Crystal Growth of $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) Thin Film by Introducing SrTiO_3 Seed Buffer Layer

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SrTiO_3 シードバッファ層の導入による $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) 薄膜の結晶成長

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It has been reported that preparation of crystallized single phase $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) (perovskite structure) thin film on $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ and $\text{Pt}/\text{Ir}/\text{SiO}_2/\text{Si}$ substrates by pulsed laser deposition (PLD) method is difficult, and a pyrochlore-type compound forms instead of PZT; however, the reason for this has not been clarified. In this work, it was found that such instability of PZT is caused by the evaporation of Pb during the deposition. It was also found that the evaporation of Pb can be suppressed by introducing a very thin SrTiO_3 (ST) seed buffer layer to the surface of $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ and $\text{Pt}/\text{Ir}/\text{SiO}_2/\text{Si}$ substrates. Moreover, it was found that the peak intensity of PZT changes with the thickness of the ST seed buffer layer, and maximum peak intensity was obtained when the thickness of ST was 2 nm. When the thickness of the ST seed buffer layer was less than 1 nm, considerable coexistence of the pyrochlore-type compound was detected, therefore the remanent polarization (P_r) was lowered. Single-phase PZT thin films can be obtained if the thickness of ST is over 2 nm, however, if the thickness of ST is over 4 nm, the P_r value is decreased.

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1. Introduction

Ferroelectric thin films are of great interest for a wide range of applications such as ferroelectric random access memories (FeRAM) and piezoelectric sensors and micro-actuators.^{1)–3)} For these device applications, $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT) is one of the most promising ferroelectric materials, and $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ is one of the most promising substrates. Therefore, the PZT thin films have been prepared on $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrates by several methods such as metal-organic chemical vapor deposition (MOCVD),^{4),5)} sputtering,⁶⁾ chemical solution deposition (CSD)⁷⁾ and pulsed laser deposition (PLD).⁸⁾ In the preparation of PZT thin films on $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrates, a pyrochlore-type compound may form, which lowers the ferroelectric properties. It is well known that pyrochlore formation temperature is lower than PZT (perovskite) formation temperature.⁹⁾ Moreover, it is also reported that if the pyrochlore-type compound is formed during the preparation of perovskite PZT, it is difficult for it to change into the perovskite-type compound.¹⁰⁾ Therefore, in the literature, the following two methods have been reported:

- (a) rapid thermal annealing (RTA),
- (b) use of a seed buffer layer.

RTA is a method in which an amorphous thin film with PZT composition is heated rapidly to the perovskite formation temperature without allowing the nucleation of the pyrochlore-type compound.⁹⁾

It should be emphasized that the RTA method is a post-annealing method, therefore it is impossible to obtain “as-depo” crystallized PZT thin films. On the other hand, the seed buffer layer method is a kind of template method and the nucleation of the pyrochlore-type compound is suppressed by the introduction of an appropriate seed buffer layer. It should also be emphasized that this method is applicable for obtaining “as-depo” crystallized PZT thin films. Thus far, several kinds of seed buffer layers, such as PbTiO_3 (PT),^{4),11)–13)} Ti ,¹⁴⁾ TiO_2 ,¹⁵⁾ and $(\text{La}, \text{Sr})\text{CoO}_3$ (LSCO),^{8),16)}

have been introduced on the surface of $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrates to promote the crystallization of PZT. Actually, it was reported that the introduction of such a seed buffer layer is essential to crystallize a PZT thin film on a $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate, particularly by pulsed laser deposition.^{8),16)–18)}

The lattice parameter of SrTiO_3 (ST) (0.3905 nm) is very close to the a -axis of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (0.4036 nm) at room temperature (–3.3% lattice mismatch). Moreover, it is also reported that the estimated stability of ST is very high.¹⁰⁾ This suggests that ST is expected to be a good seed buffer layer for PZT. To the best of our knowledge, however, there have been no reports on introducing a ST seed buffer layer between PZT and $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$. This concept was derived from the fact that the introduction of a BaTiO_3 (BT) seed buffer layer on $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrates is effective for the crystallization of $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN).^{19),20)}

The purpose of this work is to clarify the effect and role of the ST seed buffer layer in the crystallization of PZT.

2. Experimental

PZT thin films were deposited by PLD with a KrF excimer laser ($\lambda = 248$ nm). The repetition rate of the laser was 7 Hz. In this work, a SrTiO_3 (ST) seed buffer layer was also deposited by PLD. The laser beam was focused by a quartz lens up to an energy density of about 1.5 J/cm² at an angle of 45° on targets of stoichiometric ST and PZT, which were rotated during the deposition. These targets were located on the multiple target holders, therefore, PZT/ST thin films were prepared in a single run. 10 mm × 10 mm $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}(001)$ (Furuya Metals Corporation) and $\text{Pt}/\text{Ir}/\text{SiO}_2/\text{Si}(001)$ (Fujitsu) were used as the substrates. The deposition was carried out in O_2 ambient. The pressure for SrTiO_3 and PZT deposition was set at 7.3×10^{-2} and 2.93×10^{-1} Pa, respectively. The composition and thickness of the thin film were analyzed by wavelength dispersive spectroscopy (WDS; PW2404, Phillips). The constituent phase

and texture of the films were identified with a powder X-ray diffractometer (X' Pert-MPD (θ - θ), Phillips) using Cu K α radiation operated at 40 kV–40 mA. The ferroelectric properties were measured between Pt bottom and top electrodes using a ferroelectric tester (RT-6000HVS, Radiant). The Pt top electrodes having 200 μ m diameter and 30 nm thickness were deposited by DC magnetron sputtering at room temperature. The surface and fractured cross section of the films were observed using a scanning electron microscope with a field emission gun (S-800, Hitachi).

3. Results and discussion

3.1 Pt/Ti/SiO₂/Si substrate

Figure 1 shows the change of XRD spectra with substrate temperature for PZT thin films deposited on Pt/Ti/SiO₂/Si without the ST seed buffer layer. This figure indicates that trace PZT with perovskite structure was detected at 500 and 600°C. The predominant phase was the pyrochlore-type compound below 600°C, and ZrTiO₄ (ZT) above 700°C. It should be noted that Pb-containing pyrochlore-type compound has a wide range of solid solutions.^{21),22)} The result shown in Fig. 1 suggests that the nucleation of PZT on the surface of Pt/Ti/SiO₂/Si occurs below 600°C. The formation of ZT above 700°C suggests that considerable vaporization of Pb occurs in the film. To stabilize the nuclei of perovskite PZT, the effect of introducing a ST seed buffer layer was investigated. Figure 2 shows the change of XRD spectra for PZT thin films with substrate temperature deposited on Pt/Ti/SiO₂/Si with an 8-nm-thick ST seed buffer layer. This figure shows that the formation of pyrochlore-type compound is markedly suppressed and PZT with the perovskite structure is stable between 450 and 650°C. This figure also shows that the maximum peak intensity of PZT was obtained at 600°C. Figure 3 shows the change of XRD spectra for PZT thin films with the thickness of the ST seed buffer layer deposited on Pt/Ti/SiO₂/Si at 600°C. In this figure, the thickness of the ST seed buffer layer was determined on the basis of the deposition rate and deposition time. Figure 3 indicates that coexistence of the pyrochlore-type compound is detected if the thickness of the ST seed buffer layer is below 1 nm. This suggests that a ST seed buffer layer more than 2 nm thick is needed to cover the entire surface of Pt. This figure also shows that the intensity of PZT(110) decreases with increasing thickness of the ST seed buffer layer. The same tendency was also observed for other PZT

diffraction peaks such as (100) and (111). This indicates that the crystallinity of PZT is decreased with increasing thickness of the ST seed buffer layer. This suggests that the ST seed buffer layer promotes the crystallization of PZT until the entire surface of Pt is covered with ST. However, after the surface is fully covered, increasing the ST seed buffer layer thickness lowers the crystallinity of PZT. To clarify this phenomenon, the composition of an 8-nm-thick ST seed buffer layer deposited on Pt/Ir/SiO₂/Si substrate was determined by WDS. The analyzed composition was Sr_{0.90}Ti_{1.00}O_x. It was reported that TiO₂-excess ST thin film consists of the ST crystalline phase and Ti-excess amorphous phase.²³⁾ Therefore, our ST seed buffer layer with Sr_{0.90}Ti_{1.00}O_x composition would contain amorphous TiO₂ in the film. This amorphous TiO₂ brings about the lowering of the crystallinity of the over laying PZT thin film. It is also expected that the fraction of the amorphous phase on the surface of the film would correspond to that of amorphous TiO₂ in the ST seed buffer layer. Consequently, from the view point of crystal structure it was concluded that PZT thin film with maximum crystallinity is obtained if the thickness of the ST seed buffer layer is 2 nm.

Fig. 2. Change in XRD spectra for PZT thin films with substrate temperature deposited on Pt/Ti/SiO₂/Si with 8-nm-thick ST seed buffer layer. (PY: pyrochlore, ZT: ZrTiO₄, PZT: Pb(Zr, Ti)O₃)

Fig. 1. Change in XRD spectra for PZT thin films with substrate temperature deposited on Pt/Ti/SiO₂/Si without ST seed buffer layer. (PY: pyrochlore, ZT: ZrTiO₄, PZT: Pb(Zr, Ti)O₃)

Fig. 3. Change in XRD spectra for PZT thin films with the thickness of ST seed buffer layer deposited on Pt/Ti/SiO₂/Si at 600°C. (PY: pyrochlore, ZT: ZrTiO₄, PZT: Pb(Zr, Ti)O₃)

Fig. 4. Change in (a) XRD intensity and (b) composition of PZT thin film with substrate temperature deposited on Pt/Ir/SiO₂/Si without ST seed buffer layer.

3.2 Pt/Ir/SiO₂/Si substrate

On the Pt/Ti/SiO₂/Si substrate, it is impossible to determine the composition of PZT thin film because Ti is included in both the PZT thin film and the substrate. Therefore the results of PZT and PZT/ST thin films deposited on Pt/Ir/SiO₂/Si are discussed below. Figure 4 shows the changes of (a) XRD intensity and (b) composition of PZT thin films with substrate temperature for the films deposited on Pt/Ir/SiO₂/Si without a ST seed buffer layer. Comparing the results in Fig. 4(a) with those in Fig. 1, the change of the resultant phase with substrate temperature agrees well. Figure 4(b) indicates that the Zr/(Zr + Ti) ratio is constant irrespective of the substrate temperature, while the Pb/(Zr + Ti) ratio decreases with increasing substrate temperature. This indicates that vaporization of Pb started above 500°C and considerable vaporization occurred above 600°C. Figure 5 shows the changes of (a) XRD intensity and (b) composition of PZT thin films deposited on Pt/Ir/SiO₂/Si with a 2-nm-thick ST seed buffer layer with substrate temperature. The change of the resultant phase with substrate temperature on Pt/Ir/SiO₂/Si substrates was very close to that on Pt/Ti/SiO₂/Si substrates, as shown in Fig. 2. Figure 5(b) indicates that the Zr/(Zr + Ti) ratio was also constant irrespective of the substrate temperature, as the result shown in Fig. 4(b). However, for the Pb/(Zr + Ti) ratio, it was apparent that the vaporization speed of Pb was lowered when the ST seed buffer layer was introduced on the surface of Pt. To highlight this phenomenon, the change in the weight of the PZT thin film with substrate temperature with and without the ST seed buffer layer is replotted in Fig. 6. This figure clearly indicates that the ST seed buffer layer suppresses the vaporization of Pb, particularly at 600°C. This enhances the crystallization of PZT with perovskite structure. Figure 7 shows the change in the *P*-*E* hysteresis curve of PZT thin films with the thickness of the ST seed

Fig. 5. Change in (a) XRD intensity and (b) composition of PZT thin film with substrate temperature deposited on Pt/Ir/SiO₂/Si with 2-nm-thick ST seed buffer layer.

Fig. 6. Change in the weight of PZT thin film with substrate temperature deposited on Pt/Ir/SiO₂/Si with and without 2-nm-thick ST seed buffer layer.

buffer layer deposited on Pt/Ir/SiO₂/Si. The films were deposited at 600°C. The PZT film deposited on a 0.25-nm-thick ST seed buffer layer did not show the ferroelectric property because the film was composed of the pyrochlore-type compound. The ferroelectric property was observed when the thickness of the ST seed buffer layer was between 0.5 and 8 nm. It should be noted that these *P*-*E* curves are not well saturated since the films were leaky. Therefore, it is difficult to determine precise remanent polarization from Fig. 7. However, in this work, "apparent" remanent polarization was plotted against the thickness of the ST seed buffer layer to determine the relationship between the ferroelectric property and the thickness of ST (Fig. 8). Figure 8 shows that the ferroelectric property was im-

Fig. 7. Change in P - E hysteresis curve of PZT thin film with the thickness of ST seed buffer layer deposited on Pt/Ir/SiO₂/Si. The values indicated in the figure are the thickness of ST seed buffer layer.

Fig. 8. Change in remanent polarization of PZT thin film with the thickness of ST seed buffer layer deposited on Pt/Ir/SiO₂/Si.

proved when the thickness of the ST seed buffer layer was between 1 and 4 nm. This result also agrees well with that of XRD shown in Fig. 1. When the thickness of the ST seed buffer layer is less than 1 nm, remanent polarization (P_r) is lowered due to the coexistence of the pyrochlore-type compound. If the thickness is over 4 nm, the P_r value also decreases since ST is paraelectric at room temperature and the dielectric constant is lower ($\epsilon_r = 400^{24}$) than that of PZT ($\epsilon_r = 1280^{25}$). Consequently, it can be considered that the introduction of a thin ST seed buffer layer suppresses the vaporization of Pb and stabilizes perovskite PZT. Therefore the introduction of a thin (around 1–4-nm-thick) ST seed buffer layer improved the ferroelectric property of PZT. However, when the thickness of ST was more than 4 nm, the ferroelectric property was degraded.

4. Conclusions

A method of stabilizing perovskite PZT on Pt/Ti/SiO₂/Si and Pt/Ir/SiO₂/Si substrates was established. It has been reported that preparation of crystallized single-phase Pb(Zr, Ti)O₃ (PZT) (perovskite structure) thin film on Pt/Ti/SiO₂/Si and Pt/Ir/SiO₂/Si substrates by PLD method is difficult, and a pyrochlore-type compound forms instead of

PZT; however, the reason for this was not clarified. In this work, it was found that such instability of PZT was caused by the evaporation of Pb during deposition. It was also found that the evaporation of Pb can be suppressed by introducing a very thin SrTiO₃ (ST) seed buffer layer on the surface of Pt/Ti/SiO₂/Si and Pt/Ir/SiO₂/Si substrates. Moreover, it was found that the peak intensity of PZT changes with the thickness of the ST seed buffer layer, and maximum peak intensity was obtained when the thickness of ST was 2 nm. When the thickness of the ST seed buffer layer was less than 1 nm, considerable coexistence of the pyrochlore-type compound was detected, therefore the remanent polarization (P_r) was lowered. Single-phase PZT thin films can be obtained when the thickness of ST is over 2 nm, however, when the thickness of ST is over 4 nm, the P_r value is decreased.

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