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

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Tetragonal 30-nm thick Pb(Zr$_x$Ti$_{1-x}$)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 Pb(Zr$_x$Ti$_{1-x}$)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 with except for an anomalous Pb(Zr$_{0.45}$Ti$_{0.55}$)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 Pb(Zr$_{0.7}$Ti$_{0.3}$)O$_3$ thin films with $x = 0.22$ and 0.30. On (100)-SrTiO$_3$ substrates, however, the (001) orientation was obtained for Pb(Zr$_{0.7}$Ti$_{0.3}$)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 Pb(Zr$_{0.45}$Ti$_{0.55}$)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.

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. 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. The influence of the in-plane strain on film orientation has been widely investigated for (100)/(001)-oriented films. The stable constituent phases and their orientations as functions of temperature and in-plane strain have also been studied using theoretical approaches. 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 Pb(Zr, Ti)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. 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 Pb(Zr, Ti)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 Pb(Zr, Ti)O$_3$ films with various Zr/(Zr+Ti) ratios were grown on (100)-KTaO$_3$ and (100)-SrTiO$_3$ substrates to enable detailed study of the orientation behavior of these systems. High temperature X-ray diffraction (XRD) measured at 600°C showed that
the desired in-plane strain was present in Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$ films grown on the (100)-K-TaO$_3$ 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 Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$ (PZT) 30-nm thick films were prepared at 580°C by pulsed metalorganic chemical vapor deposition (pulsed-MOCVD) from a Pb(C$_{11}$H$_{19}$O$_2$)$_2$-Ti(O-i-C$_3$H$_7$)$_4$-ZrO$i$-C$_4$H$_6$O$_4$-O$_3$ system. The proportion of Zr[Zr + 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) K-TaO$_3$ 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$^{4+}$. The tensile and compressive strains were as expected for Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$ thin films with $x$ values below and above those of 0.15 on (100)-K-TaO$_3$ substrates.$^{25}$ A compressive strain was expected for Pb(Zr$_{1-x}$Ti$_x$)$_2$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 K-TaO$_3$ 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)-K-TaO$_3$. The horizontal and vertical axes in Fig. 1 correspond to the reciprocal lattice spacing along the in-plane and out-of-plane directions, $l/d_1$ and $l/d_2$, respectively. One Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$ 202 diffraction spot was observed near the K-TaO$_3$ 202 spot for all compositions. Furthermore, the Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$ 202 and K-TaO$_3$ 202 diffraction spots were located at the same $1/d_1$ value, indicating that the in-plane lattice spacing of PZT was the same as that of K-TaO$_3$ for $x = 0, 0.22, 0.30$ [Figs. 1(a)–1(c)]. This suggests that the PZT lattice was clamped by the K-TaO$_3$ substrate at these compositions. Conversely, the PZT film with $x = 0.45$ showed a different $1/d_1$ value from that of K-TaO$_3$, 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 Pb(Zr$_{1-x}$Ti$_x$)$_2$O$_3$ 202 spot had $1/d_1$ 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 $1/d_1$ value of the Pb(Zr$_{1-x}$Ti$_x$)$_2$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 $1/d_1$ 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 film 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-
variances between lattice parameters of the Pb(Zr\(\text{Ti}
\text{Ta})\text{O}_3\) thin films and KTaO\(_3\) and SrTiO\(_3\) substrates are also indicated in Fig. 3 by solid and dashed lines, respectively. In the case of the PZT films grown on KTaO\(_3\) 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 SrTiO\(_3\) substrate deviated from the expected parameters as \(x\) increased, although the PZT films grown on the SrTiO\(_3\) 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)-SrTiO\(_3\) substrates and \(x = 0.45\) grown on KTaO\(_3\). 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)-KTaO\(_3\) and (100)-SrTiO\(_3\) substrates.\(^{26,27}\) Here we assume the misfit dislocation to be a type (110) 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)-KTaO\(_3\) was greater than the film thickness of the present study. This suggests that PZT films will be clamped by KTaO\(_3\) 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) SrTiO\(_3\) 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 SrTiO\(_3\) 202 measured at room temperature for PZT films grown on SrTiO\(_3\) substrates. Only the Pb(Zr\(\text{Ti}
\text{Ta})\text{O}_3\) 202 diffraction peaks were detected and no Pb(Zr\(\text{Ti}
\text{Ta})\text{O}_3\) 220 peaks appeared in any films, indicating a perfect (001) out-of-plane orientation. This result is consistent with our previous reports on 30-nm thick PZT films.\(^{28}\)

The PZT 202 spots were located at the same 1/\(d_\|\) value as that of the SrTiO\(_3\) 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/\(d_\|\) value of the PZT 202 spots was smaller than that of SrTiO\(_3\) 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 SrTiO\(_3\) 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 SrTiO\(_3\) 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 KTaO\(_3\) 202 spots measured at room temperature for 30 nm-thick PZT films with various \(x\) values deposited on (100) KTaO\(_3\) substrates. As shown in Fig. 6(a), Pb(Zr\(\text{Ti}
\text{Ta})\text{O}_3\) 202 and 220 spots with the same out-of-plane lattice spacing were observed around the KTaO\(_3\) 202 spot for films with \(x = 0\), i.e., PbTiO\(_3\), 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-
composition, as reported in a previous letter. These orientations with degree orientation mixing controlled by the parameters show a gradual decrease with temperature up to 500°C and then begin to increase at this temperature. This restriction indeed implies that strong clamping from the substrate might restrict the growth temperature plays a critical role in determining the formation. Moreover, a-domain formation requires satisfaction of mechanical boundary conditions, which determine the minimum domain width. Previous reports 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 Pb(Zr0.30Ti0.70)O3 thin films epitaxially grown on (100)KTaO3 and (100)SrTiO3 substrates was investigated. The in-plane misfit strain was controlled by the x value of Pb(Zr0.30Ti0.70)O3 thin films, which tuned the film orientation. When the films were grown on KTaO3, 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 = 0.22 or 0.30 owing to lower strain at the film growth temperature. A perfect (001) orientation was achieved for Pb(Zr0.30Ti0.70)O3 thin films grown on (100)SrTiO3 for x = 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 KTaO3 substrates showed some deviations from the predictions. The perfect (001) orientation in Pb(Zr0.30Ti0.70)O3 thin films grown on KTaO3 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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References

1) N. Setter, “Piezoelectric Materials in Devices”, EPFL, Switzerland (2002).
2) R. Waser, “Nanoelectrics and Information Technology”, Wiley-VCH, Weinheim, Germany (2003).
3) D. G. Schlom, L. Q. Chen, C. B. Eom, K. M. Rabe, S. K. Streiffer and J. M. Triscone, Annu. Rev. Mater. Res., 37, 589–626 (2007).
4) O. Díequez, K. Rabe and D. Vanderbilt, Phys. Rev. B, 72, 144101 (2005).
5) C. Ederer and N. Spaldin, Phys. Rev. Lett., 95, 257601 (2005).
6) J. X. Zhang, D. G. Schlom, L. Q. Chen and C. B. Eom, Appl. Phys. Lett., 95, 122904 (2009).
7) K. J. Choi, M. Biegalski, Y. L. Li, A. Sharar and J. Schubert, Science, 306, 1005–1009 (2004).
8) J. H. Haeni, P. Irvin, W. Chang, R. Uecker, P. Reiche, Y. L. Li, S. Choudhury, W. Tian, M. E. Hawley, B. Craigio, A. K. Tagantsev, Y. Q. Pan, S. K. Streiffer, L. Q. Chen, S. W. Kirchoefer, J. Levy and D. G. Schlom, Nature, 430, 758–761 (2004).
9) M. D. Nguyen, M. Dekkers, E. Houwman, R. Steenwelle, X. Wan, A. Roelofs, T. Schmitz-Kemen and G. Rijnders, Appl. Phys. Lett., 99, 252904 (2011).
10) K. S. Lee, J. H. Choi, J. Y. Lee and S. Baik, J. Appl. Phys., 90, 4095–4102 (2001).
11) M. J. Highland, D. D. Fong, G. B. Stephenson, T. T. Fister,
12) G. Catalan, A. Lubk, A. H. G. Vlooswijk, E. Snoeck, C. Magen, A. Janssens, G. Rispens, G. Rijnders, D. H. A. Blank and B. Noheda, Nat. Mater., 10, 963–967 (2011).
13) S. Matzen, O. Nesterov, G. Rispens, J. A. Heuver, M. Biegalski, H. M. Christen and B. Noheda, Nat. Commun., 5, 4415 (2014).
14) G. Rispens, J. A. Heuver and B. Noheda, Appl. Phys. Lett., 97, 262901 (2010).
15) V. Koukhar, N. Pertsev and R. Waser, Phys. Rev. B, 64, 214103 (2001).
16) V. Kukhar, N. Pertsev, H. Kohlstedt and R. Waser, Phys. Rev. B, 73, 214103 (2006).
17) N. Pertsev, V. Kukhar, H. Kohlstedt and R. Waser, Phys. Rev. B, 67, 054107 (2003).
18) G. Sheng, J. X. Zhang, Y. Li, S. Choudhury, Q. X. Jia, Z. K. Liu and L. Q. Chen, J. Appl. Phys., 104, 054105 (2008).
19) L. Q. Chen, J. Am. Ceram. Soc., 91, 1835–1844 (2008).
20) N. Khakpash, H. Khassaf, G. A. Rossetti and S. P. Alpay, Appl. Phys. Lett., 106, 082905 (2015).
21) H. Khassaf, N. Khakpash, F. Sun, N. M. Sbrockey, G. S. Tompa, T. S. Kalkur and S. P. Alpay, Appl. Phys. Lett., 104, 202902 (2014).
22) F. Sun, H. Khassaf and S. P. Alpay, J. Mater. Sci., 49, 5978–5985 (2014).
23) D. Ichinose, T. Nakashima, Y. Ehara, T. Oikawa, T. Shimizu, O. Sakata, T. Yamada and H. Funakubo, Appl. Phys. Lett., 107, 022902 (2015).
24) K. Nagashima, M. Aratani and H. Funakubo, Jpn. J. Appl. Phys., 39, 996–998 (2000).
25) R. D. Shannon and C. T. Prewitt, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem., 25, 925–946 (1969).
26) J. S. Speck and W. Pompe, J. Appl. Phys., 76, 466–476 (1994).
27) Y. Kuroiwa, Y. Terado, S. J. Kim, A. Sawada, Y. Yamamura, S. Aoyagi, E. Nishihori, M. Sakata and M. Takata, Jpn. J. Appl. Phys., 44, 7151–7155 (2005).
28) H. Morioka, T. Yamada, A. K. Tagantsev, R. Ikariyama, T. Nagasaki, T. Kurosawa and H. Funakubo, Jpn. J. Appl. Phys., 44, 7151–7155 (2005).
29) B. S. Kwak, A. Erbil, J. D. Budai, M. F. Chisholm, L. A. Boatner and B. J. Wilkens, Phys. Rev. B, 49, 14865 (1994).
30) C. D. Theis and D. G. Schlom, J. Mater. Res., 12, 1297–1305 (1997).
31) A. H. G. Vlooswijk, B. Noheda, G. Catalan, A. Janssens, B. Barcones, G. Rijnders, D. H. A. Blank, S. Venkatesan, B. Kooi and J. T. M. de Hosson, Appl. Phys. Lett., 91, 112901 (2007).