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Thickness dependence of piezoelectric property of ultrathin $BiFeO_3$ films

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ABSTRACT

Effects of film thickness on the piezoelectric property of the ultrathin $BiFeO_3$ films (t=1–150 nm), grown on the (0 0 1)-$SrTiO_3$ substrates with a $La_{0.67}Sr_{0.33}MnO_3$ cover layer, have been studied by the technique of piezoresponse force microscope. Special attention has been paid to the evolution of the piezoelectric response with film thickness. Well ferroelectric property maintains in the BFO film with a thickness down to 6 nm, below which no obvious ferroelectric domains are observed. Based on careful analysis of the piezoelectric response images of the ferroelectric domains upwards or downwards poled by external field, a quantitative description of the piezoelectric coefficient d_{33} can be obtained. d_{33} is found to display a monotonic decrease with the decrease of film thickness, descending from ~46 pm/V for t=150 nm to ~8 pm/V for t=6 nm. A corresponding growth of the out-of-plane lattice parameter of the film from 4.011 Å to 4.077 Å is also observed. The effects of depolarization, lattice strains and substrate clamping on the piezoelectric property of the films are discussed.

1. Introduction

Multiferroic effect has recently attracted intensive attention because of its great potential in the development of multifunctional materials/devices. A typical multiferroic material is the perovskite $BiFeO_3$ (BFO), for which ferroelectricity coexists with antiferromagnetic order (T_C=830 °C and T_N =370 °C) [1,2]. The bulk BFO single crystal has been shown to possess a rhombohedral distorted perovskite structure ($a=b=c$=5.63 Å, $\alpha=\beta=\gamma$=59.4°) at the room temperature, belonging to the space group of R3c [3,4]. The spontaneous polarization P of the single crystal is oriented along the (1 1 1) direction [2,5]. However, cases are different for the epitaxial BFO films, because of the presence of lattice strains due to the film-substrate lattice mismatch, observed by various authors. For example, Wang et al. [6] reported on a monotonic variation of the out-of-plane lattice parameter (c) from ~3.99 Å to ~4.05 Å, the ferroelectric polarization from ~50 μC/cm^2 to ~95 μC/cm^2 and the out-of-plane piezoelectric coefficient (d_{33}) from ~85 pm/V to ~40 pm/V when the thickness of the BFO film on STO decreases from 400 nm to 70 nm. Similar phenomena are observed in the BFO films grown on Si substrates [7]. Based on a systematic theoretical study, Jiang and Qiu [8] and Ma et al. [9] concluded that the remarkable change of the ferroelectric properties of the BFO film originate from the compressive strains.

It is obvious that the strain plays an important role in the film system. However, the relation between ferroelectric property and film thickness may not be so simple. In fact, it has been declared that the film with a thickness below 2 nm will lose the ferroelectricity [10]. It is interesting to study how the BFO film behaves when film thickness continuously reduces. This is an issue deserving special attention in a sense that the evolution of the multiferroic property with the dimensionality of the materials could be helpful for the understanding of the considerable ferroelectric–magnetic coupling. On the other hand, the knowledge on ultrathin films is also usually desired for the designing of artificial devices. We noticed that most of the previous studies have focused on the BFO film with a typical thickness between 100 nm and 600 nm. Due to the existence of severe leakage current, sometimes it is difficult to get a quantitative, or even a semi-quantitative analysis of the ferroelectric properties of the ultrathin films. In this letter, we report the thickness effect on the ferroelectric properties of the BFO films with the thickness between 1 nm and 150 nm, prepared by pulsed laser ablation on STO (0 0 1) substrates with a $La_{0.67}Sr_{0.33}MnO_3$ cover layer. It is found that the ferroelectric properties are preserved and the polarization can be switched by external electric field when film thickness is above 6 nm. Based on the analysis of the piezoelectric response images of the oppositely poled ferroelectric domains of the film, the piezoelectric coefficient d_{33} of the film can be derived, and it exhibits a monotonic decrease with the decrease of film thickness. A sharp reduction of the d_{33} is observed for the film of 3 nm, which could be the threshold thickness for ferroelectricity in the BFO film.

2. Experiment

The samples have been grown by the pulsed laser ablation technique using a KrF excimer laser (λ=248 nm). As bottom electrode, a $La_{0.67}Sr_{0.33}MnO_3$ (LSMO) layer of 50 nm was first grown on

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the (0 0 1)-SrTiO3 substrate under the substrate temperature of 700 °C and the oxygen pressure of 46 Pa. BFO layers of the thickness t=1 nm, 3 nm, 6 nm, 10 nm, 20 nm, 30 nm, and 150 nm, respectively, were then deposited at a lower temperature of 630 °C and a lower oxygen pressure of 15 Pa. The BFO target with the nominal composition $Bi_{1.15}FeO_3$ was used, where excessive Bi has been introduced to compensate for the high volatility of Bi. After deposition, the samples were slowly cooled down to the ambient temperature in an oxygen atmosphere of 200 Pa. The structure of the films was analyzed by an X-ray diffractometer with the Cu Kα radiation (D8 Advance, Bruker, German). The surface morphology and ferroelectric properties were measured by a piezoresponse force microscope (PFM) (Nanonavi E-Sweep) with a Rh-coated Si tip, with the tip radius being ~25 nm, force constant ~1.3 N/m, and resonant frequency ~25 kHz. The PFM cantilever was parallel to the [0 1 0] axes, and the scans were performed along the [0 1 0] axes at ambient conditions. The amplitude (R) of the piezoelectric response was recorded during scanning.

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) pattern of a typical sample, the 30 nm BFO film. In addition to those of the substrate, only the diffraction peaks of BFO and LSMO can be detected for the 2ϑ angle from 15° to 80°, and there are no signatures for the Bi_2O_3 and related impurities. Similar results are obtained for other BFO films above 6 nm. Below 6 nm, the XRD peaks of the film are too weak to be identified. As expected, the variation of the film thickness causes a systematic change in peak intensity and a slight change in peak position. The out-of-plane lattice parameter (c) of the BFO films is presented in the inset plot of Fig. 1, as a function of the film thickness. The compressive in-plane strain imposed by the substrate allows the growth of a single phase BFO thin film and makes the out-of-plane lattice parameter greater than that of the bulk counterpart. The lattice parameter decreases first slightly from ~4.077 Å to ~4.072 Å as film thickness increases from 6 nm to 30 nm then rapidly from ~4.072 Å to ~4.047 Å as t grows from 30 nm to 70 nm. This means that the lattice strain is nearly constant when t is below 30 nm and relaxes when t is greater than 30 nm. The out-of-plane lattice parameter of the LSMO film is 3.844 Å. The lattice parameters of BFO and LSMO are consistent with the reported values of ~4.051 Å and ~3.860 Å for the corresponding films on STO [6,11,12].

The surface morphology and the corresponding in-plane (IP) and out-of-plane (OP) piezoelectric response (PR) images of the BFO films measured by the piezoresponse force microscope are exemplified in Fig. 2, with a scanning area of 2 × 2 μm^2. As shown by Fig. 2(a)–(d), the film surfaces are rather smooth, and the root-mean-square roughness is 4.6 Å, 3.8 Å, 5.7 Å and 8.7 Å for the films of 6 nm, 10 nm, 20 nm, and 30 nm, respectively. The IP and OP PR images were recorded under an ac bias with a peak–to–peak amplitude of V_{PP}=12 V and a frequency of 6 kHz, applied to the conducting tip. The color contrasts of the in-plane and out-of-plane images show the differences of the electrostriction of BFO in the directions of [1 0 0] and [0 0 1], respectively. As shown by the IP PR images in Fig. 2(e)–(h), all BFO films exhibit clear PR contrasts, indicating the presence of ferroelectric domains. With the increase of film thickness, both the color contrast and the domain sizes grow. According to Catalan et al. [13], the sizes of the IP domains follow the Landau–Lifshitz–Kittel scaling law against film thickness. In contrast, the OP PR images [Fig. 2(i)–(l)] show the domains separated by labyrinth-like domain walls. Similar to the IP images, the domain size and color contrast also vary with film thickness, and the OP domains cannot be identified in the films of t<10 nm. It could be a consequence of depolarization, which enhances with the decrease of t. These results primarily reveal the evolution of the ferroelectric properties of BFO with film thickness.

To get a quantitative analysis of the ferroelectric properties of the film, the OP PR images of the samples are measured after the electric poling of the polarization of the domains. Fig. 3(a)–(d) shows the OP-PR images of the BFO films with different thicknesses under an ac bias with a peak-to-peak amplitude of V_{PP}=10 V and a frequency of 6 kHz. The images are measured after first poling the domains upwards by applying a dc field (8 V for t=6 nm and 10 nm and 9 V for 20 nm and 30 nm) then downwards, by applying a dc field

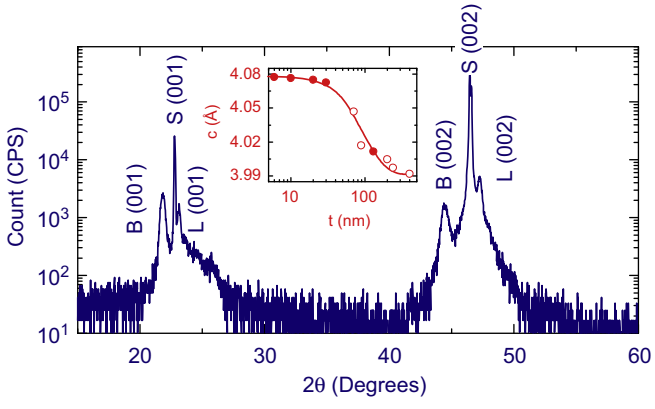

Fig. 1. XRD patterns of BFO film of thickness of 30 nm, measured at the ambient temperature. The peaks are indexed based on the cubic perovskite structure. The labels B, S, and L in the figure represent BFO, STO and LSMO, respectively. The out-of-plane lattice parameter of the BFO films is shown in the inset plot. Data from Ref. [6] were also presented for comparison (hollow symbols).

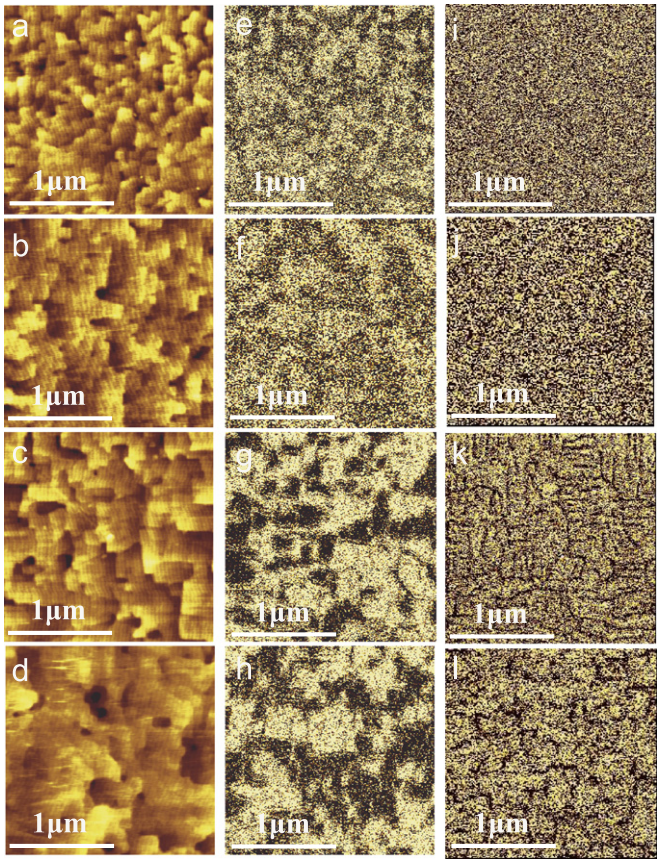

Fig. 2. The surface morphology of the BFO films of 6 nm (a), 10 nm (b), 20 nm (c) and 30 nm (d) and the corresponding in-plane [(e), (f), (g) and (h)] and out-of-plane [(i), (j), (k), and (l)] PR images (the amplitude of the piezoelectric response), measured under the ac voltage of 12 V and the frequency of 6 kHz.

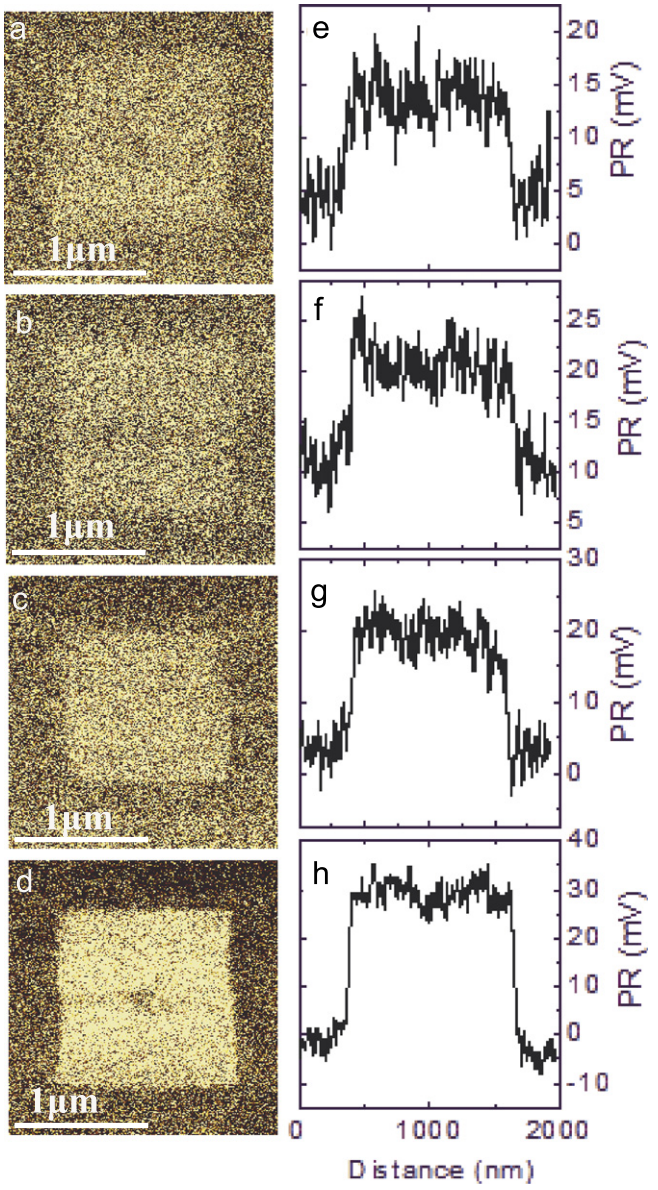

Fig. 3. Out-of-plane PR images of the ferroelectric domains of the BFO films (the amplitude of the piezoelectric response) of the thickness of 6 nm (a), 10 nm (b), 20 nm (c), and 30 nm (d), measured under the ac voltage of 10 V and the frequency of 6 kHz. The scanning area is $2\times2\ \mu m^2$, and the interior image is $1.2\times1.2\ \mu m^2$. The average line profiles of the PR images are shown in (e), (f), (g) and (h).

(−8 V for t=6 nm and 10 nm and −9 V for 20 nm and 30 nm). The scanning areas are $2\times2\ \mu m^2$ and $1.2\times1.2\ \mu m^2$ and the latter locates at the center of the former. All of the images show a clear dark–bright contrast. The dark region represents the domain with an upward component of polarization, while the bright region the downward component. Domain regions are clearly defined and produce an uniform piezoresponse, suggesting a homogeneous polarization. The magnitudes of the piezoresponse signals of the dark domains and the bright domains are essentially uniform, indicating a single polarization switching. Therefore, the PFM images show clear evidence of filed-induced ferroelectric polarization switching at the room temperature, even in the film of 6 nm. From the first glance, the dark–bright contrast shows a monotonic decrease with the decrease of film thickness. This indicates the weakening of the PR of BFO with the decrease of film thickness. The BFO films of 1 nm and 3 nm are also measured, and there are no signatures for definite ferroelectric domains. This means that the lower critical thickness for ferroelectricity in BFO is ~3 nm, consistent with the report ~2 nm [14].

As well established, when the structure symmetry is high and the ferroelectric anisotropy is weak, the OP component of the PR has a close relation with the field-induced deformation of the crystal structure for the PFM with the lock-in technique, and it can be expressed as $\Delta Z\approx\pm d_{33}V$ [15,16], where V is the bias voltage, and the $\pm$ sign corresponds to upward and downward poled ferroelectric domains. To the first approximation, these requirements are well satisfied by the BFO film, and the above equation should be applicable. These analyses actually indicate the possibility to deduce the piezoelectric coefficients of the BFO film from its PR.

In fact, the dark–bright contrast of the PR image can be quantitatively analyzed, and a line scan of the PR image from left to right gives the quantified PR of the domains with different polarizations. Fig. 3(e)–(h) shows the magnitude of the PR as a function of the distance, obtained by averaging the line scans at different vertical positions of the PR images. In our equipment, the sample deformation ΔZ is translated into electric signals ΔZ_E as amplitude of PR by $\Delta Z=k\Delta Z_E$, in the unit of mV. The different PR magnitudes have been obtained for dark and bright domains. Averaging the plateau and the background of the ΔZ_{-x} curves, two ΔZ values, $\Delta Z_\uparrow$ and $\Delta Z_\downarrow$, can be obtained, respectively. The difference of $\Delta Z_\uparrow$ and $\Delta Z_\downarrow$, divided by 2, gives a quantitative description of the piezoelectric response of the BFO film, and the piezoelectric coefficient can be determined as $d_{33}\approx(\Delta Z_\uparrow-\Delta Z_\downarrow)/2\ V=k(\Delta Z_{E\uparrow}-\Delta Z_{E\downarrow})/2\ V$. In order to determine the coefficient k, a typical ferroelectric material (0 0 1) $BaTiO_3$ crystal was measured using PFM under the ac bias of V_{PP}=15 V and 6 kHz. Following the same procedure for the determination of d_{33} for the BFO films, the pre-factor k can be obtained adopting the $d_{33(BTO)}$= 85.6 pm/V [17], and it is ~17.13 pm/mV. Noting that k is a parameter of the Nanonavi E-Sweep PFM used here, it should be applicable to the BFO films. Based on this parameter and the ΔZ data, the d_{33} of the BFO films are calculated. The ferroelectric coefficients thus obtained are shown in Fig. 4 as a function of film thickness. Results reported by Wang et al. [6] are also presented for comparison. The two set data fit each other quite well and situate at the same master curve, specifying the reasonability of our data. With the increase of film thickness, d_{33} grows monotonically from ~8 pm/V to ~85 pm/V, and d_{33}=0 below t=3 nm. It is interesting to note that the d_{33}–t relation is far from linearity, and a simple analysis yields $d_{33}\approx3.0+2.95[\ln(t)-0.745]2$. This is a mathematical fitting, showing the compatibility of the $d_{33}-t$ relation obtained here with that given by Wang et al. [6]. The physical meanings of this relation, if any, are not clear at present.

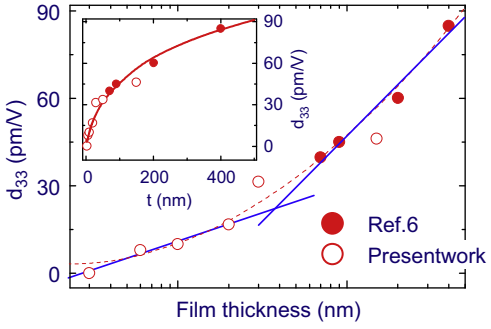

Fig. 4. A semilogarithmic plot of the piezoelectric coefficient d_{33} of the BFO films against film thickness. A linear plot is shown in the set plot. For a solid and hollow symbols represent respectively that data of the present work and those in Ref. [6]. Solid line is the results of $d_{33}\approx3.0+2.95[\ln(t)-0.745]2$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

It is obvious from the inset plot in Fig. 4 that the thickness effect is especially strong when the films are ultrathin, indicating the possibility of the different mechanisms affecting the piezoelectric response of the BFO films. In fact, there are three main factors that may affect the ferroelectric properties of the BFO films: the lattice strains, the clamping of the substrate to film, and the effect of depolarization. It is possible that the different factors take dominant roles in different thickness ranges. When film thickness is above 30 nm, the effect of lattice strains could be important. This can be clearly seen from the data of Wang et al. [6]. Although both the lattice constant and the ferroelectric polarization show a monotonic increase with the decrease of film thickness, the P–t and c–t relations are obviously different. For example, the growth of polarization displays a slowdown while c speeds up with the decrease of film thickness. Noticing the synchronic variation of d_{33} and the ferroelectric polarization versus t, lattice strains may be the determinative factor affecting d_{33} for $t > 30$ nm. However, when film thickness is so thin that the film is nearly fully strained and the lattice parameters almost do not change with t, the clamping effect of the substrate to the film may be more important. It depresses the PR of the film to the external field. This is understandable noting that as the clamping effect prevents lattice relaxation, it prevents the piezoelectric response of the films to external field simultaneously. The slope of the d_{33}–t curve changes around 30 nm (shown by the blue lines in Fig. 4), which demonstrates the different effects of substrate clamping and lattice strains.

The depolarization process in ultrathin films may also have a negative effect on d_{33}. It is a pity that the evolution of the ferroelectric polarization cannot be read from the PR of the ultrathin film, though it seems that P and d_{33} show the exactly opposite tendencies against film thickness for $t > 70$ nm [6]. However, the depolarization effect may mainly influence the size of the ferroelectric domains. This explains the reduction of the domain size as film thickness decreases.

4. Conclusion

Effects of film thickness on the piezoelectric property of the ultra-thin $BiFeO_3$ films (t=1–150 nm), grown on the (0 0 1)-$SrTiO_3$ substrates with a $La_{0.67}Sr_{0.33}MnO_3$ cover layer, have been studied by the technique of piezoelectric force microscope. Special attention has been paid to the evolution of the piezoelectric response with film thickness. Well ferroelectric property maintains in the BFO film with a thickness down to 6 nm, below which no obvious ferroelectric domains are observed. Based on a careful analysis of the piezoelectric response images of the ferroelectric domains upwards or downwards poled by external field, a quantitative description of the piezoelectric coefficient d_{33} can be obtained. d_{33} is found to display a monotonic decrease with the decrease of film thickness, decreasing from $\sim$46 pm/V for t=150 nm to $\sim$8 pm/V for t=6 nm. A corresponding growth of the out-of-plane lattice parameter of the film from 4.011 Å to 4.077 Å is also observed. The effects of depolarization, lattice strains and substrate clamping on the piezoelectric property of the films are discussed.

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