$PbTiO_3$ thin films prepared by metalorganic chemical vapor deposition on $LaAlO_3$

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High-quality $PbTiO_3$ thin films have been grown on $LaAlO_3$ substrates by metalorganic chemical vapor deposition, using purified metalorganic precursors titanium-iso-propoxide and tetra-ethyl-lead. The results of the cross-section scanning electron microscopy and x-ray diffraction (XRD), including theta and phi scan, show that the films are epitaxy, and *a* domains and *c* domains may align alternately in the thin films. The experiments of high-temperature XRD reveal the nature of the phase transition of grown $PbTiO_3$ thin films from tetragonal to cubic phase. The transition temperature is around 460 °C which is far lower than that of bulk $PbTiO_3$ and the thin films deposited on fused quartz substrates. © *1995 American Institute of Physics.*

Lead titanate, $PbTiO_3$, is a well-known perovskite-type ferroelectrics with a large spontaneous polarization, high Curie temperature, a small dielectric constant, and a small coercive field. Possible applications to electric and photoelectron devices have brought much attention to the preparations of high-quality $PbTiO_3$ thin films. Among the preparation techniques of $PbTiO_3$ thin films, the sputtering[1] is the most widely used, but this method has some disadvantages such as low deposition rate, generation of surface defects, and composition change between film and target materials. The sol-gel,[2] which is also widely used, suffers from the generation of microcracks, and poor uniformity in the thickness and composition. Metalorganic chemical vapor deposition (MOCVD), which has been well developed to prepare device-quality thin films and superlattices of semiconductors since 1968,[3] recently has been used to prepare $PbTiO_3$ and other oxide ferroelectric thin films, like PZT[4] and $BaTiO_3$.[5] For example, the epitaxial $PbTiO_3$ thin films have been obtained on (001)$SrTiO_3$ substrates by MOCVD.[6–8]

In this letter, we report the results of the preparation and characterization of $PbTiO_3$ thin films grown on $LaAlO_3$ substrates by MOCVD. The MOCVD apparatus[7] used in this study, consisted of three main parts: a gas supplying system, reactor, and an exhaust gas handling system. A horizontal quartz reactor with an inner diameter of 47 mm was connected with a fast switching manifold in which the precursors mixed with oxygen and carrier gas. Two purified metalorganic precursors named titanium-iso-propoxide (TIP) and tetra-ethyl-lead (TEL) were used. The source vapor was guided by a purified N_2 carrier gas into the reactor chamber under reduced pressure, with the gas pressure of 1 atm in the evaporator. O_2 was used as oxidizing gas. The growth conditions are summarized in Table I.

Lanthanum aluminate, $LaAlO_3$, is a pseudoperovskite crystalline.[9] At room temperature, $LaAlO_3$ has a pseudocubic structure with lattice constant of 3.792 Å. Due to the similar crystal structure and small mismatch (2.8%) of the lattice constant, $LaAlO_3$ might be a promising substrate for the deposition of high-quality $PbTiO_3$ thin films.

The structure of grown $PbTiO_3$ thin films was analyzed using scanning electron microscopy (SEM) and x-ray diffraction (XRD), including theta and phi scans. For XRD measurement, a Ragaku x-ray diffractometer with nickel filtered Cu $K\alpha$ was used. In a temperature-dependent XRD measurement, the sample was placed in the center of a Nichrome heated high-temperature stage with a chromel-alumel thermocouple fixed on the back of the 0.5-mm-thick sample in order to avoid a difference of measured temperature and the film's temperature. The programmable rate of heating/cooling and the time of thermostat at measuring temperature was controlled in 4–5 °C/min and 15 min, respectively.

Mirror-smooth $PbTiO_3$ thin films were grown on $LaAlO_3$ at 650 °C. The films were transparent and firmly attached to the substrates. Figure 1 shows a cross-section SEM photograph of $PbTiO_3$ film. It can be seen that the film is dense and has no apparent grain boundaries. Under the conditions of Table I, the growth rate was 0.45 μm/h.

Figure 2 shows the XRD pattern of a MOCVD-grown thin film on $LaAlO_3$. Obviously the pure perovskite phase has been obtained. In this pattern, only (001) and (100) planes of $PtTiO_3$ can be found. It means that there are two oriented crystallines in the films, one with its spontaneous polarization direction being normal and another with its spontaneous polarization direction being parallel to the surface of the film. The measured *c*-axis constant is 4.111 ±0.003 Å which is significantly smaller than the 4.15 Å (Ref. 10) of the bulk $PbTiO_3$ and the 4.125 Å (Refs. 6 and 7) of the epitaxial $PbTiO_3$ thin films on (001) $SrTiO_3$ substrates.

An x-ray phi scan diffraction pattern is shown in Fig. 3.

TABLE I. Typical growth conditions.

Substrate	(012) $LaAlO_3$
Substrate temperature	~650 °C
Reactor pressure	13.3 Torr
Carrier gas	N_2
T_{TIP}	65 °C
T_{TEL}	35 °C
TEL carrier flow rate	~100 sccm
TIP carrier flow rate	~100 sccm
O_2 flow rate	~150 sccm

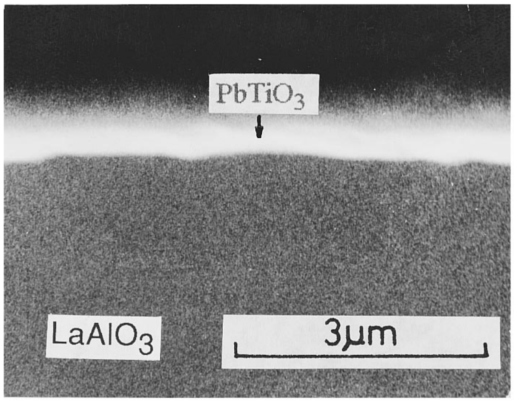

FIG. 1. A scanning electron micrograph of the cross-sectional $PbTiO_3$ thin film on (012) $LaAlO_3$.

In the measurements, two theta angle was fixed at 70.7° corresponding to the (212) and (122) planes of the $PbTiO_3$ thin film while the chi angle was tilted 43.1° off the surface normal. In Fig. 3, three sets of diffraction were measured. Each set consists of four peaks separated from each other by 90° rotation angle which reveals a (001) axis of $PbTiO_3$ and (012) axis of $LaAlO_3$, a fourfold symmetric axis, while the interval of the rotation angle between two adjacent sets of diffraction are 26.5° and 37°, respectively. Depending on the measured angles, say theta, chi, and phi angles, the three sets of diffraction were certified to contribute, respectively, to the (212) plane and (122) plane of $PbTiO_3$ thin film and the (220) plane of $LaAlO_3$ substrate. The measured angle between the (212) and (122) planes of $PbTiO_3$ and the angle between the (212) plane of $PbTiO_3$ and the (220) plane of $LaAlO_3$ are about 27° and 76°, respectively, which almost equal the calculated values (26.6° and 75.2°).

It might be reasonable to conclude, from XRD measurements, that the in-plane lattice vectors of both the c- and a-axis oriented crystallines in the as-grown $PbTiO_3$ thin films on $LaAlO_3$ are aligned with some vectors of the $LaAlO_3$ substrate. So the films were epitaxy. In fact, 90° domains were spontaneously formed in the films when the phase transition from paraelectrics to ferroelectrics took place during the cooling of films grown at high temperature.

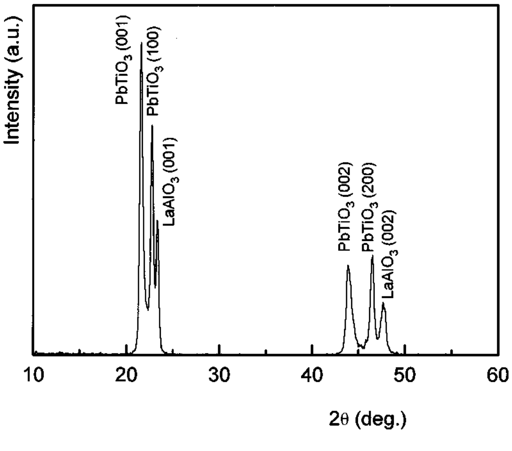

FIG. 2. XRD pattern of a $PbTiO_3$ film grown on $LaAlO_3$ at 650 °C. Only (001) and (100) planes of $PbTiO_3$ were measured.

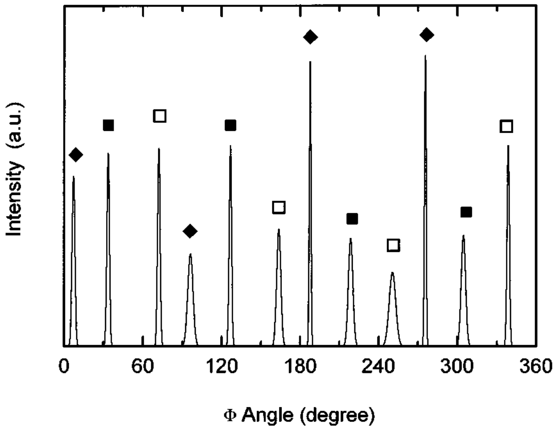

FIG. 3. A Φ scan XRD pattern of $PbTiO_3$ thin film. ♦, ■, and □ indicate the (212), (122) planes of $PbTiO_3$ and the (220) plane of $LaAlO_3$ substrate, respectively.

Figure 4 shows the temperature dependence of the XRD pattern. During the measurements, two cycles, heating and cooling, were performed. An evident phase transition in each process was observed with the transition temperature of 460 °C in the heating cycle and 450 °C in the cooling cycle. The results show that the transition in the films is reversible but with about 10 °C hysteresis between heating and cooling cycles.

The results of high-temperature XRD measurements also

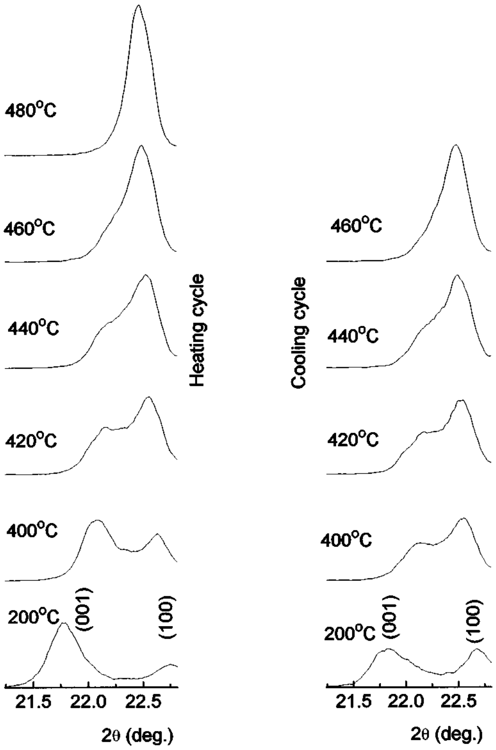

FIG. 4. XRD patterns of the $PbTiO_3$ thin film on $LaAlO_3$ substrate vary with temperature.

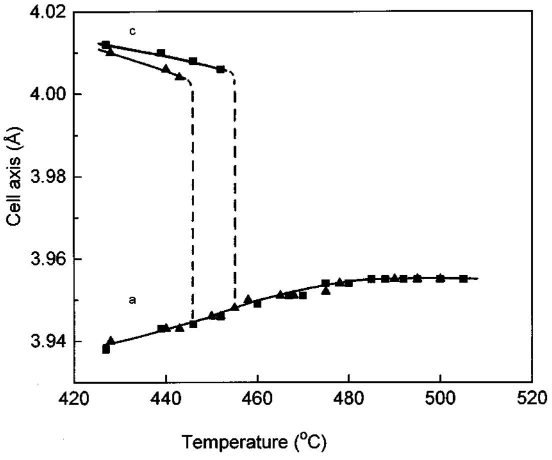

FIG. 5. The temperature dependence of the lattice constants *a* and *c* of $PbTiO_3$ thin film grown on $LaAlO_3$ substrate. ▲: the cooling cycle, ■: the heating cycle.

provided evidence of the temperature dependence of the lattice parameters *a* and *c*, which are plotted in Fig. 5. One can see clearly that a phase transition from a tetragonal to a cubic phase occurs at 460 °C during heating and reverse transition occurs at 450 °C upon cooling. The corresponding phase transition from the tetragonal to the cubic phase in the bulk $PbTiO_3$ takes place at 490 °C,[10] and in the film forms, the upshift of the Curie temperatures to 560 °C has been reported in the $PbTiO_3$ thin films on fused quartz substrates.[11] The downshift of the Curie point of $PbTiO_3$ thin films was, to our knowledge, first observed. It may be attributed to the strain energy in twins which destabilizes the ferroelectric phase. The change in the *a*-axis constant with temperature is almost the same in both heating and cooling cycles while the *c* axis exhibits hysteresis. This result is the same as the report of the upshift.

In summary, high-quality $PbTiO_3$ thin films have been prepared by MOCVD under reduced pressure. The as-grown films were confirmed to be epitaxy with 90° domains, whose in-plane vectors were aligned with the vectors of the $LaAlO_3$ substrate. The phase transition of the epitaxial film on $LaAlO_3$ takes place at about 460 °C which is considerably lower than those of the bulk $PbTiO_3$ and the thin film on fused quartz. The transition is reversible but with about 10 °C hysteresis between cooling and heating.

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