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# Nanoscale Switching and Domain Structure of Ferroelectric $BaBi_4Ti_4O_{15}$ Thin Films

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Ferroelectric domain structures of epitaxial $BaBi_4Ti_4O_{15}$ (BBiT) thin films with different orientations have been imaged for the first time at the nanometer scale. Using the piezoresponse mode of scanning force microscopy it was demonstrated that the spontaneous polarization of BBiT has no component along the *c*-axis of the unit cell. Local piezoelectric hysteresis loops from non *c*-oriented grains with lateral sizes of 300 to 500 nm were recorded. The saturation values of the piezoelectric constant perpendicular to the *c*-axis are comparable to those measured macroscopically. A distinct ferroelectric behavior was still found in grains as small as 300 nm in lateral size.

KEYWORDS: scanning force microscopy, piezoresponse, layered ferroelectrics, epitaxial thin films, domains, switching

Ferroelectric thin films with Bi-layered perovskite structure are very attractive for applications, mostly for nonvolatile memories. While the macroscopic dielectric and ferroelectric properties of these so-called Aurivillius compounds have intensively been investigated,[1–4] only a few reports concerning the observation of the ferroelectric domain structure of $SrBi_2Ta_2O_9$ (SBT) thin films can be found.[5,6] Moreover, since the lateral size of a capacitor cell of a Gigabit density FeRAM (Ferroelectric Random Access Memory) should have a size of only a few hundred nanometers, it is important to find out whether and how the behavior of an individual ferroelectric nanostructure is influenced by the respective environment and external conditions (scaling down the ferroelectric properties with size). Therefore, it is both of fundamental and practical interest to study the influence of local and external conditions (in particular of the crystallographic orientation and of the applied electric field) on the equilibrium ferroelectric domain structure. The piezoresponse mode of scanning force microscopy (SFM) has proven to be the most suitable method to study and to control the ferroelectric domain structure at the nanometer scale,[7] since its resolution is determined by the contact area between sample and probing tip only. This paper reports the first observations performed by SFM of the domain structure and switching behavior of epitaxial $BaBi_4Ti_4O_{15}$ (BBiT) ferroelectric thin films at the nanoscale level. It is demonstrated by local measurements on a *c*-oriented grain that the spontaneous polarization has no component along the crystallographic [001] direction.

Ferroelectric BBiT thin films were grown on epitaxial $LaNiO_3$ (LNO) films on $SrTiO_3$(100) single crystalline substrates by pulsed laser deposition. The conductive 150 nm thick LNO layer serves as template to favor the epitaxial growth of the BBiT film and also as bottom electrode. Details about film deposition and characterization were given in a previous paper. As measured macroscopically, the 400 nm thick BBiT film exhibits a remanent polarization of 2 $\mu$C/cm$^2$ and a coercive field of 60 kV/cm.[8] The experimental set-up for nanoscale imaging is basically the same as that reported elsewhere.[7,9] In the experiments presented here, a Dimension 5000 (Digital Instruments) SFM with a conductive tip was used to image and control the ferroelectric domain structure. A testing AC signal with a frequency of 16.3 kHz and an amplitude of 2.7 V was applied between the SFM tip and the bottom electrode of the sample while scanning the tip over the surface. The image of the ferroelectric domain structure is obtained by simultaneously monitoring the topography and the induced piezoelectric oscillations of the sample (first harmonic signal), using a lock-in amplifier (EG&G Instruments, Model 7260). The nanoscale piezoelectric hysteresis loops were recorded in the same manner as described by other authors.[10,11] The point of the hysteresis loop having the coordinates [$U_p$, $d_{33}(U_p)$] represents the piezoelectric coefficient measured after a delay time $T_d$ from the suppression of the poling voltage $U_p$ applied for a duration $T_p$. It is important to note that this kind of measurement describes the ***remaining*** piezoelectric coefficient as a function of a given bias pulse applied ***previously***. The envelope of the $U_p$ sequence traces a triangular wave form (commonly used for normal hysteresis loop measurements). Since for single-domain ferroelectric single-crystals with a centrosymmetric paraelectric phase the piezoelectric constant is related to the polarization via the formula $d_{33} = 2Q\varepsilon_{33}P$,[12] assuming no dependence of the electrostriction coefficient $Q$ and dielectric constant $\varepsilon_{33}$ on the spontaneus polarization $P$, the measured piezoelectric loops reflect the polarization hysteresis.[13] In these experiments, the values $T_p = 100$ ms and $T_d = 2$ s were chosen.

The morphology of the investigated epitaxial BBiT film deposited on epitaxial LNO on (100) $SrTiO_3$ consists of distinct grains embedded in a *c*-oriented film matrix. From transmission electron microscope (TEM) analysis it was found that the rectangular and spherical grains protruding 50 nm–100 nm out of the surface are either (100)- or (110)-oriented, whereas the background is entirely and only *c*-oriented.[14] The topography and the simultaneously acquired initial domain structure of the as-deposited sample are presented in Figs. 1(a) and 1(b), respectively. The *c*-oriented regions of the surface in the topographical image correspond to the noise level signal zones (gray contrast) in the piezoresponse image. This fact leads to the conclusion that the regions of the sample surface corresponding to *c*-oriented BBiT regions do not exhibit any piezoelectric activity and therefore possess no polarization normal to the surface, at least in the initial state. It will also be demonstrated later that these regions do not exhibit a ferroelectric hysteresis. The regions of the sample which show a high piezoelectric response (black or white areas) correspond to (100)- or (110)-oriented crystallites in the topographical image. The reference phase of the lock-in amplifier was adjusted so that positive DC voltages applied to the

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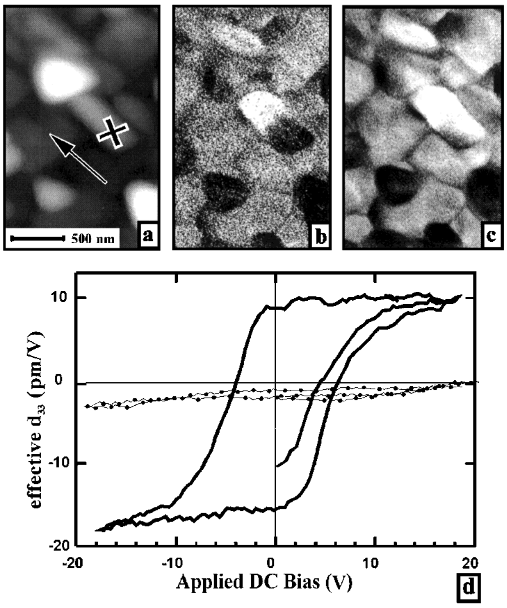


Fig. 1. Topography (a) and piezoelectric response images of a (110)-oriented crystallite of $BaBi_4Ti_4O_{15}$ before (b) and after (c) acquirement of the piezoelectric hysteresis loop. Piezoelectric hysteresis loops (d) acquired at the place marked by a cross in the topographic image (——) and in the *c*-oriented region (—●—) at the place marked with an arrow in the topographic image. Note that the *c*-oriented region exhibits no piezoelectric activity. The piezoelectric coefficient was measured 2s after the corresponding poling voltage was reduced to zero (see text for details).

bottom electrode (electric field towards the sample surface) produce a white contrast in the piezoresponse image. Therefore, the white (black) regions represent ferrolectric domains having the polarization oriented upward (downward). By scanning different regions of the sample it was observed that the major part of the (100)- or (110)-oriented crystallites are negatively polarized (polarization towards the bottom electrode). This fact was also reported for SBT/Pt heterostructures[5] and was explained by the asymmetry of the conductive tip-ferroelectric-bottom electrode system. The electrode asymmetry could generate a built-in electric field which can favor the switching of polarization in one direction (towards the LNO electrode in this case). The ferroelectric behavior was tested on different grains, having both (100)- or (110)-orientations. No significant difference was found between the two types of grains. A typical example of ferroelectric switching performed on a (110)-oriented rectangularly shaped grain is shown in Fig. 1. By probing the negative domain of the rectangular grain (point marked by a cross in Fig. 1(a)) a piezoelectric hysteresis loop was recorded (Fig. 1(d)). Note that at the starting point of the curve the piezoelectric coefficient is negative, which is consistent with the initial domain state seen in Fig. 1(b). The saturation values of $+d_{33}^{\rm rem} = 10$ pm/V and $|-d_{33}^{\rm rem}| = 18$ pm/V obtained are comparable with the value of $d_{33} = 12$ pm/V measured for poled ceramic disks of BBiT by Subarao.[1] The coercive voltages of $+V_{\rm c} = 5.8$ V and $|-V_{\rm c}| = 4.5$ V of the nanoscopic hysteresis loop are comparable with $V_{\rm c} = 4.48$ V obtained from classical macroscopic ferroelectric hysteresis measurements performed on the same sample.[8] The imprint in the LNO-BBiT structure is confirmed by the shifts of the hysteresis loop in the negative direction along the piezoelectric signal axis and in the positive direction of the electric field axis (i.e. switching of polarization in the positive direction requires a higher field). Figure 1(c) presents the piezoresponse image of the same area after having performed the piezoelectric hysteresis loop measurement. As the last voltage applied was +20 V, the polarization and piezoelectric constant remained positive after the acquirement of the hysteresis loop and it can be easily seen that the entire grain became positive. Therefore, a single ferroelectric domain as small as 300 nm in size was switched within a (110)-oriented crystallite of BBiT.

BBiT is an even member of the Aurivillius family, having four oxygen octahedra between 2 bismuth oxide planes. Due to this symmetry it is expected that the spontaneous polarization has no component along the *c*-direction. Measurements performed by Kim *et al.* on BBiT single crystals[15] revealed a strong anisotropy of the dielectric constant. They found that $\varepsilon_{\rm a,b}/\varepsilon_{\rm c} = 6$ at room temperature and $\varepsilon_{\rm a,b}/\varepsilon_{\rm c} = 58$ at Curie temperature, concluding that the $Bi_2O_2$ planes act as paraelectric layers in BBiT. However, there are to date very few experimental proofs of the absence of the spontaneous polarization in the *c*-direction.[16] In order to investigate the ferroelectric behavior along the *c*-axis, the piezoresponse of a point located on the *c*-oriented region was thus measured. The hysteresis loop measurement shown in Fig. 1(c) (the dotted curve) was performed at the place marked by the arrow in Fig. 1(a). The absence of the piezoelectric hysteresis definitely demonstrates that the polarization vector in BBiT has no component along the *c*-axis.

The lateral size of a capacitor cell in a Gbit density FeRAM is expected to be of the order of 200 nm. At such low dimensions the fundamental question arises whether or not the nanostructures still exhibit a ferroelectric behavior.[17] The ferroelectric behavior of a distinct nano-sized (100)-oriented crystallite was investigated in order to answer this question. In Figs. 2 and 3 measurements carried out on a crystallite of 300 nm diameter protruding 75 nm out of the surface are presented. The initial domain structure of the grain is shown in Fig. 2(b): Most of the grain is negative, but there are some positive domains with lateral sizes between 30 and 50 nm located mainly at the edge of the grain. The SFM tip was fixed at the edge of the grain (place marked by the cross in Fig. 2(a)) in the middle of a negative domain and the piezoelectric hysteresis loop shown in Fig. 3 (——) was acquired. The last voltage applied was 20 V, so that the final state of the probed area was positive. This is confirmed by the next piezoresponse image (Fig. 2(c)), where it can be seen that the previously poled area became positive. However, not only the exposed area was influenced by the polarizing voltage, but also the other positive domains have laterally grown in size so that only the center of the grain remained in a negative polarization state. In contrast, no effect of the biasing procedure was observed in the vicinity of the grain.

The SFM tip was then positioned in the center of the grain (place marked by the cross in Fig. 2(d)) and the first half of the hysteresis loop shown in Fig. 3 (—●—) was measured. (The amplitudes of the DC bias pulses applied were increased from zero to 20 V and back to zero). The image presented in Fig. 2(e) shows the domain structure of the grain after this poling procedure: The area previously negatively poled was effectively switched and the entire grain became positive. However, a needle-shaped negative domain of 30 nm × 250 nm at the right edge of the grain remained unchanged (negative)

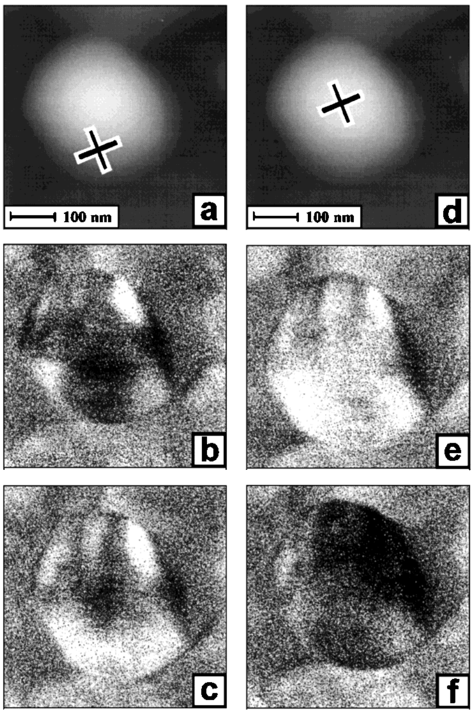


Fig. 2. Topography (a, d) and piezoresponse images of a crystallite 300 nm in lateral size showing the domain structure of the grain before (b) and after (c) the hysteresis loop measurement was performed at the edge of the grain, at the point marked by a cross in (a). Piezoresponse images after the positive (e) and negative (f) poling procedure were performed in the center of the grain, at the point marked by a cross in (d).

by the poling procedure. In order to get a closed hysteresis loop, the SFM tip was then again positioned in the center of the grain and the second half of the hysteresis loop was acquired by applying biasing pulses decreasing from 0 to −20 V, and then increasing to 4 V. The image in Fig. 2(f) represents an intermediate stage of the grain switching towards its positive polarization state, since at the end of the measurement the last applied voltage was approximately equal to the coercive voltage. While the upper half of the grain remained negative (net black color), the lower half already started to switch to the positive direction (dark gray color). This is consistent with the smaller positive coercive field of the local piezoelectric hysteresis loop measured at the edge of the grain (3.7 V), compared to that at the center (4.2 V). Therefore, two parts of the same crystallite behave differently under the influence of an external biasing stimulus. The asymmetry of the silicon tip-BBiT-LNO structure is confirmed by comparing the slopes and the coercive fields of the hysteresis loops: the ferroelectric domains can switch more easily in the negative direction (the coercive field is 3 V with a very steep slope) than in the positive direction, for which the coercive field is 3.7 V to 4.2 V with a flatter slope.

In conclusion, the ferroelectric domain structure of epitaxial $BaBi_4Ti_4O_{15}$ thin films with nanometer-sized grains was imaged for the first time using SFM in the piezoresponse mode. Ferroelectric domains as small as 150 nm in lateral

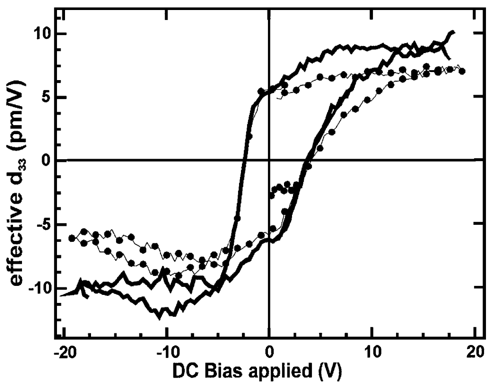


Fig. 3. Piezoelectric hysteresis loops at the edge (——), respectively in the center (—●—) of the crystallite shown in Fig. 2, measured with no bias applied (see text for details).

size were switched within single crystallites. A fine stable ferroelectric domain structure with lateral sizes ranging from 30 nm to 250 nm was revealed in sub-micron *a*-oriented crystallites and found to be stable. Furthermore, different ferroelectric behaviors were detected at the center and at the edge of the same *a*-oriented grain of 300 nm in diameter. Finally, no piezoelectric activity was detected in the *c*-oriented background, showing the absence of ferroelectricity along the *c*-axis and evidencing the fact that in BBiT the spontaneous polarization is confined in the *ab* crystallographic plane.

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