Thickness dependence of structural and electrical properties in epitaxial lead zirconate titanate films

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We have studied the effect of misfit strain on the microstructure and properties of ferroelectric lead zirconate titanate thin films. We have changed the misfit strain by varying the film thickness and studied the thickness effect on the domain formation of epitaxial PbZr0.2 Ti0.8 O3 (PZT) films grown by pulsed laser deposition on (001) LaAlO3 substrates with La0.5 Sr0.5 CoO3 (LSCO) electrodes. The nominal thickness of the PZT films was varied from 60 to 400 nm with the LSCO electrode thickness kept constant at 50 nm. X-ray diffraction experiments show that the films relax via the formation of a domains, the fraction of which increase with the ferroelectric film thickness. The c-axis lattice constant of PZT films calculated from the 002 reflection decreases with increasing film thickness and approaches the bulk value of ~0.413 nm in the films thicker than 300 nm. Cross-sectional transmission electron microscopy images reveal that the a-domain fraction and period increase with increasing film thickness. The relaxation of misfit strain in the film is accompanied by systematic changes in the polarization properties, as well as the switching fields, quantified by the coercive field and the activation field. © 1999 American Institute of Physics.

I. INTRODUCTION

The bistable polarization states of ferroelectric materials is the fundamental property that enables nonvolatile information storage in a ferroelectric random access memory device. Among the many desirable attributes for a memory device, the ferroelectric thin film capacitors should show large values of switched polarization (∆P) for short read and write pulses and low coercive voltages. This is motivated by the fact that they will be used in circuits that will typically be integrated using 100 ns wide pulses. Therefore, it is necessary to understand the complex interplay between film microstructure and the switching properties and subsequently control it. The earliest studies on the switching behavior of lead zirconate titanate thin films suggested that the intrinsic switching speed is faster than 1 ns, and is limited only by the intrinsic resistance-capacitor time constant of the device and by instrumental limitations.1 One measure of switching speed, the “activation field,” was identified by Merz in his pioneering work on barium titanate single crystals.2 More recently, the activation field for polarization reversal has been demonstrated to be independent of circuit parameters and directly related to the tetragonality ratio (c/a) of the ferroelectric layer.3 Cillesen, Prins, and Wolf4 have investigated the thickness dependence of the switching voltage in textured oxide ferroelectric thin films prepared by pulsed laser deposition (PLD) where they reported that the coercive field is independent of thickness in films with oxide electrodes for films with thicknesses ranging from 200 to 800 nm. On the other hand, the coercive field was shown to increase with decreasing ferroelectric layer for capacitors with a metallic top electrode.4 In order to understand the effects of heteroepitaxy-induced strain and its relaxation with film thickness, it is important to carry out studies on films that span the range over which strain relaxation occurs by dislocation formation. Furthermore, the impact of epitaxial strain on the polarization properties, as well as ease of switching under pulsed fields need to be understood. Our work has thus focused on the impact of strain relaxation, including relaxation due to 90° domain formation, on the ferroelectric properties under pulsed switching conditions.

In order to systematically understand the effect of strain on the ferroelectric properties, specifically the switching dynamics, we have chosen lattice-mismatched epitaxial heterostructures as the demonstration vehicle. The observed microstructures of tetragonal lead zirconate titanate films with different thicknesses on a (001) LaAlO3 (LAO) substrate are a result of an interplay of two different mechanisms for strain relaxation: misfit dislocation generation at the deposition temperature (T D) and polydomain formation below the paraelectric to ferroelectric transformation temperature (T C). While it is not the primary intention of the article to address misfit dislocation formation at T D, it is very possible that these dislocations assist in the nucleation of the polydomain structure. Polydomain formation in epitaxial films undergoing a phase transformation is a mechanism that relaxes the total strain energy which is a result of the lattice misfit due to the structural phase transformation, the difference in the thermal expansion coefficients of the film and the substrate, and misfit dislocation formation.5 In Fig. 1, we show all possible orientational variants of the ferroelectric phase (inner circle)
and possible polydomain structures (outer circle) due to a cubic-tetragonal transformation.\(^8\) Previously we have obtained a map showing regions of stability of possible domain structures and relative fractions of domains in polydomain structures for epitaxial ferroelectric or ferroelastic films, which undergo a cubic-tetragonal transformation.\(^7\)–\(^11\) The map is constructed in the coordinates of the misfit strain between the substrate and the film, and the tetragonality of the film. These parameters, together with an “effective” substrate lattice parameter to incorporate relaxation by misfit dislocations,\(^12\) conveniently combine the effects of earlier mentioned sources of strain energy. For relatively thick films with \(h \gg h_{\text{ct}}\), where \(h\) is the film thickness and \(h_{\text{ct}}\) is the critical film thickness for the formation of the \(c/a_1\) or the \(c/a_2\) polydomain structure, the domain structure is controlled only by the elastic energy density.\(^7\),\(^10\) It was also shown that the \(c/a_1\) and the \(c/a_2\) polydomain structures are energetically equivalent and will be referred to as the \(c/l\) structure hereafter.\(^7\)–\(^12\) The existence of such a critical thickness is due to microstresses, which are a result of the periodic deviation of the actual misfit strain from the average misfit on the interface between the polydomain structure and the substrate.\(^9\) The effect of film thickness was accounted for using a simple approximation for microstresses.\(^9\),\(^10\) It was shown that the fraction of \(c\) domains in a \(c/l\) domain structure depends on the film thickness.\(^10\) The task of this article is to establish a correlation between the strain relaxation, polydomain formation, and the ferroelectric properties.

In the lead zirconate titanate family of ferroelectrics, the switching properties can be systematically varied by one of many microstructural parameters, such as the film tetragonality, strain, grain size, etc. Heteroepitaxy provides us with a powerful approach to control the elastic strain that is introduced into the ferroelectric layer, by systematically changing the thickness of the ferroelectric layer. In this work, we have studied the influence of the thickness of PbZr\(_{0.2}\)Ti\(_{0.8}\)O\(_3\) (PZT) films on strain relaxation, domain formation and its effect on switching properties. The switching behavior was studied by pulsed measurements with the pulse amplitude and width as key variables. The familiar ferroelectric hysteresis loop provides a quasistatic (i.e., low frequency) measure of the polarization and the switching field, i.e., the coercive field. However, under pulsed testing conditions, the remnant polarization, i.e., the difference between the switched response (\(P^+\)) and the nonswitched response (\(P^-\)), and the activation field are better measures of the switchability of the capacitor. The activation field is obtained via the Merz approach\(^13\) from a plot of \(\ln(i_{\text{max}})\) vs \(1/E\), where \(i_{\text{max}}\) is the switching current and \(E\) is the applied field.

### II. EXPERIMENT

The oxide heterostructures were deposited by PLD at 650 °C under 100 mTorr of oxygen partial pressure. Prior to deposition, the substrates were sequentially cleaned with trichloroethylene, acetone, and methanol. The films were cooled under 760 mTorr of oxygen partial pressure at 5 °C/min until 200 °C and then by Newtonian cooling to room temperature. The thickness of the PZT layer was varied from 60 to 400 nm. La\(_{0.3}\)Sr\(_{0.7}\)Co\(_3\) (LSCO) electrodes were used to contact the ferroelectric layer with the thickness of top and bottom electrode kept constant at 50 nm. All the films were grown on (001) LAO substrates.

The heterostructures were investigated by x-ray diffraction (XRD) using standard \(\theta–2\theta\), \(\omega\), and, \(\phi\) scans to evaluate crystalline quality and domain structure. A Siemens D5000 four-circle diffractometer was used to obtain the \(\theta–2\theta\), \(\omega\), and \(\phi\) spectra. Epitaxial quality of the films was confirmed by the presence of only 00l or 000 type of peaks in the Bragg scans. From the 200 reflections, the lattice constants were calculated after normalizing with respect to the 200 peak of LAO with a lattice parameter of 0.379 nm. The thickness of the films was measured by Rutherford backscattering spectroscopy.

Cross-sectional transmission electron microscopy (TEM) samples were prepared by gluing the films face to face and mechanically thinning them down to 15 μm. In addition to the standard tripod, a novel tool developed by one of the co-authors, was used in the last stage of mechanical polishing. A Bal-Tech Ion Milling RES-010 was used to ion mill the sample. For the first 1 1/2 h the conditions were 7 kV and 2.5 mA. Then, 5 kV and 1 mA was used for 30 min to finish the ion milling. TEM studies were carried out on a JEOL 4000FX microscope operated at a voltage of 300 kV.

The electrical measurements used square bipolar pulse trains with the sequence that transverses the entire hysteresis loops. We obtained polarization data from the output responses observed at the top of the read pulse which immediately follows the delay time after the read pulse. The high-speed tests were performed using an Analogic polynomial waveform generator and the signal responses were measured on a Tektronix oscilloscope. The pulse responses were measured using applied voltages that kept a constant applied field of 250 kV/cm across the ferroelectric capacitor. The signal generator produced square bipolar pulses that were varied in width from 1 μs to 1 s. The delay between each pulse was 1 s. For activation field measurements the bipolar pulse widths were kept constant at 1 μs. The delay time between write and read pulses was 1 s. The applied voltage was varied from 1 to 10 V. The net current response were acquired at each voltage level from which current maximum peak was noted.
sumed to be cubic) requires a biaxial strain state with equal orthogonal in-plane components concentrated in the LSCO film (thickness of substrate is much larger than the thickness of LSCO). In the absence of misfit dislocations at the LAO–LSCO interface, if the substrate and the LSCO layer are assumed elastically isotropic and their elastic constants are equal, the out-of-plane component of the misfit strain tensor, \( \varepsilon_{zz} \), is related to the in-plane components as

\[
\varepsilon_{zz} = -\frac{2\nu}{(1-\nu)} \varepsilon,
\]

where

\[
\varepsilon = \varepsilon_{xx} = \varepsilon_{yy} = \frac{a_s - a_{LSCO}^0}{a_s},
\]

and \( a_s \) is the lattice parameter of the LAO substrate, \( a_{LSCO}^0 \) is the unconstrained (bulk) lattice parameter of LSCO, and \( \varepsilon_{xx} \) and \( \varepsilon_{yy} \) are the in-plane components of the misfit strain. The value of \( \varepsilon \) is approximately \(-1.01\%\) at room temperature (compression). Therefore, Eq. (1) finds \( \varepsilon_{zz} \) as 0.90\% (tension). Then, the out-of-plane lattice parameter of the LSCO layer, \( a_{LSCO}^0 \), can be calculated using

\[
\varepsilon_{zz} = \frac{a_{LSCO}^2 - a_{LSCO}^0}{a_{LSCO}^0},
\]

which gives \( a_{LSCO}^0 = 0.386 \text{ nm} \). Compared to the experimentally observed value of 0.387, we conclude that the intermediate LSCO layer is coherently strained. Thus, the first layers of PZT are deposited on a highly strained LSCO layer. A clear shift in the peak position of the 002 PZT peak towards higher peak positions is observed with increasing thickness. The \( c \) lattice parameter drops from 0.416 nm for the 60-nm-thick film to 0.413 nm for 400-nm-thick film. This indicates that the epitaxial strain in the film relaxes as the film thickness is increased.

To determine the domain fractions, \( \omega \) rocking curves have to be used. Foster et al. have demonstrated that depending on the \( \chi \)-angle resolution, \( h00 \) type of peaks from the PZT layer may disappear. This is due to the tilting of the \( a \) domains away from the \( (00l) \) planes of the substrate because of the tetragonality of the PZT film. The \( (h00) \) planes of the \( a \) domains are tilted from the \( [00l] \) direction of the substrate theoretically by \( \sim 2.9^\circ \) along \([h00], [\bar{h}00], [0k0], \) and \([0k0] \) directions resulting in a fourfold symmetry. Thus, using the integrated intensities of the 002 and 200 peaks of the PZT layer from the standard \( \theta \sim \theta \) XRD pattern to calculate domain fractions of the PZT film may give misleading results (usually an overestimation of the \( c \)-domain abundance). To obtain the domain populations in the twinned PZT layer more accurately, the integrated intensities of either the \( \omega \sim \chi \) scans (area maps) or the \( \omega \) rocking curves of the \( 00l \) and \( h00 \) PZT peaks should be employed. If the rocking curves are used, the \( c \)-domain fraction \( \alpha_c \) is given by

\[
\alpha_c = \frac{\prod_{002}^c}{\prod_{002}^c + 4\prod_{200}^c}.
\]
where $\Pi_{002}^R$ and $\Pi_{200}^R$ are the integrated x-ray rocking curve intensities of 002 and 200 reflections of the PZT layer, respectively. $\Pi_{200}^R$ is the volume under one of the $a$-domain lobes observed in the 200 rocking curve. Measurement of the total intensity of x-rays diffracted from $a$ domains requires complete mapping of the relrods in reciprocal space lattice. Therefore, to calculate the volume fraction of $a$ domains, their integrated intensity must be multiplied by a factor of four.

To accurately locate the positions of the 200 peak of PZT, the samples were tilted by $\pm 2.1^\circ$ along $\chi$. The intensities of both the 002 LAO and 002 PZT peaks were drastically reduced. This way, the positions of the 200 PZT peaks were located and specular $\omega$-rocking curves around 002 and 200 PZT were obtained. The results are illustrated in Fig. 3. From the $\omega$-rocking spectra around 200 PZT for all the films, it can be seen that there is only one peak. Therefore, we can conclude that the PZT films grown on (001) LAO consist of a single $c$-axis oriented growth plane. The $\omega$-rocking curves around the 200 peaks illustrate the fourfold symmetry of the $a$ domains [see Fig. 3(b) and 3(c)]. The reflections indicate the presence of [101] and [011] type 90° domain structures on the film (i.e., the $c/a/c/a$ polydomain structure), except for the 60-nm-thick film for which the $\omega$ rocking did not show any appreciable amount of $a$ domains. It can be observed that the angular separation between the terminal peaks of the 200 reflections is $\sim 4.1^\circ$. Therefore, the $a$ domains are tilted away from the (00$l$) planes of the substrate by $2.05^\circ$ in a fourfold symmetry which is lower than the theoretical value of $2.9^\circ$. It should be noted that, from Fig. 3(b), the 200 nm film does not reveal a 200 PZT peak, but when we follow the aforementioned method we were able to map around 20% $a$ domains.

Figure 4 shows that $c$-domain abundance measured this way decreases continuously to a value of 67% for the film 400-nm-thick film. Figure 4 also plots the $c$ lattice parameter of the PZT film as a function of film thickness. The lattice parameter changes from 0.416 nm for the 60 nm film to 0.413 nm for the 400 nm film. The lattice parameter for the
60 nm film indicates that the film is under high internal stresses. A comparison to 0.413 nm, the bulk PZT \( c \)-lattice parameter,\(^{14}\) indicates that the film is under very high in-plane compressive stresses. The 300- and 400-nm-thick films show a lattice parameter of 0.413 nm indicating almost full relaxation.

This is further confirmed from electron diffraction. Figure 5 plots the \( c/a \) ratio from electron diffraction as a function of ferroelectric film thickness. The \( c/a \) ratio calculated from the electron diffraction decreases from 1.08 for the 60 nm film to 1.051 for the 400 nm film. Figures 6 and 7 are the cross-sectional TEM images for 60- and 400-nm-thick films. These micrographs clearly show that the relative volume fraction of the 90° domains increases with film thickness. The measured fractions match reasonably well with the results obtained from XRD. The average twin period increases with increasing film thickness. Notice that 90° domains are present in as low as 60-nm-thick films, which could not be observed by XRD probably because of instrumental limitations. Further studies of thinner PZT films (~30 nm) show the absence of 90° domains. These results are to be published elsewhere.

It is evident that the contraction of \( c \)-lattice parameter is commensurate with the relaxation behavior of the film. In other words, it begins to decrease when the film relaxes via polydomain formation. This decrease in the \( c \) lattice parameter causes a decrease in the tetragonality of the ferroelectric layer. The decrease in tetragonality, as indicated by the electrical characterization, has a significant influence on the switching behavior.

**B. Electrical characterization**

For the electrical characterization we investigated primarily films in the 100–400 nm range. The properties do not change very much for films just below this range and we were limited by the equipment to achieve high fields for thicknesses higher than 400 nm. Figure 8 shows the polarization as a function of applied field for 100-, 200-, and 300-nm-thick films. It can be seen that at a field of just below 150 kV/cm the thicker films show a pulsed switched polarization, \( \Delta P \), of more than 80 \( \mu \)C/cm\(^2\). However, the 100 nm film shows negligible switching. But at higher applied fields the value of \( \Delta P \) for the 100 nm film rises sharply to a value nearly equal to the saturation value of 200- and 300-nm-thick films (it should be noted that \( \Delta P \approx 2P_s \), where \( P_s \) is the saturation polarization, since the hysteresis loops are almost square shaped). As we further increase the applied fields, the value of \( \Delta P \) for 100 nm films is the highest.

As the thickness of the PZT films increase, volume fraction of \( c \) domains, absolute value of \( \Delta P \), and the \( c \)-lattice parameter decrease. To isolate the effect of tetragonality and the domain fraction on \( \Delta P \), we have plotted in Fig. 9 a normalized \( \Delta P \) as a function of film thickness. The normalized polarization is defined as

\[
\Delta P_N = \frac{\Delta P_M}{\alpha_c},
\]

where \( \Delta P_M \) is the average switched polarization measured over different regions of the film. A comparison of Figs. 4, 8, and 9 shows that when the tetragonality of the lattice becomes constant, \( \Delta P_N \) does not change. This shows that the switching of 90° domains is not likely under the used electrical fields. At lower thicknesses, \( \Delta P_N \) increases indicating
that the increase is not purely an effect of 90° domain formation but an effect of strain as evidenced from higher \( c/a \) ratios. The 100 nm film shows a \( \Delta P_N \) close to 140 \( \mu \text{C/cm}^2 \) and then the polarization remains constant at \( \sim 125 \) \( \mu \text{C/cm}^2 \) after the initial rise.

The increase in the polarization of the 100-nm-thick film is due to high in-plane stresses which are not relaxed by 90° domain formation. To calculate the in-plane stress, \( \sigma \), the out-of-plane component of the strain in the PZT layer is given by

\[
e_{zz} = \frac{c_{1}^{PZT} - c_{0}^{PZT}}{c_{0}^{PZT}},
\]

where \( c_{1}^{PZT} = 0.416 \text{ nm} \) is the \( c \) lattice parameter from the \( \theta-2\theta \) scan, and \( c_{0}^{PZT} = 0.413 \text{ nm} \) is the bulk \( c \)-axis lattice parameter of PZT.\(^{14} \) Equation \( \sim 6 \) finds \( e_{zz} \) as \( -0.007 \) (tension). Therefore, for a film containing only \( c \) domains, the in-plane components of the strain can be found by noting that the normal stress in the \( 001 \) direction is zero. Then

\[
e = e_{xx} = e_{yy} = -\frac{C_{33}}{2C_{13}} e_{zz},
\]

where \( C_{ij} \) are the components of the tensor of elastic constants of the tetragonal film. Therefore, the in-plane stress can be determined by

\[
\sigma = \sigma_{xx} = \sigma_{yy} = \left( C_{11} + C_{12} - \frac{2C_{13}^{2}}{C_{33}} \right) e.
\]

Equation \( \sim 8 \) yields \( \sigma = 3.185 \times 10^9 \text{ N/m}^2 \) by using the elastic constants as cited by Kwak \textit{et al.}\(^{21} \) for PbTiO\(_3\) (\( C_{11} = 1.433 \times 10^{11} \text{ N/m}^2 \), \( C_{12} = 0.322 \times 10^{11} \text{ N/m}^2 \), \( C_{13} = 0.241 \times 10^{11} \text{ N/m}^2 \); and, \( C_{33} = 1.316 \times 10^{11} \text{ N/m}^2 \)). A thermodynamic analysis similar to the one carried out in Ref. 22 shows that the increase in the polarization is proportional to \( \sigma \)

\[
\delta P_S / P_S \approx (2Q_{12}/\kappa)\sigma,
\]

where \( Q_{12} \) is the electrostrictive coefficient and \( \kappa \) is the dielectric stiffness. Substituting \( Q_{12} = 2.5 \times 10^{-2} \text{ m}^4/\text{C}^2 \) and \( \kappa = 1.3 \times 10^9 \text{ m/F}^2 \) yields \( \sim 10\% \), consistent with the experimental observation.

We next investigated the activation field, \( E_a \), as function of film thickness. Figure 10 plots \( \ln(i_{\text{max}}) \) as function of \( 1/E \) where \( i_{\text{max}} \) is the switching current and \( E \) is the applied field. \( E_a \) was correlated to switching current \( i_{\text{max}} \) by Merz\(^{2,24} \) by the following relationship:

\[
i_{\text{max}} \propto \exp(-E_a / E).
\]

Therefore, the slope of \( \ln(i_{\text{max}}) \) vs \( 1/E \) plot gives the value of \( E_a \). There is a distinct increase in the slope as the thickness is decreased. This clearly indicates a decrease in activation field with increasing thickness.

Figure 11 shows the plot of \( E_a \), obtained from Fig. 10 as a function of thickness. It can be seen that \( E_a \) drops from 1090.9 kV/cm for the 100 nm film to 567 kV/cm for the 200 nm film and then remains more or less constant with thickness. This large drop in \( E_a \) is one of the most important

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![FIG. 7. Cross-sectional bright field TEM image of the 400-nm-thick PZT film. The \( a \)-domain fraction and period increase with PZT film thickness (compare with Fig. 6).](image)

![FIG. 8. Polarization as a function of applied field, \( E \), for 100-, 200-, and 300-nm-thick films.](image)
impacts of strain relaxation and domain formation on the electrical behavior of the film. Merz has correlated the wall
energies to the activation field and proposed that $E_a$ is proportional to the spontaneous strain to the power $n$, where $n$ is
a semi-empirical constant varying from 2 to 4.\textsuperscript{2,24} Hence, with decreasing strain we expect $E_a$ to decrease.\textsuperscript{2,24}
Fattuzo and Merz,\textsuperscript{25} Chynoweth,\textsuperscript{26} and Drougard and Landauer\textsuperscript{27} have investigated the thickness dependence of
single crystal BaTiO$_3$ and attribute a similar behavior to a “surface” layer at the ferroelectric electrode interface. Since $E_a$ is a measure of the impedance to switching, it can be concluded that the relaxed thicker films switch more easily than the thin strained films. This can also be seen in Fig. 8 where the thicker films reach the saturation polarization at much lower applied fields compared to the 100 nm film. Figure 11 also shows the coercive field, $E_c$, plotted as a function of thickness of the film. It shows a behavior very similar to $E_a$ where it drops from 225 to 90 kV/cm for an applied field of 333 kV/cm. In a subsequent article, we will present the interrelationship between tetragonality, 180° domain wall energy, activation field and the switching dynamics. Finally, the exact role of the 90° domains in the switching process, i.e., whether they facilitate the nucleation of
180° domain walls is yet to be understood. However, it is clear from Fig. 11 that the activation field is relatively independent of the volume fraction of 90° domains once the tetragonality of the lattice remains constant.

It is observed that activation field and coercive field show a trend strongly dictated by the change in tetragonality. The switched polarization follows the same dependence. An increase in tetragonality implies a larger displacement of the central Ti$^{4+}$ ion, and hence, larger switched polarization. The increase in tetragonality, a direct effect of the large in plane compressive stress in thinner films, causes higher activation fields. But once the film relaxes via domain formation the $c$-lattice parameter and the tetragonality tend to their bulk values. Consequently, the switched polarization and activation field tend to saturate towards lower values.

IV. CONCLUSION

We have investigated the effect of film thickness on structural and electrical properties of epitaxial lead zirconate titanate films. We have prepared the films by pulsed laser ablation and characterized the films using four-circle XRD, TEM, and pulsed switching measurements. A strong dependence of the domain structure of the film on the thickness of the ferroelectric layer has been shown. The fraction of $a$ domains increases as the film thickness of the ferroelectric film is increased. As the film thickness is increased, the tetragonality of the PZT film drops due to relaxation of internal stresses by polydomain formation. We also observe a large drop in activation field as the film relaxes via domain formation. We attribute the drop in switched polarization to the relaxation of internal stresses and to polydomain formation. These results illustrate that the microstructure of the ferroelectric thin film plays a significant role in the switching behavior.

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