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X-ray analysis of epitaxial PbTiO₃ thin film grown on an (001) SrTiO₃ substrate by metal–organic chemical vapour deposition

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Abstract. Using metal–organic chemical vapour deposition (MOCVD) under reduced pressure at 650 °C, stoichiometric PbTiO₃ thin films have been epitaxially grown on (001) SrTiO₃ single-crystal substrates. A series of x-ray analyses have been carried out to study the microstructures and phase transition process in the as-grown films. X-ray θ – 2θ diffraction patterns revealed a pure perovskite phase of the thin film. The epitaxial nature of the film was confirmed by a Laue back-reflection photograph and x-ray Φ scan. From the rocking curve measurement made by the synchrotron radiation method at the Beijing Synchrotron Radiation Facility (BSRF), an *a*-, *c*-domain coexisting structure in the 4500 Å PbTiO₃ thin film had been observed with the *c*-axis of the *c*-domain perpendicular to the film surface and the *a*-axis *a*-domain tilted away from the surface normal. The phase transition process of the PbTiO₃ thin film was investigated through the high-temperature θ – 2θ scan patterns; a higher T_c than in the PbTiO₃ single crystal had been observed. The strain-driven domain boundary movement in the film was studied by the relative diffraction intensity variation of the (200) and (002) planes.

1. Introduction

Because of the technological applications and theoretical value, extensive attention has been focused on the preparation and characterization of high-quality ferroelectric thin films. PbTiO₃, with a high Curie temperature of 490 °C and a very small aging rate of the dielectric constant [1], is a promising material as regards device usage. However, pure and dense PbTiO₃ ceramics are hard to obtain due to the great tensile stress occurring in the cooling process when the phase transition occurs and the fact that the bulk material may break into powder. Fortunately, the rapid progress in thin-film preparation techniques makes it possible to obtain epitaxial PbTiO₃ thin films by rf magnetron sputtering [2, 3], ion-beam sputtering [4], electron-beam evaporation [5], sol–gel [6, 7], pulsed-laser deposition (PLD) [8, 9], metal–organic decomposition (MOD) [10] and metal–organic chemical vapour deposition (MOCVD) [11–15] on various substrates. Also, the recently observed layer-by-layer growth mechanism [16] has demonstrated the MOCVD technique to be an ideal method for the growth of high-quality PbTiO₃ thin films.

Among the various insulating substrates used for the deposition of perovskite ferroelectrics, strontium titanate, SrTiO₃, is distinguished as being a perovskite-type

ferroelectric with a Curie temperature of 110 K and a cubic structure ($a = 3.905 \text{ \AA}$) from room temperature to the film deposition temperature. A similar structure and almost zero lattice mismatch with the a - and b -axis lattice constants (3.904 \AA) of PbTiO_3 favour epitaxial growth of the c -axis-oriented PbTiO_3 thin films.

In this paper, we report the preparation and x-ray investigations of epitaxial PbTiO_3 thin films deposited on (001) SrTiO_3 substrates. In the a -, c -domain-coexisting PbTiO_3 thin film, a c -axis contraction phenomenon which was attributable to the size effect and the epitaxy-driven deformation had been observed. The high-temperature x-ray diffraction measurements revealed a higher phase transition temperature (T_c), indicated the influence of strain on T_c , and provided interesting information on the ferroelectric domain boundary movement when the film suffers a compressive strain during the heating cycle.

Table 1. Typical growth conditions.

Substrate	(001) SrTiO_3
Substrate temperature	$\sim 650 \text{ }^\circ\text{C}$
Total pressure	12.0 Torr
Carrier gas	N_2
T_{TIP}	$65 \text{ }^\circ\text{C}$
T_{TEL}	$35 \text{ }^\circ\text{C}$
TEL carrier flow rate	$\sim 100 \text{ sccm}$
TIP carrier flow rate	$\sim 50 \text{ sccm}$
O_2 flow rate	$\sim 100 \text{ sccm}$

2. Experiment

PbTiO_3 thin films were deposited in a horizontal cool-wall MOCVD apparatus [17] under reduced pressure using purified titanium iso-propoxide (TIP) and tetra-ethyl lead (TEL) as the metal-organic precursors; N_2 and O_2 were used as the carrier gas and oxidant, respectively. The SrTiO_3 single-crystal wafers of size $10 \times 5 \times 1 \text{ mm}^3$ were mechanically polished and cleaned by the standard semiconductor procedure. The cleaned substrates were put on a resistor-heating stainless-steel susceptor with a thermocouple inserted into the centre of the heating block for temperature measurement. By adjusting the vapour pressure of the MO precursors, the substrate temperature, the total reaction pressure, the partial pressure of O_2 , and the flow rate of the MO vapour and N_2 , optimal growth conditions were experimentally determined and these are listed in table 1.

The as-deposited PbTiO_3 thin films were transparent and had a pale-yellow glassy surface. The film thickness was measured by profilometry at the film edge made by selective deposition through a cover-glass mask and confirmed by scanning electron microscopy (SEM) cross-section morphology. The typical PbTiO_3 thin film had a thickness of 4500 \AA , and the growth rate was determined to be 75 \AA min^{-1} .

3. X-ray analyses

XRD measurements were performed on a Rigaku D/MAX-RA powder diffractometer with nickel-filtered $\text{Cu K}\alpha$ radiation. As shown in figure 1, only the (00 k) reflections of PbTiO_3 and SrTiO_3 appeared; no PbO and $\text{Pb}_2\text{Ti}_2\text{O}_7$ phases could be observed even on a logarithmic scale. Using the lattice constant of the SrTiO_3 substrate for a calibration, the c -axis length

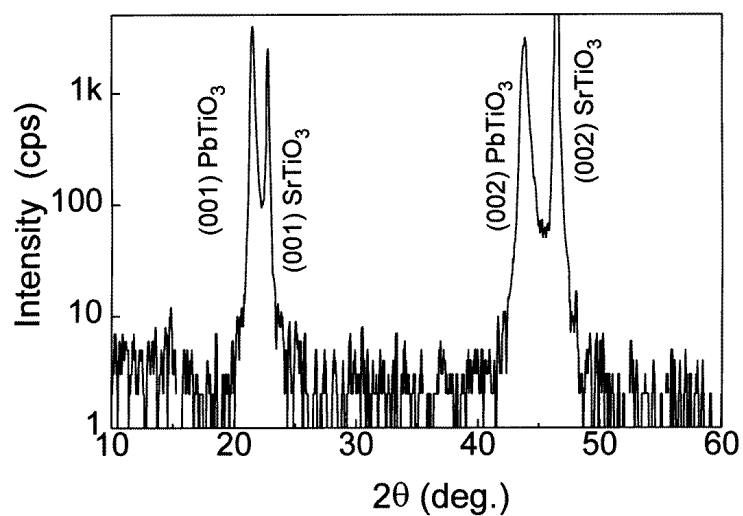


Figure 1. The XRD θ - 2θ scan pattern of PbTiO_3 thin films deposited on an (001) SrTiO_3 substrate.

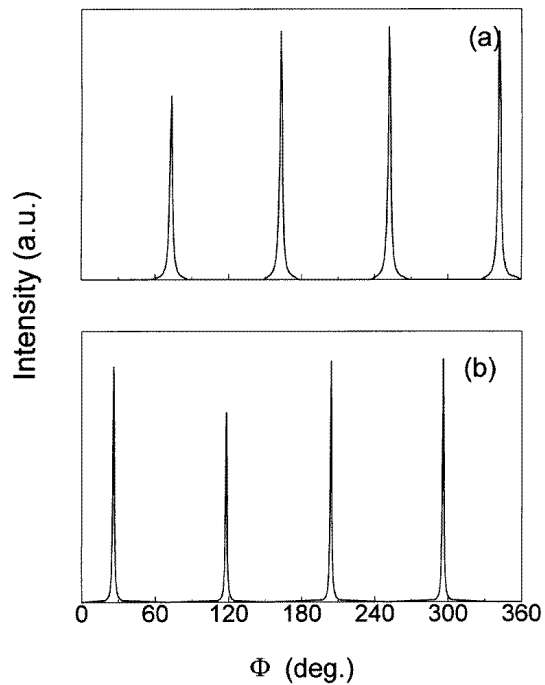


Figure 2. The x-ray intensity versus the angle Φ of (a) the (113) peak of the PbTiO_3 thin film, and (b) the (103) peak of the substrate.

of the as-grown thin film was determined to be $4.125 \pm 0.002 \text{ \AA}$, which was considerably smaller than that of the bulk material (4.150 \AA). The chemical composition of the film

investigated by a Joel JXA-8800M electron microprobe revealed that the Pb, Ti and O distributed uniformly on the surface, and that the average atomic ratio of the Pb and Ti was 1:1.02, in accordance with the result calculated from the Rutherford back-scattering (RBS) [16] spectrum. So in our case, the c -parameter change should not be caused by lead deficiency as observed by Shirasaki. We noticed that the same phenomenon of c -axis contraction had been observed for PbTiO_3 thin film deposited on almost any substrate [19–22], so we assumed that in addition to the in-plane strain influence effected through the Poisson ratio, the size effect and the relaxation of the surface layer, the nature of the epitaxy would deform the film unit cell; in other words, in the epitaxy process, the film unit cells tended to have the same lattice parameters as the substrates, so the interface energy could be reduced, and this would not only be the origin of the in-plane strain, but also resulted in c -axis contraction when $c_{\text{PbTiO}_3} > a_{\text{SrTiO}_3}$.

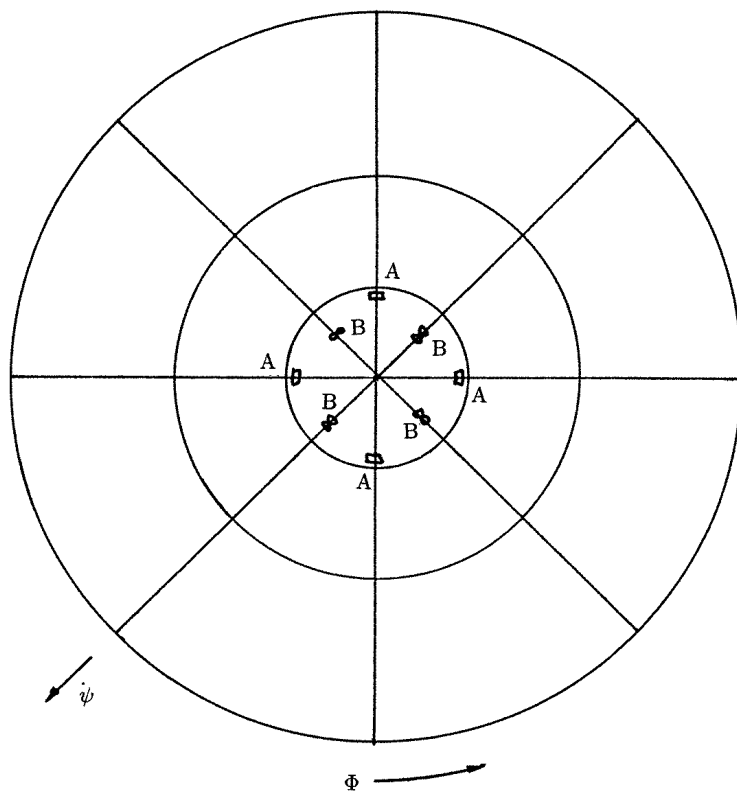


Figure 3. A simplified pole figure of a PbTiO_3 film on a SrTiO_3 substrate with a fixed 2θ -value of 77.4° . The intensities indicated as A and B are (113) reflections of the film and (103) reflections of the substrate, respectively. Two kinds of peak appear at the correct position as is expected in Wulff's projection for a PbTiO_3 film with the a -axis aligned with the [100] and [010] directions of the substrate.

Because the XRD θ - 2θ scan can only detect the crystal surfaces with normals parallel to the growth direction, back-reflection x-ray Laue photography and an x-ray Φ scan were performed to determine the epitaxial relationship between the PbTiO_3 thin film and the SrTiO_3 substrate. In the Laue photograph, only a fourfold-symmetric diffraction pattern

was clearly discerned without rings being observed. This suggests that the as-deposited thin film was not textured, but epitaxial. Precise information about the in-plane lattice vector alignment of the film and the substrate was obtained by x-ray Φ scanning. The measurement was made by rotating the sample around the surface normal at a fixed 2θ -value of 77.4° ; the 2θ -angle corresponded to the reflections of the (113) plane of the PbTiO_3 films and the (103) plane of the SrTiO_3 substrates; the tilt angles ψ of the two planes were 63.5° and 71.6° off the original surface normal, respectively. In the two Φ -scan patterns (figure 2), both curves exhibit four sharp peaks separated one from the other by a 90° rotating angle, and the measured Φ angles for the two reflections are 72° and 27° with a 45° difference. The Φ value indicates the relative positions of the surface normal projection in the (001) plane. The angle between the projections of the {103} surface normal of the PbTiO_3 and the {113} surface normal of the SrTiO_3 in the {001} plane is 45° when lattices of PbTiO_3 and SrTiO_3 are coherent, so the experimentally obtained Φ value confirms that the in-plane lattice vectors of the PbTiO_3 layer are epitaxially aligned with those of the SrTiO_3 substrate, i.e., (100) $\text{PbTiO}_3 \parallel$ (100) SrTiO_3 , (010) $\text{PbTiO}_3 \parallel$ (010) SrTiO_3 and (001) $\text{PbTiO}_3 \parallel$ (001) SrTiO_3 . The corresponding polar figure is plotted schematically in figure 3; contributions of the (113) reflections of the PbTiO_3 film and the (103) reflections of the SrTiO_3 film are indicated. A fourfold symmetry has been observed, as is anticipated for a tetragonal lattice of PbTiO_3 and the cubic structure of SrTiO_3 . In this picture, all of the reflections are at the expected positions, and it also confirms the in-plane epitaxy of the film.

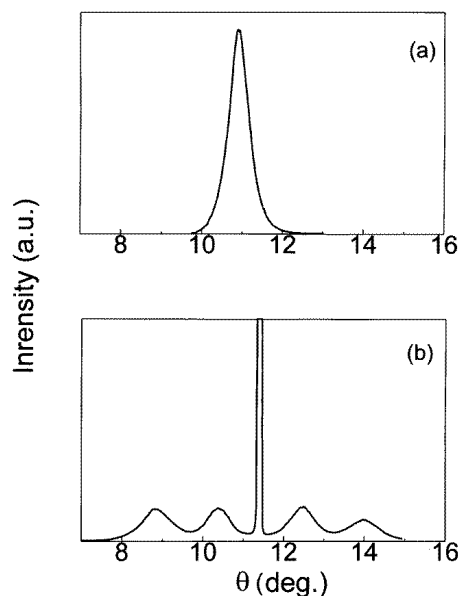


Figure 4. Rocking curves of the (a) (001) orientation of PbTiO_3 and (b) (100) orientation of SrTiO_3 ; the central peak was the reflection of the substrate, and the other four peaks correspond to the four tilted (100) orientations in the a -domain of PbTiO_3 thin film.

Because of the almost zero lattice mismatch between the a - and b -axes of the PbTiO_3 film and the lattice constant of the SrTiO_3 substrate at room temperature, the a -domain diffraction signal overlaps the substrate, and the domain configuration in the PbTiO_3 cannot be discerned by normal x-ray θ - 2θ diffraction. Theoretical analysis points out that for a -, c -domains coexisting in PbTiO_3 film, the c -axis of the c -domain should be perpendicular

to the surface, so the elastic energy in the films can be reduced, and the slight difference between the lengths of the a - and c -axes may cause the a -orientation in the a -domain to have a tilt away from the surface normal [23–24]; this tilt can be discerned by the x-ray ω -scan method through different θ -values at a fixed value of 2θ . Our rocking curve experiment was performed at the Beijing Synchrotron Radiation Facility (BSRF) using a 1.54 Å monochromatic x-ray beam which was obtained by using the {220} plane of Si single crystal as a monochromator; the detector had an energy resolution of 4.4×10^{-4} eV. Figure 4 shows the rocking curves for (001) of PbTiO₃ and the (001) orientation of the SrTiO₃ substrate; only a sharp peak with a full width at half-maximum (FWHM) of 0.48° has been recorded in figure 4(a); this confirms that the c -axis in the c -domain is perpendicular to the surface. In figure 4(b), besides the diffraction peak of the (100) orientation of the SrTiO₃ substrate, four other peaks corresponding to the (100) diffraction of the PbTiO₃ with a tilt angle have been detected. Li *et al* [23] had proposed that the fourfold symmetry along the (001) direction of tetragonal PbTiO₃ would lead the a -domains to be aligned equivalently around a c -domain. Because of the different included angles with respect to the incident x-ray, differently oriented a -domains exhibit four θ -values.

The phase transition of the PbTiO₃ thin film was investigated using a high-temperature x-ray diffraction technique. During the experiment, the sample was placed in the centre of a triangular column coiled with Pt resistance thread in order to create a uniform temperature field. A thermocouple was fixed directly on 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⁻¹ and the temperature was held steady long enough to allow thermal equilibrium to be reached before the x-ray diffraction measurement was performed. Figure 5 shows the profile near the (002) peak of PbTiO₃. The (200) peak of PbTiO₃ which could not be observed at room temperature was separated from the (002) peak of the SrTiO₃ substrate due to the different thermal expansion coefficients of PbTiO₃ and SrTiO₃ when temperature rose up to 470 °C. A computer program was developed to distinguish the (200) and (002) signals; we firstly determined the functional form of a single reflection, then used a least-squares method to determine the positions and intensities of the two diffractions. Using this computer simulation, the phase transition from a tetragonal to a cubic structure was observed at about 515 °C and in the reverse process it happened at 507 °C. Figure 6 is the lattice parameter versus temperature plot; the c -axis lattice constant has a hysteresis in the cooling process unlike in the heating process, and the a -axis length in the a -domains changes in almost the same way in both cycles

Table 2. Lattice parameters of PbTiO₃ and SrTiO₃.

Materials	Room temperature (23 °C)	Growth temperature (650 °C)	Phase transition temperature (510 °C)
PbTiO ₃	$a = b = 3.904$ Å $c = 4.152$ Å	$a = b = c = 3.990$ Å	$a = b = 3.968$ Å $c = 3.996$ Å
SrTiO ₃	$a = b = c = 3.905$ Å	$a = b = c = 3.930$ Å	$a = b = c = 3.924$ Å

From the high-temperature x-ray diffraction, it was also observed that the relative reflection intensities of the (002) and (200) planes of PbTiO₃ changed with the temperature, indicating the movement of domain walls. A c -domain reduction and a -domain enlargement in this process had been observed in the heating cycle, and a reversal process happened in the cooling cycle. According to powder diffraction patterns of PbTiO₃, the diffraction intensity ratio of the (200) plane and (002) plane is 8:15, so the c -domain ratio α can be

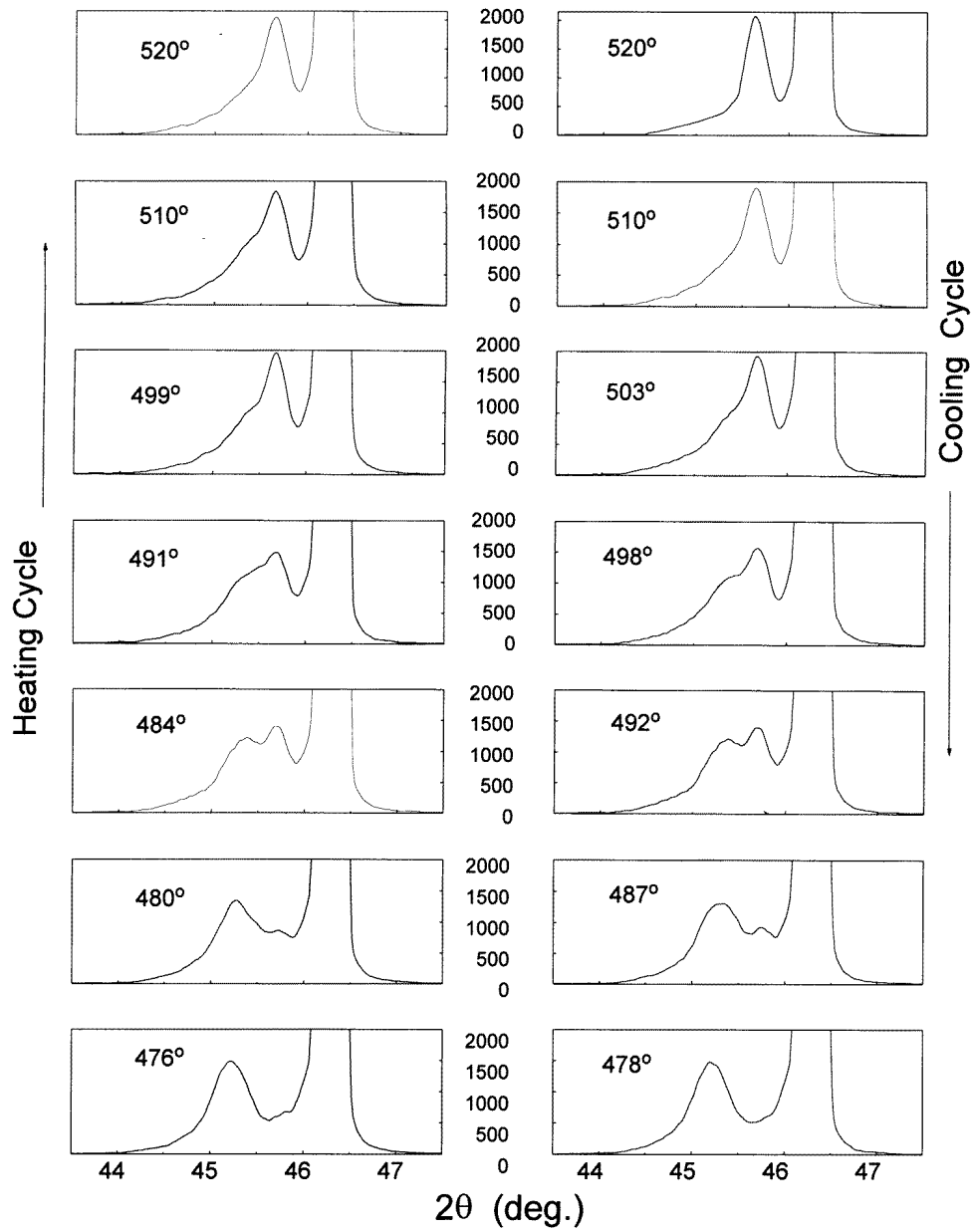


Figure 5. The temperature dependence of the x-ray diffraction profile near the (002) peak of $PbTiO_3$ thin film.

defined as follows:

$$a = I(002) / \{I(002) + I(200) \times 8/15\}$$

where $I(200)$ and $I(002)$ represent the intensities of the (002) and (200) reflections respectively. The c -domain ratio versus temperature plot is shown in figure 7. The movement of the domain boundary can be attributed to the difference between the thermal

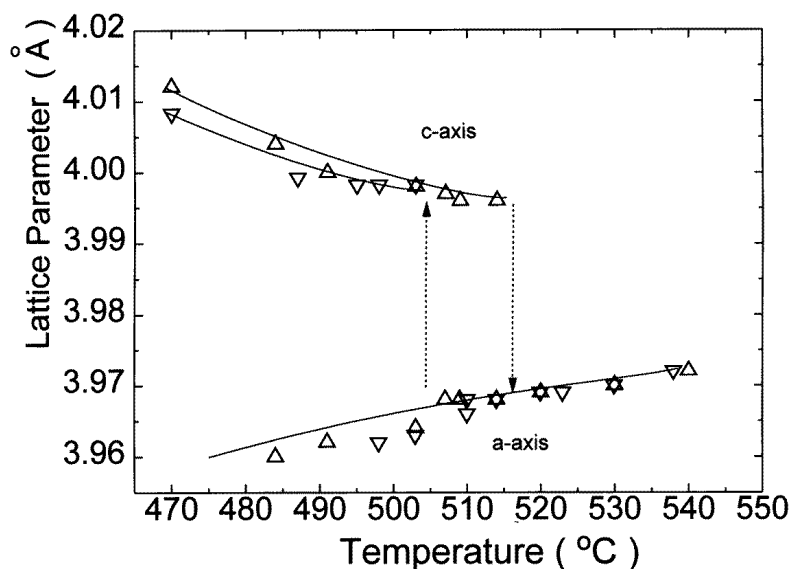


Figure 6. The temperature dependence of the lattice constants a and c of PbTiO_3 thin film. Δ : the heating cycle, ∇ : the cooling cycle.

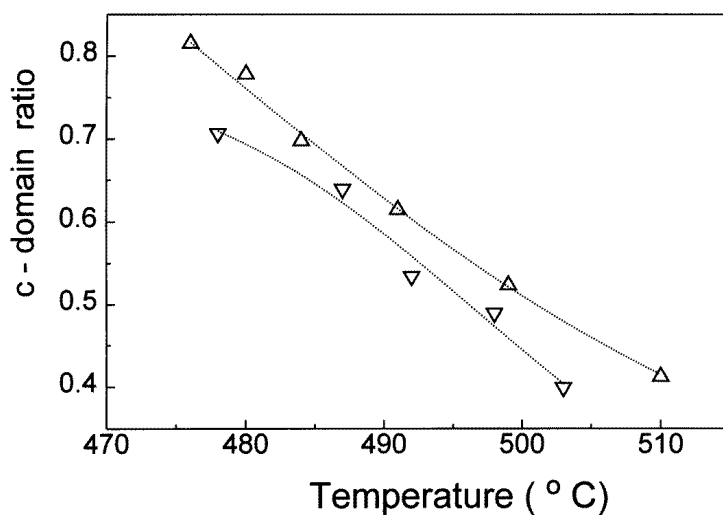


Figure 7. The temperature dependence of the c -domain ratio in the film. Δ : the heating cycle; ∇ : the cooling cycle.

expansions of the PbTiO_3 and SrTiO_3 substrates. As listed in table 2, at the growth temperature of 650°C , the PbTiO_3 has a cubic structure, and the lattice mismatch with SrTiO_3 is 1.53%. When the film is cooled to the phase transition temperature, the PbTiO_3 transforms to a tetragonal structure; the lattice mismatches between a -, b - $\text{PbTiO}_3/\text{SrTiO}_3$ and c - $\text{PbTiO}_3/\text{SrTiO}_3$ are 1.12% and 1.83%, but they change to -0.03% and 6.3% at room temperature, respectively. Recent studies have proved the domain formation to be the most

significant lattice-mismatch-relaxation mechanism in the thin-film epitaxy, so the different thermal expansion coefficients play the most important role in generating a strain in the film as Pompe *et al* reported [25]. During the heating cycle, the SrTiO_3 substrate may generate a compressive stress on the c -domain due to the smaller expansion coefficient compared to the a - and c -axis expansion coefficients of PbTiO_3 . As a result, the PbTiO_3 film prefers an a -axis orientation, so the a -domain ratio increases. We notice that the c -axis deformation caused by surface relaxation and the difference between the film–substrate unit cells decreases when the temperature rises. So the upshift of the PbTiO_3 phase transition temperature can also be understood from considering this compressive stress in the thin film.

4. Summary

The results of the investigation can be summarized as follows.

(1) Stoichiometric PbTiO_3 thin films have been epitaxially deposited on (001) SrTiO_3 substrates using a low-pressure MOCVD technique at a growth temperature of 650 °C.

(2) A c -axis shortening phenomenon has been found in the thin film and is attributable to the size-induced surface relaxation and the nature of the heteroepitaxy.

(3) Synchrotron radiation rocking curves reveal that a - and c -domains coexist in the as-grown 4500 Å PbTiO_3 thin films; (001) of the c -domain is perpendicular to the film surface and the tilted a -domain aligns around the c -domain with a fourfold symmetry.

(4) The phase transition temperature of the PbTiO_3 thin film showed an upward shift compared with that of the bulk PbTiO_3 single crystal. The content of a -, c -domains in the film changed with the temperature due to the stress caused by the difference between the thermal expansion coefficients of the PbTiO_3 and SrTiO_3 .

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References

- [1] Ikegami S and Ueda I 1967 *J. Phys. Soc. Japan* **22** 725
- [2] Iijima K, Tomita Y, Takeyama R and Ueda I 1986 *J. Appl. Phys.* **60** 361
- [3] Okawamura M, Matsui Y, Nakano H, Nakagawa T and Hamakawa Y 1979 *Japan. J. Appl. Phys.* **18** 1633
- [4] Castellano R N and Feinstein L G 1979 *J. Appl. Phys.* **50** 4406
- [5] Shiosaki T, Adachi M, Modhizuki S and Kawabata A 1985 *Ferroelectrics* **63** 227
- [6] Maeda M, Ishida H, Soe K K and Suzuki I 1993 *Japan. J. Appl. Phys.* **32** 4136
- [7] Hayashi Y and Blum B 1987 *J. Mater. Sci.* **22** 2655
- [8] Ghonge S G, Goo E and Ramash R 1993 *Appl. Phys. Lett.* **62** 1742
- [9] Okuyama M, Asano J, Imai T, Lee D H and Hamakawa Y 1993 *Japan. J. Appl. Phys.* **32** 4107
- [10] Okada M, Takai S, Amemiya M and Tominaga K 1989 *Japan. Appl. Phys. Lett.* **28** 1030
- [11] Kwak S B, Embil A, Budai J D, Chisholm M F, Boatner L A and Wilkens B J 1994 *Phys. Rev. B* **49** 14 865
- [12] de Keijsers M, Domans G J, Cillessen J F M, de Leeuw D M and Zandbergen H W 1991 *Appl. Phys. Lett.* **58** 2636
- [13] Bai G R, Chang H L M, Foster C M, Shen Z and Lan D J 1994 *J. Mater. Res.* **9** 156
- [14] Lee W G, Woo A I, Kim J C, Choi S H and Oh K H 1993 *Appl. Phys. Lett.* **63** 2511

- [15] Sun L, Chen Y F, Yu T, Chen J X and Ming N B 1995 *J. Phys. D: Appl. Phys.* **7** 6537
- [16] Chen Y F, Sun L, Yu T, Chen J X, Ming N B, Ding D S and Wang L W 1995 *Appl. Phys. Lett.* **67** 3503
- [17] Chen Y F, Chen J X, Sun L, Yu T, Li P, Ming N B and Shi L J 1995 *J. Cryst. Growth* **146** 624
- [18] Shirasaki S 1971 *Solid State Commun.* **9** 1217
- [19] Gao Y, Bai G, Merkle K L, Chang H L M and Lam D J 1993 *Thin Solid Films* **235** 86
- [20] Erbil A, Braun W, Kawk B S, Wilkens B J, Boatner L A and Budai J D 1992 *J. Cryst. Growth* **124** 684
- [21] Chen Y F, Yu T, Chen J X, Shun L, Li P and Ming N B 1995 *Appl. Phys. Lett.* **66** 148
- [22] Zhong W L, Wang Y G, Kong D S, Zhang P L and Qu B D 1994 *Thin Solid Films* **237** 160
- [23] Li Z, Foster C M, Guo D, Zhang H, Bai G R, Baldo P M and Rehn L E 1994 *Appl. Phys. Lett.* **65** 1106
- [24] Bai G R, Chang H L M, Foster C M, Shen Z and Lam D J 1994 *J. Mater. Res.* **9** 156
- [25] Pompe W, Gong X, Suo Z and Speck J S 1995 *J. Appl. Phys.* **74** 6012