MOCVD Growth and Structure of $PbTiO_3$ Thin Films*

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MOCVD Growth and Structure of $PbTiO_3$ Thin Films

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ABSTRACT

$PbTiO_3$ thin films grown on (001)MgO and (110)MgO by MOCVD have been characterized by x-ray diffraction and transmission electron microscopy. The $PbTiO_3$ films deposited on (001)MgO under the optimum conditions always show a bi-layer structure. The top layer of the films near the free surface is c-axis oriented with the orientation relationship (001)[100]$PbTiO_3$||(001)[100]MgO. The bottom layer of the films near the substrate is a-axis oriented with (100)[001]$PbTiO_3$||(001)[100]MgO. 90° domains were observed, but only in the c-axis oriented layers. The thickness of the a-axis oriented layers near the substrate decreases with decreasing the cooling rate. $PbTiO_3$ films deposited on (110) MgO, however, are single-layer, epitaxial films with (101)[001]$PbTiO_3$||(110)[001]MgO.

1. INTRODUCTION

Recently, technological applications of ferroelectric oxides in electronic and optical devices have drawn attention to study ferroelectric thin films. Ferroelectric oxides exhibit spontaneous electrical polarization, which can be switched from plus to minus by applying an external electric field. Switching between these two polarization states in ferroelectric thin films can be directly used for nonvolatile memories. In addition to the polarization switching of ferroelectric oxides, properties of interest include high dielectric constant, pyroelectricity, piezoelectricity, and electro-optic effects. These unique properties of ferroelectric oxides give them great potential for future applications in electronic and optical devices [1].

MOCVD is an economical and high-production-rate process, and can provide flexible control of deposition rate and film composition by adjusting the source temperature and carrier gas flow rate. In the last few years, ferroelectric thin films have been successfully prepared on various substrates by the MOCVD technique [2-6]. Epitaxial thin films on $SrTiO_3$ and $LaAlO_3$ were also reported for a number of ferroelectric oxides such as $PbTiO_3$ [2], $Pb(Zr,Ti)O_3$ [7], and $BaTiO_3$ [4, 6]. However, there is a lack of systematic study to correlate the processing parameters with the microstructure, which is essential for a basic understanding of the MOCVD growth of the ferroelectric thin films. Recently, such a study has been carried out for $PbTiO_3$ films grown on MgO by the present authors [8]. The most important result of that investigation was that the $PbTiO_3$ thin films on (001) MgO consist of two layers due to the substrate effect on the phase transformation. The one near the free surface is c-axis oriented with 90° domain structure, and the other near the substrate interface is a-axis oriented without the 90° domain structure. However, single-layer epitaxial films of $PbTiO_3$ were found on (001) $SrTiO_3$ [2]. Clearly, the final microstructure of epitaxial $PbTiO_3$ films will strongly depend on their substrates as well as other processing parameters. The purpose of this paper is to report the results of an extended study of the $PbTiO_3$ thin films grown on MgO. Primary emphasis is focused on the effects of the substrate orientation and cooling rate from the growth temperature to room temperature on the bi-layer structure.

2. EXPERIMENTAL

Thin films of $PbTiO_3$ were prepared in a horizontal, low-pressure, cold-wall reactor with a resistive substrate heater. Commercial extra-pure lead β-diketonate ($Pb(thd)_4$) and titanium isopropoxide ($Ti(OC_3H_7)_4$) from STREM Chemicals were used as the metal-organic precursors. The mixture of the precursor vapor was introduced into the reactor by high-purity nitrogen as a carrier gas. High-purity oxygen gas in a separate gas line was used as an oxidant. The flow rates of the carrier gas and evaporator temperature for each of the precursor chambers were controlled individually to adjust the film composition. Deposition parameters were used as follows: reactor chamber pressure, 10 torr; oxygen flow rate, 400 sccm; carrier gas flow rate for Pb, 100 sccm;

carrier gas flow rate for Ti, 10-25 sccm; Pb metal-organic source temperature, 116 °C-126 °C; Ti metal-organic source temperature, 32 °C. The $PbTiO_3$ thin films were grown on (001) MgO and (110) MgO at temperatures ranging from 550 °C to 700 °C.

The film structure and crystallinity were characterized by x-ray diffraction technique. The microstructure of the thin films was investigated by transmission electron microscopy (TEM) using both plan-view and cross-sectional specimens. TEM plan-view specimens were prepared by mechanical thinning, dimpling, and argon-ion milling at liquid-nitrogen temperature from the MgO side. TEM cross-sectional specimens were prepared using a standard technique as described in detail elsewhere [8].

3. RESULTS AND DISCUSSION

$PbTiO_3$ on (001) MgO

Fast cooling - When $PbTiO_3$ films deposited on (001) MgO at temperatures above 500 °C under optimum growth conditions were fast cooled down to room temperature by turning off the heater, x-ray diffraction spectra of the $PbTiO_3$ films show only two orientations, (001) and (100), parallel to the substrate surface. A representative x-ray diffraction spectrum is shown in Fig. 1(a). X-ray ϕ scans of appropriate crystallographic planes of the films and the substrates indicate that the films are likely to be single crystalline with two oriented regions: 1) the c-axis oriented region - $(001)[100]PbTiO_3 \| (001)[100]MgO$; and 2) the a-axis oriented region - $(100)[00\bar{1}]PbTiO_3 \| (001)[100]MgO$. The rocking curves (i.e. θ scan) of the (100) and (001) planes were performed to show the quality of each layer in the growth direction, for the a-axis and the c-axis oriented regions, respectively. The results show that the rocking curves of the (100) plane always consist of three peaks about 2° apart, while the rocking curves of the (001) plane show a single peak. A representative of the rocking curves is shown in Fig. 1(b) for the

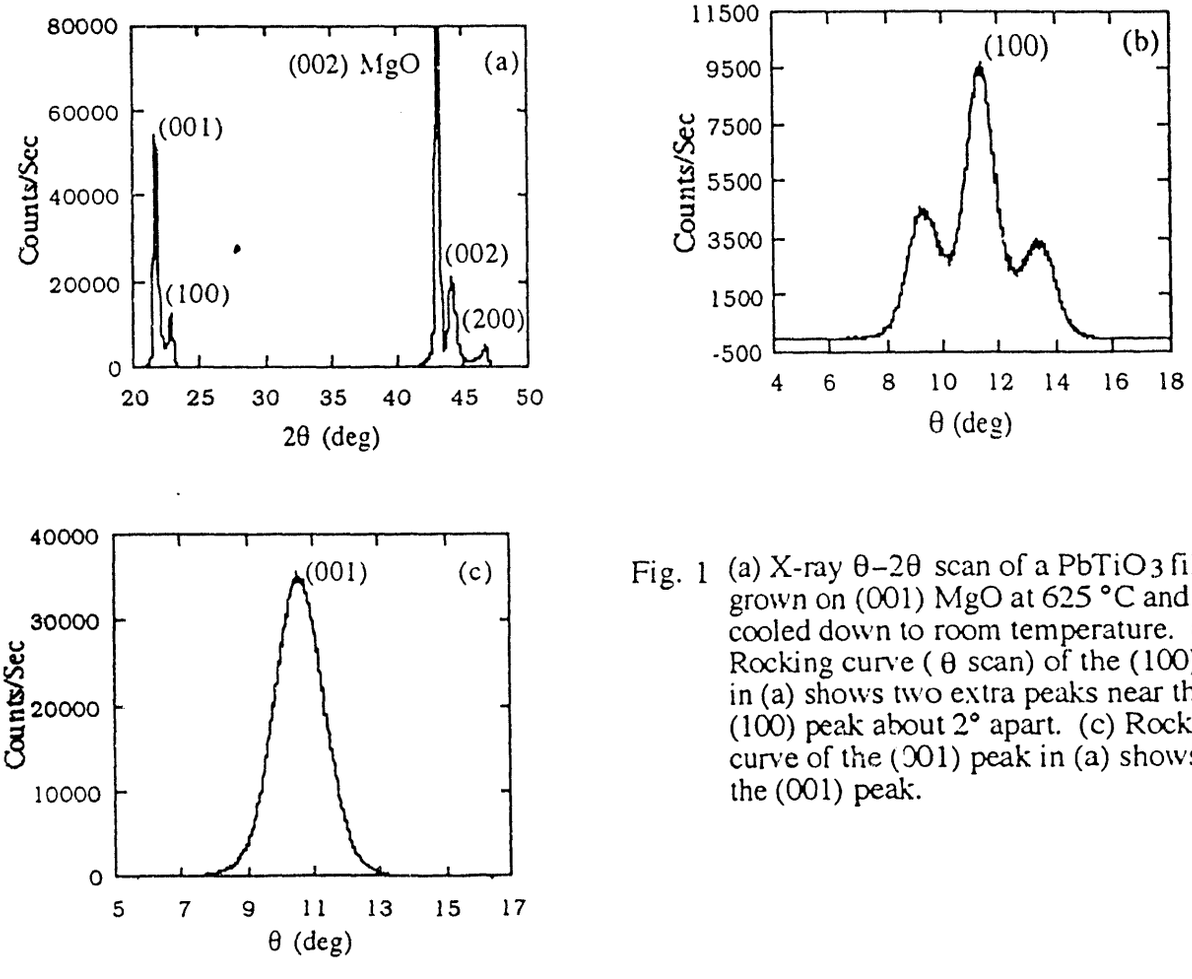

Fig. 1 (a) X-ray θ–2θ scan of a $PbTiO_3$ film grown on (001) MgO at 625 °C and fast cooled down to room temperature. (b) Rocking curve (θ scan) of the (100) peak in (a) shows two extra peaks near the (100) peak about 2° apart. (c) Rocking curve of the (001) peak in (a) shows only the (001) peak.

(100) plane and in Fig. 1(c) for the (001) plane, respectively. The two extra peaks in Fig. 1(b) could come from 90° domains in the c-axis oriented region. The 90° domain walls in $PbTiO_3$ are the {101} or {011} twin boundaries, which were formed in the films through the phase transformation during cooling. Because of the slight difference between lattice constant a (0.391 nm) and c (0.409 nm), the a axis in the 90° domains of the c-axis oriented region will not be exactly parallel to the c axis in the matrix, but tilted slightly by an angle of about 2.6° calculated from the geometry of the domain structure. The calculated value is in agreement with the value measured from Fig. 1(b). For the same reason, the 90° domains in the a-axis oriented region of the film should be formed during cooling. Therefore, one should also see the two extra peaks in the (001) rocking curve of Fig. 1(c) as in the (100) rocking curve of Fig. 1(b). However, we did not see any trace of the extra peaks in the (001) rocking curves for all films. It is not clear from the x-ray diffraction analyses why the 90° domains were formed in the c-axis oriented region, but not in the a-axis oriented region due to a lack of information about the microstructure. Thus, the x-ray diffraction analyses have been supplemented by TEM studies.

Fig. 2(a) shows a TEM micrograph of a cross-sectional specimen for the film in Fig. 1. A bi-layer structure of the $PbTiO_3$ thin film is evident from the micrograph. Moreover, the 90° domains (or twins) are clearly observed in the top layer near the free surface, while the domains are not observed in the bottom layer near the substrate. A selected-area diffraction pattern (SADP) in Fig. 2(b) taken from a small area covering the bottom layer and the substrate shows that the bottom layer is the a-axis oriented region. The epitaxial orientation relationship between the a-axis oriented region and the substrate is $(100)[00\bar{1}]PbTiO_3 \| (001)[100]MgO$. A SADP taken from an area covering both layers and the substrate is shown in Fig. 2(c), indicating that the top layer is the c-axis oriented region. Note that the diffraction spots from the bottom layer did not show up due to their weak intensity. Therefore, the epitaxial orientation relationship between the c-axis oriented region and the substrate is $(001)[100]PbTiO_3 \| (001)[100]MgO$. The two sets of the 90° domains observed in Fig. 2(a) are the $(\bar{1}01)$ and the (101) domains inclined by about 45°. The tilt angle of the (010) orientations in the 90° domains from the (001) orientation in the matrix was measured from Fig. 2(c) to be about 2.8°, which is in agreement with the scale of 2° measured from the rocking curves and 2.6° calculated from the film lattice parameters. Note that a slightly large value of the tilt angle measured from the diffraction pattern could be due to the stress relaxation in the thin TEM specimen. It is now clear that the thin films consist of a bi-layer structure; the one near the free surface is c-axis oriented with the twins, and the other near the substrate is a-axis oriented without the twins. If a rocking scan of the (100) plane is performed, one will expect to see three peaks of about 2° apart, one from the bottom layer and two from the top layer. However, only one peak will be observed for a (001) rocking scan. This is consistent with the x-ray diffraction results discussed earlier. The formation of the bi-layer structure could be due to the competition between the phase transition and the substrate constraints. The mechanisms have been discussed in some detail elsewhere [8].

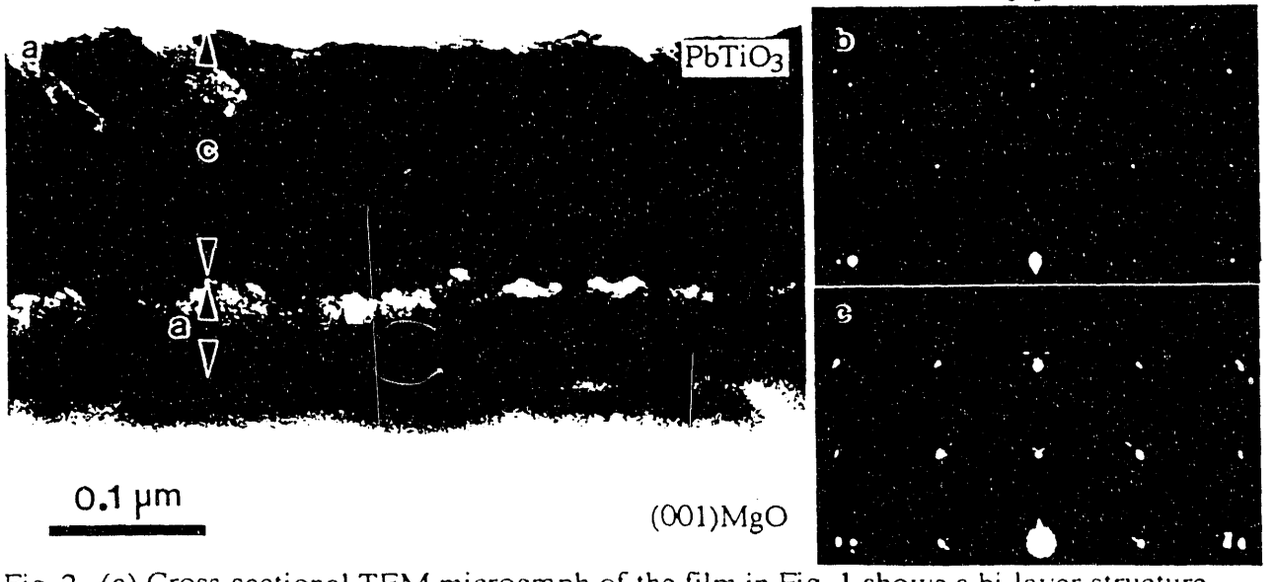

Fig. 2 (a) Cross-sectional TEM micrograph of the film in Fig. 1 shows a bi-layer structure.
(b) SADP taken from interface region shows that the bottom layer is a-axis oriented.
(c) SADP from a large area shows that the top layer near the free surface is c-axis oriented.

Slow cooling - When $PbTiO_3$ films were slowly cooled down to room temperature at a cooling rate of 20 °C/hr after deposition, x-ray diffraction spectra of these $PbTiO_3$ films are similar to those of the fast-cooled films. The θ-2θ scans show only (001) and (100) orientations; the (100) rocking curves show three peaks; and the (001) rocking curves show only one peak. However, the intensity of the (100) plane is relatively lower compared to the intensity in Fig. 1(a), indicating that the thickness of the a-axis oriented layer decreases with reducing the cooling rate.

A cross-sectional TEM micrograph of the slow-cooled thin films is shown in Fig. 3(a). The bi-layer structure is not visible in the micrograph. An electron diffraction pattern taken from the interface area shows that the film was grown epitaxially on the substrate with the c axis as the growth direction. The 90° domains are clearly observed in the film, and the domain boundaries appear to be continuous across the film thickness. In addition, some strain contrast can be seen near the interface, which could be associated with a thin, a-axis oriented layer. Such a thin layer near the interface has been observed using high resolution electron microscopy (HREM). A HREM image of the interfacial area is shown in Fig. 3(b). After measuring the lattice spacing of the thin layer, it was found that this layer is the a-axis oriented layer. The interface appears rough, which could be due to the rough surface of the MgO substrate. Large lattice distortion is likely associated with the lattice mismatch across the interface since no localized misfit dislocation has been observed at the interface.

It is found that the 90° domain size is similar in the two types of the thin films. Most of the domain boundary plane appears abrupt, but the segments near the ends of the domains consist of a number of small steps. Fig. 4(a) shows a HREM image of a flat segment of a $(0\bar{1}1)$ domain boundary near the free surface. It can be seen that this segment of the boundary is abrupt and structurally coherent. The boundary plane can be recognized by viewing the image under a shallow angle. The coherent lattice planes slightly, but abruptly, change their directions as they across the boundary. The tilt of lattice planes across the domain boundary is found to be about 3.2° along [010] or [001] directions in Fig. 4(a). Note that the tilt angle across the boundary will be 6.4° if one measures it along the [011] direction of the matrix. The corresponding diffraction pattern in Fig. 4(b) shows that the tilt due to the twinning on the $(0\bar{1}1)$ plane of the tetragonal structure is about 3.3°, which is consistent with the value measured from the HREM image in Fig. 4(a). This value is close to the calculated value (3.3°) for $PbTiO_3$ single crystal, which indicates that the c/a ratio of the slow-cooled films is close to 1.06. In other words, the structure of the slow-cooled films is much closer to the bulk structure than that of the fast-cooled films. This can be understood if the large lattice stress due to the phase transformation is reduced during the slow cooling process.

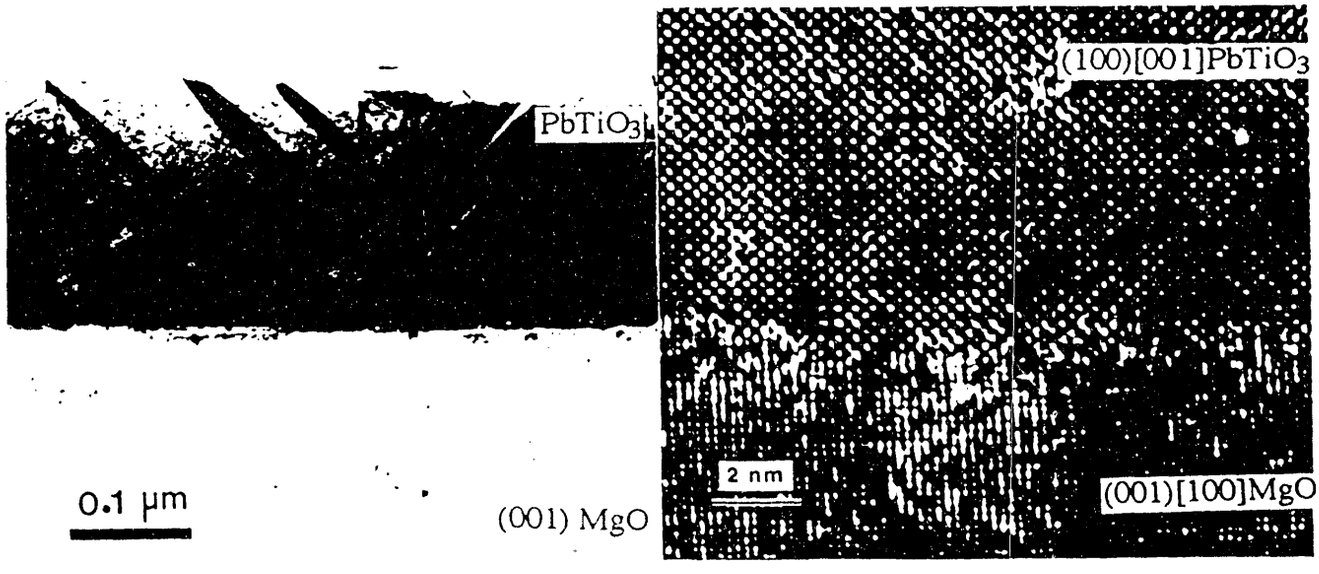

Fig. 3 (a) Cross-sectional TEM image of a film grown on (001)MgO slowly cooled down to room temperature. (b) HERM image shows that a thin layer near the interface is a-axis oriented.

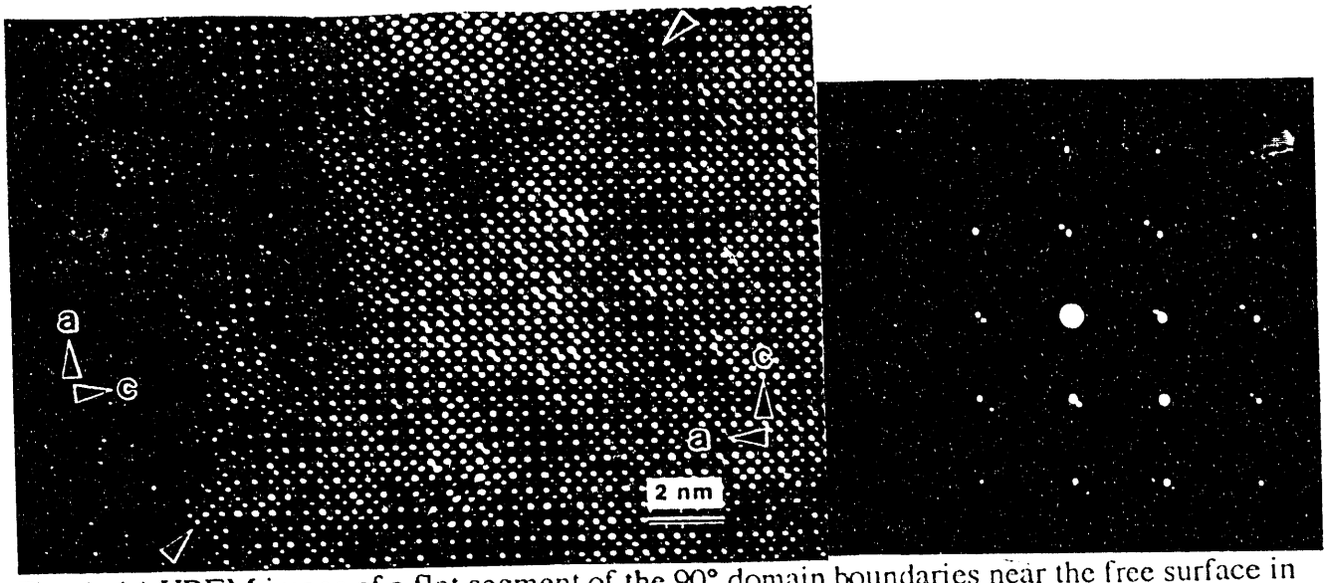

Fig. 4 (a) HREM image of a flat segment of the 90° domain boundaries near the free surface in the slow-cooled films. (b) SADP shows that the tilt angle across the boundary viewed along <100> is 3.2°, indicating that the ratio of c/a is about 1.06.

$PbTiO_3$ on (110) MgO

When $PbTiO_3$ films were grown on (110) MgO under optimum growth conditions, and then slowly cooled down to room temperature at a cooling rate of 20 °C/hr, it was interesting to note that only two diffraction peaks in the θ-2θ scans were observed from the films at 2θ=31.56° and 2θ=32.2°, as shown in Fig. 5(a). The two peaks are (101) and (110), respectively. It appears that the two orientations could also be a result of the bi-layer structure of the films. The θ rocking scans of the (101) and (110) planes were performed to see whether the formation of the two orientations was due to the bi-layer structure. A representative of the rocking curves is shown in Fig. 5(b). It is seen that the rocking curve of the (101) plane shows a single peak, while the rocking curve of the (110) plane consist of two peaks about 2° apart. More importantly, there is no (110) peak at 2θ=32.2°, indicating that only the (101) planes are parallel to the substrate surface. The intensity of the (110) planes observed in the θ-2θ curve of Fig. 5(a) is contributed by the intensity overlapping of the two (110) peaks. The results indicate that the films consist of a single, (101) epitaxial layer with the {101} twins or domains. Twinning will cause the (110) planes in the twin region to closely parallel to the (101) planes in the matrix. The tilt angle calculated from the domain geometry is about 2.8°, which is in agreement with the measured value of about 2°.

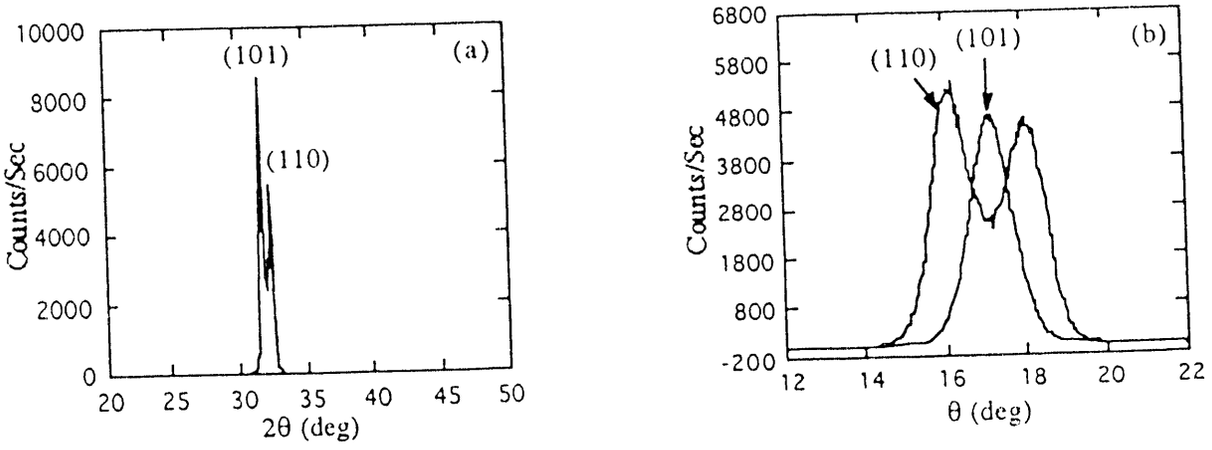

Fig. 5 (a) X-ray θ-2θ scan of a $PbTiO_3$ film grown on (101)MgO at 625 °C and slowly cooled down to room temperature. (b) Rocking curves of the (101) and (110) peaks in (a) shows one (101) peak and no (110) peak at the center, but two (110) peaks near the center about 2° apart, indicating that the (110) plane is not the growth plane.

Fig. 6 Plan-view TEM micrograph of a $PbTiO_3$ film on (110) MgO shows that the film is single crystalline with the {011} twins.

Cross-sectional TEM studies have confirmed the x-ray diffraction analyses that the $PbTiO_3$ films grown on (110) MgO are single-layer epitaxial films with the {101} domain structure. The epitaxial orientation relationship between the film and the substrate, obtained from electron diffraction patterns, is (101)[010]$PbTiO_3$||(110)[001]MgO. Most of the 90° domain boundaries are (011) or $(0\bar{1}1)$ type inclined to the interface, while the others are (101) parallel to the interface, or $(10\bar{1})$ perpendicular to the interface. The {011} 90° domains can be clearly seen in plan-view TEM micrographs as shown, for example, in Fig. 6. The angle between the two sets of the domains is about 74°, which is close to the calculated value (72°) of the angle between the projections of the (011) and $(0\bar{1}1)$ domain boundaries on the (101) plane.

4. CONCLUSIONS

The present studies have shown that the $PbTiO_3$ films grown on (001)MgO are single crystalline with a bi-layer structure at room temperature. The top layers near the free surface is c-axis oriented with the orientation relationship of (001)[100]$PbTiO_3$||(001)[100]MgO. The bottom layer near the substrate is a-axis oriented with (100)$[00\bar{1}]PbTiO_3$||(001)[100]MgO. The 90° domains were observed in the c-axis oriented layers of the $PbTiO_3$ films, but not in the a-axis oriented layers due to the substrate effect. HREM showed that the domain boundaries are abrupt and structural coherent. The formation of the bi-layer structure of the $PbTiO_3$ films appears to be the result of the combined effect of the cooling rate and the lattice mismatch across the interface on the phase transition of $PbTiO_3$ from the cubic to the tetragonal phase. The a-axis oriented layers decrease in thickness with decreasing cooling rate.

$PbTiO_3$ films deposited on (110) MgO are single-layer, epitaxial thin films with (101)[001]$PbTiO_3$||(110)[001]MgO. Most of the 90° domain boundaries in the (101) films are (011) or $(0\bar{1}1)$ type inclined to the interface, while the others are (101) parallel to the interface, or $(10\bar{1})$ perpendicular to the interface.

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