Broadening of X-ray reflections and inhomogeneous strain distribution in PbZrO$_3$/SrRuO$_3$/SrTiO$_3$ epitaxial heterostructures

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Abstract. Antiferroelectric thin film heterostructures are important in energy storage technology and have prospective applications in domain wall nanoelectronics. The improvement of functional properties of this kind of material is directly connected with the effect of epitaxial strain. Thus, the investigations of strain distribution in the antiferroelectric films volume are on demand. In this work we have studied the distribution of orientational domain states and the condition of near-interface layer in a set of PbZrO$_3$ films with different thickness grown on SrRuO$_3$/SrTiO$_3$ substrate. The analysis of X-ray diffraction curves shows that only the relatively narrow near-interface part of PbZrO$_3$ film experiences significant strain along the normal to the surface, which decays very quickly on moving away from the interface. The out-of-plane strain profiles are strongly similar in films of different thickness above d=50 nm. The inhomogeneous out-of-plane strain is surprisingly of compressive character, which we attribute to the effects of hydrostatic-like compression associated with the presence of edge dislocations. In the films of higher thickness, we observe unusual broadening of the Bragg reflections, which is also tentatively associated with relaxation through the formation of dislocations.

1. Introduction

Thin film perovskite oxides are of great importance in technology and attract intense scientific interest [1, 2]. One of the most important types of such oxides are ferroelectric and antiferroelectric crystals. These two types of crystals share the common property of having structural phase transitions resulting in particular groups of ions becoming off-centered with respect to their ideal positions in cubic perovskite structure. In ferroelectrics these off-centerings are arranged homogeneously throughout the crystal, resulting in homogeneous polarization. In antiferroelectrics the ordering of ionic shifts is anti-polar, which results in zero net polarization. However, by applying external electric field, the anti-polar pattern of displacements can be transformed to polar order, which offers unique opportunities in energy storage applications [3]. Antiferroelectric single crystals have been widely studied using x-ray diffraction [4-7]. In thin film form, the energy balance between polar and anti-polar ordering in antiferroelectrics is predicted to be tunable for attaining better practical characteristics, which stimulates enhanced attention particularly to the thin film antiferroelectrics [8, 9].
Another difference between thin films of practically important ferroelectric and antiferroelectric stems from the fact that the latter tend to have much larger lattice parameter mismatch between film and commonly used substrates. The most widely used substrate is SrTiO$_3$, which has lattice constant of 3.905 Å, while the most promising antiferroelectric material, PbZrO$_3$, has pseudocubic lattice constant of 4.16 Å. The lattice mismatch amounts to 5.5 %, which leads to intense lattice relaxation via formation of dislocations near the interface. This makes the physical picture of epitaxial PbZrO$_3$ on SrTiO$_3$ heterostructures highly complicated from the structural point of view. Moreover, the phase transitions in such structures have been shown to differ dramatically from the ones in bulk PbZrO$_3$ [10]. Building of a consistent thermodynamical model of such complex behavior appears highly difficult and better structural assessment of these structures appear essential for moving this field forward.

Here we report on the study of PbZrO$_3$/SrRuO$_3$/SrTiO$_3$ epitaxial heterostructures with different values of thickness of PbZrO$_3$ layer, ranging from 50 nm to 200 nm. By using the x-ray reciprocal space mapping we showed that these films demonstrate selective appearance of particular orientational domain states, namely – only those orientational states appear, in which the shifts of Pb ions are non-parallel to the substrate-film interface. Ruling out the possibility of other domain orientations enables us to analyze precisely the state of the out-of-plane strain distribution by means of high-resolution diffraction measurements. We show that the near-interface layer is strained compressively in the out-of-plane direction, which is in disagreement with the predictions of basic elasticity theory, but which appears logical and consistent with the specifics of the strain fields created by edge dislocations that are inevitably present due to the large lattice mismatch. Additional signature of substantial density of such dislocations is observed by us in the unusual broadening of the diffraction peaks in comparison with the theoretical model.

2. Experimental
PbZrO$_3$ thin film samples were grown using pulsed laser deposition technique at the University of California, Berkeley on the SrTiO$_3$ substrate with SrRuO$_3$ bottom electrode as buffer layer. The SrRuO$_3$ was grown at a heater temperature of 680 °C in a dynamic oxygen pressure of 100 mTorr and with a laser fluence and repetition rate of 1.0 J/cm$^2$ and 5 Hz, respectively. For the PbZrO$_3$ films, growth was completed at a heater temperature of 630 °C in a dynamic oxygen pressure of 80 mTorr and with a laser fluence and repetition rate of 1.8 J/cm$^2$ and 5 Hz, respectively. The thicknesses of the studied films were 50, 100 and 200 nm. The thickness of the SrRuO$_3$ layer was 20 nm. The pseudocubic main axes of the films were coincident with the ones of the substrate, normal to which was oriented along the [001] direction.

Oriental domain states were studied using SuperNova single-crystal XRD system using CuK$_\alpha$ ($\lambda = 0.154$ nm) source at Peter the Great Polytechnic University. Reciprocal space mapping has been done using Crysals Pro software. The strain distribution along the film normal was analyzed on the basis of $\theta - 2\theta$ scans obtained with Panalytical X’Pert 3 MRD system (University of California, Berkeley, USA). The measurements were performed using CuK$_\alpha$ ($\lambda = 0.154$ nm).

3. Results
Reciprocal space maps of heterostructures allow identifying the distribution of AFE orientational domain states in the film and identify the presence of additional superstructure reflections that are not present in bulk PbZrO$_3$.

Two-dimensional intensity distribution is shown in figure 1 for reciprocal lattice planes ($H 0 L$) and ($H K 2$) for 50 and 200 nm PbZrO$_3$ films. Qualitatively the diffraction patterns are almost same for these films. At the planes ($H 0 L$) one sees the presence of two superstructure reflection types at the $\Sigma$ and $M$ points in pseudocubic Brillouin zone, which correspond to coordinates of the form ($H+1/4$, $K+1/4$, $L$) and ($H+1/2$, $K+1/2$, $L$), respectively. These superstructure reflections are typical for this material in the bulk form. At the planes of the form ($0 0 L$) the $\Sigma$ and $M$ superstructures are absent. This indicates the absence or negligible amount of AFE domains with in-plane modulation
wavevectors (domains with axis \( c \) of the AFE unit cell [11] pointing along the normal to the film, referred to as \( c \)-domains hereafter). In addition to the reflections characteristic to bulk \( \text{PbZrO}_3 \), we note very weak reflections at \( X \) points with coordinates of the form \((H+1/2, K, L)\) in the 200 nm film. Tentatively, they should be attributed to additional cell doubling due to the presence of defects. This kind of superstructure reflections is observed for the first time in \( \text{PbZrO}_3 \) films.

The absence of \( c \)-domains allows a straightforward analysis of the high-precision diffraction profiles with wavevector transfer parallel to the film normal: due to the absence of \( c \)-domains the corresponding profiles do not contain splitting of Bragg reflections due to the differences in pseudocubic lattice parameters along \( c \) and along \( a \) and \( b \) axes of AFE structure. In order to obtain the information on the state of near-interface layer we have analysed the diffraction profiles corresponding to wavevector transfer along the normal to the film. Figure 2 shows the XRD profiles obtained in \( \theta-2\theta \) mode, which includes the \((0 0 2)\) peaks corresponding to the film \((2\theta \approx 43.5^\circ)\) and to the substrate \((2\theta \approx 46.5^\circ)\). These profiles correspond to the three different thicknesses of \( \text{PbZrO}_3 \) layer: 50, 100 and 200 nm. The characteristic oscillations around the main peak of each film occur from the interference between X-rays reflected from the surface of the film and the interface between film and substrate. The period of these oscillations is inversely proportional to the film thickness. It is consistent well with the nominal values listed earlier.

\[
(H 0 L) \quad 50 \text{ nm} \quad (H K 2) \quad 50 \text{ nm}
\]

\[
(H 0 L) \quad 200 \text{ nm} \quad (H K 2) \quad 200 \text{ nm}
\]

**Figure 1.** Two-dimensional reconstructions of the intensity distribution in reciprocal lattice planes \((H 0 L)\) and \((H K 2)\) for 50 and 200 nm \( \text{PbZrO}_3 \) films. The inset of the right bottom image depicts the one dimensional profile through \( X \) point.

The main feature associated to the peak of each film is the high asymmetry in shape. One can see that the oscillating intensity on the right of the main peak is about an order of magnitude stronger than it is on the left. Such asymmetry on XRD profile is typical for epitaxial layers and is commonly attributed to the inhomogeneous strain in the film volume [12]. Modelling the inhomogeneously
strained films has been described in a number of studies [12,13]. Within the kinematical scattering theory, the amplitude of the scattered wave distributed along surface normal is given by the equation [12]

\[ E(q_z) = \int_0^\infty (F(z) \exp[-ihu(z)]) \exp(-iq_z z) \, dz \]  

(1)

Here \( h \) – reciprocal lattice point and \( u(z) \) – shift of the elementary unit cell as a whole at the height \( z \). The intensity of X-ray scattering equals the square of (1)

\[ I(q, t) = |F \int_0^\infty \Omega(z, t) \exp[-ihu(z)] \exp(-iq_z dz)|^2 \]  

(2)

\( \Omega(z, t) \) is the shape factor of the layer. In the simplest case of a flat film with sharp surface and interface and thickness \( t \), \( \Omega(z, t) = 1 \) if \( z \in [0, t] \); otherwise, \( \Omega(z, t) = 0 \). The vertical strain profile follows from \( \varepsilon_{zz} = \frac{\partial u(z)}{\partial z} \).

Figure 2. XRD profiles of the heterostructures with different thickness of PbZrO\(_3\) layer. The left peaks correspond to the \( (0 \ 0 \ 2) \) reflection from the film and the right ones to the reflection from the substrate with same indexes.

In our previous work, we have shown that using equation (2) with exponential law of \( u(z) \) allows to reproduce the XRD profile shape of PbZrO\(_3\) films with 50 nm thickness [14]. It was also established that the penetration depth of strain into the film does not exceed 15-20 nm. In the present study, aiming to improve the accuracy of strain profile determination, we used cubic B-spline functions to model vertical strain profile. This approach was adopted from the Ref. [13]. However, unlike the Ref. [13], we model only the near-interface area of the film instead of whole thickness. This is reasonable as we showed that the strain changes predominantly in this region. Reducing the modeling area, we can use fewer fitting parameters and thus, reach the better convergence of minimization algorithm.

Given a set of knots \( x_i \ (i = 1, 2 \ldots N) \), a spline function of degree \( m \), \( S_m(x) \), is such that \( S_m(x) \) is a polynomial of degree \( m \) in each \( \{x_i, x_{i+1}\} \) interval, and \( m - 1 \) continuous derivatives over the whole \( x \) range. In the B-spline representation, any spline function can be written

\[ S_m(x) = \sum_{i=1}^N w_i B_{i,m}(x) \]  

(3)
where \( w_i \) is the weight of the \( i \)-th B-spline of degree \( m \), \( B_{lm}(x) \). Any spline function is therefore entirely determined by a set of \( N \) discrete weights. We have used 4 knots to describe the strain profile. A Levenberg–Marquardt minimization algorithm was used to refine the weights of spline function and thickness of the film. The result of fit with B-spline function presented in figure 3. One can see that the model reproduces reasonably well the higher-angle part of experimental profiles. Slight inconsistency on left side can be tentatively explained by the neglecting the possible inhomogenously strained surface layer. In case of 200 nm film, the measured profile is noticeably wider than the modeled one. The difference in the full-width-at-half-maximum is about 0.007 \( \text{Å}^{-1} \), which amounts to 50 percent of the experimental width. Such effect cannot be caused by the influence of the resolution function, because the latter is very narrow (accuracy about 0.001 \( \text{Å}^{-1} \)) and allows seeing much finer oscillations on the shoulders. One can also exclude the broadening due to presence of \( c \)-domains, as we showed that they are absent in that film (figure 1). On the one hand, broadening of Bragg reflection in epitaxial films can originate from one-dimension or two-dimension defects, such as dislocations \([15]\). On the other hand, a possible explanation could be the presence of ferroelectric domains coexisting with AFE phase \([16]\). Such domains could also influence the peak shape due to the difference in the lattice constant as compared to the one of AFE structure. In principle, the broadening could be related to both of these two effects. In general, despite the simplifications of our approach, it can be seen that the derived profiles stay very close to the XRD profiles.

\[ \frac{\partial u(z)}{\partial z} \]

**Figure 3.** X-ray diffraction patterns in \( \theta-2\theta \) geometry: (a) 50 nm, (b) 100 nm, (c) 200 nm. Black dots correspond to the experimental data and brown dashed lines correspond to the fitted profiles. The origin of the wave vector axis is chosen to correspond to the scattering maximum.

The strain profiles recalculated on the basis of fit parameters as \( \frac{\partial u(z)}{\partial z} \) are shown in figure 4. The strain magnitudes are notably large in the direct vicinity of the interface. of the value at the interface of about 4.5 percent is comparable to the value of the lattice mismatch between \( \text{PbZrO}_3 \) and \( \text{SrRuO}_3 \) amounting to about 5.5 percent. All of the strain profiles are almost equivalent. Therefore, we can conclude that the thickness of film affects remarkably weakly the strain distribution near the interface for the present range of thicknesses. For thinner films we should expect more pronounced modification of strain profile on changing the thickness. Another interesting question arises on the sign of the strain, which is negative, meaning that the \( \text{PbZrO}_3 \) lattice is compressed along the normal to the film. Interestingly, this unusual diffraction result is consistent with the observation of Ref. \([17]\),
obtained by microscopy. The contradiction is in the fact, that as long as the in-plane strain is expected to be compressive (PbZrO₃ has larger lattice spacing), the simple elasticity theory would predict the out-of-plane strain to be tensile according to the relation \( \varepsilon_{\perp} = -2 \frac{c_{12}}{c_{11}} \varepsilon_{\parallel} \), where \( c_{12} \) and \( c_{11} \) are the elastic constants of the layer [12]. On the other hand, we can expect that this situation can be reversed due to the presence of the near-interface dislocations that are going to inevitably accommodate the very large lattice parameter mismatch. In fact, such dislocations were observed in PbZrO₃/SrRuO₃/SrTiO₃ heterostructures by HRTEM [17], where the Burgers vectors were found pointing along [1 1 0] pseudocubic directions. We suggest that the observed near-interface compressive strain in both the in-plane and out-of-plane directions can be envisaged from the fact that the edge dislocations are expected to induce hydrostatic-like compression on the side of the “excess” half-plane [18], which in the case of the present heterostructure should be, and has been observed [17] on the side of the substrate.

4. Summary

The near-interface layer in PbZrO₃ films appears to be one of the key factors in modifying the phase structural state and phase transitions in these objects. By studying the films of different thicknesses we have established that only the small near-interface part of PbZrO₃ film experiences significant strain along the normal to the surface, which decays very quickly on moving away from the interface. The vertical strain profiles are very similar in films of different thickness in the range between 50 and 200 nm. The out-of-plane inhomogeneous strain is surprisingly of compressive character, which we attribute to the effects of hydrostatic-like compression associated with the presence of edge dislocations. Also, these dislocations are likely to result in the unusual reflection broadening observed in our x-ray study. Our results can be useful for engineering thin film heterostructures for energy storage applications.

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