

## Effect of thermal treatment for PZT thin film based on zirconium oxyacetate precursor

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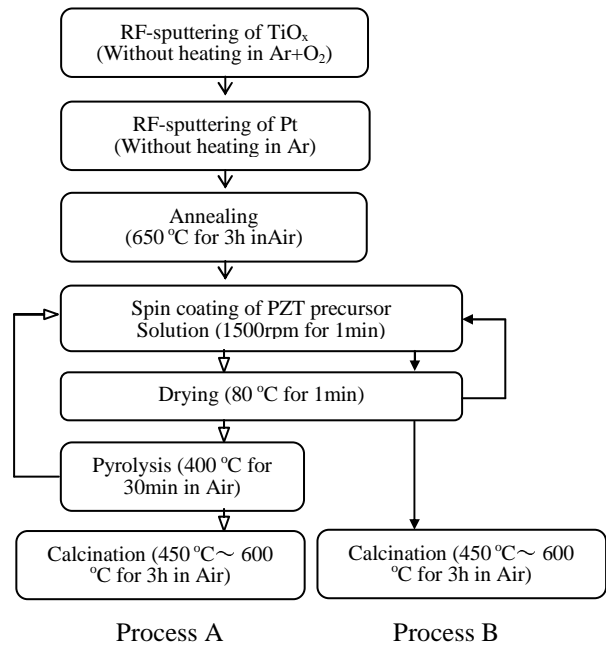
Thin film of ferroelectric material,  $\text{Pb}(\text{Zr,Ti})\text{O}_3$  (PZT), has received much attention for their applicability to high-density, nonvolatile memory devices. The PZT thin films have been prepared by using various deposition techniques, i.e., chemical vapor deposition (CVD), rf sputtering, laser ablation, sol gel process, etc. Among these techniques, the sol gel process is advantageous in process cost, composition control and adoptability to large area fabrication. Recently, we found that crystallization temperature of PZT thin films can be lowered to be below  $600^\circ\text{C}$  by using a novel precursor solution containing zirconium oxyacetate<sup>1, 2)</sup>. In this study, we report that thermal treatment for PZT thin film based on zirconium oxyacetate precursor have effects on crystalline orientation and ferroelectric properties of PZT.

Figure 1 shows preparation flow chart for the PZT thin film on  $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$  substrate annealed at  $650^\circ\text{C}$ . The concentration of the PZT precursor solution was set to be 0.05M on the  $\text{Pb}_{1.07}\text{Zr}_{0.52}\text{Ti}_{0.48}\text{O}_3$  basis. The PZT films were prepared by using two different thermal treatments (process A or B). In the case of process A, the precursor film spin-coated was pyrolyzed at  $400^\circ\text{C}$  for 30 min under air flow after drying at  $80^\circ\text{C}$ . The process from spin-coating to pyrolysis was repeated to obtain the film thickness desired. On the other hand, process B was conducted without pyrolysis of precursor films at  $400^\circ\text{C}$  in process A. The thin films obtained by both processes were finally calcined in the temperature range of  $450$  to  $600^\circ\text{C}$  for 3h under air flow. The thickness of the PZT films obtained was about 100 nm.

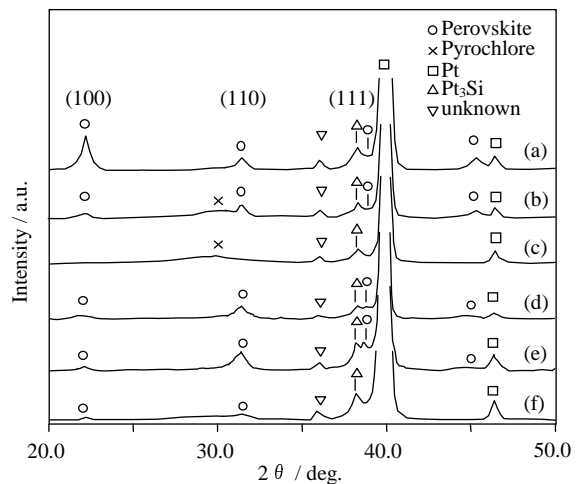
Figure 2 shows the XRD patterns of the PZT films obtained by process A and B. On the process A, the PZT film annealed at the temperature below  $500^\circ\text{C}$  indicated mixed phases mixed perovskite and pyrochlore. With increasing the calcinations temperature, however, the crystalline phase converted to a single phase of perovskite. On the other hand, the process B gave a single phase of perovskite at the calcinations temperature of  $500^\circ\text{C}$ . Compared crystalline orientation between the two process, the PZT films obtained on process B showed high crystalline orientation for (110) and (111) faces. As a result, process B seemed to be better than process A from the viewpoint of crystallinity of PZT film. Next, the thermal treatment of substrate was investigated through the process B. It was found that the PZT thin films prepared on  $\text{Pt}/\text{TiO}_x$  substrate without annealing at  $650^\circ\text{C}$  show fairly good remanent polarization as well as crystalline orientation, compared with those prepared on annealed substrate. In addition, it was also found that the remanent polarization is affected remarkably by thickness of Pt electrode. Figure 3 shows remanent polarization (2Pr) for the PZT films on non-annealed substrates as a function of the thickness of Pt electrode. The remanent polarization of the PZT films calcined at  $550^\circ\text{C}$  showed the maximum at 125nm in thickness of Pt electrode. However there is room for argument on the reason why the thermal treatments is effective for PZT thin film based on zirconium oxyacetate precursor.

### References

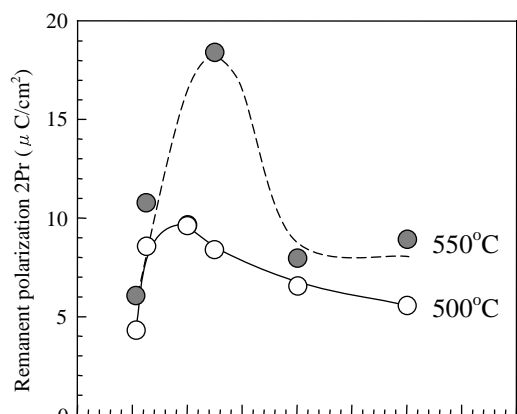
- 1) K. Nakano, G. Sakai, K. Shimanoe and N. Yamazoe, *The 42<sup>th</sup> Symposium on Basic Science of Ceramics Abstract Book*, 146 (2004).
- 2) K. Nakano, G. Sakai, K. Shimanoe and N. Yamazoe, *The Electrochemical Society Proceedings*, **2003-01**, 230 (2003).



**Fig. 1** Preparation flow chart for PZT thin film on  $\text{Pt}/\text{TiO}_x/\text{SiO}_2/\text{Si}$  substrate.



**Fig. 2** XRD patterns of the PZT thin film prepared through different two processes. (a), (b) and (c) were calcined at  $550^\circ\text{C}$ ,  $500^\circ\text{C}$  and  $450^\circ\text{C}$ , respectively, on process A. (d), (e) and (f) were calcined at  $550^\circ\text{C}$ ,  $500^\circ\text{C}$  and  $450^\circ\text{C}$ , respectively, on process B.



**Fig. 3** Remanent polarization (2Pr) of the PZT films as a function of thickness of Pt electrode.