Ferroelectric properties of Pb-excess PZT thin films prepared by Zirconium oxyacetate-based sol-gel process

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Thin films of the ferroelectric material, $Pb(Zr,Ti)O_3$ (PZT), have 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[1)], 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°C by using a novel precursor solution containing Zirconium oxyacetate[2)]. However, the surface of $Pt/IrO_2/SiO_2/Si$ substrate used was too rough to accomodate thin films less than 100nm. In this study, another kind of substrate, $Pt/Ti/SiO_2/Si$ was fabricated to prepare PZT thin films less than 100nm. The effects of excessive doping of Pb on preferred orientation and ferroelectric characteristics of the PZT crystal were also investigated.

Figure 1 shows the scheme to prepare the PZT precursor solution. The standard composition of PZT was set to be $PbZr_{0.52}Ti_{0.48}O_3$ in this study. $ZrO(CH_3COO)_2$ was dissolved in 2-methoxyethanol by refluxing at 115°C for 5h under N_2 flow. The resulting solution was added with a stabilizer ($NH(CH_2CH_2OH)_2$) and stired at room temperature for 1h under N_2 flow. Subsequently, $Ti(OCH(CH_3)_2)_4$ and $Pb(CH_3COO)_2 \cdot 3H_2O$ were dissolved respectively into the above solution in this order at room temperature under stiring for 5h in N_2 flow at each step. The concentration of the standard precursor solution was set to be 0.05M on the $PbZr_{0.52}Ti_{0.48}O_3$ basis. The starting composition of Pb was varied to be 0, 4, 7, 10 or 15 mol % in excess of this standard. Each precursor solution was spin-coated on the $Pt/Ti/SiO_2/Si$ substrate, and the resulting deposit was dried at 80°C for 30 min and then calcined at 400°C for 30min under air flow to remove organic residual. The same procedures were repeated many times, and finally the film was annealed at 650°C for 3h under O_2 flow. It was found that the film thickness increased by 7-9nm per each coating almost linearly. The $Pt/Ti/SiO_2/Si$ substrates used were found to have fairly flat surface so that the PZT thin films of about 100nm in thickness were prepared successfully.

As indicated by the XRD patterns in Figure 2, the PZT thin films annealed at 650°C showed Pb-content-depended preferred orientation. That is, preferential (100) reflection was observed at stoichiometric Pb content, whereas (100) reflection was weaken and (110) reflection was strengthened with increasing excessive Pb. This change in prefered orientation with a change in Pb content is just opposite to what has been reported for 40nm thick PZT films by Doi et al.[3)]

Figure 3 shows remanent polarizaiton (Pr) and coercive field (Ec) as a function of excessive Pb content. Pr began to increase when excessive Pb content exceed 4mol%. On the other hand, Ec went through a minimum at 7mol% Pb before increasing much at 10mol%. As judged from such behavior in Pr and Ec, an optimal Pb content seems to be 7mol% in excess of the stoichiometric composition for an application to memory devices.

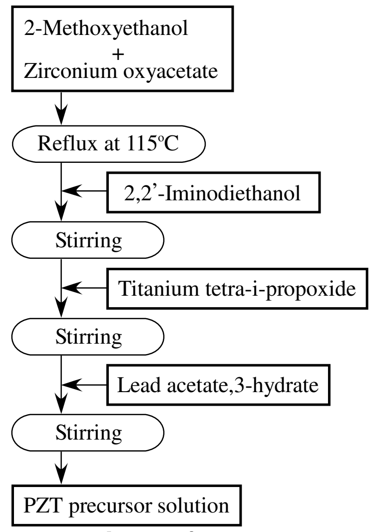

Fig. 1 Preparation scheme of PZT precursor solution.

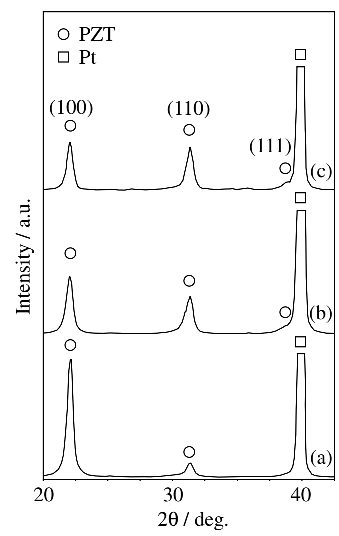

Fig. 2 XRD patterns of the thin films annealed at 650°C using the each precursor with Pb in excess of the stoichiometry. (a) Pb 0mol% excess, (b) Pb 7mol% excess, (c) Pb 15mol% excess.

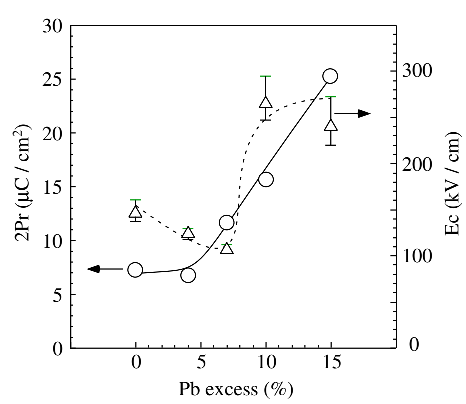

Fig. 3 Remanent polarizaiton (Pr) and coercive field (Ec) as function of the content of Pb in excess of the stoichiometry.

References

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