, Ca and Zr ions prefer to occupy A-sites (Ba-sites) and B-sites (Ti-sites) in the perovskite lattice, respectively [16]. The ionic radius of Ca^{2+} is smaller than that of Ba^{2+}, and Ti^{4+} has a smaller ionic radius than Zr^{4+} [25]. With increasing x the Ca and Ti contents are enriched which shrink the lattice of BZT–xBCT thin films, leading to the shifting of the diffraction peaks to larger 2θ value.

The dielectric constant and dielectric loss were measured at room temperature as a function of frequency ranging from 100 Hz to 100 kHz for BZT–xBCT thin films on Pt/Ti/SiO_2/Si substrates as shown in Fig. 2. The dielectric constant exhibits a slight decrease, whereas dielectric loss shows an opposite tendency in the frequency range between 100 Hz and 100 kHz. Such frequency dispersion may be ascribed to space charge polarization or Maxwell–Wagner type interfacial polarization. The space charge polarization is inherently related to the nonuniform charge accumulation near the interfaces between the film and electrode [26,27]. It is also influenced by the contact resistance between the probe and the electrode [28]. The dielectric constant and dielectric loss at 1 kHz at room temperature for BZT–xBCT thin films are listed in Table 1. According to phase diagram of BZT–xBCT system, there is a C–R–T triple point locating at x = 0.32 and at $T_c = 57$ °C [23]. It can be seen that the BZT–xBCT (x = 0.45, 0.55) thin films with tetragonal phase have the largest dielectric constant about 460 at 1 kHz. The BZT–xBCT (x = 0.30, 0.40) films near the MPB have the smallest dielectric constant near 340 at 1 kHz, and the dielectric constant of cubic BZT–xBCT (x = 0.15) thin films is 374 at 1 kHz. Generally, the dielectric properties of the thin films are affected by stoichiometry, strain, microstructure, and 'dead layer' near the interface between the film and the electrodes [8]. In ferroelectric materials the dielectric constant is also controlled by the equilibrium of elastic and domain-wall energy [12]. The smaller dielectric constant of BZT–xBCT (x = 0.30, 0.40) thin films near MPB may be due to the smaller domain size in microstructure. Moreover, the dielectric constant of the BCZT thin films prepared by pulsed laser deposition is much larger than that of the BZT–xBCT thin films prepared by sol–gel method [17–22]. This is mainly due to the grain size, strain, microstructure and dead layer of the BZT–xBCT thin films.

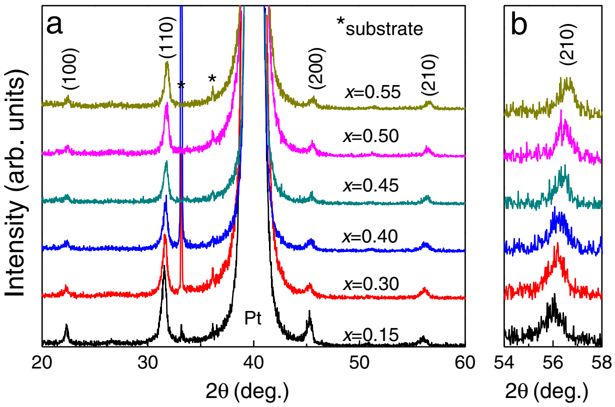

Fig. 1. XRD patterns of BZT–xBCT (x = 0.15, 0.30, 0.40, 0.45, 0.50, and 0.55) thin films on Pt/Ti/SiO_2/Si substrates.

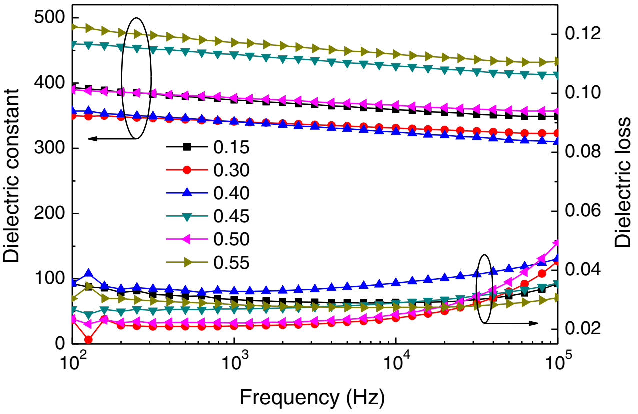

Fig. 2. Dielectric constant and dielectric loss measured at room temperature as a function of frequency for the BZT–xBCT (x = 0.15, 0.30, 0.40, 0.45, 0.50, and 0.55) thin films on Pt/Ti/SiO_2/Si substrates.