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Lead-free piezoelectric $BiFeO_3$-$BaTiO_3$ thin film with high Curie temperature

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Polycrystalline $0.67Bi_{1.05}FeO_3$-$0.33BaTiO_3$ (BF33BT) lead-free piezoelectric thin film is fabricated on $Pt(111)/Ti/SiO_2/Si(100)$ substrate by using pulsed laser deposition technique. The remnant polarization ($2P_r$) and coercive field ($2E_C$) observed from polarization hysteresis (*P-E*) loop are 18 $\mu C/cm^2$ and 208 kV/cm, respectively. The local piezoelectric constant ($d_{33,PFM}$) of BF33BT thin film is 92.5 pm/V which is as high as lead-based piezoelectric thin film results. From the temperature dependent dielectric constant result, the Curie temperature is 405 °C. These results show that BF33BT thin film is a promising candidate for lead-free piezoelectric nano- and micro-devices with high Curie temperature.

1. Introduction

Piezoelectric $Pb(Zr,Ti)O_3$ (PZT) has been widely used in commercial parts such as actuators and sensors due to its high-performance piezoelectric properties and high phase transition Curie temperature (T_C) near the morphotropic phase boundary (MPB) composition [1–3]. Because Pb-based materials have problems to the human health and environment, lead-free piezoelectric materials have been studied extensively recently. Among the lead-free materials, alkali and/or Bi-based perovskite materials, such as $(K_{0.5}Na_{0.5})NbO_3$ (KNN), $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT), and $(Bi_{0.5}K_{0.5})TiO_3$ (BKT) materials have been reported to have good piezoelectric properties with high T_C [4–6]. KNN-based materials are, however, very sensitive to moisture and have sintering problems due to the volatility of alkali elements. BNT-based materials exhibited a high piezoelectric performance, but they have low depolarization temperatures (T_d) lower than 200 °C and high coercive fields (E_C) [5,6].

$BiFeO_3$ (BF) thin films have been studied intensively in terms of multiferroic properties, but piezoelectric properties have been paid less attention [7]. $(Bi_{1-x}Sm_x)FeO_3$ thin films have been reported to have a good piezoelectric constants ($d_{33,PFM}$) of 60 pm/V to 110 pm/V with composition range of $x = 0.01$ to 0.14 in MPB. But this system has relatively low T_C of about 250 °C when $x = 0.11$ [8,9]. With complicated structures with BF, G. Lee *et al.* reported very high $d_{33,PFM}$ of 331 pm/V for highly strained epitaxial $BF/SrTiO_3/BF$ nano-laminates structure [10] and Y. F. Hou *et al.* showed $d_{33,PFM}$ = 119.5 pm/V for polycrystalline $BF/BaTiO_3$(BT) bi-layer structure [11].

Recently, it was observed that quenched (1-*x*)BF-*x*BT(BF-BT) lead-free piezoelectric ceramics had good piezoelectric properties and low leakage currents with high T_C [12]. BF-BT solid solutions were observed in the complete compositional range with rhombohedral (x = 0.00–0.33), pseudo-cubic (x = 0.33–0.92), and tetragonal (x = 0.92–1.00) perovskite crystal structures [13,14].

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Specifically, the composition around $x = 0.33$ showed that the rhombohedral and tetragonal phases co-exist with MPB [14–16]. However, the piezoelectric properties and T_C of BF-BT thin films have not been reported sufficiently. In this work, $0.67Bi_{1.05}FeO_3$-$0.33BaTiO_3$ (BF33BT) solid solution thin film was prepared by using a pulsed laser deposition (PLD) method. Its ferroelectric, piezoelectric properties, and T_C were investigated and were compared with those of BF thin film.

2. Experimental

The BF and BF33BT thin films were deposited on Pt(111)/Ti/SiO_2/Si(100) substrates. The PLD targets were prepared via a solid-state reaction process using raw powders of Bi_2O_3 (Aldrich 99.9%), Fe_2O_3 (Aldrich 99.9%), $BaCO_3$ (Aldrich 99.9%), and TiO_2 (Aldrich 99.9%). 5 mol% excess Bi was added to compensate the volatile Bi_2O_3 during the high temperature sintering and/or deposition [17]. Pellets of 1 inch in diameter and 3 mm in thickness were sintered at 830 °C for 2 h for BF and, 980 °C for 3 h for BF33BT in air. Then the sintered ceramics were quenched to room temperature in water to avoid the formation of secondary phases [18]. A KrF excimer laser with a wavelength of 248 nm was used to ablate the target materials at a repetition rate of 5 Hz. The laser energy fluence was 2.1 J/cm^2 per pulse. The substrate temperature was maintained at 540 °C and the oxygen pressure was kept at 30 mTorr during the film deposition. After the deposition for 30 min, the film was rapidly cooled down to room temperature under an oxygen pressure of 760 Torr within 10 min without post-annealing process. Circular Pt top electrodes (170 μm in diameter) were deposited on top surfaces of the films by using ion sputtering with a shadow mask.

The crystal structure and the microstructure of the films were determined by using X-ray diffraction (XRD, MiniFlex II, Rigaku) and field-emission scanning electron microscopy (FE-SEM, MIRA II LMH, Tescan), respectively. Ferroelectric hysteresis loops were measured by using a modified Sawyer-Tower circuit. Leakage current densities were measured by using a semiconductor parameter analyzer (HP4145b, Agilent). The surface morphology and local piezoelectric responses were observed with an atomic force microscope (AFM, XE-100, Park Systems) and with a piezoelectric force microscope (PFM, SPH-300HV, Seiko Instruments), respectively. Local piezoelectric coefficient $d_{33,PFM}$ value was calculated from the result of standard material of *x*-cut quartz single crystal. Temperature dependent dielectric constant (ε) and loss (tan δ) were measured at 100 kHz using an impedance analyzer (HP4192A, Agilent).

3. Results and discussion

Fig. 1 shows the XRD patterns of the polycrystalline BF and BF33BT ceramic targets for comparison with thin film results. The BF and BF33BT bulk ceramic target peaks were indexed based on the rhombohedral structure and high temperature cubic symmetry, respectively. Silicon (Si) powder was coated in a small part on the sintered ceramic targets surface serving as an internal standard to calibrate the XRD results by reducing height and tilt errors. The BF bulk ceramic target has secondary phases, such as Fe-rich and Bi-rich phases. The secondary phases marked by "■" are related to Fe-rich phases such as Fe_2O_3 and/or $Bi_2Fe_4O_9$, and the secondary phases marked by "□" are related to Bi-rich phases, such as Bi_2O_3. BF33BT bulk ceramic target, however shows a polycrystalline perovskite single phase without secondary phases. The BF and BF33BT thin films showed a single perovskite phase without any secondary phases. The XRD peaks in Fig. 2 were indexed based on high-temperature cubic symmetry. The BF and BF33BT thin films were well crystallized and had the preferred orientation of (111). The oriented ferroelectric thin films were reported to have improved ferroelectric properties and reduced E_C [19,20]. The deposition temperature (540 °C) of BF and BF33BT thin films was much lower than those of other lead-free piezoelectric thin films; 650 °C for KNN, 680 °C for BNT, and 700 °C for BKT [21–23].

The surface morphologies of the BF and BF33BT thin films were measured by using AFM and film thicknesses were measured from cross-sectional SEM image as shown in Fig. 3. The images showed dense and crack-free surfaces in both BF and BF33BT thin films. It was observed that the BF33BT thin film has a more uniform and smaller grains than those of the BF thin film. From SEM images, the thicknesses of thin films were measured to be ~300 nm.

Fig. 4(a) shows a ferroelectric polarization hysteresis (*P*-*E*) loops of the Pt/BF/Pt and Pt/BF33BT/Pt capacitors with triangular wave at 10 kHz and at room temperature. The remnant polarization ($2P_r$) and $2E_C$ values of BF and BF33BT thin films were 150 μC/cm^2 and 18 μC/cm^2 and 630 kV/cm and 208 kV/cm, respectively. $2P_r$ of the BF33BT thin film is higher than that of the (001) oriented epitaxial BF30BT thin film [24] and the E_C decreased by 60% [25]. The leakage current density ($J(E)$) characteristics of the BF and BF33BT thin films are presented in Fig. 4(b). Higher leakage current densities were observed in the BF thin film compared to those of the BF33BT thin film. The leakage current density of 7.3×10^{-3} A/cm^2 at 430 kV/cm for the BF33BT capacitor is approximately two orders of magnitude lower than that of the polycrystalline BF30BT thin film under the same electric field [26].

Fig. 5 shows the local piezoelectric $d_{33,PFM}$ hysteresis loops of the BF and BF33BT thin films. The local piezoelectric behaviors of the BF and BF33BT thin films were measured by using PFM with the in-field hysteresis method. This method uses a probing *ac* voltage 0.7 $V_{p\text{-}p}$ and a frequency of 17 kHz superimposed on a *dc* bias varied in steps from 0 V to V_{max} (10 V) and then decreased down to V_{min} (−10 V) and increased again up to 0 V in order to measure simultaneously $d_{33,PFM}$ as a function of the applied *dc* bias voltage [27]. The high E_C and poor local piezoelectric properties were observed in the BF thin film compared to those of BF33BT thin film. BF33BT thin film showed good local piezoelectric properties with $d_{33,PFM} = 92.5$ pm/V (positive $d_{33,PFM} = 67$ pm/V and negative $d_{33,PFM} = 118$ pm/V). The observed $d_{33,PFM}$ value is similar to the value reported in other lead-free piezoelectric thin films; 94 pm/V for $0.94(Na_{0.5}Bi_{0.5})TiO_3$-$0.06BaTiO_3$ thin film [28], 64 pm/V for $[Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}]TiO_3$ [23], and 61 pm/V for $(K_{0.5}Na_{0.5})NbO_3$ [29]. This value is comparable with those of 85–125 pm/V in PZT thin films [30,31].

Compared with other lead-free piezoelectric materials, BF-BT

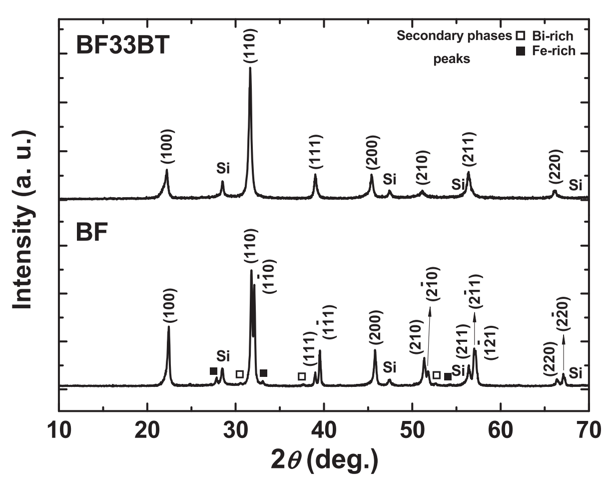

Fig. 1. The X-ray diffraction patterns of BF and BF33BT ceramic targets.