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ABSTRACT

Ferroelectric superlattice structures composed of three-dimensionally epitaxial $PbTiO_3$ and PLT thin films have been successfully grown on $SrTiO_3$ substrates by metalorganic chemical vapor deposition. The modulation structures were confirmed by θ-2θ XRD, and the excellent in-plane orientational relationship between the superlattice film and the substrate by (100), (110), and (111)-pole figures. The ϕ-scans through the (110) and (111) reflections were used as additional evidence for three-dimensional epitaxy. The substrate dependence of the epitaxial orientation of PLT and $PbTiO_3$ single-layered thin films was investigated. $PbTiO_3$ thin films with very high crystalline perfection can be successfully grown on $KTaO_3$ substrates.

INTRODUCTION

One of the most exciting recent developments in materials science is the ability to produce artificial superlattice structures, which are composed of alternating epitaxial thin films. Many exotic properties have been observed in the artificial superlattice structures made from semiconductors[1] and metals[2].

Because of the complexity of the crystal structures and the compositions of ferroelectric materials, even the growth of a ferroelectric single-layer film with three-dimensional epitaxy can be difficult. To date, many attempts to prepare PLT and $PbTiO_3$ thin films have been made by using rf magnetron sputtering[3], sol-gel[4], and MOCVD[5], and some synthesis of three-dimensionally epitaxial films have been reported[5]. Even ferroelectric thin films with a superlattice structure have been obtained by using multi-target sputtering technique[6]. However, the sputtering method has some disadvantages, such as low deposition rates, high density of defects, and composition changes between the film and target, while the MOCVD method provides flexible control of the deposition rate and film composition by adjusting the source temperatures and carrier gas flow rates. The synthesis of ferroelectric superlattices by using MOCVD techniques has not been previously reported.

In this paper, we report the epitaxial growth of $PbTiO_3$ and lanthanum-modified $PbTiO_3$(PLT) thin films, as well as layered $PbTiO_3$/PLT superlattices.

EXPERIMENTAL

The deposition is carried out in an inverted vertical, warm-wall reactor with a resistively heated susceptor. The substrate temperature was measured with a K-type thermocouple embedded in the susceptor about 1 mm from the substrate. The metalorganic precursors used were tetraethyl lead, $Pb(C_2H_5)_4$, lanthanum β-diketonate, $La(C_{11}H_{19}O_2)_3$, and titanium isopropoxide, $Ti(OC_3H_7)_4$ for the PLT thin film while tetraethyl lead, $Pb(C_2H_5)_4$ and titanium isopropoxide, $Ti(OC_3H_7)_4$ were used for $PbTiO_3$ thin films. During the deposition process, the substrate temperature was fixed at 600 °C and the reactor pressure was maintained at 70 torr. Growth conditions for $PbTiO_3$ and PLT thin films as well as layered $PbTiO_3$/PLT superlattices are given in the table 1. The deposition rates were about 1260 Å/h and 240 Å/h for PLT and $PbTiO_3$ thin films, respectively.

The crystal structure was examined by x-ray diffraction (XRD) methods using a Siemens digitized horizontal diffractometer employing Cu-K_α radiation and a sample stage that was equipped with both rotational and rocking capabilities in order to provide statistically correct

Table 1. Growth conditions for PLT and PbTiO₃ thin films.

Thin Film	Flow Rate (sccm)	Source Temperature (°C)

PLT	O₂: 50
	Ar;
	    La : 250
	    Pb: 140
	    Ti : 1000
		La: 176.5
		Pb: 9.0
		Ti : 22.0

PbTiO₃	O₂: 8
	Ar;
	    Pb: 100
	    Ti : 1000
		Pb: 4.2
		Ti : 22.0

averaging over the reciprocal lattice points. In-plane epitaxial relations between the film and substrate were examined by pole figure and ϕ-scan measurements by using a Philips X'Pert Materials Research Diffractometer. Rutherford backscattering (RBS) and ion channeling experiment were performed to determine the film thickness, composition, and crystallographic perfections.

RESULTS AND DISCUSSION

PLT single-layer thin films

The selection of the substrate is very important in the growth of an epitaxial thin film, because the crystal growth of the film is strongly affected by lattice matching between the film and substrate, and the substrate surface crystalline quality. The epitaxy of PLT thin films on $Al_2O_3(1\bar{1}02)$, $Al_2O_3(0001)$, MgO(100), KTaO₃(100), and SrTiO₃(100) was examined by x-ray diffraction (XRD) methods. At room temperature, KTaO₃ and SrTiO₃ have the same perovskite structure with the cubic phase as PLT, and lattice constants are 3.989 Å and 3.905 Å, respectively. MgO has a sodium-chloride structure with a lattice constant of 4.203 Å. The θ-2θ XRD patterns for PLT ($Pb_{1-x}La_xTiO_3$) films with x=0.39 grown on KTaO₃, SrTiO₃, and MgO substrates are shown in Fig. 1. The films had single perovskite cubic phase with dominant (100) planes parallel
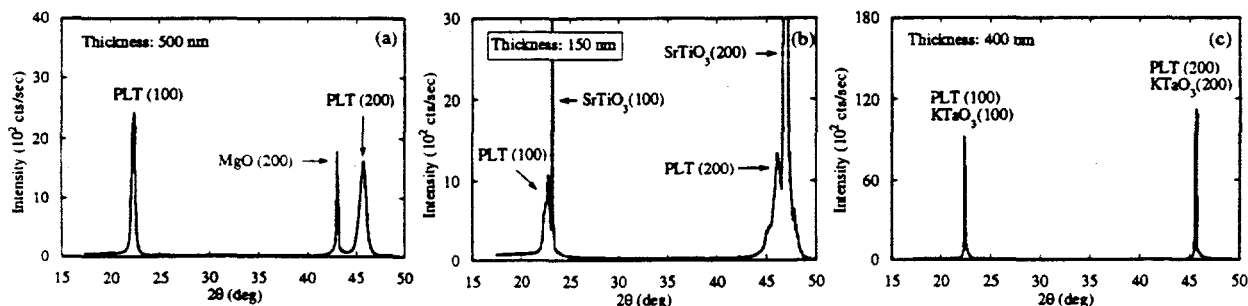

Figure 1. θ-2θ XRD patterns for PLT thin films grown on (a) MgO (100), (b) SrTiO₃ (100), (c) KTaO₃ (100).

to the substrate surface. Sapphire, α-Al_2O_3, has a trigonal crystal structure with $R\bar{3}c$ space group. Its unit cell is hexagonal with a=4.76 Å and c=13.00 Å. The θ-2θ XRD patterns for PLT films grown on $Al_2O_3(1\bar{1}02)$ and $Al_2O_3(0001)$ substrates are shown in Fig. 2. There were two different growth orientations on $Al_2O_3(0001)$ depending on the growth temperature. PLT films grown at 600 °C and 650 °C have [100] and [111] orientations, respectively, perpendicular to the substrate surface.
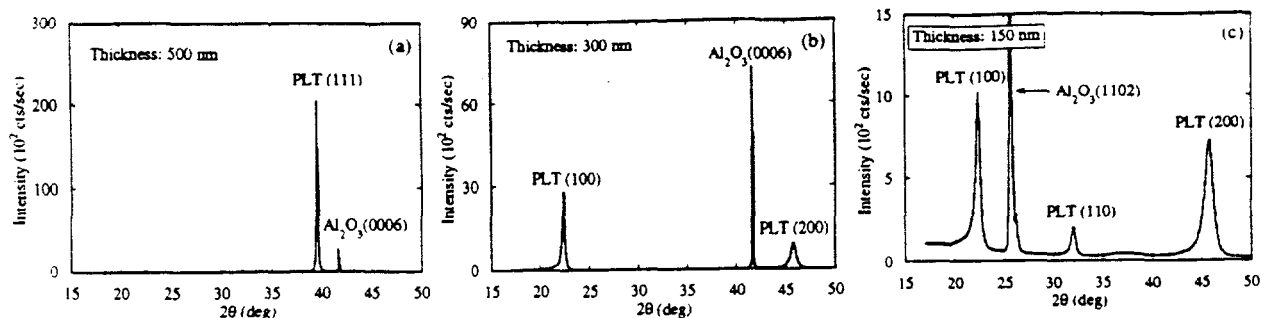
Figure 2. θ-2θ XRD patterns for PLT thin films grown on (a) Al_2O_3 (0001) at substrate temperature of 650 °C, (b) Al_2O_3 (0001) at substrate temperature of 600 °C, (c) Al_2O_3 ($1\bar{1}02$) at substrate temperature of 600 °C.

Fig. 3 (a) shows an RBS spectrum from an epitaxial PLT thin film deposited on $SrTiO_3$(100). The dotted-dashed line represents the simulation of stoichiometric PLT ($Pb_{0.61}La_{0.39}TiO_3$) as determined by the Rump program[7], while the solid line shows the experimental data. Ion channeling experiments were also performed on the sample in the [100]-direction, and the results are shown by a dashed line in Fig. 3. The minimum channeling yield χ for this sample along the [100] direction is about 72% as determined by using the Pb signal , while χ for PLT grown on $KTaO_3$(100) is about 32%.
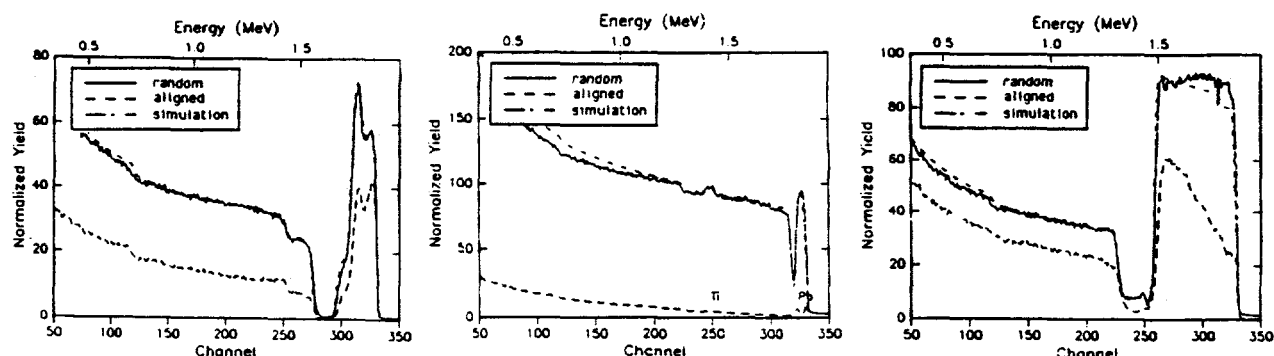

Figure 3. RBS and channeling spectra from (a) an epitaxial PLT film on a $SrTiO_3$ (100) substrate, (b) a single-domain $PbTiO_3$ film on $KTaO_3$ (100) substrate, (c) $PbTiO_3$/PLT superlattice film on $SrTiO_3$ (100) substrate.

PbTiO₃ single-layer thin films

θ-2θ XRD patterns of epitaxial $PbTiO_3$ films deposited on $KTaO_3$(100) and Al_2O_3(0001) substrates are shown in Fig. 4. Only single a-domain $PbTiO_3$ films were grown on $KTaO_3$
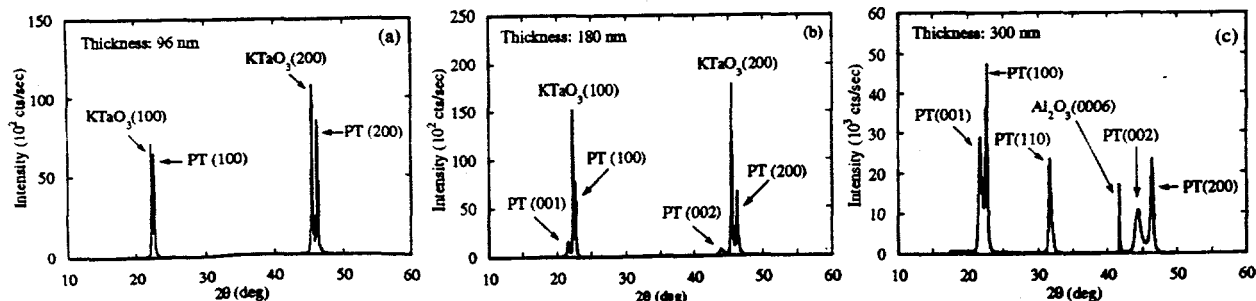

Figure 4. θ-2θ XRD patterns for $PbTiO_3$ thin films grown on (a) $KTaO_3$ (100) with single-domain, (b) $KTaO_3$ (100) with a- and c-domain, (c) Al_2O_3(0001).

for thicknesses less than 1000 Å. Above this thickness, PbTiO$_3$ thin films form a- and c-domains due to strain relaxation. Compared to the previous paper[5], the critical thickness for domain formation has increased possibly due to a lower growth rate of 240 Å/h. XRD patterns from the PbTiO$_3$ films deposited on Al$_2$O$_3$(0001) had reflections from the (001), (100), and (110) planes.

Fig. 3 (b) shows the result of RBS and ion channeling experiments for PbTiO$_3$ film on KTaO$_3$ with a thickness of 480 Å. The minimum channeling yield in the [100] direction is 3%. This indicates that a single-domain PbTiO$_3$ film grown on KTaO$_3$(100) has a single-crystal structure since a perfect crystal usually exhibits a χ of 2 to 3%.

PbTiO$_3$/PLT superlattice

Two PbTiO$_3$/PLT superlattices having ten periods were grown on SrTiO$_3$. One had a growth time of 15 minutes for each layer and the other had a 30 minute growth time. We estimate the individual layer thickness of the first sample to be 60 Å and 315 Å for PbTiO$_3$ and PLT, respectively. Fig. 5 (a) and (b) show θ-2θ XRD patterns of these two PbTiO$_3$/PLT superlattices with different modulation
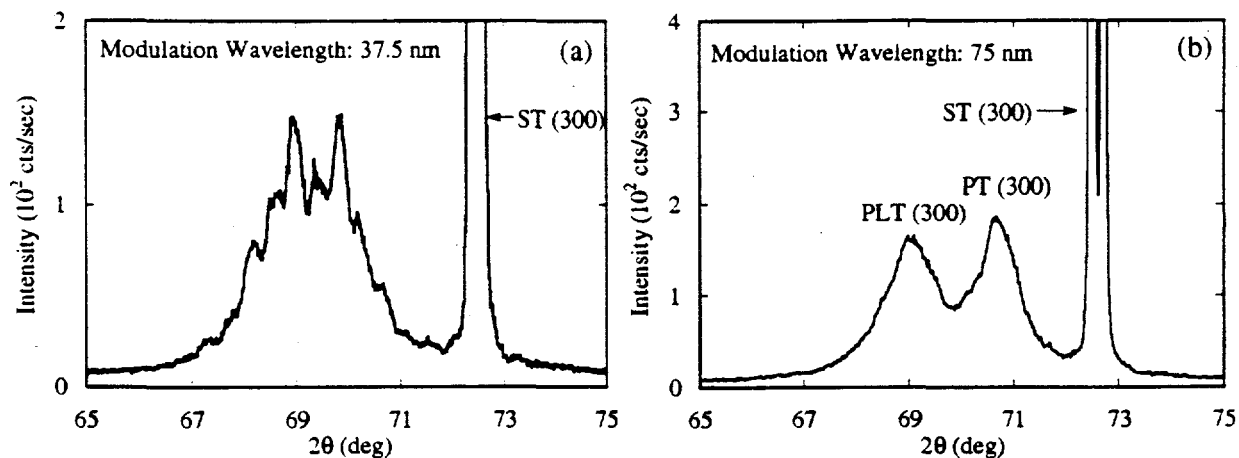

Figure 5. θ-2θ XRD patterns of (300) peak of PbTiO$_3$/PLT superlattice with growth time of (a) 15 minutes for each layer, (b) 30 minutes for each layer.

wavelengths. The XRD pattern of the (300) peak shown in Fig. 5 (a) exhibits satellite peaks up to fourth order. The XRD pattern of the second sample shown in Fig. 5 (b) exhibits only two split peaks which correspond to the PbTiO$_3$(100) and PLT(100) planes. The calculated modulation wavelength of 375 Å for the first sample obtained from the angular distance between satellite peaks is in good agreement with the expected period of 375 Å from the film-growth rates.

In-plane epitaxial relations between the superlattice film and substrate were determined by pole figure and φ-scan measurements. The plots of (100), (110), and (111) pole figures of the
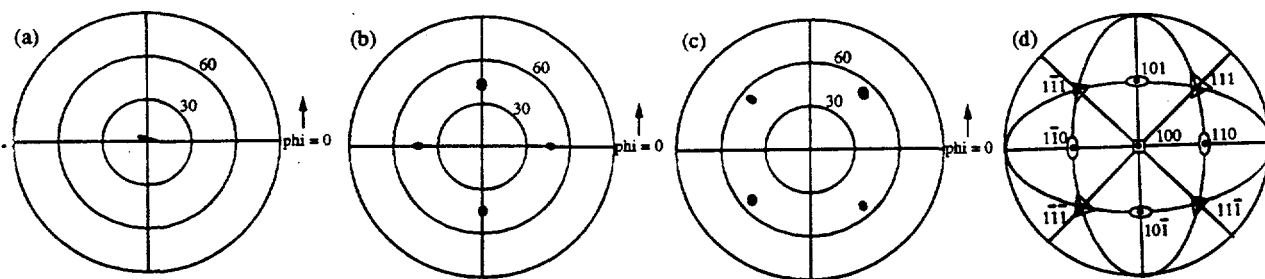

Figure 6. Pole figure plots from PbTiO$_3$/PLT superlattice layer with modulation wavelength of 375 Å (a) (100) pole, (b) (110) pole, (c) (111) pole, (d) stereographic projection on (100).

superlattice layer with a modulation wavelength of 375 Å are shown in Fig. 6 (a), (b), and (c), respectively. The stereographic projection of the superlattice layer on (100) is shown in Fig. 6 (d). There are (100) poles at $\chi=0°$, 4 poles such as (110), (101), ($1\bar{1}0$) and ($10\bar{1}$) at $\chi=46°$, and 4 poles such as (111), ($1\bar{1}1$), ($1\bar{1}\bar{1}$), and ($11\bar{1}$) at $\chi=56°$. ϕ-scans from (110) and (111) reflections are shown in Fig. 7 (a) and (b), respectively. As can be seen from Fig. 7 (a) and (b), the (110), (101), ($1\bar{1}0$) and ($10\bar{1}$) peaks are separated by 90°, and there are no other peaks; while (111), ($1\bar{1}1$), ($1\bar{1}\bar{1}$), and ($11\bar{1}$) peaks are separated by 90°, and there are no other peaks. These scans demonstrate the excellent in-plane relations between the superlattice layer and the substrate, indicating that the superlattice layer is indeed three-dimensionally epitaxial.
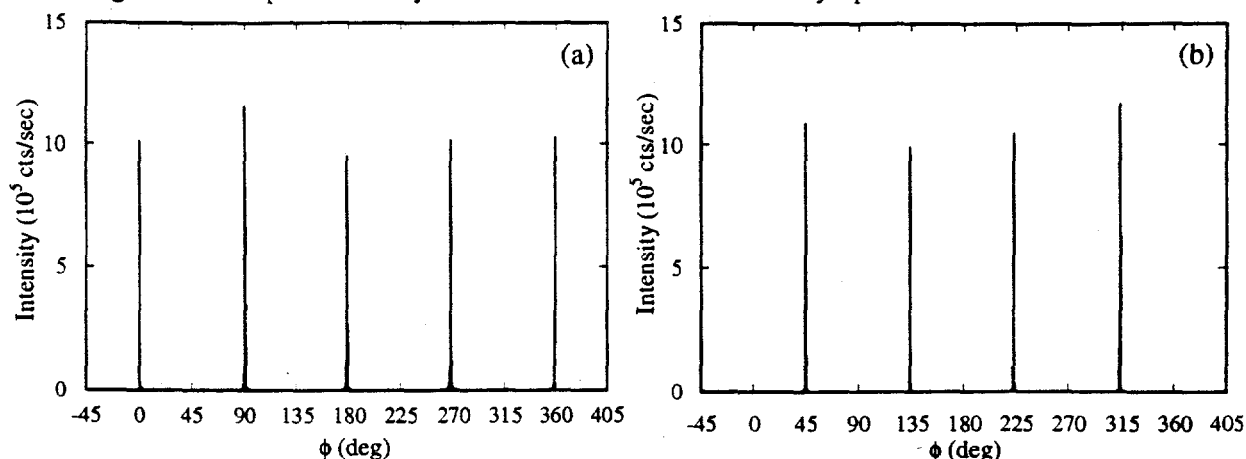

Figure 7. ϕ-scan XRD patterns of PbTiO$_3$/PLT superlattice layer with modulation wavelength of 375 Å from (a) (110) reflection, (b) (111) reflection. $\phi=0°$ is the in-plane SrTiO$_3$ [100] direction.

Figure 3 (c) shows the result of RBS and ion-channeling experiments for a PbTiO$_3$/PLT superlattice with a modulation wavelength of 375 Å. Due to the limitation from the resolution of the system, the compositional modulation structure could not detected. The minimum channeling yield in the [100] direction is 25%.

CONCLUSIONS

We have successfully grown ferroelectric superlattice structures composed of three-dimensionally epitaxial PbTiO$_3$ and PLT thin films on SrTiO$_3$ substrates. The modulation structures were confirmed by θ-2θ XRD, and the excellent in-plane orientational relationship between the superlattice film and the substrate by (100), (110), and (111)-pole figures. The ϕ-scans through the (110) and (111) reflections were used as additional evidence for three dimensional epitaxy. The substrate dependence of the epitaxial orientation of PLT and PbTiO$_3$ single-layered thin films was investigated. PbTiO$_3$ thin films with very high crystalline perfection can be successfully grown on KTaO$_3$ substrates.

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