Effect of a Single Dislocation in a Heterostructure Layer on the Local Polarization of a Ferroelectric Layer

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We study, on an atomic scale, the influence of a single dislocation in a $SrTiO_3$ sublayer on the local ferroelectric polarization of the neighboring ferroelectric $PbZr_{0.2}Ti_{0.8}O_3$ (PZT) sublayer in an epitaxial $SrTiO_3/PbZr_{0.2}Ti_{0.8}O_3/SrTiO_3$ three-layer heterostructure. The strain field of the dislocation in the $SrTiO_3$ layer propagates across the interface into the PZT layer and leads to a strong variation of the c-lattice parameter of the PZT layer. Accompanying a strong reduction of the c-lattice parameter, the off-center displacements of the Zr/Ti atoms away from the center of the oxygen octahedra are also strongly decreased, resulting in a decrease of the local spontaneous polarization by up to 48%.

Owing to their excellent properties, perovskite ferroelectrics have become important materials in electronics applications [1–3]. In more complex systems like perovskite ferroelectric-paraelectric superlattices or tricolor superlattices intriguing properties and effects arise due to the combination of materials with similar structure [4,5]. Adjusting the composition/periodicity in these superlattices allows for an additional degree of freedom and results in the possibility to tune the final properties. As has recently been shown [6], a classical ferroelectric-paraelectric system, such as $PbTiO_3/SrTiO_3$ can, under certain conditions, behave like an improper ferroelectric only due to a ferroelectric/antiferrodistortive coupling at the interface between the two materials. In experimental and theoretical analysis of these effects one usually assumes that one is dealing with perfect materials. Oxides and, in particular, ferroelectric perovskite oxides are, however, far from being perfect materials. When the characteristic sizes of the investigated systems are scaling down to nanometer sizes even a single lattice defect can be very detrimental to ferroelectric properties. An example is the case of dislocations that are not avoidable in most crystalline materials. In the surrounding area a dislocation produces strain which depends on the Burgers vector of the dislocation and the location with respect to the dislocation core [7].

The effect of dislocation strain fields on the local ferroelectric polarization has been investigated theoretically [8,9] in ferroelectric $PbZr_{1-x}Ti_xO_3$. It was demonstrated that the coupling between the strain field of the dislocation and the polarization results in high local polarization gradients, leading to strong depolarization fields within a distance of about 10 nm from the dislocation core. In experiment, a high density of threading dislocations occurring in epitaxial $PbZr_{0.2}Ti_{0.8}O_3$ films has been reported to affect the ferroelectric switching properties [10]. A study on epitaxial $PbZr_{0.52}Ti_{0.48}O_3$ nanoislands on Nb-doped $SrTiO_3$ substrate has related a poor piezoresponse to the

strain field resulting from interfacial dislocations [11]. A study on the role of misfit dislocations in destabilizing the polar state was reported in epitaxial ferroelectric thin films [12]. However, a genuine measurement of polarization change in a dislocation field has so far not been carried out. The atomic-resolution study of the behavior of a unit cell dipole near a dislocation requires direct imaging or determining the atomic structure at subangstrom accuracy [13,14].

Here we employ the negative C_S imaging (NCSI) technique [15] to study the change of the local polarization in a ferroelectric $PbZr_{0.2}Ti_{0.8}O_3$ (PZT) layer due to the presence of a single dislocation in the neighboring dielectric $SrTiO_3$ (STO) layer, in a model sample consisting of three epitaxial layers of STO/PZT/STO, all prepared by pulsed laser deposition on a STO (100) substrate [16].

Figure 1(a) shows an image of an interface area between the bottom STO layer and the c axis oriented, tetragonal PZT layer at a low magnification. The image is recorded with electron beam parallel to the [110] direction of both compounds under the NCSI conditions. The interface is marked by a dotted line. A dislocation is denoted in the lower-left part of the STO layer by a symbol "⊥". A Burgers circuit surrounding the dislocation core leads to a closure failure with a projected displacement vector $a[\frac{1}{2}\,\bar{\frac{1}{2}}\,\bar{1}]$ along the [110] direction. Since no other defects are found to accompany the dislocation, the real Burgers vector must include a component along the viewing direction. This consideration leads to the possible Burger vector either $a[011]$ or $a[\bar{1}01]$. In the core area of the dislocation the image contrast is smeared out due to a short-distance dissociation of the dislocation and strong lattice distortion. Above the dislocation core the (001) planes bend upward as shown by a curved open arrow. The upward bending of the lattice plane is seen to propagate through the interface into the PZT film area, resulting in a compressive stress along the c axis of the PZT film. This bending gets weaker
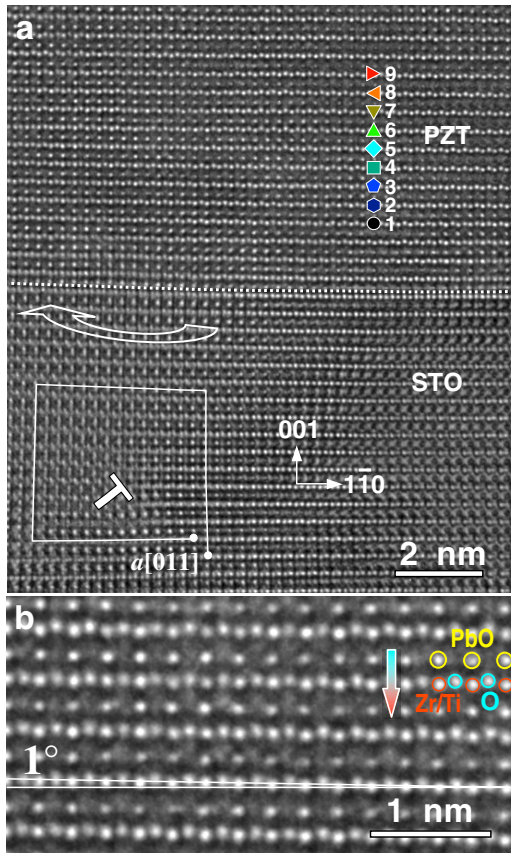
FIG. 1 (color online).   (a) Atomic-resolution [110] image of
part of a STO/PZT/STO heterostructure including a dislocation
denoted by "⊥", recorded under NCSI conditions. The interface
between the bottom STO and PZT layers is marked by a dotted
line. The curved arrow shows the strong upward bending of the
(001) planes. The numbered symbols mark the (001) $(Zr/Ti)O_2$
planes for quantitative analysis. (b) A magnification of an area
directly above the interface in (a). The columns of PbO, Zr/Ti
and O are denoted. The relative displacements between posi-
tively charged cations (Pb, Zr/Ti) and negatively charged anion
(O) result in an electric dipole in the unit cell and define the
spontaneous polarization vector as show by an arrow. Two lines
trace the lattice bending from left to the right of the image, which
amounts to about one degree.

as going from the left to the right, i.e., as going from the
area right above the core to the area far from the core.
Figure 1(b) shows a magnification of a PZT film area above
the interface. In the NCSI image the atoms appear bright on
a dark background. The PbO, Zr/Ti, and O columns are
marked by circles. The shifts of the oxygen atoms are
evidently directed upward, resulting in an upward shift of
the negative charge center in the unit cell. As a conse-
quence, the polarization in this area points downward, from
the net negative charge to the net positive charge in the unit
cell.

Various properties related to the bending of the lattice
planes in the PZT layer are studied by quantitatively map-
ping the image in the area from the left edge (zero position)
to the place marked by a group of circles where the lattice

bending is seen to vanish in Fig. 1(a). In order to minimize
the effects of the contrast noise, before mapping the image
is filtered in such a way that the quantitative results should
not be affected [13]. In image mapping the positions of the
bright dots, which correspond to the atom columns, are
determined using a least square fit by two-dimensional
Gaussian profiles to each of the individual atomic intensity
profiles [17]. All of the measurements are based on the
positions of the intensity maxima corresponding to the
oxygen and the Zr/Ti columns. The upward bending of
lattice planes is first investigated by checking the relative
vertical position of the individual unit cells. The relative
positions are presented by the relative vertical shifts $\Delta_j(d_i)$
of individual Zr/Ti columns in a given (001) $(Zr/Ti)O_2$
plane j ($j = 1$–9, marked by a group of symbols). In a
given j plane the values of $\Delta_j(d_i)$ are defined by $\Delta_j(d_i) =
Z_j(d_i) - Z_j(\infty)$, where $Z_j(d_i)$ is the vertical coordinate of
the Zr/Ti column No. i at a distance d_i from the left edge of
the image in Fig. 1(a) and $Z_j(\infty)$ is the mean of the vertical
coordinates of the Zr/Ti columns at the area of the symbol
group. Figure 2 displays the values of $\Delta_j(d_i)$ as a function
of the distance d_i. It is evident that the shifts of the Zr/Ti
columns in planes $j = 1$–6 decrease when the columns are
going from left to the right and reach essentially zero in the
area relatively far from the dislocation core (near the
position of the symbol group).

Based on the coordinates of the Zr/Ti columns the
c-lattice parameter for individual unit cells is calculated
and calibrated referring to the lattice constant ($a =
0.3905$ nm) of $SrTiO_3$. We note that depolarization fields
can be significant in a ferroelectric thin film on an insulat-
ing substrate [18,19]. The presence of a depolarization
field may result in rather complex polarization patterns
near the interface. These may imply vertical and lateral
gradients, especially when 180° stripe domains are pres-
ent. As a consequence, the local spontaneous polarization
and the c-lattice parameter of the unit cells can be changed
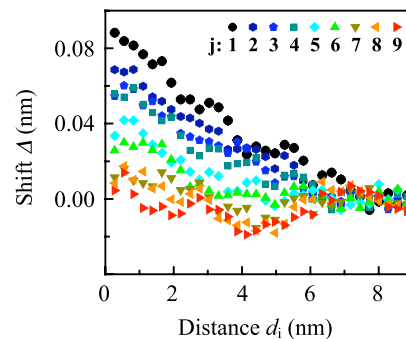[14,20]. In our specific case the mapped area is far from

FIG. 2 (color online).   Lattice plane bending in the PZT layer
as a function of the distance from the left edge of the image in
Fig. 1(a). The bending is represented by the vertical shifts Δ of
the Zr/Ti columns in a given (001) $(Zr/Ti)O_2$ plane ($j = 1$–9)
with respect to the Zr/Ti columns in the perfect area at the
position of the symbol group in Fig. 1(a).

domain walls. In the studied area no 180° stripe domains and other complex polarization patterns are found employing the NCSI imaging technique which allows any lateral or vertical polarization gradients to be directly visualized [13]. Therefore, the effect of lateral gradient can be neglected. In addition, inhomogeneous strain can exist in a film due to the lattice mismatch between STO and PZT, which depends on the location with respect to the interfaces [21]. Such effects of the vertical gradient on the studied parameters can be mitigated by averaging the values of the measured parameters along the normal of the interface, concentrating on the effect of the dislocation. This results in the observation of the dependence of the c-lattice parameter as a function of the lateral distance from the left edge of the image, i.e., from the area near the dislocation core. The mean values of the c-lattice parameters are calculated by averaging over 6 unit cells along the [001] direction. Figure 3(a) displays the c-lattice parameter as a function of the distance from the left edge. A continuous increase of the c value is evident from about 0.405 nm at the left edge of the image to about 0.416 nm representing the value in the perfect film matrix at the position of the circle group. At the area right above the dislocation core the value of the lattice parameter c is reduced by about 3%.

Accompanying the reduction in c-lattice parameter, the reduction of the vertical spacing $\delta_{O\text{-}Zr/Ti}$ between the oxygen columns and the neighboring Zr/Ti columns is also measured. Figure 3(b) displays the vertical spacing $\delta_{O\text{-}Zr/Ti}$ as a function of the distance from the left edge of image in Fig. 1(a). In the perfect area at the position of the circle group the value of the spacing is about 0.0296 nm while in the area right above the dislocation core near the left edge of the image the minimum value is about 0.0166 nm. The maximum reduction of the vertical spacing is about 44% in the mapped area. Since the spontaneous polarization P_S arises from the electric dipole which forms by the relative displacements of ions in the unit cells, the dependence of the O-Zr/Ti spacing on the distance from the dislocation shows also evidence for the dependence of the local polarization.

The spontaneous polarization can be derived from c-lattice parameters based on Landau-Ginzburg-Devonshire theory by the formula [14]

$$P = \left(\frac{x_3 - 2s_{12}x_m/(s_{11} + s_{12})}{Q_{11} - 2s_{12}Q_{12}/(s_{11} + s_{12})} \right)^{1/2}, \quad (1)$$

where x_3 and x_m are the spontaneous strains defined by $x_3 = (c - a_p)/a_p$ and $x_m = (a - a_p)/a_p$ (a_p is the lattice parameter of the paraelectric cubic phase extrapolated to room temperature), and s_{ij} and Q_{ij} are elastic compliances and electrostrictive coefficients, respectively. The c values are the measured values shown in Fig. 3(a) and the a value is the lattice parameter of the STO substrate. The values of a_P, s_{ij}, and Q_{ij} for PZT are adopted from Refs. [22–24]. The calculated result is presented by the circles in Fig. 3(c).
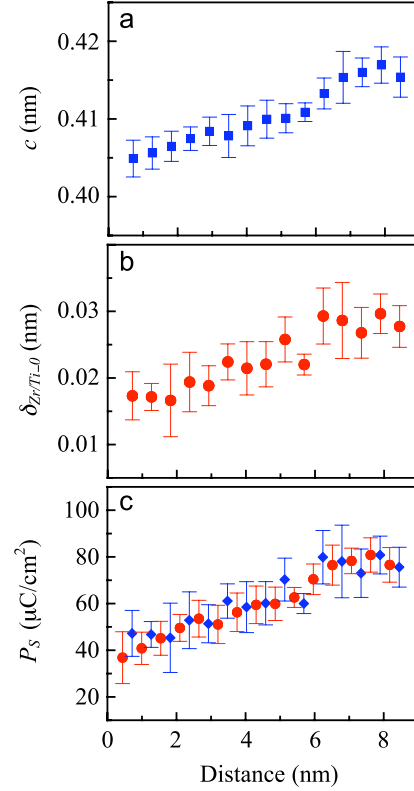

FIG. 3 (color online). c-lattice parameter (a), vertical spacing $\delta_{O\text{-}Zr/Ti}$ between O and Zr/Ti columns (b) and spontaneous polarization (c) of the PZT layer as a function of the distance from the left edge of the image in Fig. 1(a). In (c) circles display the result calculated from relation (1) and diamonds from (3). The error bars represent the mean error with a confidence level of 95%.

The local spontaneous polarization P_S can also be calculated based on the off-center displacement of atoms in the unit cell by the relation [14]:

$$P_S = 1/\nu \sum Z_i \Delta_i, \quad (2)$$

where ν, Δ_i, and Z_i are the volume of the unit cell, the off-center displacement of atom i, and the effective charge of atom i, respectively. We note that we are directly measuring the spacing between the oxygen column and the Zr/Ti column. The spacing represents the displacement of the Zr/Ti column from the center of the oxygen octahedron if we neglect the small distortion of the oxygen octahedron. Based on the data in hand [Fig. 3(b)] the local spontaneous polarization P_S is roughly estimated using a linear relation [25]:

$$P_S = \kappa \delta_{Zr/Ti}, \quad (3)$$

where κ is a constant and $\delta_{Zr/Ti}$ is the displacement of the Zr/Ti column from the center of the oxygen octahedron. In calculation of P_S a value of κ of $2726 (\mu C/cm^2)$ nm^{-1} [20] is used. Based on the data of atom displacements in the same film system published in [13], a test to evaluate the

deviation of the P_S values calculated using relation (3) from those calculated from relation (2) leads to the absolute values <10 $\mu C/cm^2$ of the deviation. For comparison, the polarization calculated from (3) is presented by diamonds in Fig. 3(c). The result calculated from (3) agrees well with that from (1). An increase of the local polarization is evidently with the distance from the dislocation core. Considering the mean values of the results from (1) and (3), the value of P_S is about 80 $\mu C/cm^2$ in the area far from the dislocation core. In the area directly above the dislocation core the value of P_S is about 42 $\mu C/cm^2$, 52% of the value in the defect-free area.

Figure 3 provides evidence for the effect of the dislocation on the local properties of the PZT layer. In addition, we estimate the possible errors created by residual lens aberrations, local change of sample thickness, and small (unavoidable) tilts away from the fully symmetric Laue orientation. This is achieved by carrying out an iterative procedure in which the experimental image is compared with images calculated on a computer following the established procedures [13,26]. The estimation shows that the errors are less than ± 0.002 nm for the vertical spacing between the oxygen and Zr/Ti columns, much smaller than the mean error bars (about ± 0.005 nm) shown in Fig. 3(b).

In the ideal case of a dislocation located at the center of a perfect lattice matrix, the strain distribution is expected to be symmetric with respect to the extra half plane. In the reality of the TEM specimen, this symmetric feature is broken by the off-central location of the dislocation, the inhomogeneity of the specimen thickness, and difference in mechanical properties of the heterostructure layers. Therefore, the measured various properties in real specimens may deviate from those expected for the ideal case. Nevertheless, the asymmetry of real specimens does not principally influence the result obtained on the effect of a single dislocation, though distant from the ferroelectric layer, onto the local polarization of the latter. In addition to the effect of strain, we note that a possible charge of the dislocation core can be induced by local chemical deviations from the ideal stoichiometry. A deficiency of oxygen can, e.g., result in a positive charge of the dislocation core [27,28]. The positive charges at the dislocation site create a depolarization field with respect to the polarization domain in the affected region of the PZT layer. The observed strong bending of the STO lattice planes at the interface, which is not expected to be affected by the electric field, shows that the lattice strain propagates into the neighboring PZT layer and thus plays a major role in depressing the spontaneous polarization. A recent study showed that a strain gradient can induce a polarization in a STO crystal [29]. A local polarization of about 1–10 $\mu C/cm^2$ was estimated around a dislocation in STO at room temperature. The flexoelectric polarization induced by the strain field of the dislocation may also produce a depolarization field with respect to the polarization domain of the PZT layer.

Our experimental study shows, on atomic scale, the behavior of unit cell dipoles of ferroelectric PZT in the field of a dislocation. In a region of the PZT layer about 8 nm away from the dislocation core a strong reduction of the c-lattice parameter is measured. A corresponding strong reduction of the off-center displacements of the Zr/Ti atoms reflects the strain-polarization coupling of the ferroelectric material. This study demonstrates that a single lattice defect, such as a dislocation, even though it is located well outside the ferroelectric material, can have a detrimental effect on the properties of the ferroelectric layer.

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