Observation of [110] surface band within {101} *a*-domain of heteroepitaxial $PbTiO_3$ thin film fabricated by hydrothermal epitaxy

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Heteroepitaxial $PbTiO_3$ film on an Nb-doped (001) cubic $SrTiO_3$ substrate was fabricated by hydrothermal epitaxy at 200 °C. Piezoresponse force microscopy and x-ray Θ rocking curves confirmed that the film showed a *c*/*a*/*c*/*a* multi-domain structure even though it did not undergo a cubic paraelectric (PE) to tetragonal ferroelectric (FE) phase transition. After heat treatment of this film at 600 °C, we observed the [110] surface band within the *a*-domain, which was formed through the PE to FE phase transition. We also found that a [110] surface band existed along the $(1\bar{1}1)$ plane within the *a*-domain. We predicted that the [110] surface band would be monoclinic phase due to the interaction of two different variants of *a*-domains in the presence of a *c*-domain in the heteroepitaxial $PbTiO_3$ film. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2171489]

Heteroepitaxial perovskite ferroelectric films ($PbTiO_3$ and $PbZr_{1-x}Ti_xO_3$) on a cubic single crystal oxide substrate undergo a phase transition from a high symmetric cubic paraelectric (PE) phase to a low symmetric tetragonal ferroelectric (FE) during cooling from the growth temperature.[1,2] The bulk strain due to the phase transition can be relaxed by domain formation, as suggested by Roitburd.[3] The relaxation mechanism for heteroepitaxial tetragonal films on a cubic oxide substrate has been examined in the literature.[1,2,4,5] The typical structure is a *c*/*a*/*c*/*a* multi-domain pattern, which consists of alternating *c*-domains with the tetragonal axis normal to the film/substrate interface, and a *a*-domain (90° domains) with the *c* axis of the tetragonal film along either [100] or [010] directions of the interface. The formation of the *a*-domain is related to four coherent {101} twins, because the tetragonal ferroelectric has fourfold rotational symmetry on the *c* axis and the {101} planes become the *c*/*a* domain boundary (i.e., 90° domain wall). The *c* axis of the *a*-domain and that of the *c*-domain are not at right angles to each other, and theoretically the tilt angle is determined by $\omega = 2\tan^{-1}(c/a) - 90$.[6] In the case of a heteroepitaxial $PbTiO_3$ film [$(c/a) = 1.061$],[12] the tilt angle is 3.39°. Experimentally, the tilted angle can be determined from x-ray Θ rocking curves,[1,7] the topography of atomic force microscopy (AFM),[6,8] and a cross-sectional view attained via high-resolution transmission electron microscopy (HRTEM).[9] Four {101} variants of the *a*-domains exist with a crossed stripe along the [100] and [010] directions on the (001) tetragonal film surface. This surface *a*-domain structure has been observed with a piezoresponse force microscope (PFM).[6,10]

Recently, heteroepitaxial $PbTiO_3$ film on an Nb-doped (001) cubic $SrTiO_3$ (NSTO) substrate was fabricated by hydrothermal epitaxy at a temperature lower than Curie temperature (T_c) without undergoing a phase transition.[11,12] When the film was fabricated at 160 °C, it had only a single +*c*-domain structure at an as-synthesized state, and also displayed switchable large remanent polarization ($2P_r = 144\ \mu C/cm^2$).[11] After heat treatment at 600 °C, the film showed a typical *c*/*a*/*c*/*a* multi-domain structure, which resulted from the PE to FE phase transition during cooling. In this study, we fabricated heteroepitaxial $PbTiO_3$ film on a NSTO substrate by hydrothermal epitaxy at 200 °C. The *c*/*a*/*c*/*a* multi-domain structure was observed at the as-synthesized state even though the film did not undergo a phase transition. Upon annealing at 600 °C, the film showed surface bands within the *a*-domain, which was formed through the phase transition. In this letter, we report, for the first time, the observation of surface bands (hereafter: [110] surface band), which are restricted within the *a*-domain on the (001) film surface.

The heteroepitaxial $PbTiO_3$ film was fabricated by hydrothermal epitaxy on an Nb-doped (001) cubic $SrTiO_3$ substrate (also used as the bottom electrode) at 200 °C, far below the Curie temperature, T_c(=490 °C). Typical growth conditions have been described previously.[11,12] The heteroepitaxial structure was annealed at 600 °C, and cooled to room temperature. Before and after heat treatment, the topography and the domain structure on the (001) tetragonal film surface were observed with AFM and PFM, and x-ray Θ rocking curves (ω scan). During the PFM imaging, the film was scanned with an oscillating tip bias of 5 V_{pp} (peak to peak) at 8 kHz to the bottom electrode. A HRTEM was also used to observe the cross-sectional and in-plane view of the domain structure.

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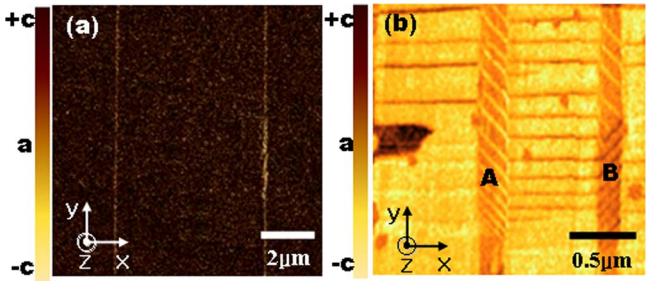

FIG. 1. (Color online) PFM images of (a) as-synthesized $PbTiO_3$ film, where the stripes along the [010] direction indicate the *a*-domain, and (b) 600 °C annealed $PbTiO_3$ film, where a [110] surface band exists within the *a*-domain.

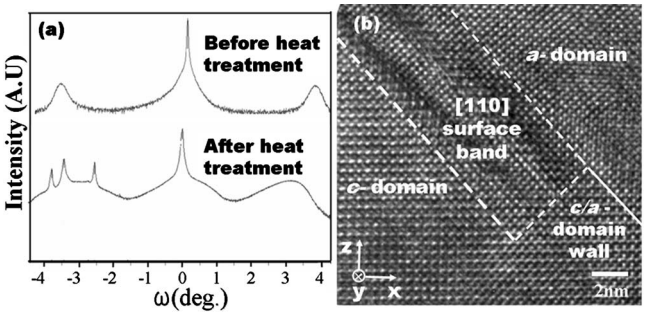

FIG. 2. (a) X-ray Θ rocking curves: the upper profile was obtained from an as-synthesized $PbTiO_3$ film, while the lower profile from the 600 °C annealed $PbTiO_3$ film, and (b) HRTEM image observed from the 600 °C annealed $PbTiO_3$ film. Note that the dashed line represents the interface of [110] surface band and *a*-domain (or *c*-domain) and the solid line represents *c*/*a*-domain wall.

Figure 1(a) shows the PFM image of the (001) film surface before heat treatment. Surprisingly, the film clearly shows stripes (i.e., no piezoresponse signal) along the [010] direction. These stripes are *a*-domains, which were not formed through the PE to FE phase transition: they were formed directly with the tetragonal structure during the hydrothermal epitaxy.[11,12] Note that the dark color represents the polarization vector directing towards the film surface (+*c*-domain).[13] It was found that below a critical hydrothermal pressure (190 °C) only a single *c*-domain was stable, while above this pressure (200 °C) the *c*/*a*/*c*/*a* multi domain was stable during the hydrothermal epitaxy process.[12] The domain stability including the *a*-domain under the hydrothermal epitaxy process has been discussed on the basis of the Landau–Ginsburg–Devonshire free energy function.[12] Arbitrarily, we can designate *a*-domain stripes of Fig. 1(a) as the (101) *a*-domain. After heat treatment at 600 °C, as shown on the PFM image of Fig. 1(b), the film clearly revealed a [110] surface band within the *a*-domain, as well as the conventionally observed *c*/*a*/*c*/*a* multi-domain pattern.

We believe that the [110] surface band was formed during the phase transition on cooling. Here, we could again designate *a*-domain stripes with the [110] surface band as the (101) *a*-domain. Utilizing a mark of a micro-Vickers indenter on/near the (101) *a*-domain before heat treatment, we confirmed that the position of the (101) *a*-domains before and after heat treatment did not vary. The [110] surface band has an angle of about 45° to the [010] direction, indicating that it exists along the [110] or $[1\bar{1}0]$ direction, as shown in Fig. 1(b). We can also see another *a*-domain along the [100] direction, which could belong to two variants, i.e., (011) and $(0\bar{1}1)$ twins. This *a*-domain, which is also formed through the phase transition, is precisely connected with two [110] surface bands on both sides. With the aid of careful AFM topography observations,[6,8] we verified that two *a*-domains, which were connected to one [110] surface band, had the same twin variant. Therefore, we could designate the *a*-domain along [100] direction as the $(0\bar{1}1)$ *a*-domain. The PFM signal from the [110] surface band clearly reveals a negative polarization vector (white signals: region "A") and a positive polarization vector (dark signals: region "B").

The observed x-ray Θ rocking curves are shown on the upper profiles (before heat treatment) and the lower profiles (after heat treatment) of Fig. 2(a). Before heat treatment, the film shows a middle rocking curve for Bragg diffraction from (100) $SrTiO_3$ and (001) $PbTiO_3$ planes, as well as two satellite peaks, which are ~3.3° away from the middle rocking curves. The left and right side satellite peaks correspond to a_1 domain [(101) variant] and a_2 domain [$(\bar{1}01)$ variant], respectively,[7] indicating that, under hydrothermal epitaxy of 200 °C, *a*-domains were formed in the film. However, after heat treatment, as shown on the lower profile of Fig. 2(a), three new peaks clearly appear near the left side satellite peak of the a_1-domain. The new center peak appears near the peak position of the a_1-domain. Meanwhile, a new left peak is about 0.3° away from the new center peak, and a new right peak about 0.7° away from the center peak. However, these new peaks are not observed near the $(\bar{1}01)$ satellite peak, i.e., a_2-domain. Nevertheless, we strongly believe that the new peaks near the (101) satellite peak are related to the [110] surface band within the (101) *a*-domain in Fig. 1(b).

The [110] surface band was observed on the cross-sectional HRTEM image. As shown in Fig. 2(b), the *c*/*a* domain wall is clearly seen on the HRTEM image. In our HRTEM observations, the *c*/*a* domain wall thickness was about 2–3 unit cells after heat treatment. On the HRTEM image, the [001] direction of the *a*-domain is tilted about 3° against the [100] direction of the *c*-domain. On the lower rocking curves of Fig. 2(a), this tilted angle was measured to be 3.2°. A new band clearly exists between the (101) *a*-domain and *c*-domain, and seems to run along the (101) plane of the tetragonal film. However, as describe later, the plane of this new band is not the (101) plane. The width of this band is clearly much wider than the *c*/*a* domain wall thickness. We believe that this new band is just the [110] surface band within the (101) *a*-domain. The ⟨100⟩ or [001] direction of this new band is clearly tilted from both [100] direction of the *c*-domain and [001] direction of the (101) *a*-domain.

The three-dimensional {101} *a*-domain structure including the [110] surface band was schematically constructed on the basis of the above experimental results (Fig. 3). The outside of the {101} *a*-domains is *c*-domains with the polarization vector normal to the interface. The [110] surface band can exist only within the (101) *a*-domain. This figure clearly shows that the [110] surface band exists along the $(1\bar{1}1)$ tetragonal plane within the (101) *a*-domain. Therefore, a new band in Fig. 2(b) actually runs along the $(1\bar{1}1)$ plane of the tetragonal film. This raises two interesting questions: What are the crystal structure and the origin of the [110] surface band that exists along the $(1\bar{1}1)$ plane within the (101)

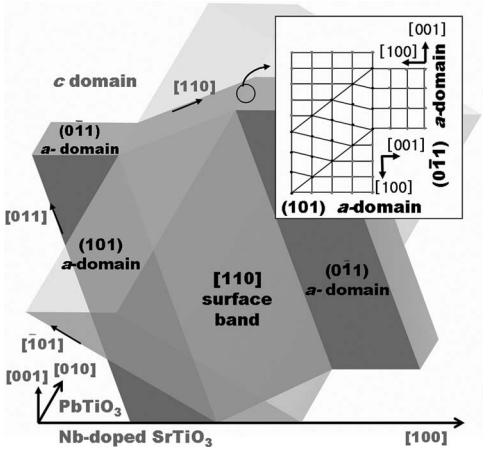

FIG. 3. Schematically constructed three-dimensional {101} *a*-domain structure including the [110] surface band. Note that the outer side of the {101} *a*-domain is the *c*-domain. The inset shows lattice distortion within the [110] surface near the interface between the [110] surface band and the $(0\bar{1}1)$ *a*-domain on the (001) film surface.

a-domain? Because the *c* axis (i.e., polar axis) of the *a*-domain is nearly parallel to the interface between the thin film and the substrate, the *a*-domain does not display piezoresponse signals during PFM observations. The [110] surface band in Fig. 1(b) clearly shows $+c$ and $-c$ piezoresponse signals, indicating that the lattices within the [110] surface band have polarization vector components to the [001] direction of the film. Therefore, the lattices within the [110] surface band must be another phase, i.e., the monoclinic lattice. Recently, the appearance of the monoclinic phase forbidden in crystal was observed in a bulk $Pb(Zr_{1-x}Ti_x)O_3$(PZT) ceramics experimentally[14] and predicted in epitaxial $PbTiO_3$ film.[15] Noheda *et al.*, reported the observation of a low temperature monoclinic phase near the morphotropic phase boundary in a bulk ceramic $Pb(Zr_{1-x}Ti_x)O_3$ system.[15] From the positions and intensity ratios of the peak, they described a monoclinic cell in which a_m and b_m lie along the tetragonal $[\bar{1}\bar{1}0]$ and $[1\bar{1}0]$ directions ($a_m \approx b_m \approx \sqrt{2}a_t$), c_m is close to the [001] ($c_m \approx c_t$), and the polar axis lies in the monoclinic ac plane close to the pseudo cubic[111] direction. The angle between a_m and c_m (β), which depends on the temperature, was tilted about 0.5° away from c_t. The new center peak on the lower profiles of Fig. 2(a) is precisely 0.3° away from the (101) satellite peak, corresponding to the tetragonal *ac* plane. Therefore, we believe that the new center peak is correspondent to the monoclinic *ac* plane. Pertsev, Zembilgotov, and A. K. Tagantsev, suggested that, due to the in-plane strain of the film, a monoclinic phase could exist by phenomenological thermodynamic theory on $PbTiO_3$ film.[14] However, in view of the white and dark piezoresponse signals from the [110] surface band, we cannot exclude the possibility of an rhombohedral phase, in which the polar axis lies in the pseudocubic [111] direction.[16]

Here, we consider the case where the film with a (101) *a*-domain before heat treatment is heated above T_c. The *c*-domains of the film undergo FE to PE phase transition: above T_c, the [100] directions of all cubic PE lattices will be exactly perpendicular to the film surface. This phase transition leads to a biaxial compressive stress state in the film. And there would be interaction of two different variants of *a*-domains in the presence of a *c*-domain. The *c*/*a* domain boundaries which existed before heat treatment could be responsible for a kind of memory because the (101) *a*-domain before and after heat treatment has the same position. At the same time, the formation of the $(0\bar{1}1)$ *a* domain on both sides will cause lattice distortion (i.e., the monoclinic lattice) within the [110] surface band, as shown in the inset of Fig. 3. Here, it should be noted that this lattice distortion does not occur within the *a*-domain, which is formed through the normal PE to FE phase transition.[11] A more detailed investigation on the crystal structure and the origin of the [110] surface band is currently in progress.

In summary, we fabricated heteroepitaxial $PbTiO_3$ film on an Nb-doped (001) cubic $SrTiO_3$ (NSTO) substrate by hydrothermal epitaxy at 200 °C. The film showed a *c*/*a*/*c*/*a* multi-domain pattern without undergoing a phase transition. After heat treatment of this film at 600 °C, employing PFM, x-ray Θ rocking curves, and HRTEM, we observed the [110] surface band within the *a*-domain, which was formed through a paraelectric to ferroelectric phase transition. We also found that a [110] surface band existed along the $(1\bar{1}1)$ plane within the *a*-domain. Owing to the interaction of two different variants of *a*-domains in the presence of a *c*-domain in the heteroepitaxial $PbTiO_3$ film, we speculate that the [110] surface band is monoclinic phase.

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