Piezoresponse and ferroelectric properties of lead-free $[Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}]TiO_3$ thin films by pulsed laser deposition

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(Received 15 January 2008; accepted 10 May 2008; published online 6 June 2008)

Polycrystalline lead-free piezoelectric $[Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}]TiO_3$ (BNKLT) thin films were grown on $Pt/Ti/SiO_2/Si$ substrates using pulsed laser deposition (PLD). In this letter, we report the ferroelectric properties and piezoresponse of the PLD-produced BNKLT thin films. X-ray diffraction characterization revealed a good crystallinity and a pure perovskite structure in the films. The films exhibited a well-defined polarization hysteresis loop with a remnant polarization P_r of 13.9 $\mu C/cm^2$ and a coercive field E_c of 10.2 MV/m. The domain structure and its thermal-driven evolution from the ferroelectric to nonferroelectric phase were observed by piezoresponse force microscopy. The results were consistent with the phase transition profile of BNKLT bulk ceramics. Typical butterfly-shaped piezoresponse loop was obtained and the effective piezoelectric coefficient $d_{33,f}$ of the BNKLT thin films was about 64 pm/V. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2938364]

Piezoelectric thin films for use in microelectromechanical systems, microactuators, and transducers have been extensively studied. The dominant materials for these applications are lead-based systems, such as $Pb(Zr_xTi_{1-x})O_3$ (PZT) because of their superior ferroelectric and piezoelectric properties. Due to the high toxicity of lead, there is an increasing interest in developing alternative piezoelectric materials, which are lead-free, environmental friendly, and biocompatible.[1] To date, most of the research works on the lead-free piezoelectric materials were focused on the bulk forms. There are only a few studies on lead-free piezoelectric thin films.

Among various lead-free piezoelectric ceramics, bismuth sodium titanate $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) is considered to be one of the promising candidates because of its pronounced ferroelectricity.[2] In recent years, great efforts have been made in the growth and characterization of BNT-based thin films. Zhou *et al.*[3] and Tang *et al.*[4] reported the dielectric, ferroelectric, and leakage current characteristics of sol-gel derived BNT thin films grown on platinized silicon substrates. Subsequent research work[5] has shown that modified BNT thin film $(Na_{0.8}K_{0.2})Bi_{0.5}TiO_3$ grown on $Pt/TiO_2/SiO_2/Si$ substrates using a metal-organic solution deposition method do not possess better ferroelectric and dielectric performance than those of pure BNT thin films. Yu *et al.*[6] and Rémondière *et al.*[7] studied the piezoelectric properties of pure BNT thin films. Yu *et al.* quantitatively evaluated the piezoelectric properties of their sol-gel derived BNT thin films and a relatively low d_{33} coefficient of 24.8 pm/V was reported. It should be noted that chemical approaches were adopted in most of the previous works to prepare the BNT-based thin films due to the good chemical homogeneity and the ease of stoichiometric control. However, the residual fine pores may deteriorate the properties of the sol-gel derived films. BNT-based thin films are now studied in an early stage and no high-performance BNT-based thin films thus far were achieved. In our previous work, it has been shown that the *A*-site substituted BNT ceramic $[Bi_{0.5}(Na_{1-x-y}K_xLi_y)_{0.5}TiO_3$, (BNKLT)] possesses excellent ferroelectric and piezoelectric properties.[8] Among these systems, $Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}TiO_3$ ceramics exhibited the best piezoelectric properties with $d_{33}=231$ pC/N and $k_t=0.505$ at room temperature, which are certainly desirable for piezoelectric device applications. In this letter, we reported the deposition of polycrystalline BNKLT thin films by pulsed laser deposition (PLD). The ferroelectric properties and piezoresponse of BNKLT thin films were presented.

The stoichiometric target of $[Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}]TiO_3$ used for laser ablation was prepared by the conventional solid state reaction route. The BNKLT thin films were deposited on $Pt/Ti/SiO_2/Si$ substrates by PLD using a krypton fluoride (KrF) excimer laser (Lambda Physik COMPex 205) with a wavelength of 248 nm. A laser energy of 250 mJ and a repetition rate of 5 Hz were adopted. The distance between the target and the substrate was fixed at 5 cm. The substrate temperature was maintained at 680 °C. The oxygen partial pressure was kept at 25 Pa during the laser ablation process. BNKLT thin films with thickness of ~350 nm were prepared by irradiating the stoichiometric target for 20 min. After deposition, the as-grown thin films were cooled down to room temperature without any postannealing process.

The crystallographic characterization of the as-grown BNKLT thin films was performed on a Bruker AXS D8 Discover x-ray diffractometer. Figure 1 shows the x-ray diffraction (XRD) patterns of the films as well as a bulk BNKLT ceramic for comparison. It can be seen that the film is polycrystalline, exhibiting a single-phase perovskite with no preferred orientations.

The ferroelectric characterization was performed using a metal-ferroelectric-metal configuration. Au top electrodes with a diameter of 0.2 mm and a thickness of 200 nm were prepared by rf magnetron sputtering, followed by the standard photolithography process. The polarization hysteresis (*P-E*) loop was measured using a TF Analyzer 2000 equipped with a FE-Module (HV) (aixACCT). Figure 2 shows the *P-E* loops of the BNKLT thin film measured under different electric fields. Well-defined *P-E* hysteresis loops

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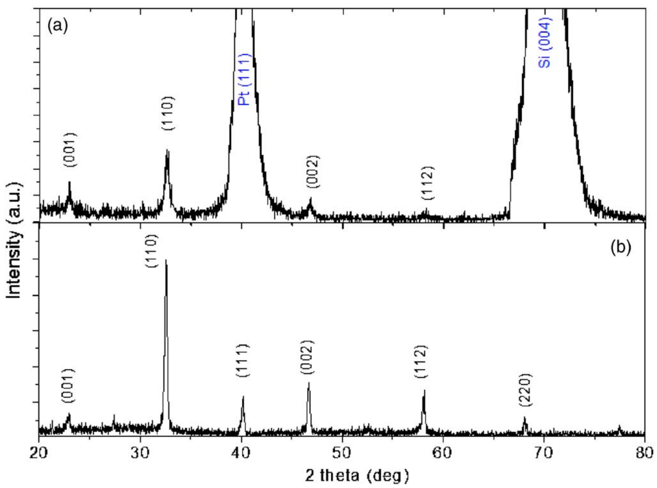

FIG. 1. (Color online) XRD patterns for (a) the BNKLT thin film deposited on $Pt/Ti/SiO_2/Si$ substrate and (b) the BNKLT bulk ceramic.

are observed. It is also seen that the hysteresis loops show an offset in the vertical direction, which may be caused by non-switchable domains pinned near the electrode-film interface.[9,10] Probably due to the size effect and multidomain state,[10] the observed remnant polarization P_r is much smaller than that of a bulk BNBKL ceramic (13.9 versus 37.5 $\mu C/cm^2$, inset of Fig. 2), while the observed coercive field E_c is much higher (10.2 versus 2.5 MV/m). Similar results have generally been observed in PZT films. The piezoelectric coefficient d is related to the (net) polarization P (which may be approximated by P_r), the permittivity ε, and the electrostriction coefficient Q via a general equation[11] $d=2Q\varepsilon P$. Therefore, because of the large P_r value, it is expected that our BNKLT thin films will exhibit a relative high piezoelectric coefficient.

Piezoresponse force microscopy (PFM) is one of the most powerful techniques widely used to study the ferroelectric domains due to its high resolution and ability for dynamic switching.[12–14] In this study, analysis of the surface morphology and the evolution of domain structure under different temperatures were carried out by simultaneous acquisition of photographic views and domain imaging using an atomic force microscope (Digital Instruments, NanoScope IV) equipped with a Pt/Ir coated Si tip in PFM mode. The tip

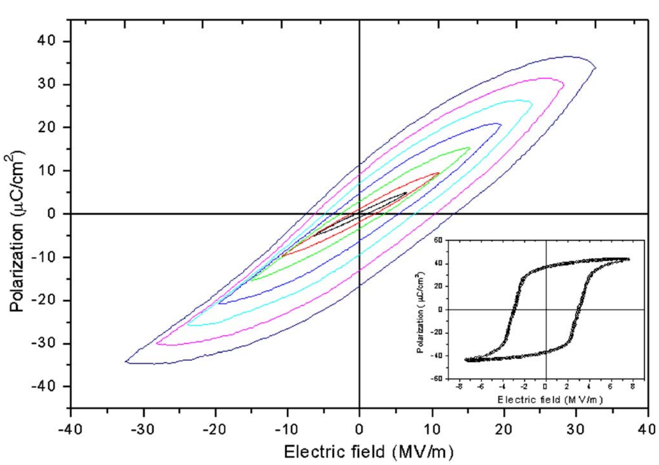

FIG. 2. (Color online) *P-E* hysteresis loops of the BNKLT thin film grown on $Pt/Ti/SiO_2/Si$ substrate.The inset is the *P-E* hysteresis loop of the BNKLT bulk ceramic.

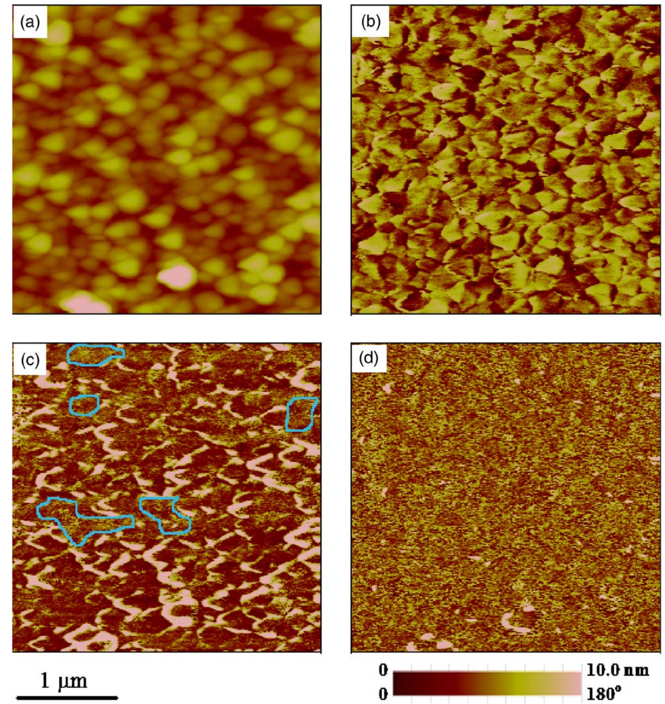

FIG. 3. (Color online) (a) Surface morphology of the BNKLT thin film and the piezoresponse phase images of the BNKLT thin film at different temperatures: (b) 25 °C, (c) 100 °C, and (d) 180 °C.

radius was less than 25 nm and a force constant of 2.8 N/m was used to study the piezoresponse of the regions without top electrodes. For the PFM imaging, an ac modulating voltages of 10 V (peak to peak) at 12 kHz was applied to the bottom electrode of the thin film, while the tip was electrically grounded. The BNKLT thin film possesses a relatively smooth surface with average grain size of 100–120 nm, as shown in Fig. 3(a). Figures 3(b)–3(d) show the local piezoresponse phase image of the BNKLT thin film at 25, 100, and 180 °C, respectively. All the images were taken at the same region as in Fig. 3(a). At room temperature, the contrast of the piezoresponse image is weak and most of the domains appear yellow in color [Fig. 3(b)]. Most of grains are of single domain structure and only a few of them contain multidomain structure. No obvious lamellar domains, as reported in PZT or PT thin films,[13,15] were observed. As the temperature increases to 100 °C, which is slightly below the depolarization temperature T_d of BNKLT, the domain structure shows a great change [Fig. 3(c)]. Some of the domains became partially depolarized (the circled regions), showing a blurry contrast. Nevertheless, the domain structures were maintained at the outer part of some grains, especially near the grain boundary regions (the white patterns), which could be explained by the domain pinning near the grain boundaries. Moreover, the contrast between opposite domains becomes sharper than that at room temperature. This indicates that the domain switching becomes much easier at high temperatures, which is consistent with our macroscopic measurement of the coercive field in BNKLT bulk ceramics: the higher the temperature, the smaller the coercive field.[8] At 180 °C, which is well above T_d, no obvious domain structure can be identified in the piezoresponse image [Fig. 3(d)], implying that the film is almost completely depolarized. The image shows mainly a gray contrast, except for a few small white regions which may correspond to the normal ferroelec-

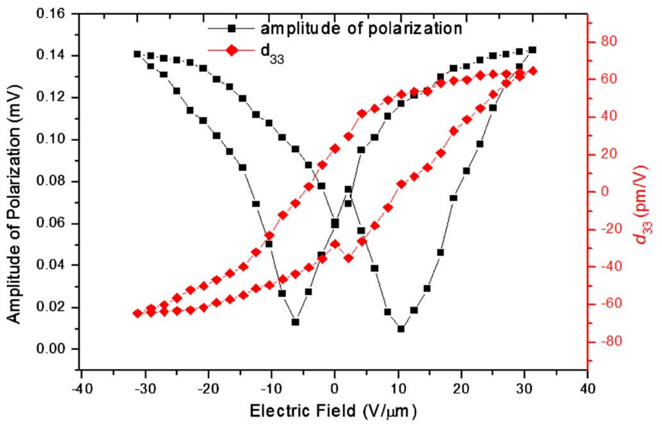

FIG. 4. (Color online) Variations of the amplitude of the static piezoresponse and the effective $d_{33,f}$ with the bias dc field for a grain of the BNKLT thin film measured at room temperature.

tric domains or defective pinned domains. In general, BNT-based ceramics undergo two phase transitions: one is the transition from a rhombohedral phase to a tetragonal phase at T_d and the other is the transition from a tetragonal phase to a cubic phase at T_m. Although a number of researchers have suggested that the ceramics are of the "antiferroelectric phase" at temperatures between T_d and T_m,[16,17] the nature of this phase is still a matter of debate. Nevertheless, the BNKLT ceramics will lose most of their ferroelectric activities (nonferroelectric state) when the temperature exceeds T_d ($\sim$130 °C),[8] which is consistent with the domain structure evolution observed in our BNKLT thin film.

The small displacement of the BNKLT thin film induced by the converse piezoelectric effect was measured by the atomic force microscope (in PFM mode) incorporated with a lock-in technique.[18,19] A small ac voltage with an amplitude of 1.5 V and a frequency of 12 kHz was applied to the sample via the PFM tip which was in contact with the ferroelectric layer without top electrodes. The converse piezoelectric response was recorded as an electrical signal in the unit of millivolts, which was then converted to the effective $d_{33,f}$ value using a $BaTiO_3$ single crystal as a piezoelectric standard. Figure 4 shows the variations of the static piezoresponse (amplitude) and effective $d_{33,f}$ with the bias dc electric field for a grain of the BNKLT thin film. It can be seen that the film exhibits a typical well-shaped "butterfly" loop. The observed E_c from the piezoresponse hysteresis loop is slightly smaller than that from the *P-E* hysteresis loop (10.2 MV/m, refer to Fig. 2). Such a discrepancy in E_c is often observed in ferroelectric thin films.[20,21] This may be due to the difference in the switching mechanism between the microscopic PFM and macroscopic *P-E* measurement.[20] As shown in Fig. 4, the film exhibits a maximum $d_{33,f}$ value of $\sim$64 pm/V under a bias field of $\sim$34 MV/m, which is about one-third of the value for a bulk sample. Owing to the clamping effect imposed by the substrate or the bottom electrode, a piezoelectric thin film usually exhibits a reduced mechanical strain, and thus, a smaller piezoelectric coefficient as compared to a bulk counterpart.[22] Nevertheless, the observed $d_{33,f}$ value for the BNKLT film is relatively large, showing its potential for replacing the toxic piezoelectric PZT films in future environment-friendly piezoelectric devices. For PZT thin films, the $d_{33,f}$ value varies from 10 to 110 pm/V,[21,23] while those for lead-free $CaBi_4Ti_4O_{15}$ films,[10] $Na_{0.5}K_{0.5}NbO_3$ films,[24] $Bi_{3.25}Nd_{0.75}Ti_3O_{12}$ films,[25] and $Bi_{0.5}Na_{0.5}TiO_3$ films[6] are 65, 40, 38, and 24.8 pm/V, respectively.

In summary, this study investigated the ferroelectric properties and piezoresponse of polycrystalline lead-free piezoelectric $[Bi_{0.5}(Na_{0.7}K_{0.2}Li_{0.1})_{0.5}]TiO_3$ thin films grown on $Pt/Ti/SiO_2/Si$ substrates using PLD. The BNKLT thin films exhibited a well-defined *P-E* hysteresis loop with a P_r of 13.9 $\mu C/cm^2$. Temperature-dependent PFM imaging clearly revealed the domain evolutions from the ferroelectric to nonferroelectric phase. Typical butterfly-shaped piezoresponse loop as a function of dc bias field was observed in the static piezoresponse measurement. The effective piezoelectric coefficient $d_{33,f}$ of the BNKLT thin films was 64 pm/V. On the basis of these properties, the BNKLT thin film is considered as a promising alternative for replacing PZT thin films in piezoelectric device applications.

This work was supported by the Research Grants Council of the Hong Kong Special Administrative Region (Project No. PolyU 5188/06E), the Niche Area Projects (1-BB95), and the Centre for Smart Materials of The Hong Kong Polytechnic University.

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