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LETTER

Enhanced electrical properties of multilayer $Ba(Zr_{0.2}Ti_{0.8})O_3$/$Ba_{0.6}Sr_{0.4}TiO_3$/$Ba(Zr_{0.2}Ti_{0.8})O_3$thin films for tunable microwave applications

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Introduction

Ferroelectric thin films based on $BaSrTiO_3$ (BST) have been intensively studied for a large field of applications, such as ultra-large-scale integrated dynamic random access memories (DRAM), and field effect transistors [1, 2]. To develop a high performance microwave tunable devices, it is required a material with suitable dielectric constant, high tunablility, and low dielectric loss, to achieve high figures of merit. However, the disadvantages of ferroelectric films include high dielectric constant, relatively high dielectric loss, and the degradation of ferroelectric in hybrid structures. In order to further increase the figures of merit, much effort has been made to develop modified BST thin films. The introduction of dopants, such as Al_2O_3 and MgO, into BST has been demonstrated to be an effective way to improve the figures of merit for microwave tunable devices application. Usually it has been observed that the reduction in losses of BST thin films doped with Al_2O_3 or MgO is accompanied by the reduction in tunability [3, 4]. In addition, their reproducibility and the stability of the materials needs to be improved [5, 6].

In recent years, Barium zirconium titanate $Ba(Zr,Ti)O_3$ has attracted immense attention for it's potential applications for the microwave technology, due to its low dielectric loss and large tunability, because the substitution of Zr^{4+} for Ti^{4+} has a benefit to the stability of the system [7–13]. As is well-known, a multilayer approach, in which the film is composed of alternating layers of different compositions or even different materials, appears to be very promising in optimizing the properties of materials. There have been a few reports on the growth and electrical properties of single crystal $BaSrTiO_3$ and $Ba(Zr,Ti)O_3$ [14–20]. However, works on BZT/BST/BZT multilayer thin films has not been reported. In this letter, we report the preparation and characterization of $Ba(Zr_{0.2}Ti_{0.8})O_3$/$Ba_{0.6}Sr_{0.4}TiO_3$/$Ba(Zr_{0.2}Ti_{0.8})O_3$ (BZT/BST/BZT) multilayer films deposited by Pulsed laser deposition (PLD) technique, using two individual BZT and BST targets. Our results showed that the multilayer films demonstrated a lower dielectric loss tangent while retaining relatively high dielectric tunability and some permittivity, making them a promising candidate for microwave device applications.

Experiment

BST and BZT/BST/BZT multilayer thin films were deposited on $LaNiO_3$ (LNO) coated $LaAlO_3$ (LAO) substrate by Pulsed laser deposition (PLD) technique. KrF excimer laser radiation (λ = 248 nm, 650 mJ, 25 ns) was focused on a rotating target set in the chamber though a quartz window. The incident angle of laser beam to the target surface was fixed to be 45°. Substrate was placed parallel to the target surface with a target–substrate distance of 50 mm. Oxygen was used as a reactive agent during deposition, and was introduced into the chamber though a needle valve. The substrate was heated by radiation from Pt resistive heater with a thermocouple embedded in the heater. Disk-type $Ba(Zr_{0.2}Ti_{0.8})O_3$ and $Ba_{0.6}Sr_{0.4}TiO_3$ ceramic targets were prepared by conventional ceramic process, which mixed the appropriate ratio of precursor oxide powders, pressed the powders into pellets, and sintered

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them to high density. The LNO bottom electrodes about 100 nm was deposited on the LAO substrate at 600 °C in oxygen pressure of 20 Pa by PLD (a laser fluence of 2.0 J/cm^2, a repetition rate of 3 HZ). The bottom electrodes were in situ annealed at 600 °C for 30 min in O_2 ambient to improve the crystallinity of the films. Three hundred nanometer BST and BZT (50 nm)/BST (200 nm)/BZT (50 nm) multilayer thin films were grown on (LNO) coated $LaAlO_3$ (LAO) substrate, respectively. The substrate temperature and the oxygen ambient pressure during the growth of the films were 650 °C and 25 Pa, respectively. To reduce any oxygen deficiency, the samples were also in situ annealed in 0.5 atm oxygen at 700 °C for 1 h, and then cooled down slowly to room temperature. For dielectric measurements, the metal–insulator–metal (MIM) capacitor configuration was fabricated. Pt top electrodes with an area of 0.03 mm^2 were deposited on the films by direct current sputtering though a shadow mask.

The crystal structure and crystallographic orientations of the thin films were obtained by X-ray diffraction (XRD) using a BeDe1 Scientific diffractometer (Cu Kα radiation). Atomic force microscope (AFM, SPM-300HV, SEIKO) was performed to investigate the morphologies and grain size of the film surface. Capacitance and dielectric loss were measured using an HP 4284 impedance analyzer. The current–voltage characteristic was measured with a HP4155B semiconductor parameter analyzer.

Results and discussion

X-ray diffraction patterns of the BST and BZT/BST/BZT multilayer thin films are shown in Fig. 1. Only (*l*00) type reflections of BST, BZT, LNO, and LAO were observed for both the BST and ML thin films, indicating that both the films have been successfully grown in single-oriented perovskite phases for the two samples. These confirmed the out-plane orientation relationship BST (100) ‖ LNO (100) ‖ LAO (100) and BZT (100) ‖ BST (100) ‖ BZT (100) ‖ LNO (100) ‖ LAO (100). The high (*l*00) orientation of BST and BZT/BST/BZT multilayer thin films on LNO-coated LAO substrate has been attributed to the small lattice mismatch. The surface morphologies of the corresponding samples were observed by a scanning probe microscope operating in the contact atomic force microscope (AFM) over an area of1 × 1μm^2, as shown Figs. 2a and 1b. It can be seen clearly that both films are very smooth surface, dense, and without any cracks. The single-layered BST films are composed of small grains, whose typical size is about 42 nm. In comparing, larger grains with the size of about 47 nm are observed in the multilayered films. It is indicated that the grain size slightly increased in case of the ML BST films.

Electrical properties of the both films are obtained through investigating the capacitors with the configuration of Pt/I/LNO, where "I" means BST or BZT/BST/BZT multilayer. The dc bias field dependence of dielectric constant and dielectric loss at room temperature (25 °C) was measured to evaluate the tunability of the BST and BZT/BST/BZT multilayer thin films. The measurements were conducted by applying a small ac signal of 0.1 V amplitude and 100 Hz frequency while the dc field was swept from positive bias to negative bias. The applied electric field dependence of the dielectric constant for BST and BZT/BST/BZT multilayer thin films grown on LNO/LAO is shown in Fig. 3. The BST film has a maximum dielectric constant of 648, while BZT/BST/BZT multilayer film shows a maximum dielectric constant of 380.

The tunability is defined as $(\varepsilon_{max} - \varepsilon_{min})/\varepsilon_{max}$, where ε_{max} and ε_{min} are the maximum and minimum measured dielectric constant, respectively. The tunability of the BZT/BST/BZT multilayer film was value of 61.58%, while that of BST films was 65.27% for 300 kV/cm. However, the dielectric loss tangent of BZT/BST/BZT multilayer film (0.8%) is lower than that of BST (2.1%) fabricated with the same process. Obviously, leading BZT layer between the BST films and electrodes should decrease the dielectric loss.

In order to compare films with varied dielectric properties for use in tunable device applications, the figure of merit (FOM) defined as $K = \text{tunabilty}/\tan\delta$ is a frequently

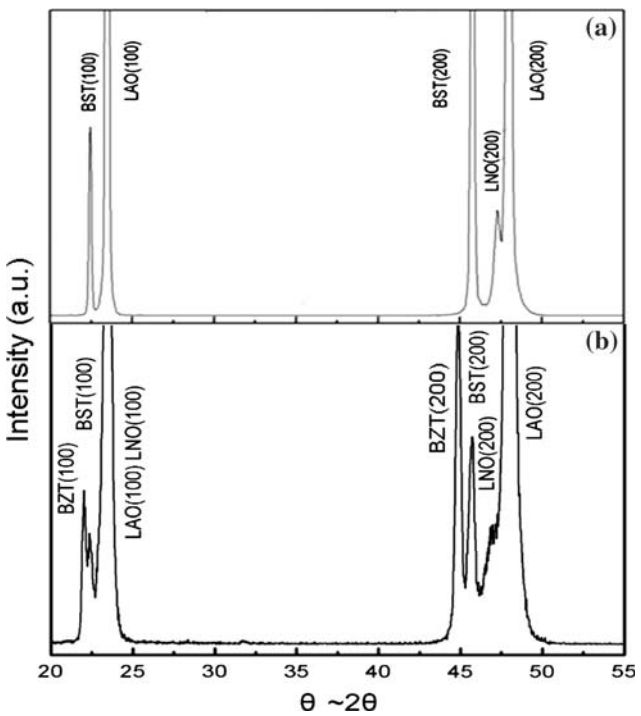

Fig. 1 XRD patterns of the (**a**) BST single layered films and (**b**) BZT/BST/BZT multilayered films

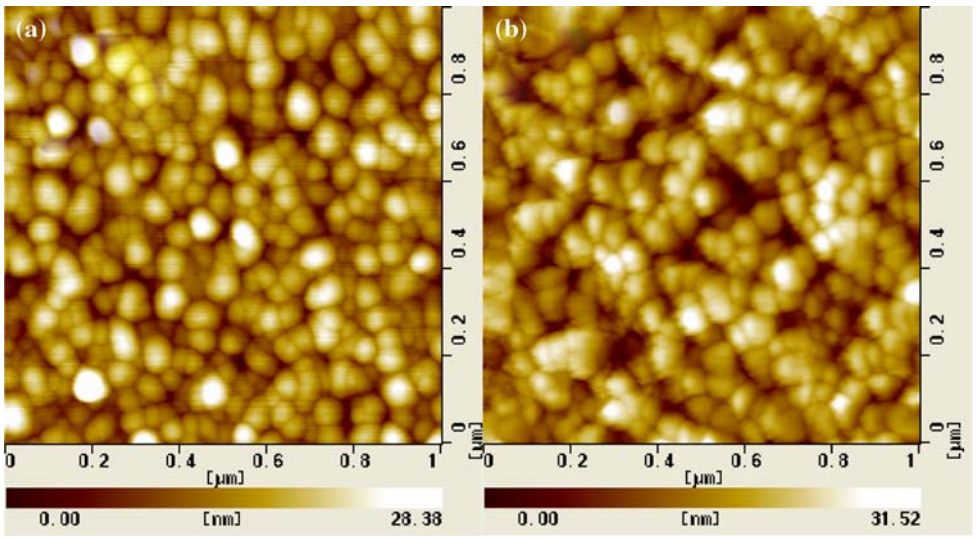

Fig. 2 AFM micrographs($1 \times 1\mu m^2$) of (**a**) BST single layered films and (**b**) BZT/BST/BZT multilayered films

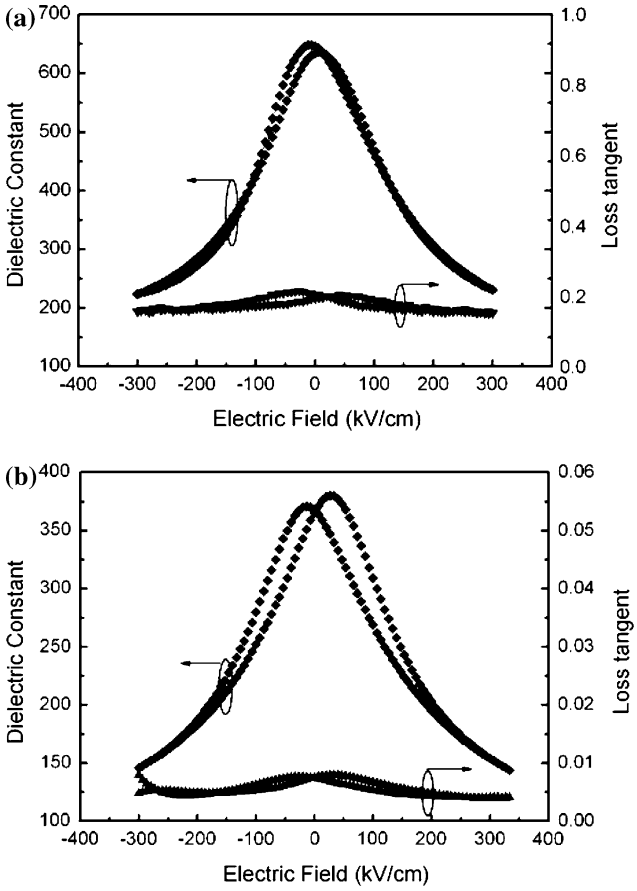

Fig. 3 Dielectric constant and dielectric loss of the two samples as a function of electric field (**a**) BST and (**b**) BZT/BST/BZT

used parameter to characterize the correlations between the tunability and the dielectric loss. Although the tunability of the BZT/BST/BZT multilayer film is smaller than that for the BST film, the K factor of BZT/BST/BZT multilayer film is more than that of the BST film since the dielectric

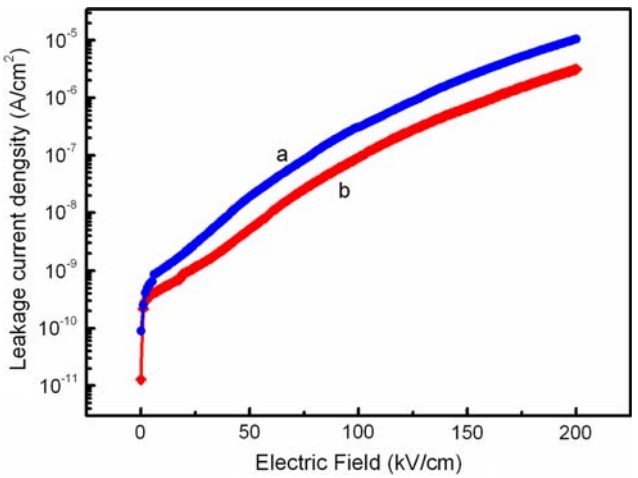

Fig. 4 I–V characters of the two samples (a) BST and (b) BZT/BST/BZT

loss tangent is considerably reduced. FOM for the BZT/BST/BZT multilayer film was 76.98. These values are relatively higher in comparison with those of BST thin films (31.08).

For practical application, the leakage current should be as low as possible. Figure 4 shows the variations of leakage current density with the applied voltage up to 200 kV/cm for the two samples measured at room temperature. It is clear that the leakage current density of BZT/BST/BZT multilayer film is lower than that of BST thin films. As shown in the figure, the leakage current density at a positive electric field intensity of 100 kV/cm is 3.07×10^{-7} A/cm^2 for the BST film, whereas the value decreases down to 9.14×10^{-8} A/cm^2 for the BZT/BST/BZT multilayer film. It is considered that an electrically stable interface or uniform microstructure is established in the multilayered BZT/BST/BZT multilayer thin film.

Conclusion

In conclusion, BST and BZT/BST/BZT multilayer thin films were deposited on $LaNiO_3$ (LNO) coated $LaAlO_3$ (LAO) substrate by Pulsed laser deposition (PLD) technique. The dielectric constant and tunability of the BZT/BST/BZT multilayer thin film slightly decreased, while the dielectric loss decreased synchronously. At room temperature, the FOM-factor value increases from 31.08 to 76.98 at 100 kHz by applying an electric field of 300 kV/cm, and the leakage current density of the BZT/BST/BZT multilayer thin film at a positive bias field of 100 kV/cm decreases from 3.07×10^{-7} A/cm^2 to 9.14×10^{-8} A/cm^2.

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