Formation and atomic structure of the (PbTi)O phase for epitaxial super-tetragonal $PbTiO_3$

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Abstract

Lattice strain has been used to modify the properties of ferroelectric oxide films. Introducing strain in thin film is usually realized based on the lattice mismatch of the heterostructural materials, which form multilayer systems or composite structure. For the composite structure of $PbTiO_3$/α-PbO-type (PTO/PO-T) structure phase, the PO-T structure phase plays the key role in introducing a high strain in the PTO phase and resulting in a giant polarization of the PTO phase. Here, we perform a detailed study on the PO-T structure phase on atomic scale by means of high-resolution (scanning) transmission electron microscopy. The atomic details including cations and oxygen of the PO-T structure phase are revealed, which show the α-PbO structure with parts of the Pb atoms being substituted by Ti atoms. Local inhomogeneity in Ti atom distribution is found in nanometer scale. Experimental investigations show that the PO-T structure phase is formed on a layer of the PTO phase with a thickness of one or two unit cells, which grows covering the underneath $La_{0.3}Sr_{0.7}MnO_3$ (LSMO) electrode layer. The formation mechanism of the PO-T structure phase is discussed on the basis of the atomic details of the PO-T/PTO/LSMO interfaces and the growth condition of the film.

1 INTRODUCTION

Thin films of $PbTiO_3$ (PTO) and PTO-based perovskite ferroelectric oxides epitaxially grown on diverse substrates have attracted tremendous attention of research for their excellent piezoelectric and ferroelectric properties. The intrinsic spontaneous polarization of the ferroelectric oxides is an important figure of merit for the ferroelectric properties, which depends on the structure details such as the axial ratio c/a, constituting a typical structure-property coupling relations.[1-3] Super-tetragonal PTO with large c/a (> 1.2) was reported in the PTO/PbO composite films prepared by means of magnetron sputtering deposition system.[4] In these films PbO nanoparticles were embedded in the PTO film matrix, introducing giant tetragonality and polarization of the PTO films. Recently, self-assembled vertically aligned nanocomposite thin films with embedded nanometer PTO columnar grains in matrix of α-PbO-type (PO-T) structural phase were prepared by pulsed laser deposition (PLD).[5] The PO-T structure was primarily characterized by electron diffraction analysis.[6] Under the constraint of the PO-T structural phase, the nanometer PTO columnar grains show a huge tensile strain, which results in giant off-center displacements of ions verified experimentally with quantitative high-resolution transmission electron microscopy (HRTEM). Based on the giant strain the experimental results were reproduced by first-principle calculations and a largely enhanced polarization was concluded.[6,7] In comparison with composite films of PTO/PbO reported in Ref. 4, the PO-T structure phase was found to be in main part (65%) of the composite film, and a high-level solution of Ti atoms in the PO-T structure phase was confirmed by High-angle annular dark field (HAADF) imaging and energy dispersion X-ray spectroscopy (EDS) analysis.[6] However, the atomic structure and formation of the PO-T structure phase are still unclear, which are the key issues for understanding the formation mechanism of the composite film growth and controlling the strain and thus the properties.

The atomically controlled interface in epitaxial heterostructures, such as multilayers,[8] superlattices,[9-11] and ultrathin films[12,13] play a prominent role in determining the microstructure evolution[14-17] and functionalities of the films .[18-21] The crystal structural quality and growth behavior of the films can be understood with the knowledge of atomic details of the interface structure between the films and the substrates. Jin *et al.* reported that the $La_{0.3}Sr_{0.7}MnO_3$ (LSMO) hillocks on Nb doped $SrTiO_3$ (STO) substrates could induce regular 180 ° domains in subsequently deposited PTO films.[14,20] A close investigation showed that interdiffusion across the LSMO/Nb-STO interface leads to distinct structural and physical properties in the PTO/LSMO/Nb-STO system. The polarization direction and strength were also reported to be influenced by chemical adsorbates and electronic processes occurring at the PTO/$SrRuO_3$ epitaxial interface and at the surface.[22] It is thus clear that in order to engineer stable ferroelectricity of a thin film, microstructure and interface effects play a pivotal role. A detailed investigation of interfaces in thin films, particularly on atomic scale, is thus the key and basic step for study of various properties of thin film systems.

In the present work, we present a detailed study on microstructure and interfaces in the PTO/PO-T structure composite thin films grown on LSMO buffered (001) STO substrate[5] by means of HRTEM and scanning TEM (STEM). The PO-T structure phase is investigated on atomic scale using negative spherical aberration imaging (NCSI) technique.[23] The PO-T structure phase is confirmed with Ti atom substitution of the Pb atom in the α-PbO structure by quantitative comparison of the atomic-resolution images with image simulation, and the distribution of the Ti atoms is found to be inhomogeneous on nanometer scale. The atomic-resolution NCSI images show that the first unit cell layer, which covers the surface of the LSMO layer, is the bulk-like PTO phase without high strain. The PO-T structure phase forms subsequently above the layer of the bulk-like PTO phase layer. The formation mechanism of the PO-T structure phase as well as the composite film is discussed in the light of structural similarity and oxygen deficiency.

2 EXPERIMENTAL PROCEDURE

The samples used in the present study are the thin film systems of PTO/PO-T composite film, which were grown on LSMO/(001) STO substrates by PLD. In the deposition process, a 3 Hz repetition rate of the KrF laser and a fluence of around 1.5 J cm^{-2} were used. A LSMO film layer was firstly grown at 780 ℃, which was desired as the bottom electrode. Then the PTO/PO-T composite film was grown subsequently at 600^{o}C. After film preparation, high-resolution X-ray diffraction (XRD) was employed to investigate the structure parameters, crystalline quality and orientation relationship of the film. More details of the film growth and XRD data are given in Ref. 5.

Cross-sectional specimens for HRTEM and STEM investigations were prepared in two directions to obtain the views along the crystallographic [100] and [110] directions of the films by focused ion beam (FIB) milling on an FEI Helios 600i FIB/SEM system. In order to minimize the damaged layer by the FIB milling process, the FIB-prepared samples were polished by a Leica EM RES102 Multifunctional Ion Milling System at 0.5 kV. HRTEM investigations under NCSI condition were performed on an objective C_S corrected FEI Titan 60-300 transmission electron microscope, operated at 300 kV. The images were recorded using a GATAN UltraScan 1000 2k × 2k charge-coupled device (CCD) camera at a sampling rate of 11 pm per pixel. HAADF imaging was performed on a probe C_S corrected JEOL ARM 200F scanning transmission electron microscope, operated at 200 kV. The HAADF images were obtained under the condition with a probe size of 0.1 nm, a semi-convergence angle of $\alpha = 22$ mrad and the collection angles ranged from 90 to 176 mrad. A Fourier-filtering procedure[24] was applied to the raw high-resolution images in order to remove the noise originated from various sources and keep the final results unaffected. Modeling and image simulation of the PO-T structure phase were carried out employing the Crystal Kit-MacTempas software package.[25]

Quantitative analysis of the NCSI images was based on comparison with the simulated image on absolute value of image contrast, which results in determination of imaging parameters and sample thickness. In practical experiments, unavoidable residual lens aberrations and a slight misorientation of the specimen from an ideal orientation are unavoidable, which have effects on the contrast. In order to obtain the true information of the atomic structure, quantitative comparison of the experimental image with the simulated one was performed following an iterative procedure. In this procedure, image simulations are performed using the imaging parameters that were estimated from experiment with two-fold astigmatism < 2 nm, three-fold astigmatism < 40 nm, axial coma < 30 nm, and objective defocus C1 in an range of 4-8 nm. The Debye-Waller factors for PTO were taken from the structure data in Ref. 26, which were also used for PO-T simulation as first order approximation. In addition, other effective factors dampening image contrast, such as the modulation transfer function (MTF) of the used CCD camera[27] and image contrast spread function,[28] were also taken into account. The aliasing artifact was also avoided by using sufficient phase grating in the image simulation. The comparison between the experimental and simulated images was iteratively performed with changes of the imaging parameters and sample thickness, until the best match with respect to positions and magnitudes of the intensity peaks as well as the absolute values of the image contrast was obtained. The best matching simulated image is considered as the representative of the experimental image and the used image parameters and sample thickness are determined.

3 RESULTS

Figure 1 shows a high-resolution HAADF-STEM image of a PTO/PO-T composite film, which was recorded from a cross-sectional specimen along the [100] direction of the PTO, presenting an overview of the film on the LSMO electrode layer. The film exhibits a structure with PTO columnar grains separated by the PO-T structure phase, which show slight difference in image contrast under the low magnification. The interface between the PTO/PO-T film and the LSMO electrode layer is clear and lattice-coherent. Interfacial steps with a height of single unit cell scale are frequently observed, as marked by arrows in Figure 1. No misfit dislocations were found in experimental investigations. As reported in our previous work,[6] the PTO columnar grains are surrounded by the PO-T structure phase matrix. Electron diffraction analysis showed that the *c*-lattice parameters of the PTO columnar grains and the PO-T structure phase matrix are 0.469 nm, while the in-plane *a*-lattice parameters are different, 0.384 nm for the PTO grains and 0.395 nm for the PO-T structure phase. Based on the *a*-lattice difference, spatial distribution of both phases can be numerically distinguished in a large field of view.[6]

Figure 2a displays a magnified [100] HAADF STEM image of the PTO/PO-T structures, providing details of the cations arrangements of the two phases. The image of the PTO phase shows clearly the stacking sequence of two different atomic planes along the [001] direction with evidently different image contrast resulted from the Z-contrast nature of the HAADF STEM image, which depends proportionally on Z^2 (Z: atomic number). In comparison with the atomic structure of PTO projected along the [100] direction (Figure S1, Supplementary materials) the image dots with the high bright contrast appear at the Pb atom column positions, while the less bright dots are at the Ti-O atom column positions. In the areas of the PO-T phase, the image contrast does not show evident different for the corresponding two stacking planes, which agrees with the crystal structure of α-PbO (Figure S1, Supplementary materials) with both stacking planes being the Pb planes. By a detailed investigation one can find that the intensity of the image dots in the PO-T phase is in general lower than those of the Pb atomic planes in PTO. The differences in the intensity of the different atomic planes can be clearly revealed by the intensity profiles of the image for these atomic planes, as shown in Figure 2b, which were obtained by scanning the atomic planes marked by two arrows in Figure 2a. From the crystal structures of PTO and α-PbO in Figure S1, it is clear that in the [100] projection the Pb atoms do not overlap with other types of atoms. The lower intensity in the PO-T phase areas than that of the Pb columns in the PTO grain observed in Figure 2 can be understood as the result of the partial substitution of the Pb atoms by Ti atoms based on the EDS studies.[6] The same results were also obtained from the images recorded along the [110] direction.

To investigate the atomic details of the PO-T structure phase, atomic-resolution NCSI was performed to investigate the PTO/PO-T film samples in two crystallographic directions, the [100] and [110] directions. In the image acquired under the NCSI condition the atom positions appear bright on a dark background, and all of the atomic columns, including cations and oxygen, are simultaneously revealed. Therefore, the individual atomic columns in the sample can be identified and analyzed quantitatively by comparison with quantum-mechanical and optical image contrast calculations. It has been demonstrated that the high quality and high contrast of the NCSI images provide advantage to study the oxygen-atom columns together with the cation columns.[29] Quantitative comparison of the experimental image to the simulated image allows for evaluating the effects of the residual lens aberrations and unavoidable crystal tilt and thus for removing the imaging artifacts.[28] Figure 3A, 3B shows a [100] experimental image of the PO-T structure phase and a corresponding simulated image, respectively. The simulated image was obtained based on the structural model of α-PbO (Figure S1, Supplementary materials), in which 50% of the

Pb atoms were replaced by the Ti atoms, as shown by the superposed structure model. The reproduction of the experiment image by the simulation evidences that the PO-T phase has the same structure as the α-PbO phase with partial substitution of the Pb atoms by the Ti atoms.

This conclusion is further confirmed by the NCSI image of a film area including both PTO and PO-T phases, which was recorded along the [110] direction, as shown in Figure 4A. In this image, the contrast of the PTO area has been quantitatively analyzed in comparison with image simulations, which leads to determination of the imaging parameters with a sample thickness of 4.7 nm and a +8 nm over focus of objective lens.[6] Figure 4B displays a zoom-in image of the PO-T phase marked by a white frame in Figure 4A, which shows evidently the structure same as that of α-PbO projected along the [110] direction (Figure S1, Supplementary materials), in agreement with the conclusion obtained from the image viewed along the [100] direction (Figure 3). In addition, variation of the contrast for the cation columns is clearly seen along the arrow in Figure 4B. The image contrast of the columns becomes apparently lower from the left to the right and the size of the image dots gets smaller. The influence of abrupt sample thickness variation can be excluded, since as comparison, along the row directly below the arrow, the contrast changes are not evident. Thus the most possible reason is that different amount of the Pb atoms are replaced by the Ti atoms in these columns. Taking the image of the PTO phase in the same area as a reference and applying the determined imaging parameters [6] to calculate the images of the PO-T area allow us to investigate the compositional changes in individual atomic column according to the changes of the image contrast. Figure 4C shows the simulated image based on a structure model with variation of the Ti concentration in the Pb/Ti columns under the determined imaging condition.[6] The simulated image reproduces well the experimental image in Figure 4B. In particular, the image intensity profiles of the columns along the arrows are displayed in Figure 4D, which show an excellent fit between the experiment and the simulation, representing the concentration variation of Ti in individual Pb/Ti column. These results show that the present PO-T phase has essentially the structure of α-PbO with partial replacement of the Pb atoms by the Ti atoms. The replacements of the Pb atoms by the Ti atoms are inhomogeneous on nanometers scale (in the case of Figure 4).

For understanding the evolution of the film microstructure and the formation of the PO-T structure phase, the interfaces between the composite film and the LSMO electrode layer were investigated on atomic scale. Figure 5A shows a low magnification image of the interface, recorded along the [100] direction of the film under the NCSI condition. In the image two PTO and a PO-T areas are identified as denoted. A yellow dashed line marks the interface between the PTO/PO-T film and the LSMO layer. The interface is determined by investigating the lattice parameters of PTO and LSMO across the interface area along the ***c***-axis direction of PTO, and by comparison of the experimental image with simulation. In the left part of the interface an interface step is seen, where strain is induced in the film due to the lattice mismatch between LSMO and PTO along the ***c***-axis direction of PTO. The rest part of the interface appears to be atomically flat and sharp. Figure 5B shows a high magnification of the middle part of Figure 5A, for studying atomic details across the interface. A detailed investigation reveals that in this area the terminating atomic plane of the LSMO layer at the interface is a (LaSr)O plane as denoted by a yellow arrow. The LSMO layer can be identified by its lattice parameter along the out-of-plane direction, which differs from that of the PTO phase.[6] The (LaSr)O plane terminating at the interface was determined by comparison of the experimental image with with image simulation and by investigation of the stacking sequence across the interface of lattice planes. Directly above the LSMO layer a continuous layer of PTO with one or two unit cell thickness forms starting from a TiO_2 atomic plane. This layer of PTO can be directly identified by comparing the image with the structure projected along the [100] direction of PTO (Figure S1, Supplementary materials), as shown by the overlapped structure model. In this layer of PTO the oxygen atoms exhibit downward displacements with respect to the Pb and Ti cations, resulting in a spontaneous polarization pointing upward direction. The first single-unit-cell-thick PTO continuously covers the surface of the LSMO layer even across interface step. In the second unit cell layer, the right part keeps the structure of PTO, while the left part shows a different contrast from the PTO structure (pink dashed line). The difference is evident for the contrast at the column positions of oxygen. The contrast for the oxygen column positions aligned with the O-Pb plane of the PTO part is weak and confused as indicated by a white arrow. At other positions (see e.g. cyan arrow), image contrast appears evident at the oxygen position in the PbO structure, indicating the initialization of the PO-T phase. The intensity values of the intensity peaks at the oxygen positions (at Pb-O planes) are compared qualitatively with the intensity profiles of the first and second unit cell layers. From the obtained intensity profiles, as shown in Figure S2, the peak intensity corresponding to the oxygen positions in the first unit cell layer is evidently higher than that in the second unit cell layer. In addition, from the image the *c*-lattice parameter is measured as about 0.47 nm for the second unit cell layer, which is larger than that (about 0.415 nm) of the first unit cell layer of PTO. The values were measured with taking the lattice parameters of LSMO and STO as calibration standard.[6] The same results are further confirmed by the investigation of the interface along the [110] direction of the film sample.

4 DISCUSSION

In our previous study, chemical composition investigation by EDS showed a high-level solution of Ti element in the PO-T structure.[6] A PbO-TiO_2 solid solution phase was reported in an early research and the solubility of Ti can be as high as 80 at%.[30] In both Refs. 6 and 30 no atomic details of the Pb-Ti solution were provided. In the present study, we provide the evidence for replacement of the Pb atoms by the Ti atoms in the α-PbO lattice by means of HRTEM and STEM. The partial substitution of the Pb atoms by the Ti atoms does not change the crystal structure of α-PbO. Inhomogeneous substitution has been detected in nanometer scale by quantitative HRTEM (Figure 4). In a structure unit of α-PbO two oxygen sites are provided (i.e., 2

Pb + 2 O as shown in Figure S1, Supplementary materials). Considering the high Ti concentration in the PO-T phase (e.g., Figure 4), two oxygen positions are thus insufficient to support Ti^{4+} as expected in the PTO phase. A reasonable interpretation is that the presence of the PO-T phase in the composite film could accompany a reduction of Ti valency to 2+. Indeed, TiO in the form of thin film could be prepared on the MgO substrate.[31] In this film phase the valence of Ti^{+} is indeed 2+. Another research[32] found that the content of oxygen could also change from $TiO_{0.7}$ to $TiO_{1.25}$. Therefore, it is understandable for the presence of the PT-O phase in the composite film.

Our interface investigations (Figure 5 and Figure S2, Supplementary materials) show that the nucleation of PTO on the LSMO electrode layer is homogeneous, resulting in a PTO layer with at least a single unit cell thickness covering the surface of the LSMO layer. The first single unit cell layer exhibits a regular structure of PTO and the lattice parameter is close to that of the bulk material. The spontaneous polarization also evidences that the unit-cell-thick PTO is structurally stable under the condition of the heterostructure. The conducting nature of the LSMO layer, which compensates the polarization-induced bound charges at the interface, provides the electrical condition stabilizing the single unit cell layer of PTO. From the second unit cell layer, parts of the structure become irregular with respect to the lattice parameters and occupation of the atomic sites. In particular, the image intensity corresponding to oxygen columns in the structure of PTO changes, revealing deficiency in some sites as well as rearrangement of oxygen atoms towards the formation of the PO-T phase.

These changes are accompanied with the lattice expansion along the ***c***-axis direction. These results suggest that the oxygen deficiency for the PTO phase may play an important role in the formation of the PO-T phase and the evolution of the PTO/PO-T composite films.

One of the effective factors leading to the formation of the composite configuration is considered as the relatively low temperature (600^{o}C) used for the film growth, which allows the formation of both the PTO and PO-T phases, thus leading to the super-tetragonal PTO embedded in the PO-T matrix. Under this temperature, the competition of other factors could have effect on details of the film microstructure. The one- or two-unit-cell layer of PTO on the LSMO layer can be understood by the low energy of the interface resulted from the good lattice match between bulk PTO (a = 0.390 nm) and the LSMO/STO film-substrate system (a_P = 0.390 nm).[6] On the other hand, form the structure details of both PTO and PbO in Figure S1 (Supplementary materials), it becomes evident that the two structures are very similar. The PTO structure has one more oxygen atom in the structure unit than that in α-PbO, if disregarding the different configurations at the cationic sites (i.e., Pb and Ti). If an oxygen atom is removed in the PTO unit cell and anti-site occupancy occurs for the cations, the structure of the PTO phase can be transformed to that of the PO-T phase (Figure S3, Supplementary materials). It is well known that in the PLD deposition process oxygen deficiency is a common phenomenon for the oxide film growth. The sufficient oxygen the observed interfacial continuous layer of PTO can be partially supplied from the connecting LSMO layer. This supplement of oxygen is likely to be stopped after the formation of the continuous layer of PTO. The configuration of the PTO/PO-T composite structure can be understood as the result of fluctuation of the oxygen concentration. The anti-site occupation of Ti and Pb atoms for the PO-T phase is possibly due to the high deposition rate and low temperature used for the film growth, which may result in low mobility of the coming atomic species. These conditions allow the formation of the PO-T phase, which adopts the similar Pb/Ti ratio without the need for necessary ordering of the Pb and Ti atoms in PTO.

5 CONCLUSIONS

The atomic details of the PO-T phase in the PTO/PO-T nanocomposite films are intensively studied by means of HR(S)TEM. NCSI images reveal both cations and oxygen columns along two crystallographic directions, leading to obtaining the views of the atomic structure in the direction of [100] and [110]. The experimental images combining image simulation provide evidence for the atomic structure of the PO-T phase, which adopts the tetragonal α-PbO structure with parts of the Pb positions being occupied by the Ti atoms. Quantitative HRTEM analysis shows that the replacement of some Pb atoms by the Ti atoms is locally inhomogeneous on nanometer scale. Atomic details of the interface structure between the film and the LSMO layer show that a layer of PTO with a thickness of one or two unit cells grows regularly covering the surface of the LSMO layer. On this PTO layer the PTO/PO-T composite structure forms, resulting in the highly strained PTO columnar grains. The formation mechanism of the PO-T phase is discussed based on the film growth condition and similarity of the PTO and α-PbO structures. Our results provide structural basis for controlling growth of the composite structure with nanometer columnar PTO in order to explore the properties of the composite films for possible applications in nanoscale electronic devices.

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Figure captions

FIGURE 1 HAADF STEM image of a PTO/PO-T composite film on a LSMO electrode layer in a cross-section view along the [100] direction. The PTO columnar grains are embedded in the PO-T structure matrix, which are distinguishable with different image contrast. Two arrows denote two interface steps between the PTO/PO-T composite film and the LSMO layer.

FIGURE 2 (A) A magnified [100] HAADF STEM image of the PTO/PO-T composite structure, showing details of the cations arrangements in the two phases.

The difference in image contrast between the two phases is visually clear along the atomic plane denoted by a red arrow. (B) Image intensity profiles of the atomic columns across the PTO and PO-T areas, obtained by scanning the atomic planes following the Ti-O_2 plane (red arrow) and the Pb-O plane (blue arrow) of the PTO structure. The intensity profiles provide evident difference in image intensity of the atomic columns for the two phases.

FIGURE 3 (A) Atomic-resolution image of the PO-T phase, recorded in an across-sectional view along the [100] direction under the NCSI condition. (B) The simulated image corresponding to the experimental image (a), calculated based on a PbO structure model, in which 50% of the Pb atoms being substituted by the Ti atoms. The simulated image fits quite well to the experimental image, confirming the structure of the PO-T phase. The atom arrangement in the structure model is superposed (cyan: O, orange: Ti, purple: Pb).

FIGURE 4 (A) Atomic-resolution image of a part of the PTO/PO-T composite structure, recorded in an across-sectional view along the [110] direction under the NCSI condition. The interfaces between the PTO and PO-T phases are denoted by yellow dashed lines. (B) A high magnification of an area of the PO-T phase denoted by a white dashed line frame, showing clearly changes in the image intensity of the atomic columns following an arrow. (C) Simulated image calculated for a sample thickness of 4.4 nm and a defocus value of +7.5 nm at a negative C_S value of -13μm, which were determined by a quantitative comparison between the experimental and simulation[6] for the PTO phase area in (A). The images in (B) and (C) are displayed on the same intensity scale, showing the best match. (D) Simulated and experimental intensity profiles along the Pb/Ti plane indicated by the arrows in (B) and (C), which are related to the concentration of the substitution of the Pb atoms by the Ti atoms in different columns.

FIGURE 5 (A) Atomic-resolution of the interface between the PTO/PO-T film and the LSMO electrode layer, recorded in an across-sectional view along the [100] direction under the NCSI condition. The interface is marked by a yellow dashed line. A yellow arrow marks the terminating (LaSr)O plane of the LSMO electrode layer. (B) A magnification of the middle part of the interface area including the PO-T phase in (A). A layer of PTO with thickness of one or two unit cells is identified between the LSMO layer and the PO-T film part (between the yellow and pink dashed lines). The structure models of the PTO and PO-T phases are superposed (cyan: O, orange: Ti, purple: Pb). Cyan and white arrows denote the changes in image intensity at oxygen column positions with respect to those of the PTO structure.