Orientation change with substrate type and composition in (100)/(001)-oriented epitaxial tetragonal $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films

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Tetragonal 30-nm thick $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films were grown epitaxially on (100) KTaO_3 and (100) SrTiO_3 single crystal substrates by pulsed metal organic chemical vapor deposition. High temperature X-ray diffraction (XRD) reciprocal space mapping showed that $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films of different compositions have a misfit strain that may not be apparent from room temperature XRD measurements. The misfit strain depends on the combination of the substrate and film composition. The misfit strain revealed by high temperature XRD measurements showed good agreement with previous theoretical predictions, even for relaxed films had except for an anomalous $\text{Pb}(\text{Zr}_{0.45}\text{Ti}_{0.55})\text{O}_3$ film, perfect (100) orientation was obtained for PbTiO_3 on (100)- KTaO_3 substrates with in-plane tensile and compressive strain. A mixture of (100) and (001) orientations was found for $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films with $x = 0.22$ and 0.30 . On (100)- SrTiO_3 substrates, however, the (001) orientation was obtained for $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films grown with $x = 0$ – 0.45 . These results reveal the importance of accounting for misfit strain at the growth temperature rather than at room temperature. Anomalous $\text{Pb}(\text{Zr}_{0.45}\text{Ti}_{0.55})\text{O}_3$ films grown on KTaO_3 had a perfect (001) orientation, despite having a small misfit strain at the growth temperature owing to relaxation. The lower degree of tetragonality of the crystal structure may contribute to the perfect (001) orientation in these films.

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1. Introduction

Ferroelectric films have been receiving increasing attention for a broad range of applications, from their ferroelectric random access memory (*FeRAM*) to microelectromechanical systems (*MEMS*), owing to attractive ferroelectric and piezoelectric properties.^{1,2)} The properties of thin films of these materials are strongly affected by the film orientation and domain structure, which are related to the in-plane strain of the ferroelectric films.^{3)–8)} The influence of the in-plane strain on film orientation has been widely investigated for (100)/(001)-oriented films.^{9)–14)} The stable constituent phases and their orientations as functions of temperature and in-plane strain have also been studied using theoretical approaches.^{15)–22)} These studies have suggested that the crystallographic orientation of these films changes from a (100)-orientation to a (001)-orientation. This change involves a shift from the (100)-orientation, with in-plane polarization and positive tensile strain, to the (001)-orientation, with out-of-plane polarization and in-plane compressive strain (negative strain value). The transition occurs through a mixture of (100)- and (001)-orientations for ferroelectric films with a small absolute strain (less than 1%).

We recently reported systematic tuning of the volume fractions

of the orientations in epitaxially grown tetragonal $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ films from a perfect (100)-orientation to a (001)-orientation on (100)- KTaO_3 substrates by changing the value ratio of Ti and Zr.²³⁾ This tunability presumably resulted from a systematic change of the in-plane strain that cannot be achieved with commercially available substrates. The strain values in the study were unclear, however, because we assumed the lattice parameters of KTaO_3 and extrapolated values from the cubic paraelectric $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$. This definition is strictly valid only for coherently grown films, i.e., films completely clamped by the substrate. Additionally, the ferroelectric tetragonal lattice parameters were based on room temperature measurements, and were thus not appropriate for evaluating the misfit strain at the film growth temperature. The mixture of in-plane lattice parameters from the (001)- and (100)-orientations added to these complications. The definition of strain used in our previous study was not effective, moreover, for partially relaxed epitaxial ferroelectric films, which are often observed to have a relatively large misfit strain. To avoid these issues, the misfit strain may be defined based on the lattice parameters of the film and the substrate measured close to the film deposition temperature and above the Curie temperature of the material.

In the present study, (100)/(001)-oriented epitaxial tetragonal $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ films with various $\text{Zr}/(\text{Zr}+\text{Ti})$ ratios were grown on (100)- KTaO_3 and (100)- STiO_3 substrates to enable detailed study of the orientation behavior of these systems. High temperature X-ray diffraction (XRD) measured at 600°C showed that

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the desired in-plane strain was present in $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films grown on the (100)- KTaO_3 substrate, except when $x = 0.45$, while the in-plane strain was partially relaxed for films with $x > 0.15$ on SrTiO_3 . The in-plane strain observed at the growth temperature was useful for predicting the domain structure at room temperature, except for one case with a low degree of tetragonality near the morphotropic phase boundary.

2. Experimental procedures

Epitaxial $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) 30-nm thick films were prepared at 580°C by pulsed metalorganic chemical vapor deposition (pulsed-MOCVD) from a $\text{Pb}(\text{C}_{11}\text{H}_{19}\text{O}_2)_2\text{-Zr}(\text{O}-t\text{-C}_4\text{H}_9)_4\text{-Ti}(\text{O}-i\text{-C}_3\text{H}_7)_4\text{-O}_2$ system. The proportion of Zr $\text{Zr}/(\text{Zr} + \text{Ti}) = x$ was controlled by adjusting the input Zr and Ti source gas concentrations x values from 0 to 0.45, while the film thickness was adjusted with the deposition time.²⁴⁾ The deposition pressure was maintained at 670 Pa. Single crystals of (100) KTaO_3 and (100) SrTiO_3 were used as substrates. The in-plane strain at the deposition temperature changes with x , because the lattice parameter increases as the proportion of Zr increases owing to the larger ionic radius of Zr^{4+} as compared with that of Ti^{4+} .²⁵⁾ The tensile and compressive strains were as expected for $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films with x values below and above those of 0.15 on (100)- KTaO_3 substrates.²³⁾ A compressive strain was expected for $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films deposited on (100)- SrTiO_3 substrates for x values from 0 to 0.45.

The orientation of the deposited films was analyzed by high-resolution X-ray diffraction (HR-XRD). XRD reciprocal space mapping (XRD-RSM) was also used to analyze their crystal structures in more detail.

3. Results and discussion

To evaluate the in-plane lattice strain at the growth temperature, we performed high temperature XRD-RSM at 600°C, at which temperature PZT films should be in the paraelectric phase. **Figure 1** shows the XRD-RSMs near the KTaO_3 202 spot measured at 600°C (close to the film's deposition temperature), for 30-nm-thick films with various x values deposited on (100)- KTaO_3 . The horizontal and vertical axes in Fig. 1 correspond to

Fig. 1. XRD reciprocal space maps measured at 600°C around the KTaO_3 202 spot for 30-nm thick epitaxial tetragonal $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films with x values of (a) 0, (b) 0.22, (c) 0.3, and (d) 0.45.

the reciprocal lattice spacing along the in-plane and out-of-plane directions, $1/d_{\parallel}$ and $1/d_{\perp}$, respectively. One $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ 202 diffraction spot was observed near the KTaO_3 202 spot for all compositions. Furthermore, the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ 202 and KTaO_3 202 diffraction spots were located at the same $1/d_{\parallel}$ value, indicating that the in-plane lattice spacing of PZT was the same as that of KTaO_3 for $x = 0, 0.22$, and 0.30 [Figs. 1(a)–1(c)]. This suggests that the PZT lattice was clamped by the KTaO_3 substrate at these compositions. Conversely, the PZT film with $x = 0.45$ showed a different $1/d_{\parallel}$ value from that of KTaO_3 , suggesting that relaxation occurred during the growth stage. This relaxation was not complete, because the evaluated lattice parameters of the PZT film from Fig. 1(d) were 4.057 and 4.098 Å for the in-plane and out-of-plane, respectively.

Figure 2 shows XRD-RSM measured near the SrTiO_3 202 spot at 600°C, for 30 nm-thick films with various x values deposited on (100)- SrTiO_3 . As shown in Fig. 2(a), the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ 202 spot had $1/d_{\parallel}$ values that were the same as that of SrTiO_3 202, suggesting that the PZT film ($x = 0$) was clamped by the substrate. However, the $1/d_{\parallel}$ value of the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ 202 spot differed from that of SrTiO_3 202 for the PZT film with $x = 0.15$, as shown in Fig. 2(b). This result suggested partial release of the PZT lattice from the SrTiO_3 substrate. The PZT lattice was almost completely released from the substrate for a PZT film with $x = 0.3$, because the $1/d_{\parallel}$ value of the PZT 202 spot was different from that of SrTiO_3 202.

Figure 3 shows plots of the observed strain of a PZT films at the film growth temperature of 600°C, shown in Figs. 1 and 2, as a function of x . Theoretical predication of the strain from differ-

Fig. 2. XRD reciprocal space maps measured at 600°C around the SrTiO_3 202 spot for 30-nm thick epitaxial tetragonal $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films with x values of (a) 0, (b) 0.15, and (c) 0.3.

Fig. 3. Misfit strain calculated from differences in experimental lattice parameter at the growth temperature. Theoretical predictions of Kukhar et al.¹⁶⁾ and Sheng et al.¹⁸⁾ are also shown. The closed circle and square indicate experimental results for deposition on KTaO_3 and SrTiO_3 substrates, respectively, while the broken and dotted line are the misfit strain calculated from powder data for on deposition KTaO_3 and SrTiO_3 , respectively. The dotted and hatched areas indicate the areas where perfect (100) and (001) orientations are expected based on theoretical calculation.

Fig. 4. Critical thickness calculated from Ref. 26 and 27 as functions of x for epitaxial $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films grown on (100)KTaO₃ and (100)SrTiO₃ substrates. The solid lines are guides for the eyes and the dashed line indicates the film thickness used in this study.

ences between lattice parameters of the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films and KTaO₃ and SrTiO₃ substrates are also indicated in Fig. 3 by solid and dashed lines, respectively. In the case of the PZT films grown on KTaO₃ substrates, the experimental results were close to the theoretical values in the model, except for that of the sample with $x = 0.45$. However, the results for the PZT films grown on the SrTiO₃ substrate deviated from the expected parameters as x increased, although the PZT films grown on the SrTiO₃ substrate with $x = 0$ followed the model. These data show that a desired strain can be imposed on the film by controlling the value of x for the different substrates, except for PZT films with $x = 0.15$ and 0.30 grown on (100)-SrTiO₃ substrates and $x = 0.45$ grown on KTaO₃. The deviation of the measured strain from the predictions in films formed under these conditions can be explained by a decrease in the thickness limit of the clamped film owing to a large misfit strain, known as the critical thickness.

Figure 4 shows the calculated critical thickness for PZT films grown on (100)-KTaO₃ and (100)-SrTiO₃ substrates.^{26),27)} Here we assume the misfit dislocation to be a type $\langle 110 \rangle$ Burgers vector. The present film thickness of 30 nm is also shown in Fig. 4. The estimated critical thickness of the PZT films grown on (100)-KTaO₃ was greater than the film thickness of the present study. This suggests that PZT films will be clamped by KTaO₃ substrates for all values of x in the present study. This estimation is in good agreement with the results shown in Figs. 1 and 3, except for those of the sample with $x = 0.45$. The PZT film with $x = 0.45$ is located at the limit for relaxation, which might have prevented a coherent film from forming.

The critical thickness was larger than the present film thickness for films grown on (100) SrTiO₃ substrates with $x > 0.07$ but smaller than that for films with $x < 0.07$. This indicates that film lattices are expected to be clamped by the substrate at below $x = 0.07$ but relaxed at higher value. This prediction is in good agreement with the results shown in Figs. 2 and 3.

Next we investigated the orientation and strain state of the films shown in Figs. 1 and 2 at room temperature. Figure 5 shows XRD-RSM around the SrTiO₃ 202 measured at room temperature for PZT films grown on SrTiO₃ substrates. Only the $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ 202 diffraction peaks were detected and no $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ 220 peaks appeared in any films, indicating a perfect (001) out-of-plane orientation. This result is consistent with our previous reports on 50-nm thick PZT films.²⁸⁾

The PZT 202 spots were located at the same $1/d_{\parallel}$ value as that of the SrTiO₃ 202 for the PZT films with $x = 0$, as shown in Fig. 5(a). This indicates that the PZT films were clamped by the substrate. However, the $1/d_{\parallel}$ value of the PZT 202 spots was

Fig. 5. XRD reciprocal space maps measured around the SrTiO₃ 202 spot for 30-nm thick epitaxial tetragonal $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films with x values of (a) 0, (b) 0.15, and (c) 0.3 at room temperature. Each schematic shows the lattice of PZT films corresponding to the diffraction spot.

Fig. 6. XRD reciprocal space maps measured at 600°C around the KTaO₃ 202 spot for 30-nm thick epitaxial tetragonal $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films with x values of (a) 0, (b) 0.22, (c) 0.3, and (d) 0.45. Each schematic shows the lattice of PZT films corresponding to the diffraction spot.

smaller than that of SrTiO₃ 202 for PZT films with $x = 0.15$ and 0.3 , as shown in Fig. 5(b), suggesting partial relaxation of the film lattice. The deviation of the 202 spot on the SrTiO₃ substrate for $x = 0.3$ was larger, moreover, than that for the sample prepared with $x = 0.15$. This tendency is consistent with the high temperature XRD RSM results shown in Fig. 2.

The theoretically predicted orientations of the films at room temperature are also indicated in Fig. 3, where the dashed line shows the boundaries of changing orientations. This figure suggests that the films grown on SrTiO₃ substrates have a perfect (001) orientation for all x values in the present study, because the misfit strain obtained from Fig. 2 is around 1%. This prediction is in good agreement with the results shown in Fig. 5, even for partially relaxed films such as $x = 0.15$ and 0.30 .

Figure 6 shows the XRD-RSM around the KTaO₃ 202 spots measured at room temperature for 30 nm-thick PZT films with various x values deposited on (100) KTaO₃ substrates. As shown in Fig. 6(a), $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ 202 and 220 spots with the same out-of-plane lattice spacing were observed around the KTaO₃ 202 spot for films with $x = 0$, i.e., PbTiO₃, indicating a perfect (100) orientation. These spots suggest the existence of two orientations with the same out-of-plane lattice spacing but different in-plane spacing; thus (100) out-of-plane orientations with two orthogo-

Fig. 7. In-plane and out-of-plane lattice parameters of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ films with an x value of 0.45 on a KTaO_3 substrate as a function of temperature. The broken lines are guides for the eye.

nally intersected in-plane polarizations exist.^{29),30)} The 202 spot in Fig. 1(a) might split into two spots of 202 and 220 with domain formation accompanied by a phase transition for PZT films with $x = 0$. Figures 6(b) and 6(c) show that the 022/202 diffraction spots appeared near the KTaO_3 202 spots, indicating the coexistence of (001) out-of-plane orientations and (100) orientations for films with $x = 0.15$ and 0.3. Figure 6(d) shows that only the 202 spot is detected for the film with $x = 0.45$, suggesting a perfect (001) out-of-plane orientation. Fig. 4 suggests that the PZT film should have a mixed orientation. As a result, the film orientation can be tuned from a perfect (100)- to a (001)-orientation with degree orientation mixing controlled by the composition, as reported in a previous letter.²³⁾ These orientations are almost the same as the theoretical predictions shown in Fig. 3, except for the PZT films with $x = 0.45$ on KTaO_3 substrates, which were expected to show perfect (100) orientations for $x < 0.10$, and a mixture of (100) and (001) orientations between 0.1 and 0.3. This deviation may be explained by the induced strain measured at high temperature by XRD *RSM*, as shown in Figs. 1(a)–1(c). Figures 5 and 6(a)–6(c) reveal that the predicted domain structure, shown in Fig. 3, can be grown as predicted for fully clamped films (PZT films on KTaO_3 with $x \leq 0.3$ and on SrTiO_3 with $x = 0$) or partially relaxed films (PZT films on SrTiO_3 with $x \geq 0.15$). This means that the strain state at the growth temperature plays a critical role in determining the domain structure.

Finally, we discuss the reasons for deviation of the PZT film on KTaO_3 with $x = 0.45$ from the theoretically predicted domain structure. Figure 7 shows the lattice parameters as a function of temperature for PZT film with $x = 0.45$ deposited on a KTaO_3 substrate together with those of KTaO_3 . The out-of-plane lattice parameters show a gradual decrease with temperature up to 500°C and then begin to increase at this temperature. This suggests that a ferroelectric transition occurs near this temperature. The in-plane lattice parameter showed an almost linear increase, although the PZT powder should also show a parabolic increase like that of the out-of-plane lattice parameter. This implies that strong clamping from the substrate might restrict the large in-plane deformation of the lattice. This restriction indeed prevents any pronounced out-of-lattice deformation, leading to smaller tetragonality (c/a) of 1.022 as compared with the value of 1.030 expected from the powder XRD results. This limited increase in tetragonality might prevent the formation of an a -domain upon cooling after film deposition.

The a -domain forms to cancel mismatches produced by spontaneous deformation during cooling. However, Fig. 4 shows

that the in-plane lattice parameter of PZT with $x = 0.45$ on KTaO_3 approximately followed the change in the lattice parameter of the KTaO_3 substrate, supporting the absence of a -domain formation. Moreover, a -domain formation requires satisfaction of mechanical boundary conditions, which determine the minimum domain width. Previous reports³¹⁾ have shown that the minimum domain width increases with decreasing tetragonality. In the present case, for a tetragonality of 1.022, the minimum width was evaluated to be 20 nm. Such a large domain would not be able to extend over the entire film thickness, particularly in thin films like present film (with a thickness of 30 nm), and this might result in observation of a perfect c -axis orientation.

4. Conclusions

The crystal structure of 30-nm thick tetragonal $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films epitaxially grown on (100) KTaO_3 and (100) SrTiO_3 substrates was investigated. The in-plane misfit strain was controlled by the x value of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films, which tuned the film orientation. When the films were grown on KTaO_3 , a perfect (100)-oriented film was obtained for films with $x = 0$, where tensile strain was imposed by the substrate. A mixture of (001) and (100) oriented films was realized when x was 0.22 or 0.30 owing to lower strain at the film growth temperature. A perfect (001) orientation was achieved for $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films grown on (100) SrTiO_3 for $x = 0$ –0.30 owing to in-plane compressive strain, which agreed with the theoretical predictions. The theoretical predictions were validated by observing the in-plane strain at the growth temperature and at room temperature. However, PZT film with $x = 0.45$ on KTaO_3 substrates showed some deviations from the predictions. The perfect (001) orientation in $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ thin films grown on KTaO_3 for $x = 0.45$ might have originated from the low tetragonality of the crystal lattice and the low thickness of the film.

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