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Ferroelectric Characterization of La:BiFeO3/Bi0.5(Na0.85K0.15)0.5TiO3 Nano-composite Films

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Ferroelectric Characterization of La:$BiFeO_3$/ $Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}TiO_3$ Nano-composite Films

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Abstract: $La_{0.1}Bi_{0.9}FeO_3$(BFO), $Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}TiO_3$(BNKT) and BFO/BNKT nano-composite films were fabricated by pulsed laser deposition (PLD) method on Pt/Ti/SiO_2/Si substrate. The ferroelectric properties were enhanced in BFO/BNKT compared to single layer film of BFO and BNKT. The ferroelectric domain structures were observed using piezoresponse force microscopy (PFM). The polarization reversal was time-dependent because the inhomogeneous domains with different coercivity. Evidence can also be seen in the fatigue results which showed unusual profile. The polarization increased as the increase of switching cycles because some of domains are difficult to switch using the applied field. Nano-scale piezoresponse hysteresis loops measured by PFM also revealed the local domain switching behavior in the BFO/BNKT film.

Key words: multiferroic; thin film; pulsed laser deposition(PLD); piezoresponse force microscopy(PFM)

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La:$BiFeO_3$/$Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}TiO_3$纳米复合薄膜的铁电特性

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摘要: 采用脉冲激光沉积技术(pulsed laser deposition,PLD),在 Pt/Ti/SiO_2/Si 基片上制备了 $La_{0.1}Bi_{0.9}FeO_3$(BFO),$Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}TiO_3$(BNKT)和 BFO/BNKT 纳米复合薄膜。结果表明,复合薄膜的铁电特性比单层的 BFO、BNKT 薄膜有所增强。利用压电力显微镜(piezoresponse force microscopy,PFM)观察到了铁电畴。由于畴结构内部矫顽力分布不均匀,导致极化反转随时间改变,疲劳测试结果也证实了该结论。随着转换周期的增加,极化随之增强。运用 PFM 测量了纳米级的压电响应,同样证实了 BFO/BNKT 复合薄膜中的畴反转现象。

关键词: 多铁; 薄膜; 脉冲激光沉积; 压电力显微镜

1 Introduction

Multiferroic materials, which show coexistence of ferroelectricity, ferromagnetism and ferroelastricity, are

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attracting considerable interest due to their potential applications in spintronics, information storage and communications[1]. Among the multiferroics, $BiFeO_3$ is one of the most widely studied materials due to its high Curie temperature ($T_C \sim 1103$ K) and Neel temperature ($T_N \sim 643$ K) and it is still the only established multiferroics with ordering temperatures far above room temperature[2-4]. As a promising multiferroic, many improvements in the ferroelectric and magnetic properties for $BiFeO_3$ have been achieved. However, there are still some challenges before its application in devices. One effective method for improvement is doping small amounts of impurities at A or B sites in a perovskite structure of ABO_3[5-11]. This method is so simple that it is good for industrial technology. It has been proved that doping of La causes structural changes and improves its crystallization[12-13]. As a result, both the ferroelectric and ferromagnetic properties are significantly enhanced. $Bi_{0.5}(Na_{0.85}K_{0.15})_{0.5}TiO_3$ (BNKT) is an important lead-free compound. It has been largely investigated as a lead-free material, but little work has been done with the nano-composite film structure containing BNKT as a nanolayer. We believe it is particular interesting to investigate the nano-composite films containing La: $BiFeO_3$ and BNKT.

2 Experimental

In this study, $La_{0.1}Bi_{0.9}FeO_3$ (BFO), BNKT and BFO/BNKT thin films on $Pt/Ti/SiO_2/Si$ substrate were fabricated. The thin films were deposited using a pulsed laser deposition (PLD) system. Third harmonic generation of Nd: YAG laser with a wavelength of 355 nm and a repetition rate of 10 Hz was used as the laser source. The ceramic targets of doped $BiFeO_3$ were fabricated by a traditional solid state reaction. To sinter BFO target, the starting materials of Bi_2O_3, Fe_3O_4, La_2O_3 were weighed according to the molecular mole ratio with 10mol% extra Bi_2O_3. They were mixed, pressed into pellets and sintered at 800 ℃ for 3 h. Then the ceramics were crushed, ground, pressed into pellets and sintered again at 960 ℃ for 1 h. To sinter BNKT target, the starting materials of Bi_2O_3, $NaCO_3$, KCO_3, TiO_2 were weighed according to the molecular mole ratio with 10mol% extra Bi_2O_3. The first sintering temperature is 800 ℃ for 2 h. The second sintering temperature is at 1100 ℃ for 1 h.

The deposition process is described as follows: $Pt/Ti/SiO_2/Si$ substrates were cleaned twice using ultrasonic cleaning machine in alcohol and deionized water. The targets and substrates mentioned above were hold on the sample stage. The chamber was pumped to a pressure about 10-5 Torr and then the oxygen was filled in the chamber. The deposition time was 40 min and the sample was cooled under oxygen flow to room temperature. To fabricate the layered film, the targets of BFO and BNKT were fixed on the different sample stage and alternately switched. The film of BFO/BNKT were obtained in a layer-by-layer growth mode. All of the thin films were fabricated at 550-580 ℃ and 200 m Torr dynamic oxygen pressure. After deposition, the films were annealed in the same condition for 15 minutes and then cooled to room temperature rapidly.

The phases of the targets and films were determined by X-ray diffraction (XRD) using Cu K_α radiation. Pt upper electrodes with an area of 0.0314 mm^2 were deposited by magnetron sputtering through a metal shadow mask. The ferroelectric properties were measured at room temperature by an aixACCT EASY CHECK 300 ferroelectric tester. The ferroelectric domain morphology was studied by way of piezo-response atomic force microscopy (PFM). Nanotec's WsXM software was used to analyze the PFM images. Piezoresponse Force Microscopy (PFM) is a powerful tool to study piezoelectric/ferroelectric properties. PFM response was measured with a conducting tip (Rh-coated Si cantilever, $k \sim 1.6\ N \cdot m^{-1}$) by an SII Nanotechnology E-sweep AFM. PFM responses were measured as a function of V_{dc} with a small ac voltage (0.5 V at 5 kHz) applied to the bottom electrode in the contact mode, and the resulting piezoelectric deformations transmitted to the cantilever were detected from the global deflection signal using a lock-in amplifier.

3 Result and discussion

Figure 1 shows the XRD patterns of the films of BFO, BNKT and BFO/BNKT. However, extra peaks, which were identified as $Bi_2Fe_4O_9$, were observed in BFO and BFO/BNKT in the XRD patterns. There are some extra peaks from the substrates. The position and intensity of main peaks changed a little, which is because of the lattice shrink or influenced by the $Pt/Ti/SiO_2/Si$ substrate. The lattice mismatch between substrate and nano-composite film during rapidly annealing process also have an impact on XRD patterns.

Figure 2 shows the electrical polarization hysteresis loops (P-E loops) of the BFO/BNKT (a), BFO (b) and BNKT (c). As shown in this figure, the hysteresis loop of BFO/BNKT is improved than that of BFO and BNKT. Moreover, it can be seen that the P-E loop is asymmetry, which is because of the asymmetric upper and below electrodes or the internal bias in the films caused by the existence of oxygen vacancy [14]. Figure 2(d) shows the fatigue characteristics of BFO/BNKT. It is unusual and the polarization increased as the increase the switching cycles. Because of these complicated mechanisms, further investigation is needed.

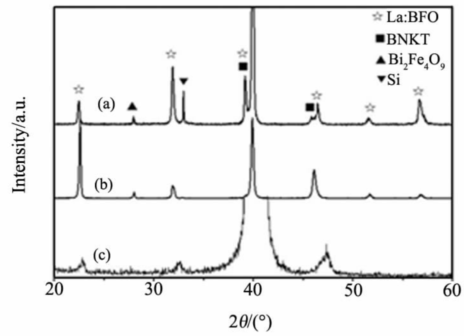

Fig. 1 XRD patterns of BFO/BNKT(a), BFO(b) and BNKT(c) films deposited on $Pt/Ti/SiO_2/Si$ substrates

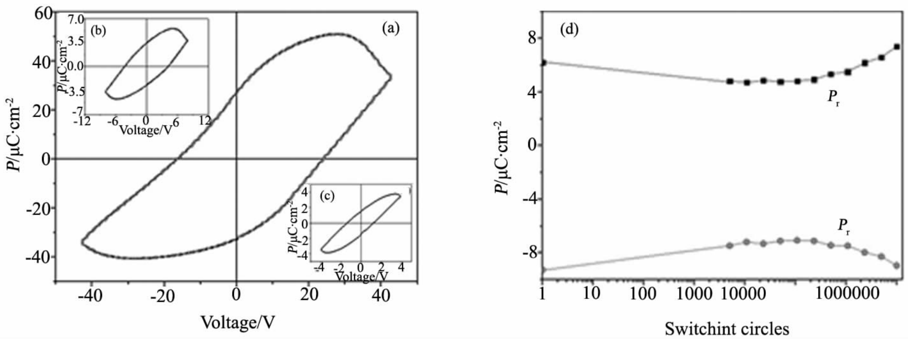

Fig. 2 Ferroelectric hysteresis loops of BFO/BNKT(a), BFO(b) and BNKT(c); (d) fatigue measurement of BNKT

As is well known, the ferroelectric property is mainly determined by the domain structures and domain wall motions. The ferroelectric domain morphology of BFO/BNKT composite film was further studied using PFM. It is proved in other materials that adsorbates can substantially modify the depolarization field and affect the out-of-plane (OP) domain morphology, therefore, only in-plane (IP) domains are shown here. Figure 3 shows the topography [(a), (d), (g)] and IP PFM images [(b), (c), (e), (f), (h), (i)] of BFO/BNKT. It shows the morphology with the special tendency to look like isosceles triangles with the vertex angle pointing in the same direction. The polarization reversal was clear after poled by ± 5 V and ± 10 V voltage. The grains in topography and PFM image are one to one correspondence. Figure 3 (h) and (i), which are obtained using longer time than Figure 3 (e) and (f), showed clearer contrast. Because the domains which are not homogeneous showed different coercivity in the film. Some of them are different to switch with applied field [15]. The fatigue measurement also gave evidence to this phenomenon, as shown in Figure 2 (d). For the unusual profile of fatigue (polarization increased with the increasing of switching cycles), we consider the different domain wall played important roles during the polarization reversal.

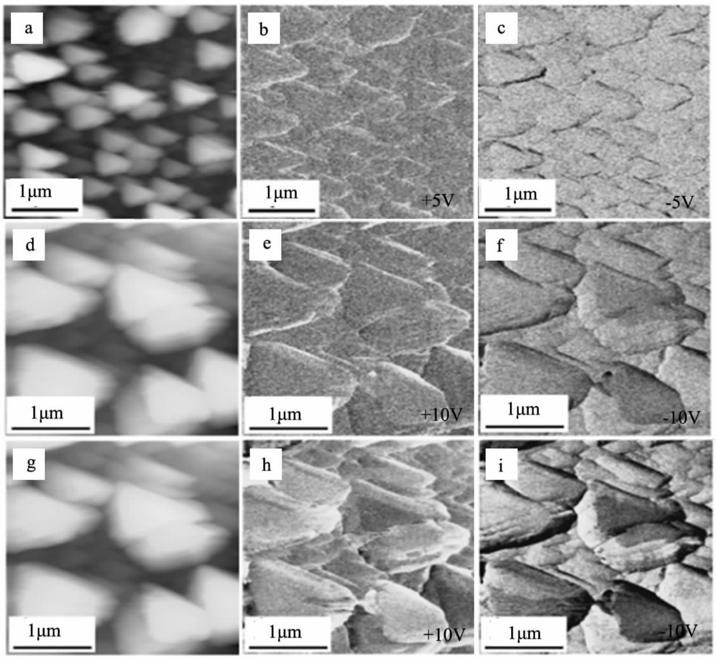

Fig. 3 (a),(d) and (g) are topography of BFO/BNKT. IP PFM images of (b),(c) polarized by ± 5 V; (e),(f) polarized by ± 10 V and (h),(i) polarized by ± 10 V with longer time

Figure 4 shows the typical "butterfly" loop and local piezoresponse hysteresis loop. It is not symmetrical well-shaped due to the asymmetry of the upper and bottom electrodes. According to the equation $d_{33} = \Delta l / V$, where Δl is the displacement, the effective d_{33} could be calculated.

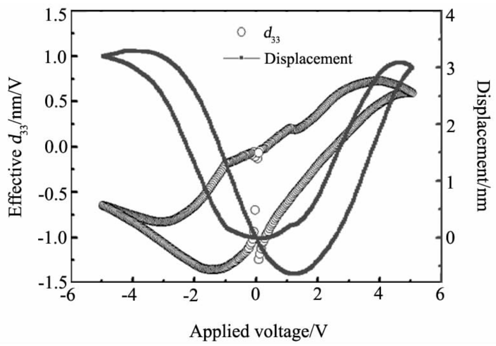

Fig. 4 Local piezoresponse hysteresis loop and piezoelectric displacement-voltage

4 Conclusions

We fabricated the BFO, BNKT and BFO/BNKT thin films on Pt/Ti/SiO_2/Si substrate by PLD method. The BFO/BNKT composite film showed improved ferroelectric properties compared single layer films of BFO and BNKT. Through PFM measurement, it is found that the polarization reversal was dynamic because the inhomogeneous domains with different coercivity and some of them are difficult to switch. Evidence can also be seen in the fatigue results which shows that the polarization increases as the increase of switching cycles.

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