

Characterization and Control of Domain Structure in SrBi₂Ta₂O₉ Thin Films by Scanning Force Microscopy

Alexei GRUVERMAN* and Yuji IKEDA

Research Center, Sony Corporation, 134 Goudo-cho, Hodogaya-ku, Yokohama 240-0005, Japan

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We used the piezoresponse mode of scanning force microscopy (SFM) to perform the first nanoscale observation of ferroelectric domain structure in as-grown SrBi₂Ta₂O₉ films. By lowering the loading force down to approximately 1 nN and by keeping the imaging voltage just below the coercive voltage, we managed to obtain a sufficiently high contrast between opposite 180° domains without affecting the original domain structure. Local and large-scale ferroelectric switching with subsequent readout in areas of about 0.01 μm² and 1.5 μm², respectively, were carried out by applying pulsed- and dc-voltage bias through the conductive tip.

KEYWORDS: scanning force microscopy, layered ferroelectrics, thin films, domain

Recently, considerable interest has been generated worldwide in ferroelectric thin films with layered perovskite structure.^{1–3)} These materials, typically represented by SrBi₂Ta₂O₉ (SBT), exhibit better fatigue properties and lower coercive fields compared to films of the PZT family. These useful features make SBT films promising candidates for ferroelectric memory applications. However, despite intensive research, some basic properties of SBT films, for example, the domain arrangement and mechanism of polarization reversal, remain unknown. Ferroelectric switching and readout of the resulting polarization state are basic operations in ferroelectric memory devices. The tendency to reduce the size of storage elements down to sub-micron dimensions in memory related SBT applications will eventually raise the issue of variations in switching parameters at the nanometer scale. How these variations will affect the writing/reading performance of sub-micron SBT capacitors is a fairly important question. These problems can be addressed by direct studies of domain structures in SBT films using high-resolution techniques such as scanning force microscopy (SFM). Recently, significant progress has been made in SFM characterization and control of domain structures in ferroelectric materials, particularly in ferroelectric thin films.^{4–15)} Arrangement of as-grown domains, polarization reversal in areas as small as 30 nm in diameter, and fatigue and retention processes have been studied in PZT thin films by means of direct observation of domain structures using the piezoresponse mode of SFM.^{9–13)} This imaging method is based on the detection of the piezoelectric vibration of a ferroelectric film (first harmonic signal) caused by an external ac modulation voltage applied through the conductive probing tip. However, the relatively low longitudinal piezoelectric coefficient d_{33} and low coercive fields of SBT films make nondestructive piezoresponse imaging of domains in these films a challenging problem. Here, we present results on the first observation of domain structure in SrBi₂Ta₂O₉ thin films performed using the SFM piezoresponse mode. By reducing the loading force down to approximately 1 nN and by keeping the imaging voltage just below the coercive voltage of the film, we have succeeded in obtaining a sufficiently high contrast between opposite domains without affecting the as-grown domain structure. We have also demonstrated nanoscale modification of the domain structure in SBT

thin films by applying a switching voltage to the probing tip.

The SBT films used in the present work were prepared by a sol-gel process on silicon wafers with a thermal 300 nm thick SiO₂ layer and sputtered layers of Ti (25 nm) and Pt (180 nm). Thin layers of nominal Sr/Bi/Ta=0.8/2.2/2.0 solution were spin coated onto a substrate, heat treated at 250°C for 7 min and then crystallized using RTA at 760°C for 30 s. A post-annealing process, performed for 1 h at 800°C in oxygen, produced SBT films with a final thickness of 170 nm. Prior to the SFM measurements, the films were characterized using transmission electron microscopy (TEM) and X-ray diffraction analysis (XRD).

Ferroelectric domain imaging in the SFM piezoresponse mode has been described in detail in previous publications.^{9–12)} The contrast between antiparallel 180° domains depends on the amplitude of the imaging voltage V_{im} and the value of the longitudinal piezoelectric d_{33} coefficient, which together determine the amplitude Δz of the piezoelectric vibration of the film: $\Delta z = d_{33} \times V_{im}$. However, there is an obvious limitation regarding the imaging voltage: to perform nondestructive visualization of domain structure, this voltage should be kept below the coercive voltage V_c of the film. The large piezoelectric coefficients ($d_{33} > 100$ pm/V) and high coercive voltages of PZT films allowed a remarkable contrast between opposite 180° domains without affecting the original domain structure.^{11–13)} In contrast, SBT films exhibit a low piezoelectric coefficient ($d_{33} \approx 20$ pm/V^{3,16)}) and relatively low coercive voltages. To obtain reasonably high domain contrast in films with a low d_{33} constant, a higher imaging voltage is required. This, in turn, can change the as-grown domain structure if the imaging voltage exceeds the coercive one, which is a likely situation in SBT films. The SFM system used in the present study (Seiko Instruments SPA 300) provides a sensitivity of about 5 pm/V for an imaging voltage of 10 V (peak-to-peak) under usual setting parameters. For comparison, the coercive voltage for the corresponding Pt/SBT/Pt capacitor was found to be about 1 V. However, there is a way to enhance the vertical sensitivity of the piezoresponse mode without increasing the imaging voltage. It has been shown in previous publications¹⁴⁾ that an increase in the loading force leads to a decrease in the measured values of the piezoelectric signal in PZT films due to the mechanical clamping of the film area underneath the probing tip. To solve the problem of non-destructive domain imaging in SBT films and to make SBT

*E-mail address: alexei@src.sony.co.jp

films suitable for memory recording in an SFM-based device, we suggest to use the lowest possible loading (contact) force between the probing tip and the film surface during scanning. It is important to note that the use of a softer cantilever ensures higher sensitivity. In our experiments, we used a gold-coated Si_3N_4 cantilever with a spring constant of 0.1 N/m and with a tip apex radius of about 20 nm. We reduced the loading force from 9 nN, the usual setting for SFM piezoelectric measurements, down to 1 nN, which resulted in a $\approx 30\%$ increase in the piezoresponse signal. This allowed us to decrease the imaging voltage down to 3.5 V (peak-to-peak) and to obtain a reasonably good domain contrast (Fig. 1). This voltage was found to be low enough not to affect the as-grown domain structure, i.e. below the coercive voltage of the film.

Figure 1 shows simultaneously obtained topographic and piezoresponse images of the SBT film. The lateral size of the grains in the topographic image ranges from about 100 nm up to 500 nm. Bright and dark areas seen in the piezoresponse image represent regions with opposite d_{33} piezoelectric constants and antiparallel polarization vectors. From comparison the topographic image (Fig. 1(a)) with the corresponding piezoresponse image (Fig. 1(b)), it can be seen that large grains which exhibit domain contrast are randomly split into opposite domains. By monitoring the phase of the piezoresponse signal it was determined that dark regions represent positive domains (polarization is towards the bottom electrode) while bright regions correspond to negative domains with the polarization vector oriented upward. At the same time, some grains appear as gray regions with no or weak domain contrast in the piezoresponse image.

Previously, several reasons have been suggested to explain the origin of the gray contrast in the piezoresponse image:¹⁵⁾ (a) presence of domains with the polarization vector in the film plane or deviating from the direction normal to the film plane; (b) several randomly polarized grains stacked in the direction normal to the film plane; (c) an amorphous or a non-ferroelectric structure, which does not exhibit piezoelectric properties; (d) polarization reversal due to the action of the imaging ac field, and with the same frequency. Film characterization by TEM and XRD allowed us to rule out premises (b) and (c) as possible explanations: it was found that the films were composed of one layer of grains and that the content of the disordered phase was quite low (less than 1%). It is difficult to directly confirm or refute hypothesis (d) and this problem calls for further quantitative experiments. However,

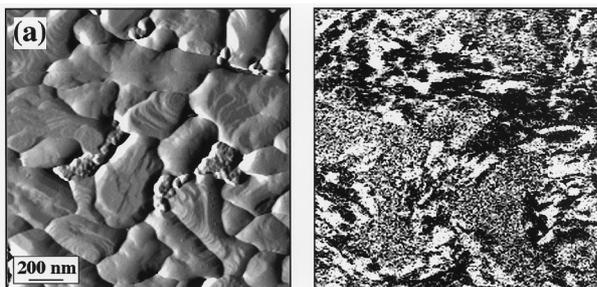


Fig. 1. Simultaneously obtained (a) topographic and (b) piezoresponse images of the $\text{SrBi}_2\text{Ta}_2\text{O}_9$ film. White and black regions in the piezoresponse image correspond to negative and positive domains, respectively.

some preliminary measurements suggested that fast polarization reversal (with the frequency of the imaging voltage) is unlikely to be the source of the gray contrast in Fig. 1(b). We tried to polarize these grains by applying a dc bias, both negative and positive, for a sufficiently long time (up to 5 min) assuming that, if there are mobile domains, the poling procedure will create more stable domains. However, this procedure resulted only in a slight change of the contrast, yielding a light gray or deep gray contrast. Moreover, piezoresponse measurements in the grains with gray contrast, carried out using the procedure described in ref. 11, did not show clear hysteresis behavior. Also, the ratio of the film area with gray contrast in Fig. 1(b) is close to the ratio of randomly oriented grains observed by XRD and TEM analysis. Therefore, we conclude that the gray contrast in Fig. 1(b) is primarily due to the crystallographic orientation of the grains, so that polarization vectors deviate from the direction normal to the film surface.

To present a detailed pattern of domain configuration and to check its correlation with grain structure, topographic and piezoresponse images of the SBT film were acquired at higher magnification (Fig. 2). In the topographic image (Fig. 2(a)), it is interesting to note the specific surface morphology of the grains which do not exhibit domain contrast in the piezoresponse image (Fig. 2(b)). A step-like structure of these grains can be attributed to their crystallographic orientation close to the (001) plane unfavorable for domain observation¹⁷⁾ supporting the earlier hypothesis (a) for the gray contrast in the piezoresponse image. Upon increasing the imaging voltage to 4.0 V (peak-to-peak), a gradual change in the original structure was observed (Fig. 2(c)). The change always occurred via lateral expansion of positive domains (dark regions) at the

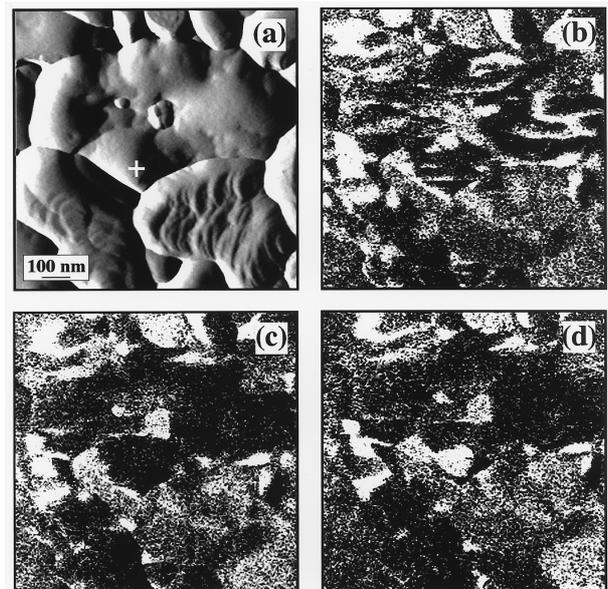


Fig. 2. SFM images of the $\text{SrBi}_2\text{Ta}_2\text{O}_9$ film at higher magnification: (a) topography; (b, c) piezoresponse images at imaging voltages 3.5 V and 4.0 V, respectively. The lower voltage does not affect the original structure. Note a change in the domain structure under the increased imaging voltage; (d) domain structure after a -4.0 V, 100 ms voltage pulse was applied to the film. The white domain of about 100 nm in diameter appeared at the center. The imaging voltage is 3.5 V. The white cross in the topographic image (a) indicates tip positioning during pulse application.

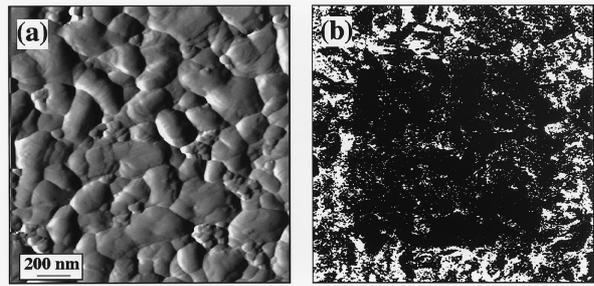


Fig. 3. Large-scale switching in the SBT film: (a) topography; (b) piezoresponse image showing a polarized $1.2 \times 1.2 \mu\text{m}^2$ area at the center produced by scanning the tip under an 8.0 V bias.

expense of negative domains (bright regions). This effect can be explained by an initial imprint in the film due to the asymmetry of the SBT/Pt heterostructure. We assume that electrons trapped near the film/electrode interface create an internal bias which increases the effective threshold voltage for positive domains. As a result, the increased imaging voltage of 4.0 V turns out to be high enough for partial switching of negative domains and for shifting 180° domain walls in the lateral direction, while it is still lower than the threshold voltage for positive domains. The effect of preferential switching could be compensated by applying a small dc bias during the imaging process. This allowed us to estimate the value of the internal bias, which was found to be -0.6 V.

In addition, we performed local and large-scale ferroelectric switching in the SBT films. An area as small as 100 nm in diameter was switched by applying a -4.0 V, 100 ms voltage pulse through the conductive tip to a selected point on the film surface. Polarization reversal was confirmed by the change of the piezoelectric contrast in the area where the external bias was applied (Fig. 2(d)). A large-scale area of $1.2 \times 1.2 \mu\text{m}^2$ was polarized by scanning the tip under an 8.0 V bias (Fig. 3). The polarized area shows a reasonably high contrast compared to the as-grown domain structure. In spite of some variation in the contrast due to crystallite misalignment, it is safe to say that the contrast is reasonably uniform after poling, suggesting little deviation in switching parameters of $1 \times 1 \mu\text{m}^2$ SBT capacitors.

In conclusion, the first observation of ferroelectric domain structure in as-deposited SBT films was carried out with nanoscale resolution using SFM. Reducing the loading force resulted in an improved vertical sensitivity of the SFM piezoresponse mode and nondestructive visualization of do-

main structure in SBT films. Opposite 180° domains within single grains were observed. At the same time, no domain contrast was found in a number of grains, presumably due to the crystallographic orientation of the grains unfavorable for domain observation in SFM. It is suggested that the observed internal bias of -0.6 V is due to electrons trapped at the film/electrode interface. Nanoscale domain switching and subsequent domain readout in an area as small as 100 nm in diameter using the SFM piezoresponse mode demonstrate the potential of the SBT films for application in as high-density recording media.

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