Strain relaxation and critical temperature in epitaxial ferroelectric Pb(Zr_{0.20}Ti_{0.80})O_3 thin films

GARIGLIO, Stefano, et al.

Abstract

Strain relaxation and the ferroelectric critical temperature were investigated in a series of epitaxial Pb(Zr_{0.20}Ti_{0.80})O_3 thin films of different thicknesses grown on metallic 0.5% Nb-doped SrTiO3 substrates. Detailed x-ray diffraction studies reveal that strain relaxation progressively occurs via misfit dislocations as the film thickness is increased from fully coherent films (for films below 150 Å) to essentially relaxed films (for thicknesses above typically 800 Å). It is found that this change in the strain state does not modify the ferroelectric critical temperature which is found for all the samples to be around 680 degrees C, a value much higher than the bulk.

Reference

GARIGLIO, Stefano, et al. Strain relaxation and critical temperature in epitaxial ferroelectric Pb(Zr_{0.20}Ti_{0.80})O_3 thin films. Applied Physics Letters, 2007, vol. 90, no. 20, p. 202905

DOI: 10.1063/1.2740171
Strain relaxation and critical temperature in epitaxial ferroelectric Pb(Zr0.20Ti0.80)O3 thin films

S. Gariglio, a) N. Stucki, and J.-M. Triscone

DPMC, University of Geneva, 24 Quai E.-Ansermet, 1211 Geneva 4, Switzerland

G. Triscone

Ecole d’Ingénieurs de Genève (EIG/HES-SO), 4 rue de la Prairie, 1202 Geneva, Switzerland

(Received 13 February 2007; accepted 21 April 2007; published online 16 May 2007)

Strain relaxation and the ferroelectric critical temperature were investigated in a series of epitaxial Pb(Zr0.20Ti0.80)O3 thin films of different thicknesses grown on metallic 0.5% Nb-doped SrTiO3 substrates. Detailed x-ray diffraction studies reveal that strain relaxation progressively occurs via misfit dislocations as the film thickness is increased from fully coherent films (for films below 150 Å) to essentially relaxed films (for thicknesses above typically 800 Å). It is found that this change in the strain state does not modify the ferroelectric critical temperature which is found for all the samples to be around 680 °C, a value much higher than the bulk. © 2007 American Institute of Physics. [DOI: 10.1063/1.2740171]

The availability of high quality epitaxial ferroelectric oxide thin films and heterostructures allows some model systems to be designed and fundamental questions related to ferroelectricity to be revisited.1–9 These high quality materials may also find their way into advanced specific applications.10 The epitaxial growth not only provides samples and structures of single crystal quality but also allows some properties to be tuned and improved, for instance, by using strain engineering. In perovskite ferroelectrics, the effect of mechanical boundary conditions has been studied both theoretically and experimentally.5–8 Theoretically, it is shown that the strain induced by the two-dimensional clamping of a film renormalizes the second-order and the fourth-order polarization terms of the Gibbs energy expansion, leading to a modification of the paraelectric-ferroelectric phase transition temperature Tc (Refs. 5 and 6) and ferroelectric polarization, both effects having been experimentally observed. Dramatic examples of the role of strain include the induction of room temperature ferroelectricity in strained SiTiO3 thin films9 and a large enhancement of polarization and transition temperature in BaTiO3 films.8

In this letter, we have studied the effect of thickness reduction on the structural and physical properties of epitaxial Pb(Zr0.20Ti0.80)O3 (PZT 20/80) thin films in order to better understand the interplay between strain and ferroelectricity. Using x-ray diffraction, the crystallographic structure and the ferroelectric phase transition temperatures were studied in a series of ferroelectric PZT 20/80 thin films, grown onto metallic (001) 0.5% Nb-doped SiTiO3 (Nb-STO) substrates, with thicknesses ranging from 150 to 1230 Å.

The deposition of PZT 20/80 films was carried out by off-axis magnetron sputtering in 180 mTorr of an oxygen/argon mixture at a substrate temperature of 510 °C. These growth conditions lead to c-axis oriented PZT 20/80 films with a low surface rms roughness ranging from 4 Å for very thin films to 12 Å for thicker films, measured over 5×5 μm2. Detailed x-ray measurements were performed with a high-resolution Philips X’Pert diffractometer using a four-bounce asymmetric Ge(220) monochromator and Cu Kα1 radiation. The (001) and (103) PZT reflections were used to determine the lattice constants as the sample was heated between 25 and 900 °C in a domed hot stage in air.

In epitaxial films and heterostructures, the strain induced by the lattice mismatch between the film and the substrate can be accommodated up to a critical thickness hcr by an elastic deformation of the film lattice which adjusts perfectly to the substrate lattice parameter. Above hcr, the strain will be progressively relaxed by the formation of misfit dislocations at the film-substrate interface.11 At room temperature, PZT 20/80 is tetragonal (P4mm space group) with a=3.9525 Å and c=4.1484 Å.12 For c-axis oriented PZT 20/80 thin films grown on top of Nb-STO (cubic, a=3.905 Å) substrates, the in-plane lattice mismatch is −1.2%. At the growth temperature, PZT 20/80 is cubic and paraelectric with a lattice parameter of 4.017 Å: the lattice mismatch with Nb-STO substrate (a=3.925 Å at 510 °C) is −2.3% and using the Matthews-Blakeslee criteria,11 a critical thickness of 20 Å is

![FIG. 1.](image-url) (a) Room temperature thickness dependence of a (■) and c (▲) lattice parameters for PZT 20/80 thin films. The continuous lines are guides for the eyes, while the dashed lines are the bulk values. (b) Room temperature in-plane film-substrate separation vs inverse of the thickness. The line is a fit to the data for strain relaxation via misfit dislocations.

---

a)Electronic mail: stefano.gariglio@physics.unige.ch

DOI: 10.1063/1.2740171

0003-6951/2007/90(20)/202905/3/$23.00 90, 202905-1 © 2007 American Institute of Physics

Downloaded 18 May 2007 to 129.194.8.73. Redistribution subject to AIP license or copyright, see http://apl.aip.org/apl/copyright.jsp
estimated. By measuring the in-plane $a$ and out-of-plane $c$ lattice parameters for different thicknesses, we quantify the elastic deformation of the strained films and track the relaxation as a function of the film thickness. We extract $a$- and $c$-axis values from (00l) and (103) diffraction peaks and the thickness from the finite size fringes.

Figure 1(a) shows the evolution of the lattice parameters as a function of film thickness $h$. A 150 Å thick film is found to be pseudomorphic with the Nb-STO substrate as shown by the analysis of reciprocal space maps around the (103) peaks, which indicates that the PZT 20/80 in-plane lattice parameter reduces to that of Nb-STO [see Fig. 2(b)]. As a consequence, the $c$-axis parameter elongates. Increasing the thickness induces a progressive relaxation of the strain, as can be seen in Fig. 1(a), where the $a$ axis is found to increase and the $c$ axis to decrease with increasing film thickness, with lattice parameter values close to those of the bulk ferroelectric phase for thick films. In Fig. 1(b), we plot the in-plane lattice separation between the film and the substrate $(a_{PZT} − a_{STO})$ measured from the (103) peaks in reciprocal space maps. Assuming that misfit dislocations accommodate the strain, the density of misfit dislocations is expected to increase as $[1 − (h_c/h)]$. The misfit strain follows a thickness dependence identical to that of the dislocation density and thus the separation value varies as

\[ (a_{PZT}(h) − a_{STO}) = \left( a_{PZT}(\infty) − a_{STO} \right) \left[ 1 − \frac{(h_c/h)}{f(h_c)} \right] \]

where $(a_{PZT}(\infty) − a_{STO})$ is the in-plane lattice mismatch for fully relaxed films. A fit to the data (line in the graph) gives a critical thickness $h_c$ of 173 Å and $(a_{PZT}(\infty) − a_{STO})$ equals to 0.059 Å. Further evidence of the presence of misfit dislocations is found in omega scans around the (001) peak of the films. Analyses of the rocking curves clearly show that the reflection contains two components: a sharp peak and a broader diffuse scattering contribution which increases as the film thickness increases, as shown in Fig. 2(a). Very similar diffraction data have been observed in epitaxial thin films grown onto mismatched substrates (ErAs/GaAs, Nb/Al$_2$O$_3$, CeO$_2$/SrTiO$_3$) and have been related to the presence of misfit dislocations.

Even if a comprehensive theory that relates the microstructural properties and the x-ray diffraction spectrum is still missing, the coexistence of Bragg and diffuse scattering components can be explained by long-range order and correlation of short-scale disorder, respectively. In this picture, the sharp Bragg component arises from the crystallographic order of the regions of the film that are in registry with the substrate. In fact, the Bragg peak appears to be similar for the substrate and for all the films: the full widths at half maximum extracted for all the scans are identical with a value of 0.025°. We note that the intensity of the maxima of this Bragg component increases with the square of the thickness, as one would expect from the diffraction theory of perfect crystals. This thickness dependence of the intensity implies that the regions in registry with the substrate keep their structural coherence throughout the whole film thickness. These observations suggest that the misfit dislocations are vertical edge dislocations. The diffuse component is related to the disorder introduced by the dislocations and the intensity of the diffuse component correlates with the density of misfit dislocations. As can be seen in Fig. 2(a), the diffuse component is absent for the 150 Å thick film, appears for the 200 Å film, and becomes progressively more intense for thicker films.

Figure 3(a) shows the temperature evolution of the $c$ lattice parameter for a 400 Å thick film. The $c$ axis shrinks up to 680 °C and then starts to expand. The change in behavior is ascribed to the ferroelectric-paraelectric transition with an estimated $T_c$ of about 680 °C. In the same figure, the behavior of the $a$ axis is also shown. At room temperature,
the $a$ axis is about 3.96 Å. As the temperature increases, the $a$-axis value increases, following the expansion of the substrate as can be seen in Fig. 3(a), where the evolution of the substrate lattice parameter is also shown. This result suggests that the dislocation density which is introduced during the growth does not change when cycling the temperature. Note that in contrast to bulk where the transition corresponds to a change from a ferroelectric-tetragonal to a paraelectric-cubic structure, the data suggest that the transition corresponds to a change from a ferroelectric–non-central-symmetric–tetragonal to a paraelectric–central-symmetric–tetragonal structure, an effect due to the clamping to the substrate.

Such measurements of the evolution of the lattice parameters with temperature allow us to extract the transition temperature of each sample. The results are reported in Fig. 3(b). As can be seen, the transition temperature does not vary significantly with thickness: strained and relaxed films display a rather similar transition temperature. Because of the large strain–polarization coupling, the modification of the strain state should induce substantial changes in the $T_c$ of the films. Using the prediction of Pertsev et al.\textsuperscript{4} for PZT 20/80, we could expect a $T_c$ of 1000 °C for the thinnest films (misfit strain $S_m=-23\times10^{-3}$, following the definition in Ref. 5). As the film thickness is increased and the strain progressively released, the $T_c$ should approach the value of 680 °C for the thickest relaxed films ($S_m=-10\times10^{-3}$), a prediction in good agreement with the data. This value is higher than the bulk (460 °C) since the film, although relaxed, still presents a misfit strain $S_m$ of $-9\times10^{-3}$ when compared to the cubic paraelectric phase. These results also seem to suggest that at the growth temperature, it is energetically more favorable for the film to relax in a tetragonal ferroelectric state than in a cubic paraelectric state, which would require more dislocations. This results in a room temperature phase with increased $T_c$ and possibly explains the large critical thickness for misfit dislocations.\textsuperscript{18} This is good news for applications since it implies that thick relaxed films can have a critical temperature substantially higher than the bulk. Finally, as mentioned above, an intriguing result is the observation of a thickness independent critical temperature despite the increase in misfit strain as the films are getting thinner. Although there is no obvious candidate to explain this result, several effects could play a role. We note that the possible change in Zr content along the film growth direction as relaxation takes place, reported in Ref. 19, may lead to a change in stoichiometry as the film thickness is increased. Also, the finite thickness of the thinnest films used in this study may influence the ferroelectric properties.\textsuperscript{2,7} Finally, an effect due to inhomogeneous strain,\textsuperscript{20} for instance, due to oxygen vacancies and other local defects, cannot be excluded. Such effects would certainly complicate the picture and may explain why in PZT thin films, the correlation between $c/a$, the polarization, and $T_c$, used for PbTiO$_3$ in Ref. 2 and demonstrated in PbTiO$_3$/SrTiO$_3$ superlattices,\textsuperscript{3,21} does not seem to hold.

The authors thank N. Reyren, C. Lichtensteiger, and M. Dawber for useful discussions. This work was supported by the Swiss National Science Foundation through the National Center of Competence in Research “Materials with Novel Electronic Properties–MaNEP,” Division II, ESF (Thiox), and the EU STREP programs Macomufi and Nanoxide.