

The effects of oxidants on the growth behavior of PbTiO₃ thin film by Atomic layer deposition

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Atomic layer deposition (ALD) is generally characterized as having a unique self-regulated growth behavior due to its surface saturating growth mechanism. However, the adoption of an ALD process to the growth of multi-cation ferroelectric oxide thin films has rarely been reported because ALD process for multi-component oxide films is very complicated.¹⁻³ In this study, the growth behavior of PbTiO₃ (PTO) thin films using different oxidants was investigated.

PTO thin films were grown using a 4-inch scale traveling wave type ALD reactor on Si and Ru substrates at 200°C. Pb(DMAMP)₂, Ti(Oi-Pr)₄ were used as Pb and Ti precursors, respectively. H₂O and O₃ were used as oxidant and Ar was used as purging gas. The deposition conditions were listed in Table 1. The Pb- and Ti-concentrations in the films and the layer density (L/D) were measured by XRF. The film thickness was measured by ellipsometry.

PTO thin films were grown using two different oxidants for Ti precursor, i.e. process A using H₂O and process B using O₃ whereas H₂O was used as an oxidant for Pb precursor for both processes. Figs. 1(a) and (b) show the variations in the Pb/Ti ratio and the L/D of PTO thin films with the Pb/Ti injection ratio for the process A and B, respectively. In process A, the L/D of PTO film shows the maximum value when the film composition is stoichiometric (Pb/Ti ratio~ 1). However, Pb-deficient- or Pb-excess-PTO films have smaller L/D per cycle. This suggests that the deposition process is the most effective under the condition where the stoichiometry can be achieved and the growth rate of films is highest. In contrast, the L/D of PTO thin films continues to increase with increasing the Pb/Ti ratio in process B. This difference can be shown more clearly in Figs. 1(c) and (d), which show the variations of Pb- and Ti-L/D per cycle as a function of Pb/Ti ratio.

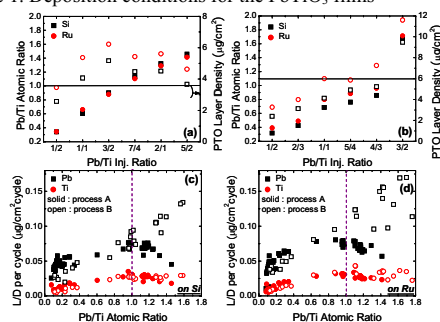
The effect of oxidant used for Ti precursor on the growth behavior of PbO layer was investigated. Figure 2(a) shows the deposition sequence of process C, D and E. Here, TiO₂ layer was deposited with 10cycles prior to the PbO layer deposition in order to make sure that the growing surface is covered with TiO₂ completely. The number of Pb cycles (n_{Pb}) was changed in the range from 1 to 4 cycles. Figure 2(b) shows that the Pb/Ti ratio increases with the n_{Pb} as a matter of course. It should be noted that the Pb/Ti ratio increases faster in process E compared to the other processes. Figure 2(c) shows that the Ti L/D increases with the n_{Pb} although

total number of Ti cycles is same in all the processes. This is due to the catalytic effect which is commonly observed in multi-component oxide ALD. Figures 2(d) and (e) show the variations of the Pb L/D per cycle for the respective Pb cycles. The Pb L/D per cycle decreases slightly at 2nd Pb cycle and increases largely at 3rd and 4th cycles. A larger amount of Pb is deposited at 3rd and 4th cycles although the area of TiO₂ surface which is uncovered with PbO decreases. This means that the adsorption of Pb component is catalyzed by PTO phase not TiO₂.

In summary, the effects of oxidants on the growth behavior of PTO thin films by ALD were investigated. It was confirmed that the growth of PbO layer is dependent sensitively on the type of oxidant used for TiO layer deposition. The incorporation of PbO is promoted by PTO not TiO₂.

	Pb	Ti	H ₂ O	O ₃
Inject/Purge time (s)	0.5/30	3/5	1/35	3/10
Carrier/Purge Ar flow rate (sccm)	35/535	-/500	-/500	-/500

Table 1. Deposition conditions for the PbTiO₃ films



Figs. 1 (a) and (b) the variations in the Pb/Ti ratio and L/D of PTO thin films for the process A and B, respectively. (c) and (d) the variations in the Pb- and Ti-L/D per cycle on the Si and Ru substrates, respectively.

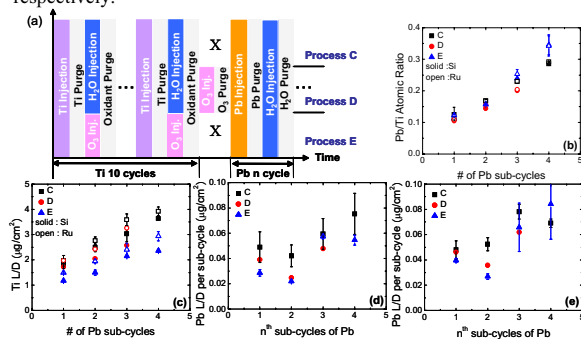


Fig. 2 (a) the deposition sequences of process C, D and E. (b) the variation in the Pb/Ti ratio. (c) the variation in the total Ti L/D. (d) and (e) the variation in the Pb L/D per cycle for the respective nth Pb cycle in case of Si and Ru, respectively.

References

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