January 2000

Nanoscopic switching behavior of epitaxial $SrBi_2Ta_2O_9$ films deposited by pulsed laser deposition

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(Received 12 July 1999; accepted for publication 8 November 1999)

We report results on scanning force microscopy (SFM) studies of epitaxial $SrBi_2Ta_2O_9$ films which, in conjunction with complementary x-ray diffraction, scanning and transmission electron microscopy data, allow us to establish direct correlation between the crystallographic structure at the submicrometer range and the nano- and macroscopic switching behavior of the films. SFM topographic analysis of the films revealed a high degree of inhomogeneity at the submicrometer level: a number of rectangular and spherical grains protruding out of the flat surface. It has been found that the ferroelectric behavior of the films is primarily due to the (110) and (100)-oriented grains, while a flat background is *c* oriented and therefore is not switchable. Remanent polarization values obtained using SFM data were consistent with the results of the macroscopic hysteresis loop measurements. [S0003-6951(00)00901-3]

Ferroelectric thin films are currently attracting significant interest due to the recent breakthrough in their integration into nonvolatile random access memories (NVFRAMs).[1] One of the most serious limitations of ferroelectric films of the Pb(Zr, Ti)O_3 family is fatigue, or the decrease in the amount of switchable polarization as a function of the number of switching cycles. One of the ways suggested to overcome this problem is to replace PZT films with Bi-layered perovskite films which were found to be free of fatigue up to 10^{12} cycles of polarization switching.[2] However, application of these films to memory devices presents some serious challenges. In particular, strong anisotropy of ferroelectric properties of the Bi-layered perovskite films impose severe requirements on controlling the film orientation. Furthermore, high uniformity of film properties over large area substrates is necessary for producing reliable, economically viable high-density memories.[3] These requirements will eventually make it imperative for engineers to use either monocrystalline (epitaxial) films or polycrystalline films with extremely fine grains. Recently, epitaxial $SrBi_2Ta_2O_9$ (SBT) and $BaBi_4Ti_4O_{15}$ (BBiT) and $LaNiO_3$ (LNO) films with good uniformity over large areas have been successfully grown using pulsed laser deposition (PLD).[4–6] This approach combines the advantages of fatigue-free Bi-layered perovskites with the high quality of PLD films. However, despite the fact that these epitaxial films have demonstrated good macroscopic homogeneity of their properties and clear ferroelectric behavior, on a microscopic level, morphologically distinct regions were observed.[5,6] In general, there is little knowledge about ferroelectric behavior of SBT films at the submicrometer level. First nanoscale studies of sol–gel grown SBT films revealed a multidomain state of *a*-oriented individual grains and showed significant variations of switching parameters from grain to grain as a result of their misalignment.[3,7,8] The purpose of the present study was to investigate the switching properties of epitaxial SBT films at the smallest possible scale for assessing a contribution of morphologically different regions to the polarization reversal signal. The experimental method, chosen for this purpose, is piezoresponse scanning force microscopy (SFM) which offers nondestructive imaging of domain patterns in ferroelectric thin films with a resolution of several nanometers.[9–12] The SFM data were substantiated by cross-section transmission electron microscopy (XTEM) analysis of the films.

The details of PLD of epitaxial SBT films and LNO electrodes can be found elsewhere.[4,5] In brief, the 140-nm-thick epitaxial $SrBi_2Ta_2O_9$ layer was grown by PLD employing a KrF excimer laser (wavelength $\lambda = 248$ nm) on Si(100) substrate coated with a stack of epitaxially grown layers of LNO/YSZ (YSZ—yttria stabilized zirconia). This multilayer serves as a template to promote the epitaxial growth of the film. The structure of the films was studied by means of XTEM and x-ray diffraction (XRD). XRD analysis of the film showed mainly *c*-oriented film with a fairly small fraction of (110) and (100)-oriented grains.[13] Measurements of macroscopic hysteresis loops, carried out using Pt top electrodes and a standard RT66A ferroelectric tester, showed that the remanent polarization of the PLD films (about 1 $\mu C/cm^2$) was much lower than values reported in the literature.[13,14]

Examination of the film nanoscopic switching behavior was carried out by direct SFM observation of the film domain structure and its change under an external switching voltage. A conductive gold coated Si_3N_4 tip, which served as a movable top electrode, was used both for domain visualization (by applying an imaging voltage below the coercive voltage of the film) and for polarization reversal (by applying a switching voltage well above the coercive voltage). The domain imaging method, described in detail elsewhere,[9,10] uses the relation between the sign of the d_{33} piezoelectric constant and the polarization direction. This method allows

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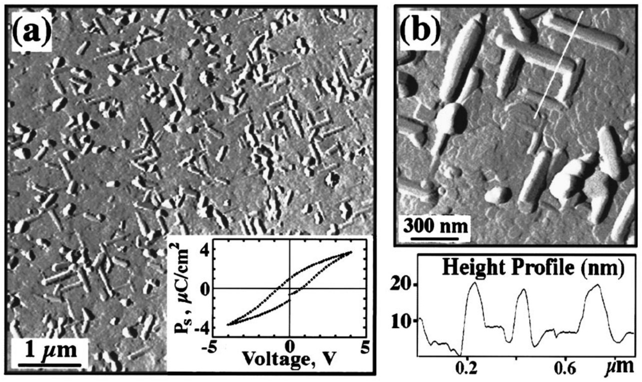

FIG. 1. (a) SFM topographic image of a PLD grown SBT film. (Inset) macroscopic hysteresis loop of the film. (b) Topographic image of the same film at the higher magnification and a cross section of surface topography along the white line.

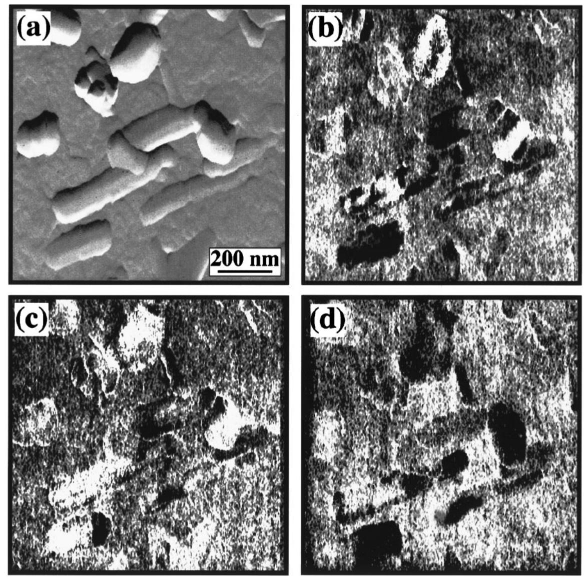

FIG. 2. Topographic (a) and piezoresponse (b) images of the as-deposited epitaxial SBT film. (c), (d) Change in the domain structure after scanning the same area with an applied dc bias of (c) 6 V and (d) −6 V.

simultaneous topographic and domain imaging of the film using a standard lock-in technique. To study nanoscopic switching parameters of morphologically different regions, local hysteresis loops were measured by monitoring the local piezoresponse signal as a function of a low frequency ac voltage (10 V, 0.5 Hz) superimposed on the imaging voltage (3.3 V peak-to-peak, 10 kHz).[15]

Investigation of the film surface with SFM revealed a number of rectangular grains of $(250-450)\times 100\,\mathrm{nm}^2$ oriented in orthogonal directions (due to the effect of crystallographic axes of the underlying layers) as well as spherical grains with an average size of about 250 nm protruding out of the flat surface (Fig. 1). The cross-section analysis showed that the average height of the grains is about 15 nm. This surface morphology is similar to that observed in PLD grown BBiT films.[6] It was suggested that morphologically different regions in BBiT films have different crystallographic orientation and, as a result, exhibit dissimilar switching behavior. The problem addressed by SFM was to analyze the difference in ferroelectric properties between rectangular and spherical grains on one hand and the flat regions of the SBT films on the other.

Comparison of simultaneously acquired topographic and piezoresponse images of the as-deposited SBT film [Figs. 2(a) and 2(b)] allows us to establish correlation between the surface morphology and domain arrangement. Dark and bright contrast, which indicates domains with out-of-plane polarization, can be seen in the above mentioned rectangular and spherical grains only (please note that most of the grains were in the polydomain state), while flat regions exhibit gray contrast associated with zero out-of-plane polarization. Variations in the gray tone are within the noise range and cannot be reliably attributed to the domain contrast. Piezoresponse images of the same area acquired after it was scanned with the tip held under a negative and then under a positive dc bias of 6 V, showed the contrast change only in the grains and not in the flat area [Figs. 2(c) and 2(d)]. Furthermore, local piezoresponse measurements carried out in several grains and in regions with a flat surface revealed remarkably different switching behavior. Application of the voltage pulses to a grain resulted in a partial or complete switching of the grain depending on the pulse amplitude and duration. This effect is illustrated in Fig. 3. A switching pulse (6 V, 10 ms) applied to the grain marked with a cross in the topographic image [Fig. 3(a)] produced a reversed domain of about 50 nm in size [Figs. 3(b) and 3(c)]. Distinct hysteresis loops were normally measured in the grains [Fig. 3(d)] while in the flat region no hysteresis loops were observed and local voltage application had no effect on its domain contrast. It has to be noted that repeated switching of the grains led to the gradual shift of the hysteresis loops in the vertical direction [Fig. 3(d)] and pinning of domains with polarization vector oriented toward the bottom electrode. A strong shift upward may indicate formation of an unswitchable layer as a result of the charge trapping at the film/electrode interface during switching. This effect could be ascribed to the asymmetry of the tip/film/electrode heterostructure.[7]

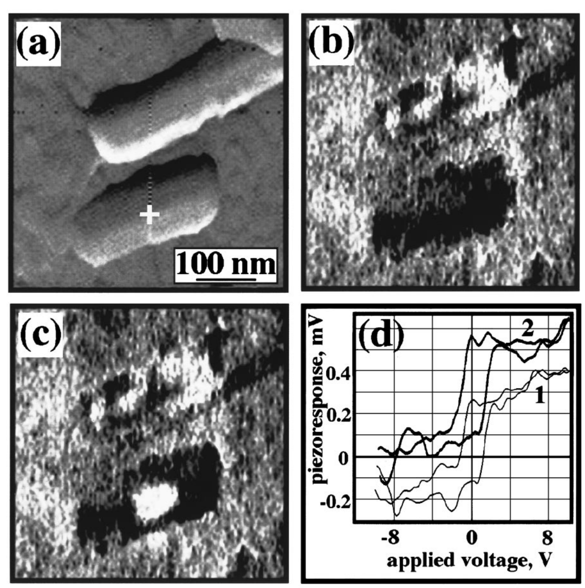

FIG. 3. Topographic (a) and piezoresponse (b) images of the the epitaxial SBT film. (c) Piezoresponse image of the same area after a voltage pulse (6 V, 10 ms) was applied to the grain marked by the white cross at the topographic image. (d) Nanoscopic hysteresis loops measured before (1) and after (2) repeated switching of the marked grain.

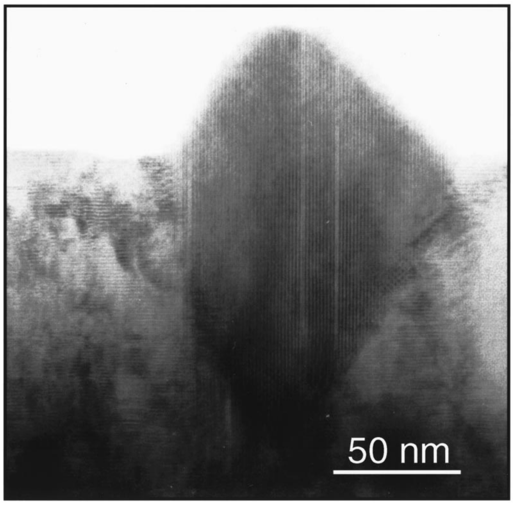

FIG. 4. XTEM image of the epitaxial SBT film. The image shows a (110)-oriented grain embedded into a flat *c*-oriented film. The periodic fringes with a spacing of 12.5 Å correspond to Bi_2O_2 layers which, in SBT films, are parallel to the polar axis.

It has been reported previously that Bi-layered perovskite ferroelectrics exhibit a high degree of anisotropy: large polarization is observed along the *a* axis, while there is no or little polarization along the *c* axis.[16] Desu *et al.*[4] observed orientational dependence of the ferroelectric properties of SBT films reporting the decrease in switchable polarization with an increasing degree of *c*-axis orientation. All these reports and our SFM data suggest that the flat regions observed in our SBT samples are predominantly *c* oriented and, therefore, are not switchable. The ferroelectric behavior of epitaxial SBT films then is due to embedded crystallites which should have a more favorable orientation. This conclusion is confirmed by the results of XTEM analysis of the film. The XTEM image of the film (Fig. 4) clearly shows an (110)-oriented[17] grain embedded into the *c*-oriented flat background. Their orientations can be easily identified by the periodic fringes which indicate the Bi_2O_2 layers running perpendicular to the surface in the grain and parallel to the surface in the flat region.

The value of the remanent polarization should, therefore, depend on the fraction of (110)- and (100)-oriented grains. SFM topographic analysis showed that rectangular and spherical grains occupy about 23% of the film surface. Assuming that the spontaneous polarization in stoichiometric SBT film is 18.2 $\mu C/cm^2$,[16] the remanent polarization in our film is expected to be at the level of about 4.1 $\mu C/cm^2$. However, it has been found that vertical spans of local SFM hysteresis loops varied significantly from grain to grain due to grain misalignment. Obviously, this should result in a lower value of the remanent polarization. Indeed, histogram analysis of the piezoresponse image in Fig. 2(c) showed that the integral polarization signal[3] will be only about 14% of the fully polarized completely *a*-oriented SBT film, or about 2.5 $\mu C/cm^2$, which is comparable with the results of macroscopic measurements of polarization hysteresis loops in epitaxial SBT films. Fully *a*-oriented SBT films on lattice-matched substrates have already been reported.[18] Although no ferroelectric measurements have been conducted as these films did not use bottom electrodes, it is expected that fully *a*-oriented Bi-layered films should have a much higher value of spontaneous polarization.

In conclusion, investigation of polarization reversal in individual grains by means of piezoresponse SFM in conjunction with XTEM analysis allowed us to establish direct correlation between nanoscopic switching parameters of the PLD grown epitaxial $SrBi_2Ta_2O_9$ films and their crystallographic structure at the submicrometer scale. Moreover, the results are fully consistent and compatible with macroscopic polarization and switching measurements. SFM domain studies showed that ferroelectric behavior of the films is primarily due to the embedded grains, while a flat background is not switchable and does not exhibit any domain contrast. This conclusion was supported by XTEM analysis which revealed that the embedded grains normally have an orientation close to (110) and (100), while flat regions have (001) orientation. Polarization reversal and evaluation of switching parameters of individual grains have been accomplished. Estimation of the remanent polarization using nanoscale SFM data produced a number of about 2.5 $\mu C/cm^2$, which is in reasonable agreement with the value obtained from macroscopic hysteresis loop measurements.

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