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The Ferroelectric Phase Transition of Thin $Pb(Zr,Ti)O_3$ Single Crystal Films grown on MgO(001) by R.F. Magnetron Sputtering : A Synchrotron X-ray Scattering Study.

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I. INTRODUCTION.

Lead Zirconate Titanate $Pb(Zr_xTi_{1-x})O_3$(PZT) is a ferroelectric material of interest for applications in microelectronics. At high ratio of Ti(>~50%), PZT shows paraelectric cubic phase(P_C) at high temperatures and ferroelectric tetragonal phase(F_T) at low temperatures. The substrate field would have considerable effect on the lattice distortion that accompanies the paraelectric cubic-to-ferroelectric tetragonal(P_C-F_T) phase transition of the film near the substrate. Up to now, many studies were focused on the effect of the Zr to Ti ratio on the tetragonal distortion of films thicker than about 1000 Å. The purpose of this study is to reveal the nature of the domain structure and the structural transformation as the film thickness is decreased to about 250 Å where the effect of the substrate field becomes significant. Understanding the effect of the substrate field would provide valuable information for the domain structure of the film.

II. EXPERIMENTALS.

We report a series of synchrotron x-ray scattering studies of the structural transformation accompanying the P_C-F_T transition in thin epitaxial PZT/MgO(001) films with thickness in the range from 5000 Å to 250 Å. The PZT films were grown on single crystal MgO(001) substrate by R.F. magnetron sputtering technique in amorphous form, and the film composition was estimated to be ~$Pb(Zr_{0.43}Ti_{0.57})O_3$. The amorphous film thus obtained were crystallized by rapid thermal annealing(RTA) process. The RTA process is necessary to avoid the intermediate nanocrystalline pyrochlore phase which is metastable. High flux synchrotron radiation was indispensable in this studies due to the weak scattering signal from the thin PZT films. Synchrotron x-rays are one of the best probes to investigate structural nature of thin films.

III. ANALYSIS AND DISCUSSION.

To study the detailed nature of the phase transition of the 500 Å and 250 Å thick film, the scattering profiles both in the out-of-plane and in-plane direction were measured at each temperatures. Figure 1 shows the scattering profiles from the 500 Å and 250 Å thick film at 300 ℃ and at 25 ℃. The 500 Å thick film had two distinct peaks in the scattering profile in the out-of-plane direction as illustrated in Fig.1(c) at room temperature. The peak at lower q_z value was originated from the domains with the long c-axis aligned the surface normal(c-domain). The a-domains with the short a-axis along the surface normal yielded the peak at the higher q_z value. Although the scattering profile of the 250 Å film had only one peak, we believe that the film was the F_T phase at low temperature, since the peak occurred at significantly smaller q value in out-of-plane direction than in the in-plane direction indicating that the film was in the F_T phase with the long c-axis aligned to the surface normal(c-domains). Different from the other thicker films, this film was always single-domained even in the F_T phase. As shown in Fig.1(d), the scattering profile in the out-of-plane direction stayed sharp keeping the interference fringe at all temperatures. We believe that the effect of the substrate field requiring the square symmetry in the film plane was prevailing through the whole film in the case of 250 Å thick films, and as a result only the c-domains with square in-plane symmetry exist.

To illustrate the change of the P_C-F_T transition as the film thickness was decreased more clearly, we have plotted the lattice constant of the c-axis and a-axis as a function of temperature in Fig. 2. Each data point was obtained from the peak positions deduced by a least-square-fit of the each scattering profile. The amount of the tetragonal distortion, $\gamma \equiv (c-a)/c$, calculated from the lattice constants were also plotted in Fig. 2. This figure vividly illustrates the suppression of the transition temperature, and the amount of the tetragonal distortion as the film thickness decreases. The transition temperature was decreased from about 450 ℃ in the bulk PZT case, to about 250 ℃ in the thinner films. The amount of the tetragonal distortion at room temperature was also decreased from 0.035 to about 0.01 with decreasing the film thickness.

We attribute the suppression of the tetragonal distortion in the thin films to the effect of the substrate field. As the film thickness decreases, the effect of the substrate field would be more stronger. It is likely that the a-domains observed in the 500 Å thick film were on the top part of the film rather than near the interface, since they were not observed in the 250 Å thick film. The substrate field is weaker away from the interface, and it is possible to have the a-domains with the rectangular symmetry in the film plane away from the interface. As a supporting evidence, the ratio of the amount of the a-domains to that of the c-domains were plotted in Fig. 3. The relative amount was calculated from the ratio of the integrated intensity of the corresponding peak. It is known that the integrated intensity is proportional to the volume fraction of a specific domain. In very thick film where the effect of the substrate field is negligible, the ratio should be 2, since there are two possible configurations for the a-type domains. Our results show that the ratio is about 1.5 in the 5000 Å film. Therefore we might conclude that the substrate field effect was significant even in the 5000 Å thick sample. We note that the bulk sputtering target would not show the ratio of 2, since it was compressed at high pressure that might change the domain structure along the direction where the pressure is applied.

From the discussions presented above, we can infer that the domain structure of the thick PZT film would be similar the one illustrated in Fig. 3(b). The part of a film near the interface with the substrate MgO is purely composed of the c-domains, while the part away from the interface was composed of the mixture of the a-domains and the c-domains. The thickness of the inner layer must be between 250 Å and 500 Å. The domain structure shown in Fig. 3 (b) is very different from the suggested ones in literature that place a-domains near the interface, which is directly opposite from the result of the 250 Å thick film.

IV. CONCLUDING REMARKS.

In summary, we have revealed the nature of the tetragonal distortion of thin PZT films grown on MgO(001) substrates using synchrotron x-ray scattering technique. The transition temperature and the amount of the tetragonal distortion were continuously decreased as the film thickness decreases. In the thinnest 250 Å thick film, the entire film was composed of the c-domains different from the other thicker films. From this, we proposed a new domain structure of thin PZT films grown on MgO(001) that is quite different from the ones suggested in literature.

The suppression of the tetragonal distortion was attributed to the effect of the substrate field. The substrate field places only the c-domains that have square in-plane symmetry near the interface. As a result the short a-axis lies in the film plane. The substrate field also suppresses the decrease of the a-axis lattice constant which is required in the tetragonal distortion to minimize the film/substrate lattice mismatch.

V. REFERENCE

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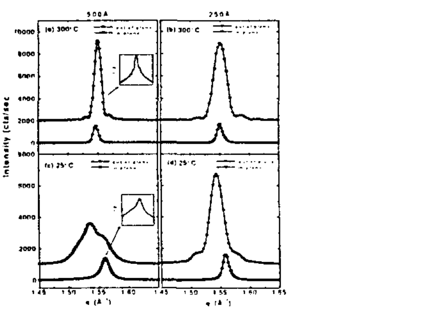

Fig.1. The scattering profile of both the 250 Å & 500 Å thick film both in the out-of-plane and in the in-plane direction.

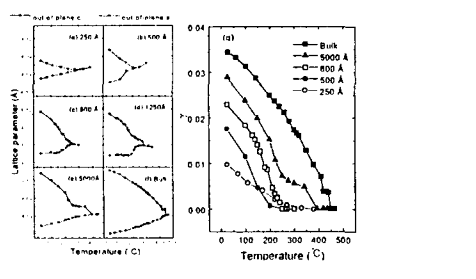

Fig.2. (a)~(f) The lattice constants of the c-axis varies thickness.(g)The tetragonal distortion calculated from the lattice constants illustrated in (a)~(f).

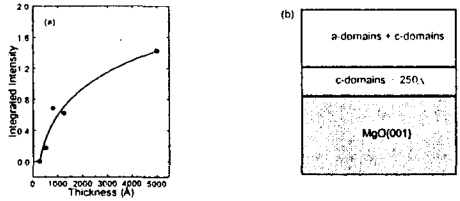

Fig.3. (a) The ratio of the amount the a-domains to that of the c-domains estimated by the integrated intensity. The upper limit is 2 for perfect random distribution. (b)Proposed domain structure of thin PZT/MgO single crystal films.