Electrical characteristics of BaTiO₃/Bi_{0.5}K_{0.5}TiO₃ multilayered thin films synthesized via metalloorganic decomposition

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ABSTRACT

Multilayered BaTiO₃(BTO)/Bi_{0.5}K_{0.5}TiO₃ (BKT) thin films have been fabricated on Pt/Ti/SiO₂/Si substrates using a metalloorganic decomposition process. XRD investigation of the resultant BTO/BKT multilayered thin films shows that they retain a perovskite-related structure type. They also exhibit a well-defined, polarization–electric field hysteresis loop with a measured remnant polarization ($2P_r$) of 5 $\mu\text{C}/\text{cm}^2$ at an applied electric field of 250 kV/cm. The measured dielectric constant and dielectric loss at 10 kHz is 470 and 0.07 respectively. These multilayer BTO/BKT films maintain an excellent fatigue-free character even after 10^9 switching cycles. The mechanism associated with the enhancement of the electrical properties of the synthesized BTO/BKT films is also discussed.

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1. Introduction

The search for high performance, lead-free piezoceramic materials to replace the current most widely used (but lead-containing) piezoceramic, $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$, has drawn considerable recent attention. Ferroelectric perovskite, tungsten bronze as well as Bi-layer structured, Aurivillius phase compounds have been widely investigated for this purpose. Ferroelectric perovskites such as BaTiO₃ [1], (Bi_{0.5}K_{0.5})TiO₃ [2], (Bi_{0.5}Na_{0.5})TiO₃ [3], and KNbO₃ [4] are currently among the most promising candidate materials due to their relatively large piezoelectric coefficients. Thus considerable efforts have been put towards the fabrication and electrical characterization of thin films of these materials for use in a wide range of potential applications e.g. in micro-electromechanical systems (MEMS) and microsensors. There have been a significant number of publications along these lines involving thin films of BaTiO₃, (Bi_{0.5}Na_{0.5})TiO₃ and KNbO₃. Only a very few such papers on pure (Bi_{0.5}K_{0.5})TiO₃ (BKT) thin films [5,6], however, have been reported to date.

The high conductivity of BKT bulk ceramics typically causes difficulties in poling and a significant deterioration in polarization properties [7]. This might well be expected to worsen if synthesized in thin film form due to the size effect and lattice mismatch between the film and substrate. Large lattice mismatch would induce an incoherent interface, which may hinder the films growth and degrade dielectric properties of the films. The use of appropriate multilayered thin films, on the other hand, is known to sometimes dramatically improve, or even create new, properties of the overall films [8–10], ascribed to the

interactions between layers with different compositions and/or structures [9,11–13]. Polycrystalline BaTiO₃/SrTiO₃ multilayer ferroelectric thin films [14], for instance, have been shown to double the dielectric constant (~367 at 10 kHz) of Ba_{0.5}Sr_{0.5}TiO₃. Again, the electrical fatigue characteristics of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ [15] have been shown to be able to be significantly improved via the fabrication of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3/\text{PbZrO}_3$ heterostructures. Likewise, multilayered $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3/\text{PbTiO}_3$ [12] and $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3/(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$ [16] thin films have led to significant improvements in various dielectric, ferroelectric and pyroelectric properties. Park et al. [17], for example, recently reported that $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3/\text{SrBi}_2\text{Ta}_2\text{O}_9$ thin films reduce the leakage current of $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ films.

Barium titanate (BTO) is a well-known ferroelectric perovskite with tetragonal $P4mm$ space group at room temperature [1]. It has a similar room temperature structure to BKT. The successful fabrication of multilayer BaTiO₃/(Bi_{0.5}K_{0.5})TiO₃ (BTO/BKT) thin films and the reporting of their resultant polarization properties is the subject matter of this letter.

2. Experimental

Both BTO and BKT precursors were first synthesized by a metalloorganic decomposition process. Highly pure barium acetate (99%, Sigma), bismuth nitrate (98%, Sigma), potassium nitrate (99%, Sigma) and titanium (IV) isopropoxide (97%, Sigma) were chosen as starting materials and glacial acetic acid (99%, Sigma) as a solvent. These resultant precursors were then spin-coated onto Pt/Ti/SiO₂/Si wafers. Each individual layer was heat-treated at 400 °C for 5 min before deposition of the next layer. A final annealing of the overall multilayer film was then carried out at 700 °C for 30 min to enable crystallization to take place. The total thickness of the resultant films

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Fig. 1. X-ray diffraction pattern of the as-synthesized multilayered BTO/BKT thin film. The inset shows an expanded region around the (110)* reflection in the vicinity of $2\theta \sim 32^\circ$.

with a deposition of 10 layers was ~ 400 nm. The first and last layers were selected to be BTO and BKT, respectively.

The crystalline phase of the resultant thin films was identified by powder X-ray diffraction (XRD, SIEMENS D-500). For the electrical measurements, a top gold electrode $400 \mu\text{m}^2$ in size was deposited by DC sputtering. Hysteresis loop measurements were performed in dynamic mode using a TF2000 analyzer. Dielectric characteristics were measured using a high precision LCR meter (Agilent 4284A).

3. Result and discussion

Fig. 1 shows a characteristic XRD pattern of the synthesized BTO/BKT multilayer thin film, demonstrating the formation of a polycrystalline perovskite structure. The inset in **Fig. 1** shows an expanded region of the XRD pattern around the (110)* reflection of the BTO/BKT multilayered thin film in the 2θ range from 30° to 34° . There are clearly two such (110)* peaks, one belonging to BaTiO_3 (JCPDS89-1428) and the other to $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ (JCPDS36-0339), thus confirming that a BTO/BKT multilayered structure has been fabricated.

The dielectric properties of this film were characterized using a high precision LCR meter. **Fig. 2** shows the measured room temperature dielectric constant and dielectric loss of this multilayer thin film as a function of frequency (from 1 kHz to 1 MHz). The measured dielectric constant is slightly frequency-dependent as is the measured dielectric loss. The dielectric constant and dielectric loss at a frequency of 10 kHz are ~ 470 and 0.07, respectively. The dielectric constant of this multilayered BTO/BKT thin film is significantly higher than that reported for a

Fig. 2. Dielectric constant and dielectric loss of the synthesized multilayered thin film as a function of frequency.

Fig. 3. The dielectric constant and dielectric loss of the multilayered BTO/BKT thin film as a function of applied DC electric field.

pure BaTiO_3 and $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ thin film at the same frequency and prepared under similar deposition conditions [5,18]. The measured dielectric loss, however, is also higher than that reported for pure BTO films over the entire measured frequency range, presumably because of strong structural distortion in the vicinity of the interfacial layers separating the BTO and BKT layers. Similar behavior has been reported for multilayer samples in other systems [14,19].

Fig. 3 shows a typical dielectric constant versus applied electric field (ϵ - E) loop for the multilayered BTO/BKT thin film, measured at 10 kHz at room temperature. The field-dependent behavior of the dielectric constant is consistent with the polarization versus applied electric field (P - E) hysteresis loop shown in **Fig. 4**, strongly suggesting that the polarization of the multilayered BTO/BKT thin film results from the switching of ferroelectric domains. The slight asymmetry observed in the ϵ - E curve (see **Fig. 3**) suggests that charge accumulates at one interface between the thin film and the electrode. From the data shown in **Fig. 3**, the dielectric tunability for DC bias electric fields up to an E_{max} of 250 kV/cm is $\sim 24\%$.

The ferroelectric property of the multilayered thin film was confirmed by a polarization versus applied electric field (P - E) hysteresis loop measurement where the polarization as a function of applied external electric field was measured at a frequency of 1 kHz. **Fig. 4** shows a typical room temperature, polarization-electric field hysteresis loop. The measured remnant polarization ($2P_r$) value of the multilayer thin film was $\sim 5 \mu\text{C}/\text{cm}^2$ at the maximum applied electric field of 250 kV/cm. Although a hysteresis loop could be observed, the

Fig. 4. The measured polarization versus applied electric field behavior of the BTO/BKT multilayered thin film.

Fig. 5. Fatigue behavior of a BTO/BKT multilayered thin film.

polarization was not fully saturated around the maximum of the applied voltage. We attempted to perform the polarization switching at higher electrical field. However, the higher electric field led to the electrical breakdown of the sample. Because the multilayered BTO/BKT thin film showed clear ferroelectric characteristics, a fatigue test was carried out using a bipolar square wave of amplitude ± 10 V. Fig. 5 shows the measured decay of the remnant polarization as a function of polarization reversing switching cycles. The capacitance of the multilayered BTO/BKT thin film exhibited rather good fatigue-resistant characteristics with a less than 10% decay in remnant polarization after $\sim 10^9$ switching cycles. The remnant polarization of single phase BaTiO₃ and K_{0.5}Bi_{0.5}TiO₃ thin films, by contrast, are maintained for less than 10^7 switching cycles and decrease markedly after more than 10^9 switching cycles [6,19].

Many theoretical approaches have been used to try to explain the measured electrical characteristics of multilayer thin films, including the Slater model [20], the Ising model [21], the Electrostatic analysis model [22] and finally detailed thermodynamic modeling [23]. These various approaches have yielded progressively better descriptions for the internal potentials. The latter, in particular, appears to be able to completely account for most experimental observations without any free “fitting” parameters.

In this latter model, the compositional variation across ferroelectric multilayer thin films results in broken spatial inversion symmetry that can lead to asymmetric thermodynamic potentials and free energies of the form [24]

$$F_i(P_i) = F_{0,i} + \frac{1}{2}aP_i^2 + \frac{1}{4}bP_i^4 + \frac{1}{6}cP_i^6 - \frac{1}{2}\xi E_{D,i}P_i$$

Here $F_i(P_i)$ is the total free energy for each layer, $F_{0,i}$ is the energy of layer i in its high-temperature paraelectric state, P_i is the polarization of layer i , a , b and c are Landau free energy coefficients, ξ is a parameter measuring the coupling between the bound charge at the interlayer region and the internal electric field in layer i ($\xi = 1$ implies that the material is an ideal insulator) and $E_{D,i}$ is the internal electric field in layer i . It is clear that the electrostatic energy of the internal fields in this equation introduce a symmetry breaking element in the

otherwise symmetric Landau potential in even powers of the polarization. Ferroelectric bilayers have different levels of intrinsic polarization and permittivity. A polarization difference between the two layers skews the symmetric potentials of the constituent ferroelectric materials, thereby making it more energetically favorable for the ferroelectric multilayer structure to self-pole. The findings are entirely consistent with first principles calculations that also find asymmetric potentials from inhomogeneous ferroelectric structures [25].

4. Conclusion

In conclusion, polycrystalline BTO/BKT multilayered piezoelectric thin films have been successfully fabricated on Pt/Ti/SiO₂/Si substrates by a metalloorganic decomposition technique. The dielectric constant and dielectric loss tangent, at a frequency of 10 kHz, are approximately 470 and 0.07, respectively. The multilayer BTO/BKT thin film shows excellent ferroelectric behavior with a remnant polarization ($2P_r$) of 5 $\mu\text{C}/\text{cm}^2$ and negligible polarization fatigue of up to $\sim 10^9$ cycles. These results indicate that multilayered BTO/BKT thin films are promising lead-free ferro/piezoelectric materials.

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