

Conf. 9203110--3

ANL/CP--75722

DE92 010907

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PbTiO₃ THIN FILMS PREPARED BY MOCVD***

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March 1992

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Received by OSTI
APR 01 1992

Manuscript submitted to the 8th International Conference on Advanced Science and Technology, Argonne, Illinois, March 28, 1992.

*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under contract #W-31-109-ENG-38.

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THE DOMAIN STRUCTURE FEATURES OF EPITAXIAL PbTiO₃ THIN FILMS PREPARED BY MOCVD

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Ferroelectric oxide thin films have attracted great interest in recent years because of their potential applications in numerous electro-optic, pyroelectric, acousto-optical, and nonvolatile memory devices [1], and a variety of methods such as sputtering, laser ablation, and MOCVD has been used for preparation of the films [2]. Among these ferroelectric materials, the PbTiO₃ thin film has been extensively studied because of its small dielectric constant, large spontaneous polarization, small coercive field, and high Curie temperature of ~500°C [3]. However, very little work has dealt with the detailed structural properties of the films. In this work, we have prepared epitaxial PbTiO₃ thin films by MOCVD and performed some detailed studies on the structure of the films, particularly those related to the twin domain structure, using X-ray diffraction technique. Based on the comparison of the domain structure features of the films grown at above Curie temperature with those of the films grown at below Curie temperature as well as of bulk PbTiO₃ single crystal, a model is proposed to explain our experimental results.

PbTiO₃ thin films were grown in a low pressure, horizontal cold wall reactor with a resistive substrate heater. Lead β -diketonate, Pb(thd)₃, and titanium isopropoxide, Ti(OC₃H₇)₄, were chosen as the metal precursors. The mixture of the organometallic precursor vapor was introduced into the reactor via a high purity nitrogen carrier gas. The flow rates of the carrier gas and the evaporator temperature for each of the precursor chambers could be controlled individually and were used to control the film compositions. Pure oxygen was used as the oxidant and introduced into the reactor in a separate line. The precursor delivery lines, as well as the inlet flange, were heated and maintained at temperatures higher than the highest source evaporator temperature used in a deposition run to prevent condensation of vapor phases. MgO (100), SrTiO₃ (100), and LaAlO₃ (100) were chosen as the substrates. In many occasions, all three types of substrates were placed on the susceptor for film deposition simultaneously, to study the effect of substrates on the structures of the deposited films. Typical growth conditions used in this study are shown in Table I.

The film composition was determined by energy dispersive X-ray spectroscopy (DES). The film structure and crystallinity were examined by X-ray diffractometer and four-circle diffractometer.

Table I. Growth Conditions

Substrate temperature	- 450-750°C
Reactor pressure	- 10 Torr
Precursor evaporation temperatures	- Ti: 30-32°C - Pb: 110-126°C
Flow rates of carrier gas	- Ti: 15-30 sccm - Pb: 50-70 sccm
Flow rate of reactant gas	- O ₂ : 400 sccm
Flow rate of background gas	- N ₂ : 1000 sccm
Thickness of the films	- 2000 ~ 3000 Å

A few dozen of PbTiO₃ thin films were prepared under growth conditions listed in Table I. The X-ray θ - 2θ scan data indicated that all of the films, whether grown at above or below Curie temperature, showed four peaks at 21.7, 22.8, 44.0, and 46.5° which corresponded well to the (001), (100), (002), and (200) reflections of tetragonal PbTiO₃, respectively. This means that the films possess tetragonal structure and contain both c- and a-axis oriented grains at room temperature.

In order to determine the epitaxial relationship between the differently oriented grains of film and the substrate, ϕ scans (rotation about the normal of the sample surface) of appropriate crystallographic planes of the a-grain and c-grain of film, and the substrate were carried out using four-circle diffractometer. The ϕ scan data of the (101) plane of c-grain (having (001) growth plane) of film and the (110) plane of substrate showed that two curves peaked at almost exactly the same position, which meant that the (100) plane of the c-grain of film was parallel to the (010) plane of substrate. Therefore, the epitaxial relationship between the c-grain of film and the substrate is: PbTiO₃ (001)//MgO (100); $\langle 100 \rangle // \langle 010 \rangle$. A similar ϕ scan was performed for the (101) plane of the a-grain (having (100) growth plane) of film. From the data, the epitaxial relationship was determined to be: PbTiO₃ (100)//MgO (100); $\langle 001 \rangle // \langle 010 \rangle$.

In order to study the detailed structures of a- and c-grains of films, ω scans (θ rocking) of the (100) and (001) planes of film were performed. The ω scan results indicated that the rocking curve of a-grain always consisted of three peaks about 2.0° apart and the rocking of c-grain also showed a slight shoulder providing that the films were grown at above Curie temperature. The films grown at below Curie temperature were still epitaxial and also contained both a- and c-grains, but the rocking curves of either a-grain or c-grain did not show any splitting or shoulder feature.

The (001) and the (100) diffraction peaks appearing in the film prepared at above Curie temperature can be an indication of the existence of a- and c-orientation ferroelectric domains formed through the phase transition from cubic phase to tetragonal phase during the cooling process or can be an indication of the existence of a- and c-oriented grains, as well as ferroelectric domains formed during the growth and cooling processes. On the other hand, the (001) and the (100) diffraction

peaks appearing in the X-ray diffraction pattern of the film grown at below Curie temperature can only indicate the existence of a- and c-oriented grains. This means that only the rocking curves of the domains formed through phase transition can show splitting or shoulder feature; the a- and c-oriented grains formed during growth process do not possess such features. To obtain better understanding of the complex features in the rocking curves of the films deposited at above Curie temperature, rocking curves of PbTiO_3 single crystal containing both a- and c-domains were obtained. The results indicated that the domains in PbTiO_3 single crystal showed basically the same features as those domains formed through phase transition in PbTiO_3 thin film deposited at above Curie temperature. The differences between them only lie in that these features in PbTiO_3 single crystal became more prominent: the differences of degree of angles among three peaks of a-domain increased to 3.5° and the shoulders originally superposed on main peak of c-domain also evolved to peaks with definite contour.

Why do the rocking curves of the PbTiO_3 single crystal containing both a- and c-domains and the PbTiO_3 epitaxial thin film with both a- and c-domains formed through phase transition show the above-mentioned features (fine structures)? When PbTiO_3 crystal transforms from cubic phase to tetragonal phase, it is possible to form two types of grains, A type of grains and C type of grains. The a-axis oriented domains in A type of grains are connected through $\{110\}$ twin boundaries with the tilted c-axis oriented domains as shown in Fig. 1; meanwhile, the c-axis oriented domains in C type of grains are connected through $\{110\}$ twin boundaries with the tilted a-axis oriented domains. The (100) plane of A type of grains is parallel to the (001) plane of C type of grains. As can be seen from Fig. 1, there are three kinds of a-domains, one being not tilted and existing in A type of grains, the other two being tilted and existing in C type of grains. For PbTiO_3 single crystal,

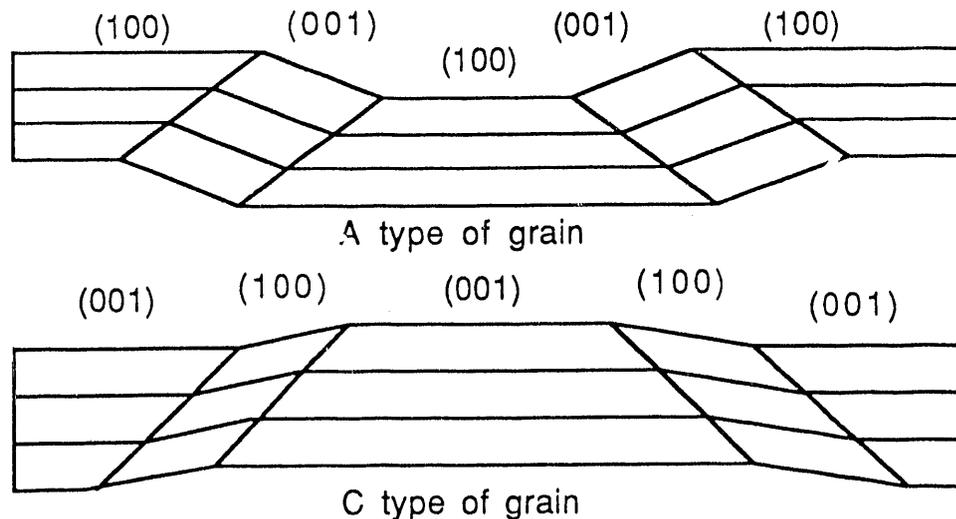


Fig.1. Schematic diagram of A type of grain and C type of grain in PbTiO_3 crystal

the degree of angle between the untilted a-domain and the tilted a-domain is 3.5° ($2 \arctan(c/a) - 90^\circ = 3.5^\circ$). The above classification is also applicable for c-domain and the degree of angle between the untilted c-domain and tilted c-domain is also 3.5° . Because there are three different kinds of a-domains in PbTiO_3 single crystal, it is reasonable to give three peaks when ω scan of a-domain is performed. The middle peak corresponds to the untilted a-domain and the other two peaks correspond to the tilted a-domains. It should be noted that the relative intensities and the differences of degree of angles among these three peaks are sensitive to the sample alignment. Keeping this in mind and considering that the amount of C type of grains is much larger than that of A type of grains in our PbTiO_3 single crystal, it is not difficult to understand the fine structure of the rocking curve of the c-domain in PbTiO_3 single crystal.

Because film was constrained by substrate, the values of lattice constant would change a little. For the PbTiO_3 thin film deposited on MgO , the c-axis length was changed from 4.16 \AA of single crystal to 4.09 \AA . This means that the differences of degree of angles among three peaks of the rocking curves of a-domain in PbTiO_3 thin film will be 2.7° , which is a little larger than the observed value of 2.0° . Considering that the phase transformation from cubic phase to tetragonal phase was also constrained by substrate, it was possible to further decrease the degree of angle between the untilted domain and the tilted domain to 2.0° . The crystallinity of PbTiO_3 epitaxial film, compared with PbTiO_3 single crystal, was much inferior to the single crystal. In this case, it is not surprising that the rocking curve of c-domain in epitaxial thin film showed a shoulder feature instead of a splitting.

In conclusion, the splitting or shoulder features of rocking curves of (100) and (001) planes of PbTiO_3 epitaxial thin film and PbTiO_3 single crystal are the intrinsic reflection of the domain structures in thin film and single crystal. Only the rocking curves of the PbTiO_3 single crystal contained both a- and c-domains and the PbTiO_3 epitaxial thin film with both a- and c-domains formed through phase transition can show the above-mentioned fine structure features.

Acknowledgement

This work was supported by the U.S. Department of Energy, Basic Energy Sciences-Materials Sciences, under contract #W-31-109-ENG-38.

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