Single-crystalline, single-domain epitaxy of $PbTiO_3$ thin films by metalorganic chemical vapor deposition

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Single-crystalline and single-domain $PbTiO_3$ films with thickness of 3000 Å have been prepared by metalorganic chemical vapor deposition (MOCVD), using metalorganic precursors of tetra-ethyl-lead and iso-propoxide titanium. The nature of single-crystalline epitaxy and single domain of as-grown films was characterized by x-ray diffraction (XRD), synchrotron radiation (SR), and Rutherford backscattering (RBS). Using atomic force microscopy (AFM), the evidence of layer-by-layer growth was observed. The growth steps on the surface may be attributable to the formation of single-crystalline and single-domain $PbTiO_3$ film with 3000-Å thickness. *© 1995 American Institute of Physics.*

A considerable amount of ferroelectric research has been focused on the preparation of ferroelectronic thin films due to their applications in a variety of fields including: nonvolatile memories,[1] ultrasonic sensors,[2] and infrared detectors[3]. Among these studies, preparation of $PbTiO_3$ thin films attracted much attention not only for the potential for the above applications but also because it is representative of displacive ferroelectrics with a large spontaneous polarization, a small dielectric constant, and high pyroelectric coefficient.[4] Recently, epitaxial $PbTiO_3$ thin films have been successfully grown by metalorganic chemical vapor deposition.[5–9]

The formation of domain in ferroelectric thin films was very interesting because the domain plays a determinant role in the device performance, such as the fatigue of ferroelectric memory,[1] and it proffers the information of film-substrate interactions, which result in film structures and properties profoundly different from those of the bulk phase. Although the single-domain single-crystal film of $PbTiO_3$ was first grown by Li *et al.*,[8] and several models were proposed to describe the formation of domain in thin ferroelectric film,[5,10,11] the mechanism of domain formation in thin films was not well-understood. In this letter, we describe the preparation of single-crystalline, single-domain $PbTiO_3$ thin films and their characterization by x-ray diffraction (XRD), synchrotron radiation (SR), and Rutherford backscattering (RBS). Atomic force microscopy (AFM) was used to observe the surface of the as-grown thin films. The growth mechanism of single-crystalline and single-domain was discussed based on the AFM observation.

$PbTiO_3$ thin films were grown in a horizontal MOCVD apparatus which has been described in detail in a previous report.[12] Purified titanium-iso-propoxide (TIP) and tetra-ethyl-lead (TEL) were used as the metalorganic precursors, highly purified N_2 and O_2 were used as a carrier gas and an oxidant, respectively. (001)$SrTiO_3$ was used as a substrate. The growth temperature was 650°C. The optimum growth conditions were established experimentally and presented in Table I.

Figure 1 shows XRD measurement of a $PbTiO_3$ thin film with θ–2θ scanning from 20° to 120°. Only reflections of (00*l*) of $PbTiO_3$ and $SrTiO_3$ were detected. This indicates that the as-grown film was perfectly *c*-axis oriented. By averaging (00*l*) of the thin film, the *c*-axis constant of the film was measured by 4.126 ± 0.002 Å, which is much less than that of the bulk. The shortening of the *c* axis was also observed in the polycrystalline $PbTiO_3$ thin films on fused silica[13] and epitaxial $PbTiO_3$ on $LaAlO_3$.[9] It seems that the shortening cannot only be attributed to the tensile strain in the films as proposed in Ref. 6. In some cases, the deficiency of Pb may also result in the reduced lattice parameter. However, the Pb/Ti ratio of our $PbTiO_3$ films was measured to be

TABLE I. Typical growth conditions.

Substrate	(001)$SrTiO_3$
Substrate temperature	650 °C
Reactor pressure	14.5 Torr
Carrier gas	N_2
T_{TIP}	65 °C
T_{TEL}	35 °C
TEL carrier flow rate	200 sccm
TIP carrier flow rate	150 sccm
O_2 flow rate	250 sccm

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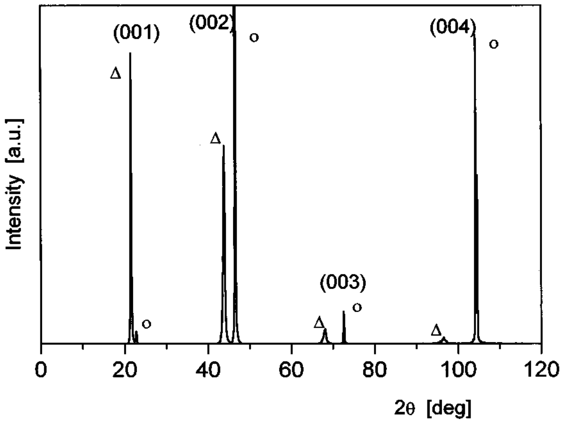

FIG. 1. XRD pattern of a $PbTiO_3$ film deposited by MOCVD at 650 °C on (001) $SrTiO_3$. The peaks indicated by (△) are (00*l*) reflections of the $PbTiO_3$ thin films, and the peaks indicated by (○) are (00*l*) reflections of $SrTiO_3$ substrates.

1 as described below. The reason for the reduction of lattice parameter *c* is still unknown. This may be evidence of ferroelectric weakening which arises from the reduction of the ferroelectrics' thickness as suggested by Tsai and Cowley.[14] The epitaxial relation between the $PbTiO_3$ thin film and $SrTiO_3$ substrate was established as $PbTiO_3(001)\|$ SrTiO3(001), $PbTiO_3(100)\| SrTiO_3$, and $PbTiO_3(010)\|$ $SrTiO_3(010)$ by Φ-scan x-ray diffraction.[12]

To detect a small signal from a small amount of a domain in the thin film, rocking curves were measured at the Beijing Synchrotron Radiation Facility (BSRF) where the maximum x-ray density was 1.6×10^9 photons/s mm^2. Using (220)Si as a monochromator, the monochromatic x ray of wavelength 1.54 Å was available with an energy resolution of 4.4×10^{-4}. The details were described elsewhere.[15] Figures 2(a) and 2(b) show the rocking curves of the (001) of $PbTiO_3$ and (001) of $SrTiO_3$, respectively. In both cases, only one peak was detected. The full width at half-maximum (FWHM) of $(001)PbTiO_3$ rocking curve [Fig. 2(a)] was 0.4°, indicating a good crystalline quality. It should be noted that, in SR measurement, both the wide detector window (5 mm×5 mm) and narrow window (0.1 mm×5 mm) were used, and the results obtained in both cases were the same. In fact, the normal double crystal rocking curve using the radiation of Cu $K\alpha$ and (004)GaAs as the first crystal, has also been measured for the same film, the measured FWHM was 0.3° which was consistent with the SR measurement. For the comparison, ω-scan XRD with Cu $K\alpha$ radiation was also

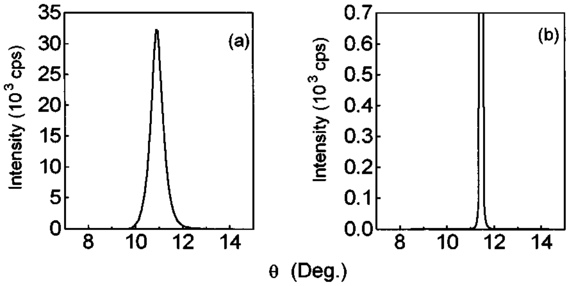

FIG. 2. Rocking curves of (a) $(001)PbTiO_3$ and (b) $(001)SrTiO_3$.

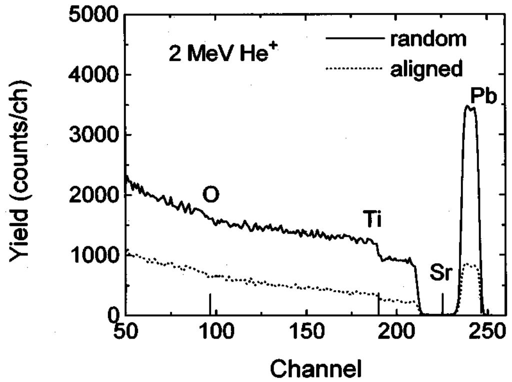

FIG. 3. Rutherford backscattering spectrum showing energy vs intensity for both channeling and random 2-MeV He^+ ions backscattering from the $PbTiO_3$ film on a $(001)SrTiO_3$ substrate.

used to measure the rocking curve with a 0.1 mm×5 mm detector window. The obtained FWHM was even as small as 0.10°. This result was good as the result by Li *et al.*[6] of 1400-Å-thick $PbTiO_3$.

We investigated the crystalline quality of the same film by ion channeling. Figure 3 shows the aligned (001) and random RBS spectra (2 MeV He^+ ions). The ratio ($\chi_{\min}$) of the backscattered yield for the $PbTiO_3$ film along (001) to that in a random direction is 24%. One of the reasons for the 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 ion channeling spectrum exhibits a rising of yield at about channel 215 due to strontium scattering may provide the explanation. With the sample positioned exactly, the result should be improved. The RBS spectrum could be simulated by assuming a 3000-Å-thick stoichiometric $PbTiO_3$ film on a $SrTiO_3$ substrate. The thickness of 3000-Å is consistent with the measurement using a surface profilometer (Dake Take-type) on a delaminated portion of the sample. The Pb:Ti ratio calculated from the RBS spectrum is equal to 1 with the error of 1%,[16] indicating no Pb deficiency in the film.

We examined the same film 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 the scanning area of 12.5 μm×12.5 μm. Figure 4 is a typical AFM image of a 250×250 nm area. Average step height of 4 Å and the terrace width of 60 Å were clearly observed on the surface. This shows that the film was grown on a vicinal $(001)SrTiO_3$ substrate misoriented by 4.5° off to (100) of $SrTiO_3$ and the growth of the thin film occurred layer-by-layer.[17] To the best of our knowledge, the evidence of layer-by-layer growth was first observed in preparation of ferroelectronic thin films. This result is consistent with the measurements of rocking curve and RBS. Furthermore, this suggests that, within the precision of the AFM instrument, the growth layer of $PbTiO_3$ during MOCVD was a monolayer with an oxygen octahedron unity cell (4.12 Å), as in high T_c superconductors.[18]

The AFM measurement also provided an explanation

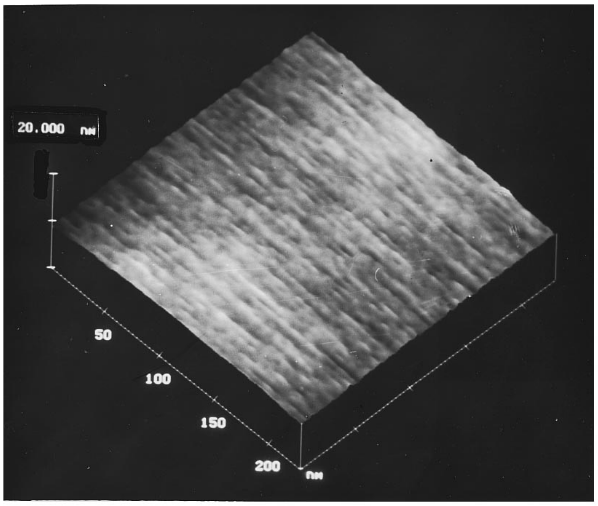

FIG. 4. AFM image of the single-crystal and single-domain $PbTiO_3$ film showing growth steps with the average height of 4.0 Å and terrace width of 60.0 Å. The size of the image is 220 nm×220 nm.

about the single-domain and single-crystal epitaxy. Although the $PbTiO_3$ (PT) and $SrTiO_3$ (ST) is matched very well at room temperature ($a_{PT}=3.9$ Å, $a_{ST}=3.902$ Å), the mismatch between them at growth temperature (650 °C) is as large as about 2.7% ($a_{PT}=4.026$ Å, $a_{ST}=3.919$ Å) and at phase transition point (520 °C)[19] about 1.4% ($a_{PT}=3.972$ Å, $a_{ST}=3.915$ Å). According to Kwak *et al.*,[5] at phase transition temperature from cubic to tetragonal, the critical thickness for the formation of a single domain at 2% misfit was about 340 Å. So, 3000-Å-thick films are much greater than the critical thickness. In fact, single domain thin $PbTiO_3$ films have been obtained up to 1400-Å-thickness by Li *et al.*,[6] where it is pointed out that in-plane compressive stress along the *a* and *b* axis of $PbTiO_3$ will eliminate domains. The AFM observation may indicate that the layer-by-layer growth is one of the mechanisms responsible for the formation of single-domain thin films with the thickness much greater than 340 Å. Qualitatively, the occurrence of the growth steps increases the surface area, which in turn makes it possible for the charge to distribute more efficiently on the surface. So when the film undergoes a structural phase transition from paraelectrics (cubic) to ferroelectrics (tetragonal) during cooling from growth temperature, the energy depending on the polarization and spontaneous strain could be accommodated entirely by the stepped surface, instead of the formation of domains and domain boundaries.

In conclusion, the single-crystal and single-domain $PbTiO_3$ thin films have been prepared and characterized by x-ray diffraction, synchrotron radiation, and Rutherford backscattering. AFM observation shows that the film was grown layer-by-layer. The stepped surface may be attributable to the single domain formation with thickness much greater than estimated critical thickness.

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[1] J. F. Scott and C. A. P. de Araujo, Science **246**, 1400 (1989).

[2] K. Iijima, Y. Tomita, R. Takeyama, and I. Ueda, J. Appl. Phys. **60**, 361 (1990).

[3] M. H. Francombe and S. V. Krinnawamy, J. Vac. Sci. Technol. A **8**, 11382 (1990).

[4] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Uarendo, Oxford, 1972).

[5] S. B. Kwak, A. Embil, J. D. Budai, M. F. Chisholm, L. A. Boatner, and B. J. Wilkens, Phys. Rev. B **49**, 14865 (1994); B. S. Kwak, A. Erbil, B. J. Wilkens, J. D. Budai, M. F. Chisholm, and L. A. Boatner, Phys. Rev. Lett. **68**, 3733 (1992).

[6] M. de Keijser, G. J. Domans, J. F. M. Cillessen, D. M. de Leeuw, and H. W. Zandbergen, Appl. Phys. Lett. **58**, 2636 (1991).

[7] G. R. Bai, H. L. M. Chang, C. M. Foster, Z. Shen, and D. J. Lan, J. Mater. Res. **9**, 156 (1994).

[8] Z. Li, C. M. Foster, D. Guo, H. Zhang, G. R. Bai, P. M. Baldo, and L. E. Rehn, Appl. Phys. Lett. **65**, 1106 (1994).

[9] Y.-F. Chen, T. Yu, J.-X. Chen, L. Shun, P. Li, and N. B. Ming, Appl. Phys. Lett. **66**, 148 (1995).

[10] J. S. Speck and W. Pompe, J. Appl. Phys. **76**, 466 (1994).

[11] T. Ogawa, A. Senga, and T. Kanasami, Jpn. J. Appl. Phys. **30**, 2145 (1991).

[12] Y.-F. Chen, J.-X. Chen, L. Shun, T. Yu, P. Li, N.-B. Ming, and L.-J. Shi, J. Cryst. Growth **146**, 624 (1995).

[13] S. L. Swartz, D. A. Seifer, G. T. Noel, and T. R. Shrout, Ferroelectrics **93**, 37 (1989).

[14] F. Tsai and J. M. Cowley, Appl. Phys. Lett. **65**, 1906 (1994).

[15] M. Jiang, W. Zheng, J. Wu, Y. Jing, and G. Liu, Rev. Sci. Instrum. **66**, 1684 (1995).

[16] W. K. Chu, J. W. Mayer, and M. A. Nicolet, *Backscattering Spectrometry* (Academic, New York, 1978), p. 223.

[17] R. E. Cavicchi, S. Semancik, M. D. Antonik, and R. L. Lad, Appl. Phys. Lett. **61**, 1921 (1992).

[18] C. Gerber, D. Anselmetti, J. G. Bednorz, J. Mannhart, and D. G. Schlom, Nature **350**, 280 (1991).

[19] L. Shun, Y.-F. Chen, T. Yu, J.-X. Chen, and N.-B. Ming, J. Phys. Condens. Matter **7**, 6537 (1995).