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Formation of the ferroelectric domains in epitaxial $PbTiO_3$ thin films grown by metalorganic chemical vapor deposition

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Abstract. Epitaxial $PbTiO_3$ thin films have been prepared by metalorganic chemical vapor deposition under reduced pressure. The formation of ferroelectric domains in films grown on $SrTiO_3$ and $LaAlO_3$ substrates was investigated by synchrotron radiation and Rutherford backscattering spectroscopy. Single-domain (3000-Å thick) and multi-domain (4500-Å thick) $PbTiO_3$ films were produced on $SrTiO_3$. For multi-domain $PbTiO_3$ film, the c-domain presented epitaxial structure with its c-axis perpendicular to the substrate surface, while a-domains aligned four-fold symmetrically with c-domains by 2.79° off the c-axis of c-domains. In the film, the measured lattice constants (a, b and c) of the a- and c-domains were different from each other, indicating that the films suffered a modulated strain during domain formation. In contrast, both the a and c domains of films on $LaAlO_3$ were alternatively aligned on substrate with the a-axis of the a-domain and the c-axis of c-domains perpendicular to the substrate surface. Two-dimensional distribution of these domains is proposed and the formation of these kinds of domains is discussed. The surface morphology and phase transition process of single and multi domain $PbTiO_3$ film on $SrTiO_3$ were studied by atomic force microscope (AFM) and high temperature X-ray diffraction, respectively.

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Investigation of the ferroelectric domain has remained one of the most important issues in studies of ferroelectric materials since their discovery. Understanding the domain and its behaviour as a function of temperature, electricity, pressure, etc. has shed light on the properties of ferroelectrics [1] and yielded some novel device applications with artificially modulated multidomains, such as optical and acoustic superlattice [2]. Recently, ferroelectric thin films have attracted much attention for their applications on integrated ferroelectric devices [3], such as nonvolatile memory [4], ultrasonic sensors, infra-detectors, etc. Although much progress has been made on the preparation and properties of ferroelectric thin films, some basic problems remain to be resolved such as the formation of domains in ferroelectric films.

Domains and domain boundaries are important because they are expected to play an essential role in controlling the properties of thin film, such as polarization and fatigue [5]. The interaction between the film and substrate results in domains and properties which are profoundly different from those of bulk materials. For $PbTiO_3$ thin films, a single domain structure was obtained on $SrTiO_3$ substrate [6], while a multi-domain was formed on $SrTiO_3$ [6, 7] and MgO [8], and a periodically aligned a- and c-domain was obtained on $KTaO_3$ [9]. Although some theories have been proposed to describe the domain formation in epitaxial overlayers [9–11], some new experimental results have been obtained [6, 8, 12] which raise questions about their formation. Furthermore, the fact that a similar situation occurred in the cuprate high T_c superconductors [13] shows that these phenomena are common in perovskite type oxides. In the present investigation, we describe the preparation of epitaxial single domain and multi-domain $PbTiO_3$ thin films, and an analysis of domains and domain boundaries by synchrotron radiation X-ray diffraction and Rutherford backscattering spectroscopy. AFM and high temperature X-ray diffraction were used to study the morphology and phase transition process of these films.

As described in a previous report [14], specimens were prepared by metalorganic chemical vapor deposition (MOCVD) under reduced pressure using metalorganic precursors: tetraethy-lead (TEL) and titanium iso-proxiode (TIP). Purified nitrogen and oxygen were used as carrier gas and oxidant gas, respectively. The optimum deposition conditions were as follows: The growth temperature was 650 °C and the pressure was 16 Torr. The mass flow rate of the TEL and TIP precursors were 150 sccm and 200 sccm, respectively, with the temperatures of precursor bubbles kept at 35 °C and 65 °C. The growth rate was 0.45 μm/h. X-ray diffraction (XRD) measurements were performed at the Beijing Synchrotron Radiation Facility (BSRF). The synchrotron radiation X-ray beam was focused using a bent triangular Si crystals monochromator (horizontal) and cylindrical mirror (vertically) onto the sample with the size of the focus spot at $0.5 \times 0.3\,mm^2$, which was supported by a Huber four-circle diffractometer. The maximum intensity of the X-ray beam was 1.6×10^9 photons/s mm^2 while energy resolution of the monochromatic beam was 4.4×10^4 eV [15].

Figure 1a shows a $\Theta - 2\Theta$ scan XRD pattern of a 3000-Å thick $PbTiO_3$ film from 20° to 60°. Only the (00*l*) diffraction peaks of the film and the $SrTiO_3$ substrate were detected; this means that the film is perfectly c-axis oriented. Figures 1b and 1c are rocking curves of (001) $PbTiO_3$ and (001) $SrTiO_3$, respectively. In order to show small peaks, an intensity scale 50 times greater than that of (001) $PbTiO_3$'s rocking curve is used in the rocking curve of (100) $SrTiO_3$ (Fig. 1c). Only the (001) peak of $SrTiO_3$ was observed in Fig. 1c , indicating that no a-axis crystalline formed in the film. The full width at half maximum (FWHM) of the (001) $PbTiO_3$ rocking curve was 0.4°, indicating a good crystalline quality. The film was thus single domain epitaxy. Rutherford back scattering spectroscopy (RBS) measurements confirmed the nature of the single domain and single crystalline by a 24% ratio(χ_{min}) of the backscattering yield along (001) and in a random direction. This ratio is higher than that reported by Li et al. [6] in single domain $PbTiO_3$ films and even higher than Forster et al. [6] reported for the multi-domain ones. One of reasons for the resulting high ratio of the backscattered yield is that the direction of ion channeling was not positioned at the exact (001) axis due to the limitation of the equipment we used. The fact that the signal of the ion channeling spectrum exhibits an increasing yield at about channel 215, due to strontium's scattering, may prove the explanation. With the sample positioned exactly, the yield should be improved [12]. It was recently found that the perovskite of ABO_3-type suffers from a reconstruction in the temperature range used during film deposition, which gives rise to the formation of new chemical phase [16, 17]. This may not be the reason responsible for the additional scattering of Sr (channel 215), because even in higher growth temperatures (700–750 °C), no new phase was observed in the $PbTiO_3/SrTiO_3$ [6], and in XRD pattern of PT/ST, no other diffraction peaks except PT and ST were detected. The results of RBS also identified the film thickness as 3000 Å, which was consistent with the measurement by a surface profilometer, within the limit of error (2980 Å). To our knowledge, this is the thickest single domain $PbTiO_3$ film prepared on $SrTiO_3$.

We examined the same film's surface with a Nanoscope III atomic force microscope (AFM) at room temperature in air. The AFM images were acquired in the constant friction mode using commercial electrochemical etched Si_3N_4 scanning tips, with a scanning area of $12.5\,\mu m \times 12.5\,\mu m$. On a typical AFM image of $250\,nm \times 250\,nm$ area, the average step height of 4 Å and terrace width of 60 Å were clearly observed on the surface [12]. This showed that the film was grown on a vicinal (001) $SrTiO_3$ substrate misoriented by 4.5° to (100) of $SrTiO_3$ and the growth of the thin film occurred layer-by-layer. To the best of our knowledge, the evidence of layer-by-layer growth was first observed in preparation of ferroelectric thin films. This result is consistent with the measurements of the rocking curve and RBS. Furthermore, this suggests that, within the precision of AFM instrument, the growth of $PbTiO_3$ during MOCVD was monolayer in nature with an oxygen octahedron unity cell (4.12 Å), as in high T_c superconductors.

However, multi-domains occurred when the thickness of films was 4500 Å. Figure 2a–d shows the rocking curves of (001) $SrTiO_3$ with Φ-scan. Notice that when the rocking curve of (001) $PbTiO_3$ is almost the same as that of single domain film, multi-peaks characteristic of multi-domain

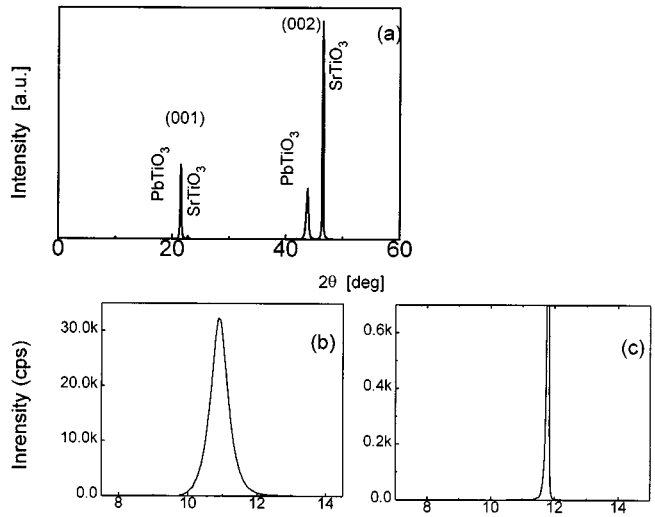

Fig. 1. a $\Theta - 2\Theta$ scan X-ray diffraction pattern of a $PbTiO_3$ film on $SrTiO_3$, showing perfect c-axis orientation. **b** Rocking curve around the (001) $PbTiO_3$ direction indicating one single domain. **c** Rocking curve around the (001) $SrTiO_3$ direction, showing a structure characteristic of a single domain

are seen [6]. A very interesting fact is that, when the sample is rotated about the Φ axis, the domains show exact symmetry about the (001) of $SrTiO_3$, which is very different from previous reports. When Φ angle is set as 0°, two peaks were detected with the same tilt angle off the (001) $SrTiO_3$ by 1.96°, and when Φ is 23.5°, two new peaks appear in addition to the two extra peaks observed at $\Phi = 0°$. At $\Phi = 45°$, the two peaks closest to the center combine to form one with increased intensity, which results in a XRD spectrum with three peaks. When $\Phi = 68.5°$, four peaks appear again around the central peak in the same position at which they appear for the $\Phi = 45°$. When $\Phi = 90°$, two peaks were detected. This process repeats for $\Phi > 90°$. The four peaks can be described as two pairs, in which the two peaks move closer to each other, and another two peaks move apart. For $\Phi = 45°$, the two peaks approaching each other combine to form a single peak, while the two separating peaks reach their maximum separation tilt angle of 2.78°. When $\Phi = 45°$, the two pairs exchange their directionality up to $\Phi = 90°$. This movement cycle repeats itself. It is clear that these domains show exact four-fold symmetry about the Φ axis, e.g (001) $SrTiO_3$. In accordance with Gao et al [8], but considering multi-domains in two-dimensions, the distribution of a-domains and c-domains is schematically plotted in Fig. 3, where four a-domains are aligned equivalently around a c-domain. So the single c-domain results in a single peak in the rocking curve of (001) $PbTiO_3$ (like Fig. 1b). On the other hand the four-fold symmetry of a-domains is responsible for Fig. 2a–d, in which the Φ scan corresponds to the rotation of four equivalent a-domains around c-axis of a c-domain. Obviously, the tilt angle of the c-axis of the a-domains with respect to the c-axis of the c-domain should be determined when the angle maintains its maximum at $\Phi = 45°$, which is measured in Fig. 2b as 2.78°. To determine the a-axis length of the a-domain exactly, before the 2Θ scan was performed, the sample must be tilted 2.78° off (001) $SrTiO_3$, e.g. the surface of the films should be at $\Phi = 45°$. The measured a-axis constant of a-domains is 3.888 Å. Considering the co-

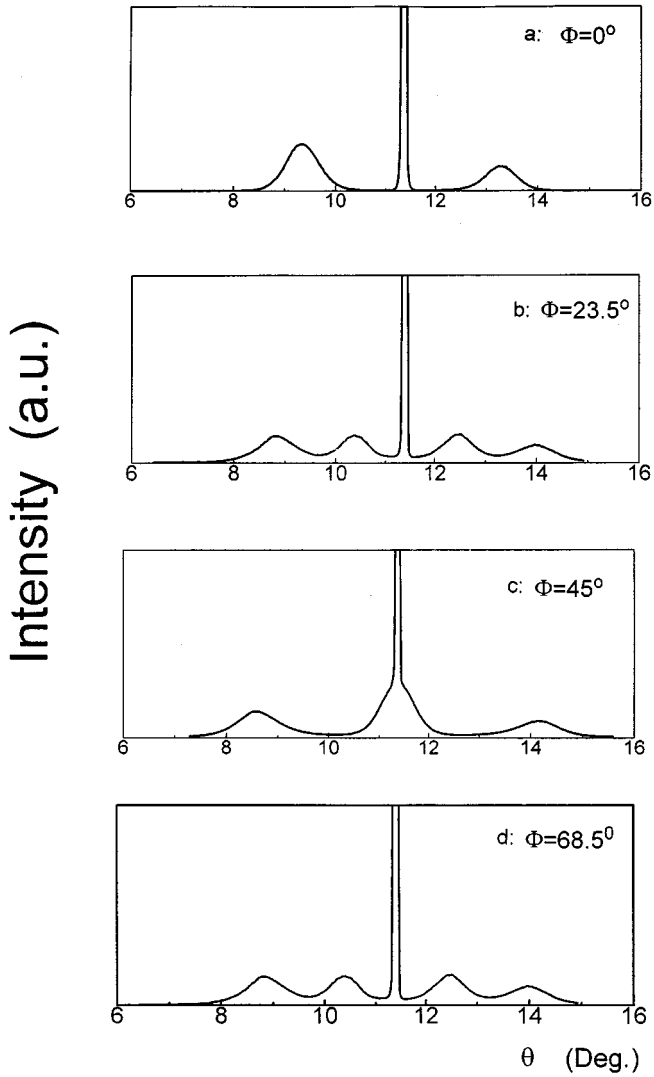

Fig. 2a–d. Rocking curves around the (001) $SrTiO_3$ direction with (**a**) $\Phi = 0°$, (**b**) $\Phi = 23.5°$, (**c**) $\Phi = 45°$, and (**d**) $\Phi = 68.5°$. The central peak corresponds to a diffraction of the (001) $SrTiO_3$ planes, while the other peaks correspond to the (100) of $PbTiO_3$ which show four-fold symmetry

herent condition [18] at the a- and c-domain walls and using the measured a-axis constant and tilt angle(2.78°), the c-axis constant of the a-domain was determined as 4.052 Å, which is different from that of the c-domain (4.124 Å). The result indicates that a- and c-domains suffer different tensile stresses, e.g. the aligned a- and c-domains consist of an imperfect twin. It seems that both the a and c axes of the a-domains were compressed. This uncommon result may be attributed to the special domain configuration in this study. In fact, the stress state of films composed of domains has not yet been explicitly addressed. For example, c-domains experienced reasonable compressive force in the a and b axes, and should extend the c constant due to the freedom of the c plane, but the measured result seemingly indicates that c-domains were under compression along the c-axis with a c-parameter of 4.124 Å, shorter than bulk $PbTiO_3$. Taking into account the continuous condition of the wall between the two domains, we believe that the spontaneous polarization directions (denoted by arrows) of the a- and c-domains are as shown in Fig. 3.

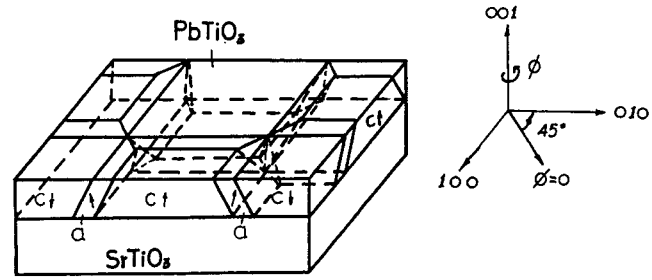

Fig. 3. Schematic drawing showing the equivalent alignment of four a-domains with a c-domain in two dimensions, which correlates with the symmetric diffraction shown in Fig. 2. The spontaneous polarization directions of a- and c-domains are indicated by arrows. The four a-domains are tilted at the same angle with respect to the film surface, while c- axis of c-domain is perpendicular to the surface. The inset shows the diffraction geometry

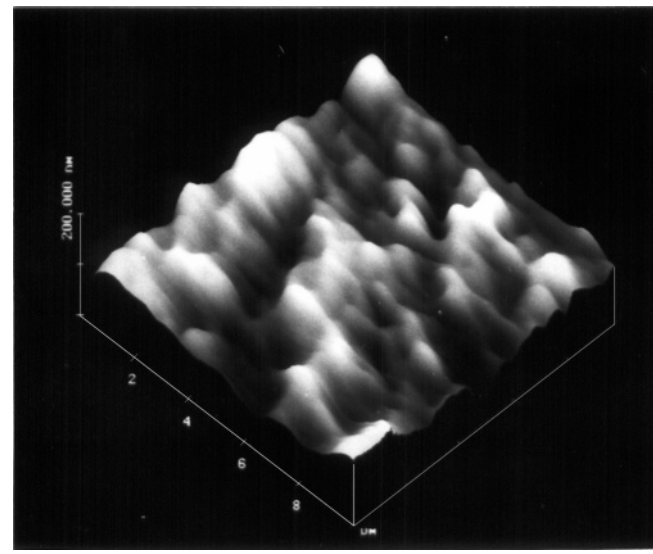

Fig. 4. An AFM image of a multi-domain $PbTiO_3$ film showing an averaged roughness of 100 nm. The size of the image is 9 μm × 9 μm

The surface of the film with multi-domains was observed by AFM. Figure 4 shows the typical morphology. The roughness was as large as 100 nm in a 9 μm × 9 μm area, much greater than the single domain case. It is interesting that no four-fold symmetric topography corresponding to a tetragonally symmetric alignment of a-domains by the c-domain was observed. A simple estimation can interpret the observation: a roughness due to the formation of twin boundaries during phase transition of $PbTiO_3$ is smaller than 20 nm which is too small to be distinguished. The result indicates that the observed morphology resultes from the growth process and not from phase transition during the cooling process.

The phase transitions of both the single and multi domain $PbTiO_3$ thin films were investigated using high temperature X-ray. During the experiment, the sample was placed in the center of a triangle-column coiled with Pt resistance thread in order to create a uniform temperature field. A thermocouple was fixed directly to the back of the sample for temperature measurement. The thermocouple was calibrated with a precision better than ±1 °C. The rate of heating and cooling was kept at 4 °C/min and the temperature was maintained long enough to reach thermal equilibrium before the X-ray

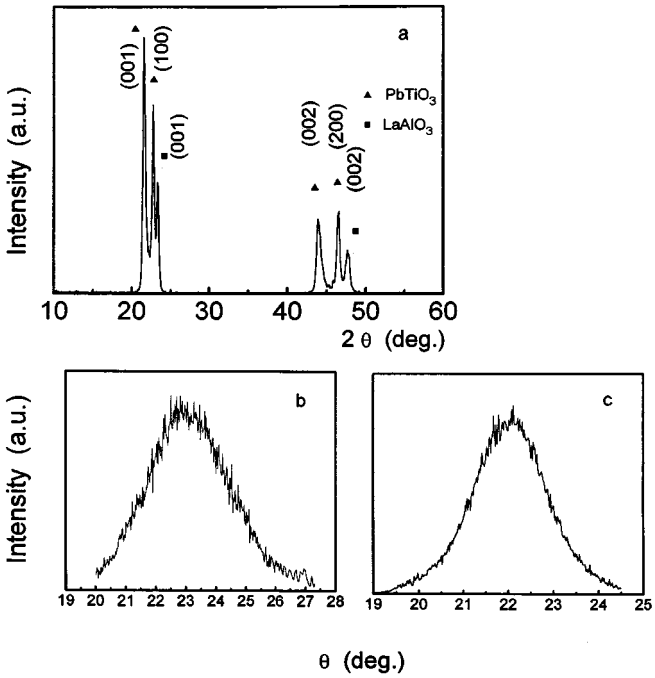

Fig. 5. a $\Theta - 2\Theta$ scan X-ray diffraction of a $PbTiO_3$ film on $LaAlO_3$ substrate. The diffraction pattern shows the presence of two orientations of $PbTiO_3$ film, (100) and (001). **b** and **c** : rocking curves around (200) and (002) directions of $PbTiO_3$, respectively, indicating single orientation of both (001) and (100)

diffraction measurement. For the single domain $PbTiO_3$ film, the phase transition temperature from a tetragonal to a cubic structure was observed at 515 °C in the heating process and at 507 °C in the cooling process, showing a hysteresis in the cooling process compared with the heating process. A similar result was observed for the multi domain film. Thus, no obvious difference in behavior during phase transition was observed in single and multi domain films by the method employed [19].

In principle, the four equivalent displacement directions of the Ti^+ ion in the oxygen octahedral of $PbTiO_3$, when the phase transition from cubic (paraelectrics) to tetragonal (ferroelectrics) phase takes place upon cooling from growth temperature, are responsible for the a-domain's distribution of $PbTiO_3$ on $SrTiO_3$. However, the situation is not so simple for the case of a- and c-domains of $PbTiO_3$ on $LaAlO_3$. Figure 5 shows $\Theta - 2\Theta$ scan and rocking curves of the (002) and (200) $PbTiO_3$ directions of a film on $LaAlO_3$. As expected, the FWHM of the (002) and (200) $PbTiO_3$ are 2° and 1.5°, respectively, which is greater than that corresponding to films grown on $SrTiO_3$. The wider FWHM resultes from a misfit between $PbTiO_3$ and $LaAlO_3$ as large as 2.8%. Another reason may be that $LaAlO_3$ tends to easily form a large number of twins, which may result in the c-axis of the c-domain and the a-axis of the a-domain inclined to the substrate normal. The a-domains of $PbTiO_3$ films on $LaAlO_3$ formed without the four fold symmetry as occurred for films grown on $SrTiO_3$. In fact, the a-domains and c-domains arrange alternately along the substrate surface [12] with the c-axis of c-domains and a-axis of a-domains perpendicular to the substrate's surface, which is similar to what happens on $KTaO_3$ [9].

The different distributions of the a- and c-domains on these substrates could be explained qualitatively as following: because the a- and b-axis lattice parameters of $PbTiO_3$ and $SrTiO_3$ are very well matched, the c-domain can be perfectly epitaxial. Then, by alignment with the c-domain through a coherent domain wall, a-domains' formation could decrease the energy related to spontaneous polarization and strain without resulting in the release of the coherent interface of the c-domain/substrate. This will raise the energy depending on the film/substrate interaction. In other words, due to the stiffness of the c-domain, a-domains must align themselves with the c-domain. In the case of $PbTiO_3$ films on $LaAlO_3$ and $KTaO_3$, the strain energy due to greater lattice misfits must be released by defects such as dislocations, small angle grain boundaries, etc. when the film thickness is greater than the critical thickness during growth [9, 11]. Then an imperfect epitaxy of c-domains makes it easier for both a- and c-domains to release their energy by misfit defect at Curie temperature. Therefore, the film/substrate system described above yields alternately arranged c- and a-domains.

Although the domain configuration described in Fig. 3 provides a reasonable explanation of how the alignment of a-domains may result in the four-fold symmetry of the rocking curves of films grown on (001) $SrTiO_3$ (Fig. 2), interesting questions remain. First, two adjacent a-domains form 90° ferroelectric domain walls, and they cross to form a special domain boundary. Along this boundary (which is vertical to the surface), these walls should show an orthogonal relationship (Fig. 3) more complex in structure than in the bulk ferroelectrics and must therefore be characterised in further research. Second, the critical film thickness needed to progress from a single to multi domain structure have been neither theoretically nor experimentally established.

In conclusion, we have used SR X-ray diffraction and RBS to investigate the nature of the domains of epitaxial $PbTiO_3$ thin films grown on $SrTiO_3$ and $LaAlO_3$ substrates. We obtain single domain films with 3000 Å thickness on $SrTiO_3$, and multi-domain films on $SrTiO_3$ and $LaAlO_3$. We find that the a-domains were four-fold symmetrically aligned with the c-domains on $SrTiO_3$, while a- and c-domains were equivalently and alternately arranged in films grown on $LaAlO_3$. The surfaces of the single and multi domain films were observed. The single domain film was grown layer-by layer with an averaged step height of 0.4 nm and a 6 nm-width terrace, while the surface of the multi-domain film was rougher than that of single domain film. The phase transition process of both these kinds of films was studied by high temperature X-ray diffraction. Similar results were observed: the transition temperatures were 515 °C in the heating process and 507 °C in the cooling process, showing a hysteresis of 8 °C. These temperatures are higher than that of bulk single crystalline $PbTiO_3$ (490 °C).

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