SUPPRESSION OF THE TETRAGONAL DISTORTION IN THIN $Pb(Zr,Ti)O_3/MgO(100)$

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ABSTRACT

The paraelectric cubic-to-ferroelectric tetragonal phase transition of the thin $Pb(Zr,Ti)O_3$ (PZT) films grown on MgO(001) substrate was investigated in a series of synchrotron x-ray scattering experiments. As the thickness of the film decreases, the transition temperature and the amount of the tetragonal distortion were decreased continuously. Different from the mixture of the *a*-domains and *c*-domains observed in the thicker films, only the *c*-domains were existent in the thinnest 25 nm thick film. Based on this, we propose a model for the domain structure of the tetragonal PZT/MgO(100) film that is very different from the ones suggested in literature. We attribute the suppression of the transition to the substrate field that prefers the *c*-type domains near the interface, and suppresses the tetragonal distortion to minimize the film-substrate lattice mismatch.

I. INTRODUCTION

Lead Zirconate Titanate $Pb(Zr_xTi_{1-x})O_3$(PZT) is a ferroelectric material of interest for applications in microelectronics such as non-volatile memory, memory-display device, pyroelectric infrared sensor, and bipolar transistor. PZT has received considerable attention for its outstanding electrical properties including high dielectric, pyroelectric, piezoelectric, and electro-optic properties[1-5]. Since the dielectric properties of PZT are originated from the lattice distortion, the structural phase diagram of PZT has been studied in-detail as a function of the Zr/Ti ratio and temperature[6,7]. The phase diagram is known to strongly depend on the Zr/Ti ratio, as well as on the concentration of dopants such as Nb, and La.

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. Many studies have been made on the F_T-P_C phase transition since its discovery by Barnett in 1962[8]. In many applications, it is desirable to obtain single crystal, ultra thin films to increase the capacity of microelectronics devices. Usually, single crystal PZT thin films are obtained by various methods of epitaxial growth such as, sol-gel

method[10], pulsed laser deposition(PLD)[11],metalorganic chemical vapor deposition(MOCVD)[12], and R.F. magnetron sputtering[13] on closely lattice-matched substrates such as MgO, $LaAlO_3$, and $SrTiO_3$. The aligning substrate field, however, 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.[14,15] It is well known that the ferroelectricity of the PZT film is caused by the lattice distortion that induces the spontaneous polarization [15]. 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 5000Å[14,16,17]. 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 250Å, where the effect of the substrate field becomes significant. The substrate field would have more significant effect on the part of the PZT film near the interface rather than away from the interface.

In this paper, 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 films with thickness ranging from 250 Å to 5000 Å. The PZT films were grown on single crystal MgO(001) substrates by RF magnetron sputtering method in amorphous form, and crystallized by RTA process. The film composition was estimated to be ~ $Pb(Zr_{0.43}Ti_{0.57})O_3$. 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.

Out results reveal that both the amount of the tetragonal distortion and the transition temperature were continuously decreased as the film thickness was decreased. In the thinnest 250 Å thick film, the entire ferroelectric domain was composed of the *c*-type domains with the long *c*-axis aligned to the surface normal direction, while in other films the films were composed of the mixture of *c*-type domains and *a*-type domains. The amount of the *a*-domains was increasing as the films become thick. This suggests a very different domain structure than the proposed ones in literature[18]. We attribute the suppression of the tetragonal distortion to the substrate field that prefers the *c*-type domains near the interface, and suppresses the tetragonal distortion.

This article is organized as follows. In Sec. II, we describe the experimental details including the film preparation conditions and the x-ray scattering measurement setup. The RF magnetron sputter deposition of the amorphous PZT films and the crystallization of them using RTA process are elaborated[19,20]. In section III, we present the x-ray scattering data on the P_C-F_T phase transition of 250 Å, 500 Å, 800 Å, 1250 Å, 5000 Å, and bulk PZT. In section IV, the amount of the tetragonal distortion was discussed, and a possible model for the domain structure was suggested. In the last section, we summarize the paper with concluding remarks.

II. EXPERIMENTAL DETAILS

A. Fabrication of PZT thin films.

The PZT thin films were grown on MgO(001) substrates using the radio frequency(R.F.) magnetron sputtering technique in amorphous form. The configuration of the RF magnetron sputtering system is shown in Fig. 1. The PZT target was 2 inch large in diameter, and was placed 8cm away from the substrate. The composition of the target was about 42% of Zr and 58% of Ti, which was later confirmed by the measurement of the tetragonal distortion at room temperature. The substrate temperature was held at RT during the entire growth process. The sputtering chamber was evacuated with a turbo molecular pump backed up with a mechanical pump; the base pressure was below 5×10^{-6} Torr. As sputtering gas, we have used 1×10^{-2} Torr of ultra-pure argon and ultra-pure oxygen(99.9999%) whose pressure was controlled with two mass flow controller.

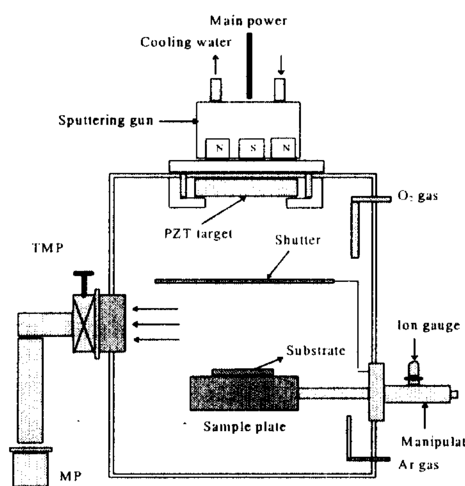

Figure 1. Schematic diagram of R.F. magnetron sputtering system used in this experiment.

The samples used in this study were prepared at relatively high RF input power density of 30watts(W)/cm^2. A movable shutter was placed between the target and the substrate to mask the substrate during cleaning the target surface by pre-sputtering prior to the deposition.

The substrates used in this experiment were MgO (001) single crystals with the dimension of 10x10x0.5mm. The MgO substrates were selected due to their smooth and stable surface morphology, and the small lattice mismatch with PZT overlayers. The lattice mismatch between MgO and the PZT(43%Zr) at room temperature is about 1.6% (with the long c-axis), and 4%(with the short a-axis). We note that PZT in this chemical composition has tetragonal crystal structure at room temperature. The substrates were first polished mechanically using SiC papers, and successively using finer grades of diamond paste down to 0.25μm. After polishing, the substrates were annealed in a tube furnace at 1200°C for 12 hr, which was heated slowly, 5K/min, in air to attain a very smooth surface morphology. Each substrate was cleaned in a ultrasonic bath using trichlorethylene, acetone, and methyl alcohol for 15 min each.

The PZT amorphous film thus obtained were crystallized by rapid thermal annealing(RTA) process. It is now well known that high quality crystal perovskite PZT films can be obtained by RTA from amorphous films[21]. The RTA process is necessary to avoid the intermediate nanocrystalline pyrochlore phase which is metastable.[Figure 2] On the closely matched MgO substrate, the nucleation of the crystallization occurs at the interface, and thus the film becomes single crystalline epitaxial films. The samples used in this experiment was heated to 500°C with the heating rate of about 200K/min. To follow the crystallization process in-detail, we have also measured the growth of the PZT Bragg reflection profile during the crystallization process in real time using synchrotron x-ray scattering method. Fig. 3. shows the growth of the perovskite PZT (001) Bragg peak. The epitaxial PZT films studied in this experiment was turned out to be 250 Å, 500 Å, 800 Å, 1250 Å, and 5000 Å thick.

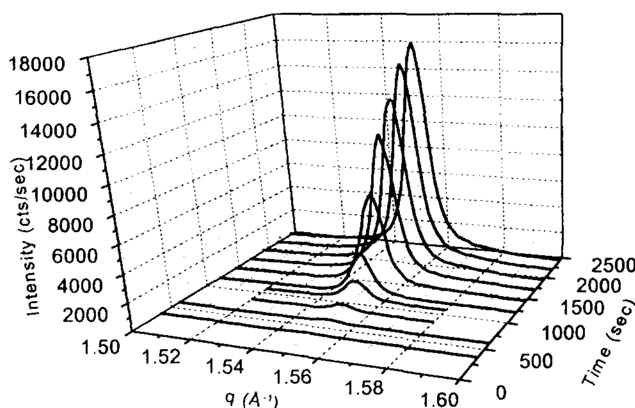

Figure 2. The x-rays diffraction profiles of PZT film on a MgO(001) substrate during the crystallization process by RTA using in-situ synchrotron x-ray scattering method.

B. Synchrotron X-rays scattering set up.

The X-rays scattering experiments were carried out at Beamline 3C2 at Pohang Light Source(PLS) at Pohang Accelerator Laboratory in Korea and Beamline 4C at Photon Factory (PF) at National Laboratory for High Energy Physics in Japan. The incident X-rays were focused both in vertical and horizontal direction by a focusing mirror. A double bounce Si(111).monochromator was used to monochromatize X-rays to 8.18keV(wavelength of 1.5142 Å). The momentum transfer resolution was controlled by two pairs of slits on the detector arm, and was set at 0.001 $Å^{-1}$ in this experiment. The instrumental configuration of the beamline is illustrated schematically in Fig. 3 (a).

A schematic illustration of the scattering geometry used in this experiment is shown in Fig. 3 (b) together with the x-ray heating chamber. The sample was heated by a Si heater that was specially designed to operate in air at high temperatures. The sample temperature was monitored with two pairs of K-type(cromel-alumel) thermocouples. The x-ray heating chamber was mounted on a Huber 4-circle goniometer that adjusts the x-ray momentum transfer to the sample.

The experiment was carried out by measuring the scattering profile mainly in the out-of-plane <001> direction along the film normal. The film lattice constant can be simply obtained from the reciprocal coordinate of the peak positions, $q_{\perp}$, by $a_{\perp} = 2\pi / q_{\perp}$ where $a_{\perp}$ is the out-plane lattice spacing. In the low temperature tetragonal phase, we expect to have double peaks in the out-of-plane direction. The peak at lower q-value represents the domains with long c-axis aligned to the surface normal (c-domains), and the one at higher q-value corresponds to the domains with short a-axis aligned to the surface normal direction (a-domains). From the separation of the peaks, one can deduce the amount of the tetragonal distortion. As the sample temperature is increased to the high temperature cubic phase, we expect to observe only one peak in the out-of-plane direction.

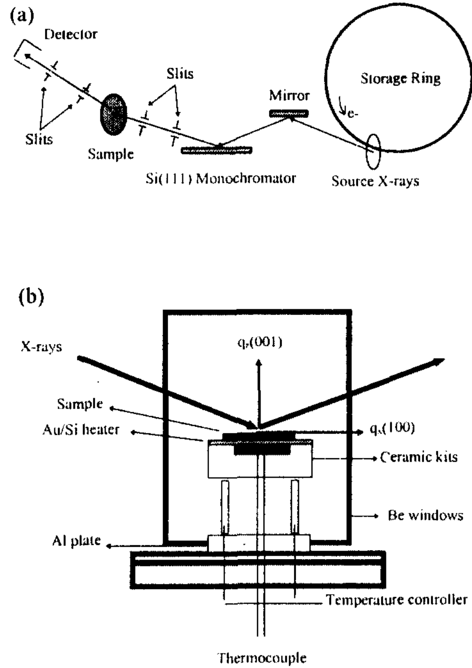

Figure 3. (a) Schematic illustration of the synchrotron x-rays setup composed of mirror, monochromator, and detector used in this experiment. (b) Schematic diagram of the heating x-ray chamber

For the 500 Å and the 250 Å thick films, we also have measured the in-plane Bragg peak, (100) in the in-plane q_X direction. Our results shows that it is possible for the thinner films to have single domain structure in low temperature tetragonal face due to the substrate field effect. In this case, it is possible to determine only one lattice constant (either the c-axis or the a-axis) from the scattering profile along the (001) direction. The other lattice constant must be measured by the scattering profile around the in-plane (100) direction. The in-plane (100) peak was accessed using the grazing incident scattering geometry [22] with the grazing incident angle of about 0.5° to open up the path for the incident and the out-going x-rays. We note that the penetration depth of the x-rays at the incident angle of 0.5° was much larger than the film thickness, which was confirmed by the x-ray reflectivity measurement on the same samples.

III. PARAELECTRIC(CUBIC)-TO-FERROELECTRIC(TETRAGONAL) TRANSITION.

A. Crystalline quality in the high temperature cubic phase.

The PZT crystal films obtained by the RTA process discussed in the previous section were very high quality epitaxial films especially in the high temperature paraelectric cubic phase. We first discuss the results obtained by the X-rays specular reflectivity method. In a reflectivity measurement the x-ray momentum transfer varies in the surface normal q_z direction in small diffraction angle ranges keeping the exit and the incident angle of x-rays equal. Using the x-ray reflectivity, we can obtain the film thickness immediately. One might also get the morphology of the film surface and the film-substrate interface by performing detailed analysis of the reflectivity.[23]

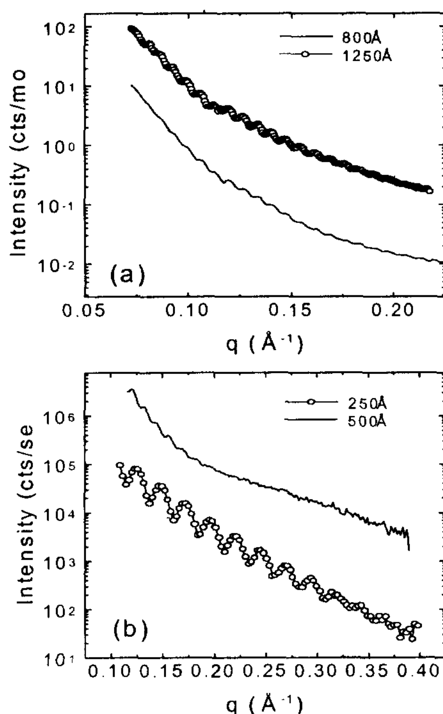

Figure 4. The X-ray reflectivity curves for the thin PZT films.

Fig. 4 shows the reflectivity of the films thinner than 1250 Å. The film thickness of a film is given by $2\pi/\Delta q$ [24], where Δq is the period of the intensity oscillations in the reflectivity curves. This is one of the best direct ways. to determine the thickness of a ultra-thin film. The oscillation amplitude in the reflectivity curves is strongly depend on the roughness of the film-substrate interface and of the film-air interface. From the data in the figure, one might conclude that the 250 Å thick film had the smoothest surface and interface morphology qualitatively. The 800 Å thick film barely showed the intensity oscillations, which suggests that the film surface was relatively rougher than that of the other films. We do not discuss the detailed analysis of the reflectivity curves, which is beyond the scope of this article.

The crystalline quality of the films could be judged by the diffraction profile around the Bragg (001) peak that was shown in Fig. 5. In the figure, the intensity profiles measured at the high temperature P_C phase were plotted in the logarithmic scale to illustrate the small features in the diffuse wings. The 250 Å and the 500 Å thick films show definite intensity oscillations in the wings of the Bragg peak. The intensity oscillations near Bragg peak immediately suggest that the

whole film was a high quality single crystal in the film normal direction. In other words, the crystal domain size in the out-of-plane direction was exceeding the film thickness, which, in turn, allows the Bragg reflected x-rays from the film surface and the film/substrate interface interfere each other. The thicker films did not show the intensity oscillations, and we conclude that the crystal domain size of them was smaller than the film thickness in this case. The crystal domain size obtained from the FWHM (full width at the half maximum) using the Scherrer's equation[25], was 447 Å, 249 Å, and 525 Å, for 800 Å, 1250 Å, and 5000 Å thick film respectively. Similarly, one might determine the crystal domain size in the film plane from the in-plane scattering profile near the (100) peak. We have measured the in-plane crystal domain size only on the 250 Å thick and the 500 Å thick film which was ~540 Å. We also have measured the azimuthal profile of the in-plane Bragg peak to confirm that the films were indeed epitaxial to the substrates (data not shown).

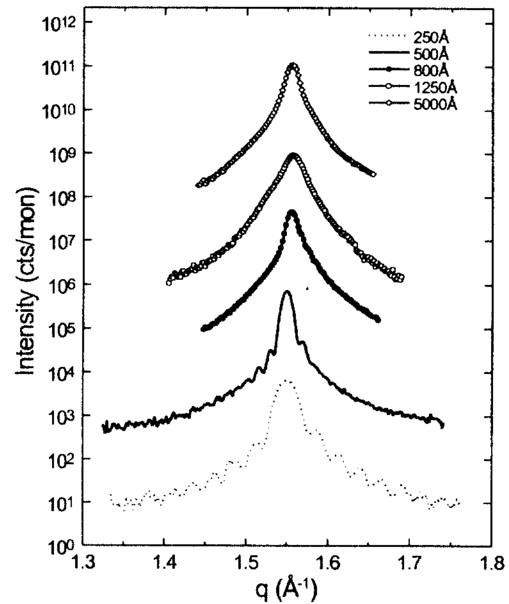

Figure 5. The x-rays intensity profile measured at the high temperature P_C phase were plotted in the logarithmic scale to illustrate the small features in the diffuse sings. The intensity oscillation in thin films indicates that the whole film was a high quality single crystal in the film normal direction.

B. Paraelectric (cubic)-to-Ferroelectric(tetragonal) transition in films thicker than 800A.

Figure 6 shows the out-of-plane scattering profile at several temperatures across the P_C-F_T transition. We first discuss the behavior of the bulk PZT target that was studied as a reference. As shown in Fig. 6(a), the bulk PZT was in cubic phase in the high temperature P_C phase as indicated by the single peak representing the reciprocal of the cubic lattice. As the sample temperature was decreased, the peak split into two peaks, which indicated that the tetragonal distortion occurred. The peak at a small q_Z value represents the domain with the large *c*-axis aligned to the surface normal, while the peak at the larger q_Z value corresponds to the domains with the small *a*-axis aligned to the surface normal. Those two kinds of the tetragonal domains were coexisting as expected in the powder sample. The splitting between the two peaks kept increasing with decreasing temperature. The difference between the lattice constant of the *c*-axis and of the *a*-axis at room temperature was

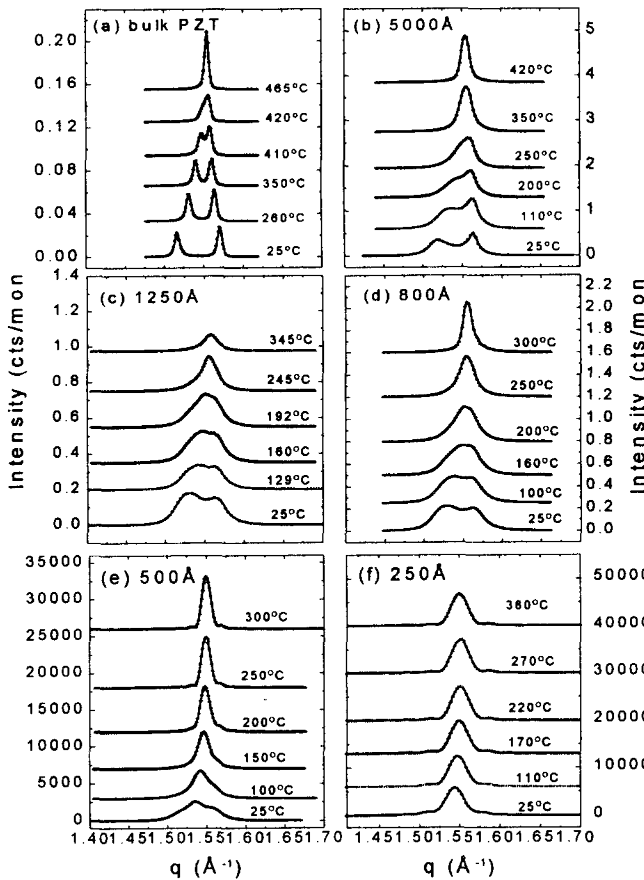

Figure 6. Phase transition of bulk and various thick films. Out of plane scattering profiles show two distinct peaks, which reveal that possible two domains coexist in surface normal direction. But 250 Å thick film has only the *a*-type domain.

about 0.15 Å. Comparing this value to the values in the reported phase diagram that shows the tetragonal distortion versus the Zr/Ti ratio[6], we determined that the composition of the target was Zr(43%)/Ti(57%). We also estimated that the composition of the thin films would be similar to that of the target bulk material based on the reported study on the film composition.

The scattering profile of the thickest film studied in this work, the 5000 Å thick film, was plotted in Fig. 6(b). There are two notable differences in the scattering profiles of this film from those of the bulk material. The first is the amount of the tetragonal distortion. At room temperature, the amount of the tetragonal distortion was significantly decreased as compared to that of the bulk PZT. The second is the decrease of the transition temperature. At 350 ℃, the scattering profile had only one peak indicating that the film was in the P_C phase, while the bulk profile still had two peaks even at 410 ℃. In the thinner films of 1250 Å and 800 Å, the transition temperature and the amount of the tetragonal distortion were decreased even further as shown in Fig6(c), and in Fig6(d).

The ultra-thin films, 500 Å and 250 Å thick films, showed rather interesting scattering features as shown in Fig.6(e), and in Fig. 6(f). In both the films, at high temperatures the scattering profile had definite intensity oscillations that were discussed in previous section indicating that the films in the high temperature cubic phase were single crystalline. As the temperature was decreased to room temperature, the 500 Å thick film showed again the two peak structure showing that it was in the tetragonal phase. However, the two peaks were very close, and the c-domains represented by the peak at low q_z value was dominant. In the 250 Å thick film, this phenomena was even more

severe. The scattering profile had always one-peak structure keeping the intensity oscillations in the wings even at room temperature as if the film was still in the cubic phase. To study the transition in the thinnest 250 Å film, it was required to measure the scattering in the in-plane (100) direction.

C. Suppression of the tetragonal distortion in the ultra thin 250 Å & 500 Å thick PZT films.

To study the detailed nature of the phase transitions 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.

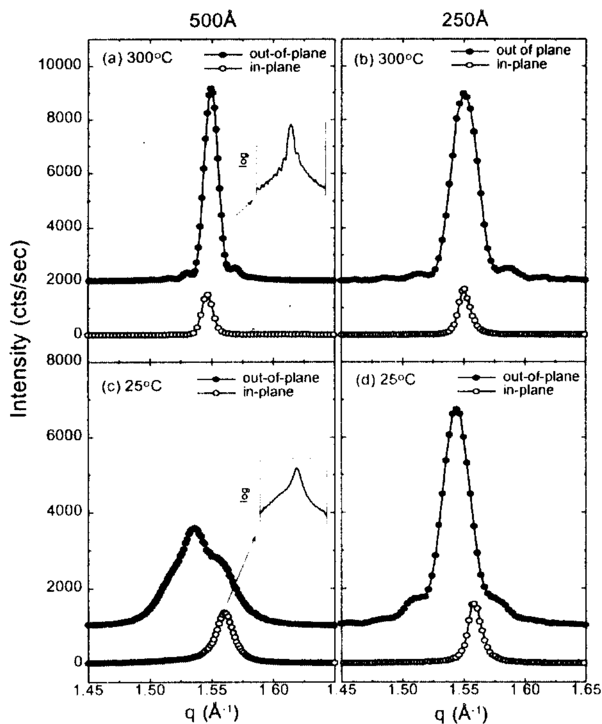

Figure 7. The scattering profile of both the 250 Å and 500 Å thick film both in the out-of plane and in the in-plane direction.

Figure 7 shows the scattering profiles from the 500 Å and 250 Å thick film at 300 ℃ and at 25 ℃. At 300 ℃, the films were in the high temperature P_C phase as indicated by the fact that the peak position in the film normal direction was almost identical to that in the film plane direction. The negligible, but finite difference between the in-plane and the out-of plane lattice constants even in the high temperature cubic phase was attributed to the stress field provided by the substrate. This is often observed tetragonal distortion of thin films on closely lattice matched substrates.

As discussed in previous section, the 500 Å thick film had two distinct peaks in the scattering profile in the out-of-plane direction as illustrated in Fig. 7(c) at room temperatures. 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. From the relative intensities, we conclude that there are more of the *c*-domains than the a-domains. The two domain structure was less obvious in the in-plane scattering profile as represented by the asymmetric feature of the in-plane scattering profile. The two peak structure in the in-plane scattering profile was well illustrated in the in-set of Fig. 7(c).

The scattering from the *a*-type domains was weak especially in the in-plane direction, since they were less aligned to the substrate due to the rectangular symmetry in the film plane that is

different from the square symmetry of the substrate. The *a*-domains with the short a-axis aligned to the out-of-plane direction must have both the long *c*-axis and the short *a*-axis in the film plane. Therefore, the *a*-domains have rectangular symmetry in the film plane which is different from the square symmetry of the substrate. It is, then, feasible for the *a*-domains develop a broad mosaic structure in the film plane, a broad distribution of the in-plane crystalline axis direction. In terms of x-ray scattering profile, this distributes the scattering intensity around the azimuthal circle, and makes the intensity in the in-plane scan rather small.

Although the scattering profile of the 250 Å film had only one peak, we believe that the film was in the F_T phase at low temperature, since the peak occurred at significantly smaller q value in the 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. 7(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.

IV. ANALYSIS AND DISCUSSIONS

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. 8. 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.8. 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. 9. 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 still effective 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 might infer that the domain structure of the thick PZT film would be similar the one illustrated in Fig. 9 (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

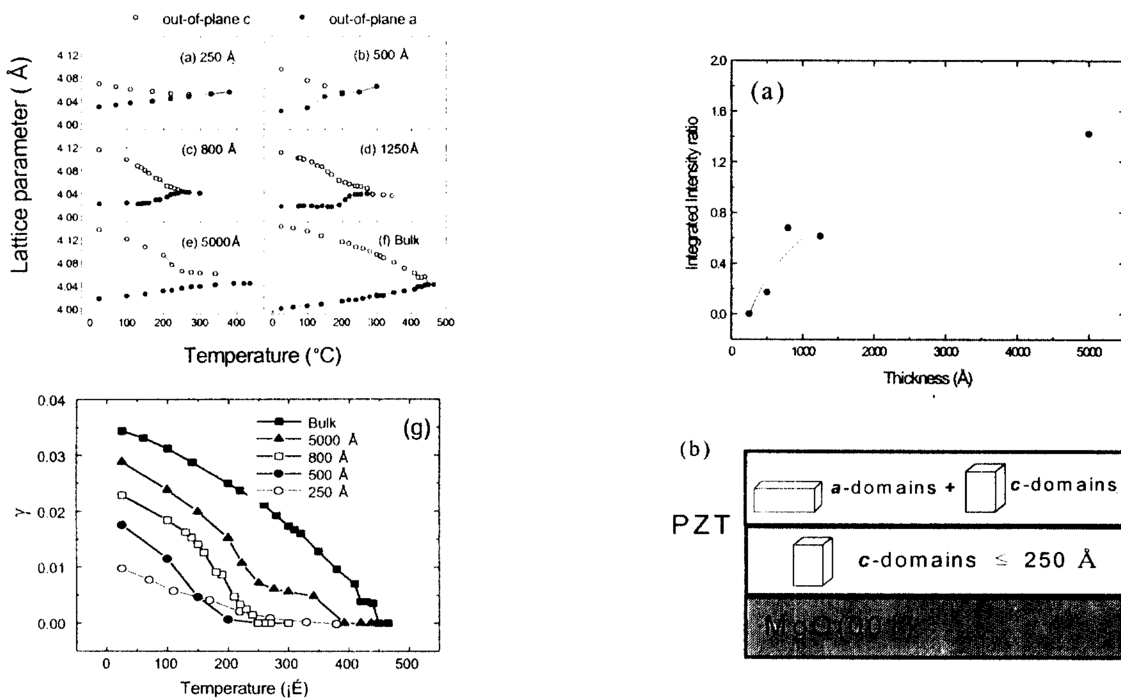

Figure 8. (a) The lattice constants of the c-axis obtained from the scattering profiles shown in figure 6 and figure 7. (b) The tetragonal distortion calculated from the lattice constants illustrated in (a).

Figure 9. (a) The ratio of the amount off 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.

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. 9 (b) is very different from the

suggested ones in literature that place a-domains near the interface[16], which is directly opposite from the result of the 250 Å thick film.

The tetragonal distortion results the lattice constant of the a-axis to decrease. Near the interface, the a-axis lies in the film plane, since only c-domains are allowed there. Since the lattice spacing of the substrate MgO is larger than that of PZT, the decrease of a-axis in the film plane would increase the film/substrate lattice mismatch, which is energetically unfavorable. Therefore, the tetragonal distortion in the thin films would decrease naturally. The substrate field effect can be summarized as following. First, it prefers c-domains with square in-plane lattice symmetry near the interface. Second it suppresses the tetragonal distortion, and consequently the P_C-F_T transition temperature to minimize the lattice mismatch.

V. SUMMARY

In summary, we have revealed the nature of the tetragonal distortion of thin PZT films grown on MgO substrates using synchrotron x-ray scattering method. The transition temperature and the amount of the tetragonal distortion were continuously decreased as the film thickness decreases. In the thinnest 250Å 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 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.

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