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Orientation control of (001) and (101) in epitaxial tetragonal $Pb(Zr,Ti)O_3$ films with (100)/(001) and (110)/(101) mixture orientations

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Epitaxial tetragonal PZT films with (100)/(001) and (110)/(101) and (111) orientations were grown on various kinds of single crystal substrates having different thermal expansion coefficient. Volume fractions of (001) and (101) orientations in respective (100)/(001)- and (110)/(101)-oriented films were almost linearly increased with increasing thermal strain of the films that was generated under the cooling process after the deposition from the growth temperature to the Curie temperature. Perfectly (001)- and (101)-oriented films were grown on (111) CaF_2 substrates with large thermal expansion coefficient. Observed saturation polarization values linearly changed with the volume fractions of (100) and (101) orientations.

Key-words : Orientation control, Epitaxial $Pb(Zr,Ti)O_3$, Tetragonal symmetry

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1. Introduction

$Pb(Zr,Ti)O_3$ has been widely investigated due to its large spontaneous polarization with good insulation characteristics. $Pb(Zr,Ti)O_3$ thin films have also been widely investigated because of the practical importance of the applications, such as ferroelectric random access memories and piezoelectric devices.[1),2)] Fundamental research has been carried out using epitaxial tetragonal PZT films grown on single crystal substrates. However, the obtained results remain sometimes complication due to the 90° domains in the films. These domains were generated at the phase transition of Curie temperature, T_c, under the cooling process, after the film growth generally above T_c.[3)] This is due to the lack of the single-oriented films, such as (001), (101) and (111) orientation, except the (001) single-oriented films below the film thickness of 100 nm.[4),5)] In fact, most of epitaxial films consists of mixed orientations, (100)/(001) and (110)/(101), when films are respectively grown on (100) and (110) oriented single crystals. These especially make difficult to understand orientation dependency of the electrical properties.

In a previous study, we demonstrated the successful growth of (001)-, (101)- and (111)-one-axis oriented epitaxial $Pb(Zr_{0.35}Ti_{0.65})O_3$ films on (111)CaF_2 substrates.[6)] However, the control methods of the film orientation, especially for (110)/(101) orientation has not been established yet. In the present study, we tried to clarify the factors determining the volume fractions of (001) and (101) orientations in (100)/(001) and (110)/(101)-oriented films.

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2. Model

Figure 1 shows the schematic model of the applied stress to the films throughout growth and the cooling process, in case of (100)/(001)-oriented tetragonal films grown above T_c by metal organic chemical vapor deposition (MOCVD). The volume fraction of (001) orientation is pointed out to be determined by the *in-plane* stress applied to the film at Curie temperature (T_c) during cooling process.[7)] This was found out to be mainly the summations of the misfit strain and the thermal strain from the deposition temperature to T_c.[8)] Misfit strain is the lattice parameter mismatch at deposition temperature between the film and the underlying layers, such as the bottom electrode layer. This strain is dominant one when the film is thin, such as below 100 nm in thickness.[4)] On the other hand, the thermal strain is the multiplication of the thermal expansion coefficients difference between the film and the substrate, and the temperature difference between the deposition temperature and T_c. Thermal strain is independent of the film thickness and become dominant in thick film case due to the decrease of the misfit strain with increasing film thickness.

When the film is under compressive strain at T_c, the orientation with smaller unit cell area along substrate *in-plane* direction becomes dominant to relax the strain, while the orientation with larger unit cell area becomes dominant in case of the tensile strain as shown in **Figs. 2**(a) and (b). **Figure 3** shows the unit cell area change with the temperature, based on the data of Ref. 9). (001) orientation is found to have smaller unit cell area than (100) one for all temperature range from T_c to room temperature. These data show that (001) orientation become dominant in the mixture orientation of (001) and (100) due to the smaller unit cell area along *in-plane* direction in case of compressive stress, while (100) one with larger unit cell area in

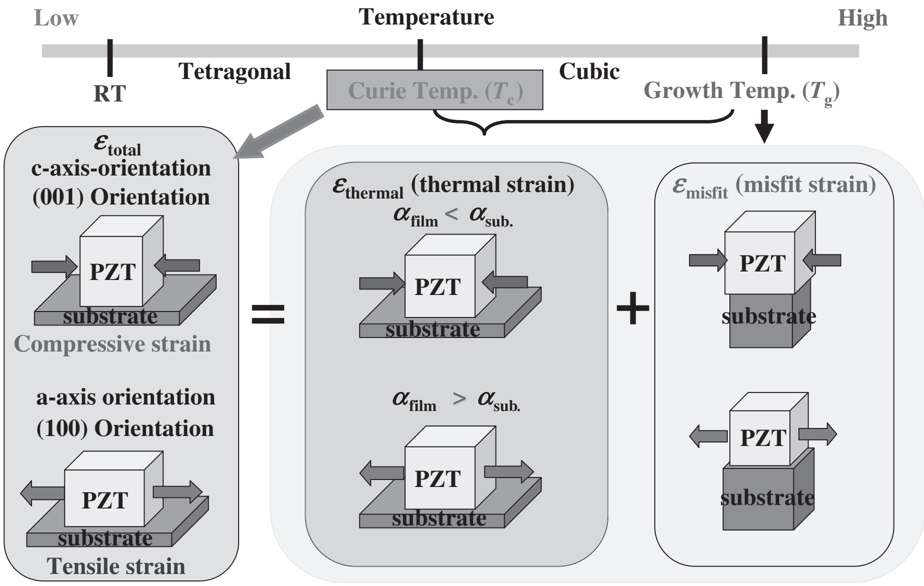

Fig. 1. Schematic model of the stress applied to the films during the film growth and the cooling process after the deposition together with the determination factors of (001) and (100) orientations in case of (100)/(001)-oriented epitaxial tetragonal PZT film.

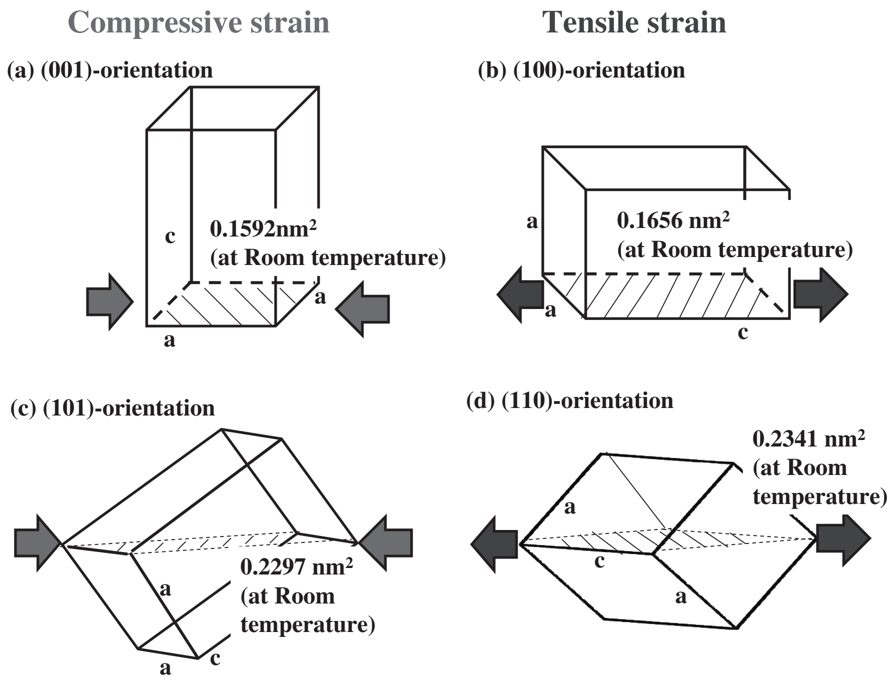

Fig. 2. Room temperature unit cell area along *in-pane* direction in case of (a) (001), (b) (100), (c) (101), and (d) (110) orientations.

case of tensile stress, even if taking into account the possibility that the orientation change with the temperature below T_c as pointed out by Kim et al.[10)]

When films are grown on various substrates having different thermal expansion coefficients with the same bottom layers, the thermal strain is considered to mainly control the orientation of the films, especially in thick film case. In fact, the volume fraction of (001) orientation in (100)/(001) mixed orientation was found to be mainly determined by the thermal strain for 150 nm-thick $Pb(Zr_{0.35}Ti_{0.65})O_3$ films.[8)]

When we expanding this idea to (110)/(101)-oriented films, (101) orientation is expected to be preferential orientation in case of compressive stress at T_c, while (110) orientation is expected in case of the tensile stress. This phenomena is due to *in-plane* unit cell area of (101) orientation which is smaller than (110) one for all temperature rage below T_c as shown in Fig. 2.

3. Experimental

Epitaxial $Pb(Zr_{0.35}Ti_{0.65})O_3$ films with ~200 nm in thickness were grown at 600°C by MOCVD from $Pb(C_{11}H_{19}O_2)_2$–$Zr(O\cdot t\text{-}C_4H_9)_4$–$Ti(O\cdot i\text{-}C_3H_7)_4$–$O_2$ system.[6),8)] The Zr/(Zr + Ti) ratio and film thickness were controlled by the input source gas concentration and the deposition time, respectively. In the present study, the Zr/(Zr + Ti) ratio was set to be 0.35 under

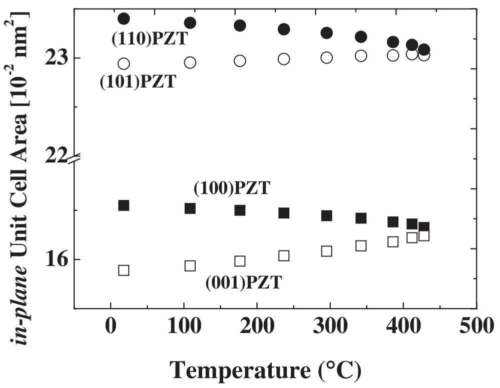

Fig. 3. Temperature dependency of the calculated unit cell area based on data of Ref. 9). closed circles: (110) orientation, open circles: (101) orientation, closed squares: (100) orientation, open squares: (001) orientation.

$Pb/(Pb + Zr + Ti) = 0.50$ and was ascertained by an X-ray fluorescence spectrometer using standard samples.

Various kinds of substrates covered with $SrRuO_3$ layers having (100)*c*, (110)*c* and (111)*c* orientations were used as substrates; $(100)_c SrRuO_3$//(111)Pt//$(111)CaF_2$, $(100)_c SrRuO_3$//$(100)(Ba,Sr)TiO_3$//(100)MgO, $(100)_c SrRuO_3$//$(100)SrTiO_3$, $(100)_c SrRuO_3$//$(100)[(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}]$(LSAT), $(100)_c$-$SrRuO_3$//$(100)KTaO_3$, $(110)_c SrRuO_3$//$(111)CaF_2$, $(110)_c$Sr-RuO_3//$(110)(Ba,Sr)TiO_3$//(110)MgO, $(110)_c SrRuO_3$//(110)Sr-TiO_3, $(110)_c SrRuO_3$//(110)LSAT, and $(111)_c SrRuO_3$//(111)Pt//$(111)CaF_2$. $SrRuO_3$ was used as common bottom electrode layer to set a constant misfit strain between PZT films and bottom electrode. $SrRuO_3$ layer and Pt top electrode were grown by rf magnetron sputtering method.

The crystal structure and the orientation of deposited films were analyzed by the high-resolution X-ray diffraction (XRD) using a four-axis diffractometer. The XRD reciprocal space mapping (*XRD-RSM*) was employed for more detail analysis of the crystal structure. Ferroelectric property was measured by ferroelectric tester (Toyo Corp. FC).

4. Results and discussions

Figure 4 shows XRD-RSM of PZT films on (a) $(110)_c$-$SrRuO_3$//(110)LSAT, (b) $(110)_c SrRuO_3$//$(110)SrTiO_3$, (c) $(110)_c$-$SrRuO_3$//$(110)(Ba,Sr)TiO_3$//(110)MgO, and (d) $(110)_c SrRuO_3$//$(111)CaF_2$ substrates. Mixture orientations of (110) and (101) were confirmed on $(110)_c SrRuO_3$//(110)LSAT, $(110)_c SrRuO_3$//$(110)SrTiO_3$ and $(110)_c SrRuO_3$//$(110)(Ba,Sr)TiO_3$//(110)MgO substrates as shown in Figs. 4(a), (b), and (c), while only (101) orientation was observed on $(110)_c SrRuO_3$//$(111)CaF_2$ substrates as shown in Fig. 4(d). It must be noticed that 1.2° off-aligned (110) orientations from the surface normal was observed in Figs. 4(a)–(c). However, this small titling angle is assumed to have a negligible contribution to the observed polarization.

Figure 5 shows the volume fraction of the (110) and (101) orientations in (110)/(101)-oriented-films as function of calculated thermal strain between growth temperature and T_c as well as (001) orientation in (100)/(001)-orientated films. Volume fractions of (101)-orientation of these films were estimated from XRD-RSMs peak intensities. Almost linear relationships were observed for both of (110)/(101)- and (100)/(001)-oriented films. These results show that the volume fractions of (110) and (101) orientations were mainly determined by the thermal strain just as (100)/(001)-oriented films. There are two things that could be pointed out from data shown in Fig. 5: One thing is that the volume fractions of (001) and (110) orientations are estimated to be equal to 0.40 and 0.33, respectively at 0 thermal strain. These values are in agreement with the volume fractions in free strain condition ($V_c = 0.33$). This suggests the relatively small contributions of the strain without the thermal strain, such as the misfit strain. This result is considered to be due to the relaxation

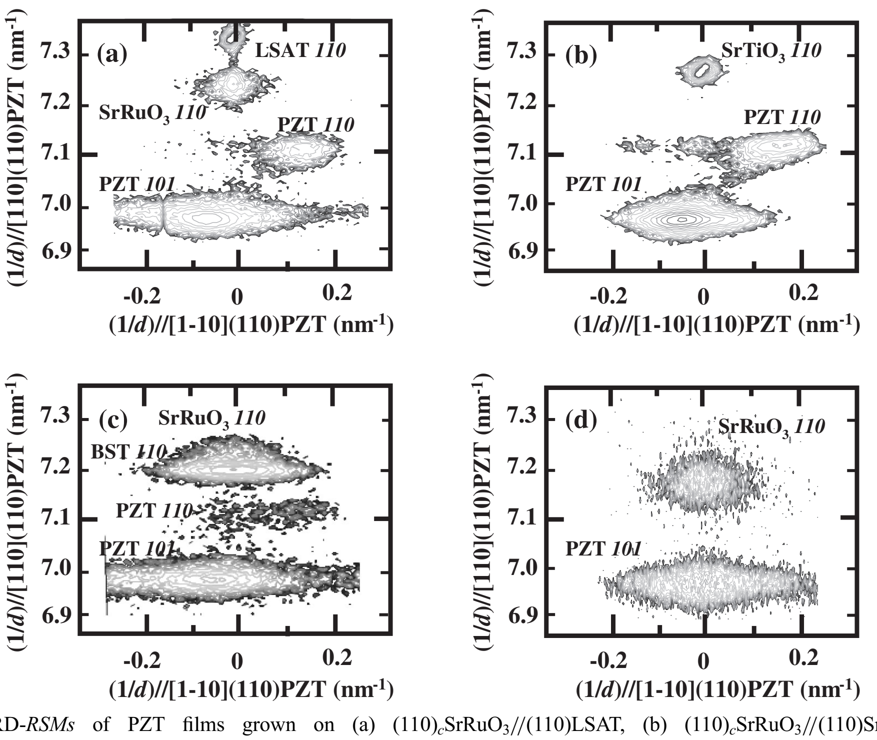

Fig. 4. XRD-*RSMs* of PZT films grown on (a) $(110)_c SrRuO_3$//(110)LSAT, (b) $(110)_c SrRuO_3$//$(110)SrTiO_3$, (c) $(110)_c SrRuO_3$//$(110)(Ba_{0.5}Sr_{0.5})O_3$//(110)MgO, and (d) $(110)_c SrRuO_3$//$(111)CaF_2$ substrates.

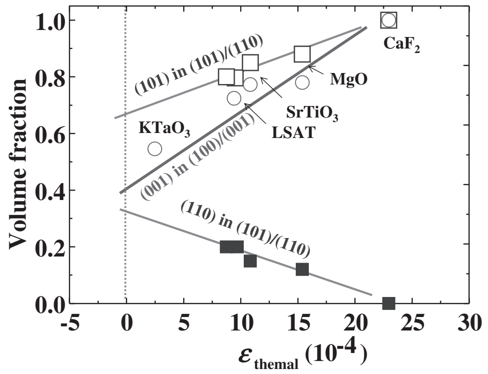

Fig. 5. Volume fraction of the (101) and (110) orientations of (110)/(101)-oriented-films as a function of the calculated thermal strain that was generated between the growth temperature and the T_c, $\varepsilon_{thermal}$, as well as that of (001) orientation of (100)/(001)-orientated films. open circles: (001) orientation in (001)/(100)-oriented films, open squares: (101) orientation in (110)/(101)-oriented films, closed squares: (110) orientation in (110)/(101)-oriented films.

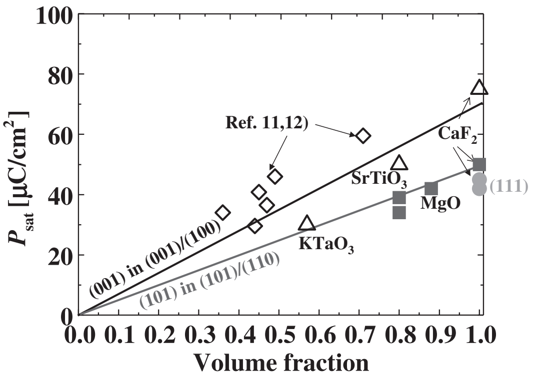

Fig. 6. P_{sat} of PZT films as a function of the volume fraction of (001) and (101) orientations in (100)/(001)- and (110)/(101)-oriented PZT films together with (111) single-oriented PZT films. open triangles and open squares: (001) volume fraction in (001)/(100)-oriented PZT,[11),12)] closed squares: (101) volume fraction in (101)/(110)-oriented PZT, closed circles: (111) single-oriented PZT.

of other strain by the increase of the film thickness, above 200 nm in the present study. On the other hand, the perfectly polar axis-oriented (001) and (101) films were obtained at similar thermal strain around 0.2% as shown in Fig. 5. Indeed, perfectly (001)- and (101)-oriented films were obtained on CaF_2 substrates having large thermal expansion coefficient (~0.23%).

Figure 6 shows the saturation polarization (P_{sat}) of PZT films as a function of the volume fraction of (001) and (101) orientations respective in (100)/(001) and (110)/(101)-oriented films. Our previous data in (100)/(001)-and (111)-oriented films were also added in the Fig. 6.[11),12)] It must be noted that the (001), (101) and (111) single-oriented films show the P_{sat} values almost expected one from the simple vector rotation of the spontaneous polarization.[6)] Continuous lines in Fig. 6 represent the trend lines of the P_{sat} based on the simple vector prediction of the polar axis, and the volume fraction of each orientation. Almost linear relationships between the volume fraction and the P_{sat} has been pointed out, and our data are coherent with the linear trend line for both of (100)/(001)- and (101)/(110)-oriented films. These results show that P_{sat} value can be mainly controlled by the thermal strain between the growth temperature and T_c in the present study.

5. Conclusions

In summary, the factor determining volume fractions of (001) and (101) in the (100)/(001) and (110)/(101) mixed orientation, respectively, were investigated for the epitaxial PZT films grown on various kinds of substrates having different thermal expansion coefficient. Both volume fractions can be almost linearly changed with the thermal expansion coefficient of the substrates. As a result, perfectly (001)- and (101)-oriented PZT films were obtained on (111)CaF_2 substrates. Linear relationships were observed between the thermal strain and the volume fraction of (001) and (101) orientations.

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