



0038-1098(95)00465-3

PHASE TRANSITION OF PbTiO₃ POLYCRYSTALLINE THIN FILM PREPARED BY METALORGANIC CHEMICAL VAPOR DEPOSITION ON YTTRIUM STABILIZED ZIRCONIUM

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(Received and accepted 25 May 1995 by Z. Gan)

PbTiO₃ thin films were grown on yttrium stabilized zirconia (YSZ) substrates by metalorganic chemical vapour deposition (MOCVD). X-Ray diffraction (XRD) pattern shows that the films are polycrystalline. The phase transition of the PbTiO₃ thin film was studied by high temperature XRD. It was found that the temperature of phase transition from a tetragonal to a cubic phase was 535°C and from a cubic to a tetragonal was 525°C, higher than the phase transition temperature of bulk PbTiO₃ (490°C). By analyzing the XRD pattern at high temperatures, different phase transition behaviors of the grains with different *c*-axis orientations were found. Scanning electron microscopy (SEM) shows that the grain boundary exposed and the surface film becoming rough after heating and cooling treatment.

Lead titanate, PbTiO₃, is a ferroelectric material with a tetragonal perovskite structure (*c/a*=1.065 for large grained powder at room temperature). It has a large spontaneous polarization ($P_s=75\mu\text{C}/\text{cm}^2$) along the *c* axis, high Curie temperature ($T_c=490^\circ\text{C}$), a small relative dielectric constant ($\epsilon_r\sim 100$) and a small coercive field.^{1,2} Many possible applications, such as pyroelectric infrared detectors and piezoelectric transducers, have brought much attention to the preparation of PbTiO₃ thin films. With the progress of thin film technology, spin-coating, rf-magnetron or ion-beam sputtering, electron-beam evaporation, chemical vapor deposition were used to deposit PbTiO₃ thin films. Among these techniques, the rf-magnetron sputtering and sol-gel were the most widely used methods.³⁻⁵ Metalorganic chemical vapor deposition (MOCVD), which has been well developed to prepare device-quality thin films and superlattices of semiconductors since 1968,⁶ recently has been used to prepare PbTiO₃ and other oxide ferroelectric thin films.^{7,8} Various substrates, such as (0001)sapphire, Si, mica, MgO, (001)SrTiO₃ and (001)LaAlO₃ were used to deposit PbTiO₃ thin films. High-quality PbTiO₃ thin films have been successfully grown on (001)SrTiO₃ and (001)LaAlO₃ substrates by MOCVD.⁹⁻¹¹ Phase transition of PbTiO₃ thin films on MgO, LaAlO₃ and fused quartz substrates also have been

investigated.^{5,10,12} In this paper, we report on the nature of the phase transition of PbTiO₃ polycrystalline thin films prepared by MOCVD on yttrium stabilized zirconium (YSZ) substrates.

The MOCVD apparatus used in this study consisted of three main parts: a gas supply system, reactor and an exhaust gas handling system. A horizontal quartz reactor with an inner diameter of 47mm is connected to a fast switching manifold in which the precursors mixed with oxygen and carrier gas. Purified titanium-iso-propoxide (TIP) and tetra-ethyl-lead (TEL) were used as metalorganic precursors. The source vapor was guided by N₂ carrier gas (99.999%) into the reactor chamber under reduced pressure, with the gas pressure of 1 atm in the evaporator. O₂ was used as an oxidizing gas.

The substrate used in this experiment was YSZ, which has a cubic structure with lattice constant of 5.139 Å at room temperature. Mirror-smooth PbTiO₃ thin films were grown on YSZ at 650°C. The reactor pressure was 13.3Torr. TEL carrier flow rate, TIP carrier flow rate and O₂ flow rate was 100sccm, 100sccm and 150sccm respectively. Under the conditions, the growth rate of PbTiO₃ film was 0.45μm/h. The film were transparent, pale

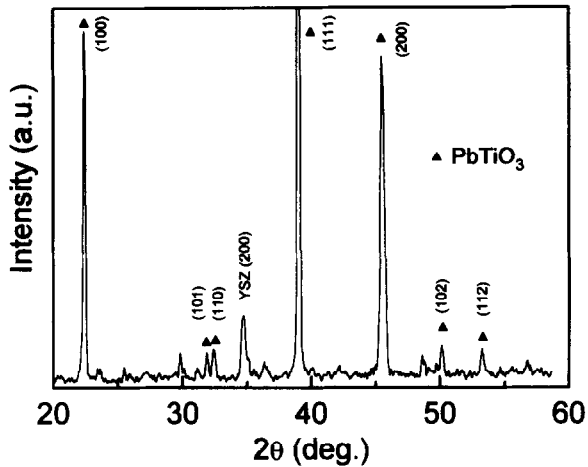


Fig.1. The XRD pattern of a MOCVD-grown PbTiO_3 polycrystalline thin film on YSZ at room temperature.

yellow in color and firmly attached to the substrates. The thickness of the film was about 3000Å.

The structure of as-grown PbTiO_3 thin films was analyzed by x-ray diffraction (XRD). For XRD measurement, a Rigaku x-ray diffractometer with nickel filtered $\text{Cu K}\alpha$ was used. In the temperature-dependent XRD measurements, an electrical furnace was attached to the θ axis of the diffractometer. The sample was placed in the center of a high-temperature stage. A chromel-alumel thermocouple fixed on the back of the 0.5mm-thick sample in order to avoid a difference between the measured temperature and the temperature of the film. The rate of heating/cooling and the time of thermostat at measuring temperature were controlled in 4-5°C/min and 15min, respectively. Fig.1 shows the XRD pattern of a MOCVD-grown PbTiO_3 thin film on YSZ. Obviously the pure perovskite phase was obtained. In this pattern, peaks of (001), (100), (101), (110), (111), (002), (200), (102), (112), (202) and (220) corresponding to PbTiO_3 perovskite structure can be found. This is a typical pattern of polycrystalline PbTiO_3 thin film.

Phase transition of the PbTiO_3 polycrystalline thin film was investigated by XRD techniques. During the temperature-dependent XRD measurements, two cycles, heating and cooling, were performed. Fig.2 shows the temperature dependence of x-ray diffraction intensities near (001) and (100) peaks. The intensities of two peaks change rapidly above 470°C. On the heating cycle, the intensity of (001) decreases and that of (100) increases. The (001) disappeared in the foot of (100) above the transition temperature 535°C. On the cooling cycle, just below to 525°C, (100) became broad and asymmetric and (001) became visible. The results show that the transition in this

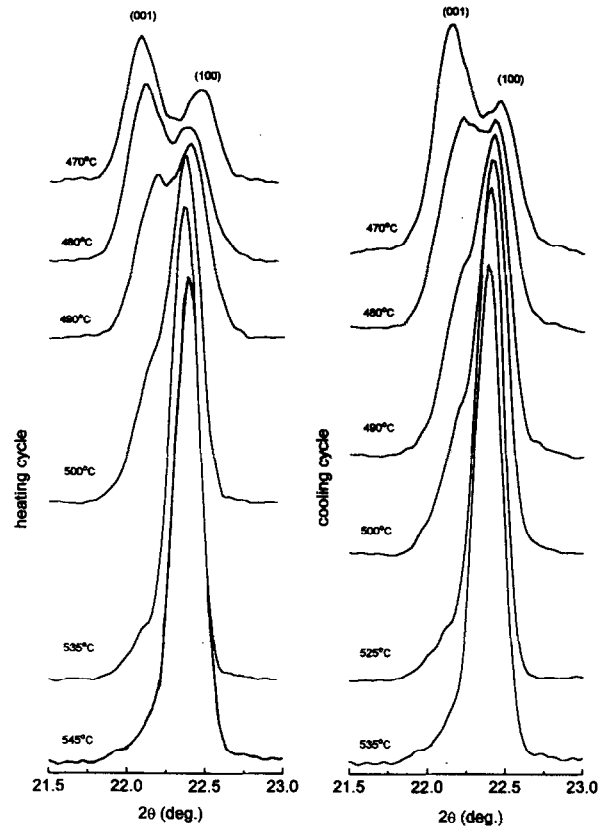


Fig.2. The temperature dependence of x-ray diffraction intensities near (001) and (100) peaks.

polycrystalline film is reversible but with about 10°C hysteresis between heating and cooling cycle. With the lowering of temperature, (001) peak became high and (100)

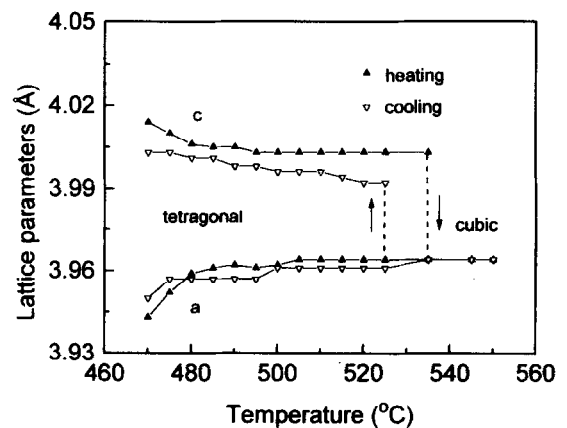


Fig.3. Relation between lattice constants and temperature in high-temperature XRD measurement.

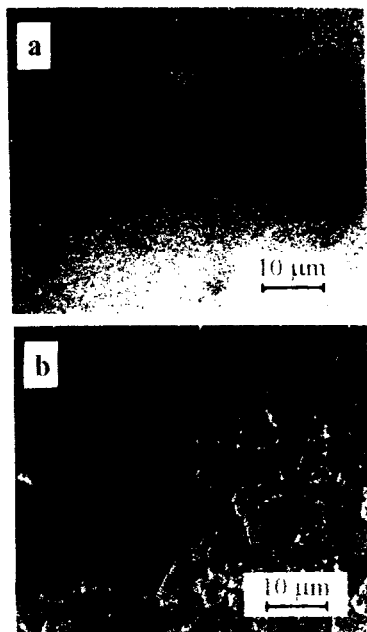


Fig.4. The SEM images of the surface of as-grown polycrystalline PbTiO_3 film on YSZ (a) before the temperature-dependent XRD measurements, (b) after the temperature-dependent XRD measurements.

became low. This change of (001) and (100) intensity corresponds to the growth of c domain in the film.⁵ The results of high-temperature XRD measurements also provided evidence of the temperature dependence of the lattice constants a and c , which are plotted in Fig.3. It shows that a phase transition from a tetragonal to a cubic phase occurs at 535°C on the heating cycle and from a cubic to a tetragonal occurs at 525°C on the cooling cycle. The a axis changed in almost the same way on both heating and cooling cycle, otherwise the change of c axis shows hysteresis on heating and cooling cycle.

Fig.4 is the SEM images of the surface of as-grown polycrystalline PbTiO_3 film on YSZ (a) before the temperature-dependent XRD measurements, (b) after the temperature-dependent XRD measurements. Fig.4(a) shows that the surface of the as-grown PbTiO_3 film was very smooth and not details of the structures could be observed on this scale. In contrast with Fig.4(a), after the heating and cooling treatment the film surface became rough and the grain boundary could be observed obviously in Fig.4(b). Fig.5 shows the XRD pattern of PbTiO_3 polycrystalline thin film at 550°C. We have analyzed this pattern and found that the peaks of (101) and (110) still existed, although the main part of the film became cubic phase whose peaks of (001) and (100) or (002) and (200) merge at this temperature. Fig. 1 shows that there were many grains in the film and their c -axis orientations were quite different. The peaks of (101) and (110) were the contribution of the grains whose

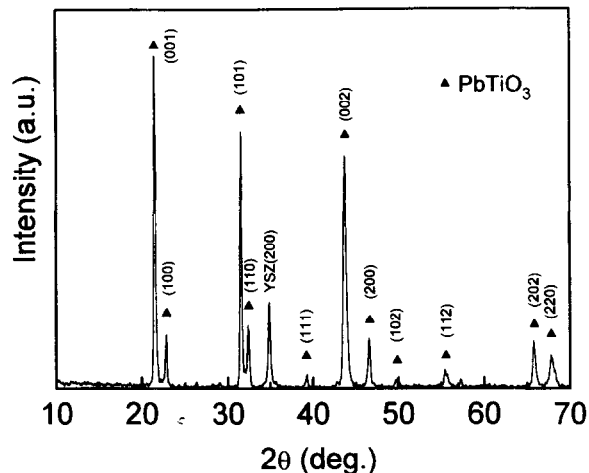


Fig.5. The XRD pattern of PbTiO_3 polycrystalline thin film at 550°C.

c -axis inclined at an angle of about 45° with the substrate. The diffraction peaks of the grains whose c -axis was parallel and perpendicular with the substrate are (100), (200), (001) and (002) respectively. Fig.5 indicates that the phase transition of the grains whose c -axis formed about 45° with the substrate was incomplete when the grains whose c -axis was parallel and perpendicular with the substrate were all in a cubic phase at 550°C. The reason for this may be that the 45° grains suffered from stronger stress than parallel or perpendicular one. Because the phase transition behavior was different in the grains with different c -axis orientations at high temperature, furthermore, the phase transition on heating cycle was not exactly same as that on cooling cycle, so the grain boundary exposed and the rough surface could be observed in Fig.4(b).

In summary, PbTiO_3 polycrystalline films were grown on YSZ by MOCVD. Temperature-dependent XRD measurements showed that the phase transition temperature from tetragonal to cubic is 535°C and from cubic to tetragonal 525°C. A different phase transition behavior of grains of different c -axis orientations was observed. The SEM images of PbTiO_3 film surface show that it becomes rough, and the grain boundary can be observed, after heating and cooling treatment.

ACKNOWLEDGEMENTS - This work was supported by the 863 National High Technology Program of People's Republic of China. The authors would like to acknowledge the assistance from Yu-Da Ye and Yu-Ping Zhu for the XRD measurements.

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