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Enhanced tunable dielectric properties of $Ba_{0.5}Sr_{0.5}TiO_3/Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ multilayer thin films by a sol–gel process

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ABSTRACT

$Ba_{0.5}Sr_{0.5}TiO_3$(BST)/$Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$(BZN) multilayer thin films were prepared on Pt/Ti/SiO_2/Si substrates by a sol–gel method. The structures and morphologies of BST/BZN multilayer thin films were analyzed by X-ray diffraction (XRD) and field-emission scanning electron microscope. The XRD results showed that the perovskite BST and the cubic pyrochlore BZN phases can be observed in the multilayer thin films annealed at 700 °C and 750 °C. The surface of the multilayer thin films annealed at 750 °C was smooth and crack-free. The BST/BZN multilayer thin films annealed at 750 °C exhibited a medium dielectric constant of around 147, a low loss tangent of 0.0034, and a relative tunability of 12% measured with dc bias field of 580 kV/cm at 10 kHz.

1. Introduction

Recently, $Ba_{1-x}Sr_xTiO_3$(BST) thin films have been intensively investigated for applications in tunable microwave components, such as frequency-agile filters, voltage-controlled oscillators, phase shifters and antennas, because of their large electric field-dependent tunability and the adjustable dielectric properties from different doping ratio of Sr and Ba [1–6]. However, the relatively large dielectric loss and the limited figure of merit (FOM) (FOM is defined as the ratio of tunability and loss tangent at room temperature) restrict the practical applications of BST thin films in tunable microwave elements. Researchers have found that BST films with high tunability, low loss at zero bias, and high dielectric breakdown fields can be grown using pulse laser deposition (PLD) with judiciously chosen process parameters [7–9]. It has been found that doping of low loss oxides into ferroelectric materials is an effective way to reduce the loss tangent. Various oxides, such as MgO, ZrO_2, TiO_2, and Al_2O_3, have been used as additives to reduce the loss tangent of BST thin films [10–16]. But in many cases, the reduction in the dielectric loss by doping is limited and the tunability of BST decreases substantially at the same time.

Recently, cubic pyrochlore phase $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ (BZN) has attracted much attention as a dielectric material for microwave tunable applications mainly due to its very low dielectric loss [17–20]. Sandwich BZN/BST/BZN films deposited by radio frequency magnetron sputtering have been reported [21]. The BZN/Mn-BST heterolayer films deposited on Nb:$SrTiO_3$ substrates by PLD has been reported [22]. These results suggest that BZN–BST composite thin films may have advantages in tunable materials design by using the compatibility and flexibility of the composites.

In our study, BST/BZN alternating multilayer thin films have been prepared on Pt/Ti/SiO_2/Si substrates by a sol–gel method. The phase composition, microstructure, dielectric properties and tunability of the resulting thin films have been investigated.

2. Experimental details

BST and BZN thin films were prepared using a sol–gel processing. The composition of BST used was $Ba_{0.5}Sr_{0.5}TiO_3$. The precursor materials used to prepare BST were barium acetate, strontium acetate and titanium tetra-n-butoxide. Glacial acetic acid and 2-methoxy ethanol were used as the solvents. Equi-molar mounts of barium and strontium acetate were dissolved in heated glacial acetic acid. Titanium tetra-n-butoxide was mixed with acetyl acetone (chelating agent) and then mixed with the barium and strontium acetate solutions under constant stirring. 2-Methoxyethanol was added to the sol to adjust its viscosity. The prepared sol was stirred for 30 min to allow complex formation. The final concentration of the BST sol was 0.5 mol/L. The composition of BZN used was $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$. The starting materials for the BZN sol were bismuth acetate, zinc acetate dehydrate, and niobium ethoxide. 2-Methoxyethonal, pyridine, and glacial acetic acid were used as solvents. The detailed synthesis procedures of used to produce the BZN sol are described in ref. [19]. The concentration of the BZN sol was 0.2 mol/L. BZN films and BST films were deposited alternatively on Pt/Ti/SiO_2/Si substrates by a spin-coating technique with a spin rate of 3000 rpm for 30 s. Each layer of wet films was pre-baked at 350 °C for

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3 min and then fired at 650–750 °C for 3 min in a rapid thermal furnace before the next layer was deposited. Thicknesses of multilayer BST/BZN thin films are 675 nm. Pure BZN and BST thin films were also prepared by the same process for comparison. Thicknesses of Pure BZN and BST layers are 400 nm and 500 nm respectively.

The structures of the thin films were characterized using a Rigaku D/Max-2400 X-ray diffractometer (XRD) with CuKα radiation at 40 kV and 100 mA. The surface and cross-section morphologies of the thin films were examined using a field-emission scanning electron microscope (FESEM, JEOL JSM-6700F) at an operating voltage of 5.0 kV. The thickness of the thin films was measured using a step profiler (Ambios Inc, XP-2). For the dielectric measurements, top Au electrodes with a diameter of 1 mm were dc-sputtered on the films via a shadow mask to form a metal-insulator-metal structure. The dielectric properties and capacitance–voltage curves were measured with an Agilent 4294A impedance analyzer.

3. Results and discussion

3.1. Crystallization and phases

Fig. 1 shows the XRD patterns of multilayer BST/BZN thin films annealed at different temperatures. The peaks present in the patterns of the multilayer thin films are believed to arise from both the BST and BZN layers. The cubic pyrochlore BZN phase can be observed in the multilayer thin films annealed at 650 °C using a rapid thermal process, but there were no peaks of perovskite BST phase in the same annealing temperature. The BZN thin films were crystalline at lower annealing temperatures than the BST layer, which is consistent with others reports [19]. The BST thin films were amorphous after rapid thermal annealing at 650 °C, so a higher temperature was required to produce crystalline BST. As the annealing temperature was increased, the perovskite BST phase emerged, and can be observed in the multilayer thin films annealed at 700 °C and 750 °C. At the same time, the intensities of the BZN diffraction peaks increased, but the layer of BZN maintained their cubic pyrochlore structure. The diffraction patterns confirm that no measurable reaction occurred between the BST and BZN components after annealing at temperatures up to 750 °C for 3 min.

3.2. Morphology

Fig. 2 shows the surface morphology of BST films, BZN films annealed at 750 °C. The surface morphology of BST films shows that the grain size is small and about 20 nm. The surface of BST films is compact and crack-free. The surface morphology of BZN films shows the grain size is around 100 nm. It is to be noted that pores appear inside the large grains in BZN films annealed at 750 °C.

The surface morphology of BST/BZN multilayer thin films annealed at 650–750 °C and a cross-section image of the BST/BZN multilayer thin films annealed at 750 °C are presented in Fig. 3. The terminating layer of the BST/BZN multilayer thin films is a BZN layer, so the surface morphology of the BST/BZN multilayer thin films is similar to that of a pure BZN thin film. The grain size is small in the film annealed at 650 °C, and it becomes larger as the annealing temperature increases. Pores appear in the BST/BZN multilayer thin films when the annealing temperature is above 650 °C. It is assumed that these pores formed during the thermal processing of the BZN thin films. Further work needs to clarify the mechanism of pore formation. The FESEM images of the BST/BZN multilayer thin films indicate that the films are smooth and crack-free. A cross-section FESEM image of the BST/BZN multilayer thin films (Fig. 3(d)) shows that each layer in the films has distinct interfaces. No obvious diffusion between the BZN and BST layers is observed.

3.3. Dielectric properties

The dielectric properties of pure BST and BZN and multilayer thin films are presented in Table 1. The BST/BZN multilayer thin films annealed at 650 °C shows the lowest dielectric constant because the layers of BST are amorphous and the layers of BZN show low crystalline degree. The dielectric constants of BST/BZN multilayer thin films increased with the annealing temperature, but are smaller than that of a pure BST thin film. The smaller dielectric constants of the BZN/BST thin films are a result of the presence of BZN phase in BST, which is similar to those observed for BST doped with oxides [23]. The BST/BZN multilayer thin films can be considered as the BST and BZN

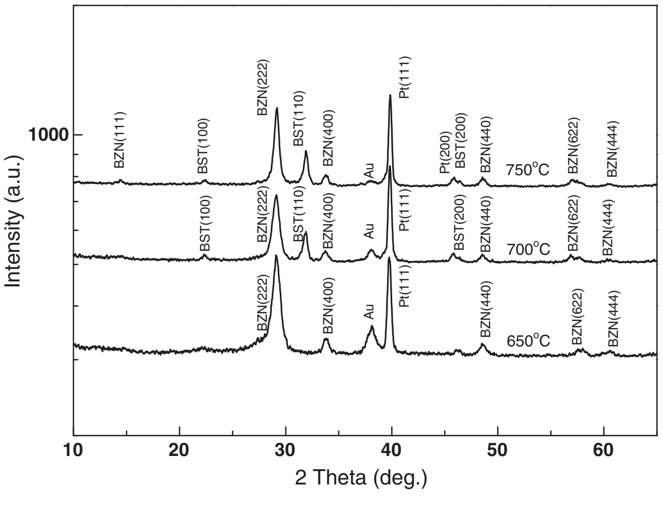

Fig. 1. XRD pattern of multilayer BST/BZN thin films annealed at different temperature.

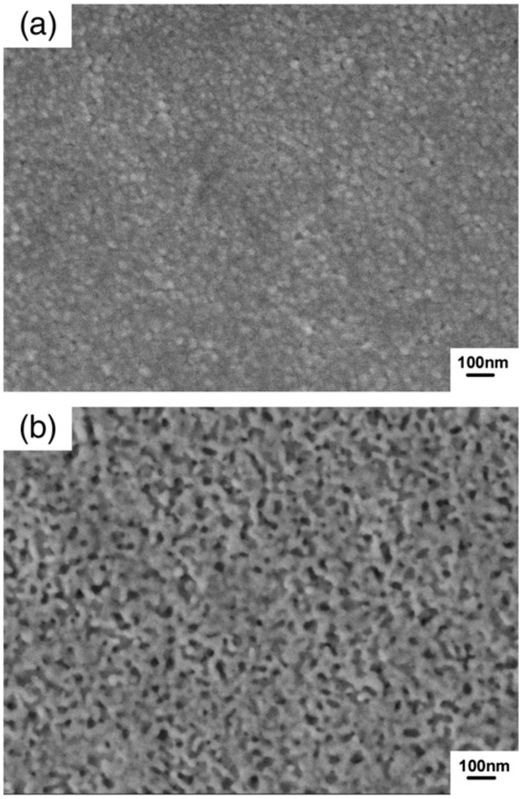

Fig. 2. SEM images of pure (a) BST, (b) BZN thin films on Pt/Ti/SiO_2/Si substrates.