Misfit dislocations in nanoscale ferroelectric heterostructures

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We present a quantitative study of the thickness dependence of the polarization and piezoelectric properties in epitaxial (001) PbZr0.52Ti0.48O3 films grown on (001) SrRuO3-buffered (001) SrTiO3 substrates. High-resolution transmission electron microscopy reveals that even the thinnest films (~8 nm) are fully relaxed with a dislocation density close to 10^{12} cm^{-2} and a spacing of approximately 12 nm. Quantitative piezoelectric and ferroelectric measurements show a drastic degradation in the out-of-plane piezoelectric constant (d_{33}) and the switched polarization (∆P) as a function of decreasing thickness. In contrast, lattice-matched ultrathin PbZr_{0.52}Ti_{0.48}O_3 films that have a very low dislocation density show superior ferroelectric properties. Supporting theoretical calculations show that the variations in the strain field around the core of the dislocation leads to highly localized polarization gradients and hence strong depolarizing fields, which result in suppression of ferroelectricity in the vicinity of a dislocation. © 2005 American Institute of Physics.

Received 8 February 2005; accepted 17 March 2005; published online 6 May 2005

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with a significantly reduced strain contrast and the density of defects is greatly reduced. Figure 2(a) shows a high-resolution image of an 8 nm thick PZT (52/48) sandwiched between the top and bottom SRO layers. An array of misfit dislocations is observed at the interface between the PZT (52/48) and the bottom SRO layer as indicated by open arrows. The majority of the dislocations are located in the SRO layer away from the interface plane. Some of the dislocations dissociate into two partials to lower the energy associated with the lattice strain. Figure 2(b) shows a magnified region around the dislocation core within the white frame. Dissociation of the dislocation can be clearly seen as indicated by two arrows. The corresponding Burger’s vectors for the two dissociating edge-type partials are \( a/2 [101] \) and \( a/2 [10\bar{1}] \), leading to a sum Burger’s vector \( \mathbf{b} = a[100] \).

Lattice strain in the vicinity of the dislocation was studied by studying the changes in lattice fringe spacings using geometric phase analysis of the lattice fringe image. In calculating the lattice spacing variations in the framed area of Fig. 2(b), the SRO lattice fringes in the bottom part of the frame were used as a spacing reference. Figures 2(c) and 2(d) show the maps of spacing changes along the in-plane axis [100] and out-of-plane axis [001], respectively. The scale in Figs. 2(c) and 2(d) quantifies the changes in the local lattice parameter with respect to the SRO fringes. It can be seen that the SRO layer is locally compressed while the PZT layer has significant in-plane tensile strain close to the core. The extra half-plane is in the SRO layer with the core penetrating into this layer away from the interface to minimize excessive elastic energy associated with the core. This is frequently observed in films on substrates where the film is elastically stiffer than the substrate. The abrupt changes of lattice strain, from compressive to tensile across the edge dislocation cores, are well characterized by variations in the color scale. Above the dislocation core, a tensile lattice strain is clearly seen in the two maps in comparison with the areas away from the dislocation cores and parallel to the interface. The lattice expansion in-plane is stronger than the one out-of-plane and extends far into the PZT (52/48) layer.

Quantitative piezoresponse force microscopy was used to extract the out-of-plane piezoelectric coefficient \( d_{33} \). To ensure a uniform electric-field distribution, the measurements were made using a top electrode and a conductive Pt-Ir tip. The displacement of the cantilever was calibrated using \( x \)-cut quartz, which has a known piezoelectric coefficient (2.3 pm/V). Figure 3(a) shows \( d_{33} \) loops for two PZT (52/48) thicknesses: 12 nm (triangles) and 160 nm (squares) thick films. The plot shows a dramatic reduction in the piezoelectric coefficient for the 12 nm film compared to the 160 nm thick film. For this composition, \( d_{33} \) for a clamped (001)-oriented epitaxial film without any suppression or extrinsic effects, is expected to be \( \sim 157 \) pm/V (Ref. 20) as shown by the 160 nm thick film. This drops significantly for the 12 nm film, which shows average remanent \( d_{33} \) of only 30 pm/V. In Fig. 3(b), we plot \( d_{33} \) at remanence as a function of film thickness. It shows a systematic and sharp fall when the thickness is below 100 nm, indicating the detrimental effect of misfit dislocations. We also measured the switchable polarization \( (\Delta P) \), which is the difference between the switched \( (P^\prime) \) and nonswitched \( (P) \) responses. We used this instead of \( 2 \cdot P_R \), where \( P_R \) is the remanent polarization,
as it is less likely to be convoluted by leakage. We find that similar to $d_{33}$, the $\Delta P$ also drops drastically for thicknesses below 100 nm. This drop begins at a thickness much greater than that predicted for fully commensurate ferroelectric heterostructures by theory or experiments. It, therefore, clearly illustrates the dominant extrinsic role dislocations play in the size effects of nanoscale ferroelectrics. This is evident in Figs. 3(c) and 3(d), where we compare $d_{33}$ and $\Delta P$ values of the PZT (20/80) versus PZT (52/48). For the sake of comparing both compositions on one scale, the values have been normalized to the unsuppressed theoretical values. The lattice-matched PZT (20/80) system shows no scaling in $d_{33}$ or $\Delta P$ down to 15 nm. In comparison, the drop in the PZT (52/48) system is much sooner; thereby exhibiting the overriding role of dislocations in the size effects of ferroelectrics.

To probe this further, we carried out a thermodynamic analysis to investigate the role of dislocations in ferroelectric materials using a methodology based on a modified mean-field Landau–Devonshire formalism incorporating the elastic energy of the dislocations, its electromechanical coupling to the polarization, and the internal field due to polarization gradients given by Maxwell’s relations. The details of this method are given elsewhere. We analyzed the polarization distribution around misfit dislocations with $b$=a[100] in (001) PZT (52/48) films with 12 and 200 nm thickness on thick (001) STO substrates with fully relaxed SRO buffer layers (SRO/STO). The internal stresses due to lattice mismatch were coupled with the stress field of dislocations in the linear elastic limit. As shown in Figs. 4(a) and 4(b), due to strong strain gradients, there is a drastic variation in the polarization near the film-substrate interface that should result in the formation of $\sim 10$ and $\sim 15$ nm thick ferroelectrically dead layers in 12 and 200 nm films, respectively. These plots also display the thickness dependence of the dead layer-to-film thickness ratio. As films get thicker, the equilibrium dislocation density increases and hence the dislocation periodicity decreases resulting in better relaxation of epitaxial stresses. The thickness of the dead layer depends on the dislocation density, which theoretically levels off above $\sim 100$ nm in PZT (52/48) films on SRO/STO.

These results have several implications in terms of properties of ultrathin ferroelectric films and nanostructures. Obviously, there exists a significant volume that will not contribute to the polarization, dielectric, piezoelectric, and pyroelectric response. Furthermore, because of this dead layer, the applied electrical field that is necessary to activate the unique properties of ferroelectrics will be screened. These regions also serve as pinning centers for reversible 180° and non-180° domain-wall motion in the presence of an applied field, and thereby reduce the extrinsic contribution to all physical properties. The detrimental effect of such regions will be enhanced in nanoscale ferroelectric films and heterostructures, and hence play a critical extrinsic role in size effect studies of ferroelectrics.

This work was supported by the National Science Foundation (NSF) under Grant Nos. DMR-0132918, NSF-MRSEC DMR-0080008, and (an NSF US-Europe program) DMR-0244288. One of the authors (V. N.) also acknowledges the support of the Alexander von Humboldt Foundation for his stay in Germany.