

Preparation and evaluation of $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ thin films by Metalorganic chemical vapor deposition

Toru Taniguchi, Youichi Kamisuki and Tadashi Takenaka

Faculty of Science and Technology, Science University of Tokyo
Noda, Chiba-ken, 278 JAPAN

Dipivaloylmethane (DPM) metalorganic precursors, $\text{Pb}(\text{DPM})_2$, $\text{Zn}(\text{DPM})_2$ and $\text{Ti}(\text{OPr}^i)_2(\text{DPM})_2$, are used as starting materials in the metalorganic chemical vapor deposition (MOCVD) method for preparation of $(1-X)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-XPbTiO}_3$ (PZN-PT100X) thin films. The films are deposited at the rate of 150 to 300 Å/min under reduced pressure of 10~30 Torr. PZN-PT50 thin film with a perovskite structure displays dielectric constant, $\epsilon_s=1000$ and Curie temperature, $T_c=360^\circ\text{C}$. The T_c value agrees with that of the single crystal or the ceramics.

1. INTRODUCTION

Recently much attention has been paid to ferroelectric thin films, since establishment of processing these materials and the necessity of integrated electronic devices. The applications of ferroelectric thin films to functional devices such as ferroelectric nonvolatile memory (FE-RAM), pyroelectric infrared sensors, piezoelectric microactuators, are expected. The high dielectric properties of ferroelectrics allow the reduction from the size of conventional device.

$(1-X)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-XPbTiO}_3$ (PZN-PT100X) phase diagram^{1,2} shows a morphotropic phase boundary (MPB) around $X=0.12$ which corresponds to a transition from a tetragonal phase to a rhombohedral phase. This boundary (MPB) is especially important for the applications because

most of the properties such as dielectric constant, remanent polarization, and piezoelectric coefficient show their maximum values near the MPB.

The most widely utilized deposition technique of ferroelectric thin films is a sputtering method. It is pointed out^{2,3}, however, that the method has some disadvantages such as low deposition rate, generation of surface damage as well as difficulty in controlling stoichiometrically film composition. On the other hand³, the metalorganic chemical vapor deposition (MOCVD) method has the following advantages over the sputtering method: higher deposition rate which is suitable for mass production, and flexible control of composition by adjusting the source temperature and the flow rate of carrier gas. As the starting material in MOCVD method, $\text{Pb}(\text{C}_2\text{H}_5)_4$

Table 1 Deposition conditions of PZN-PT films

	Pb(DPM) ₂	Zn(DPM) ₂	Nb(O ⁿ Bu) ₅	Ti(OPr ⁱ) ₂ (DPM) ₂
Source temp. (°C)	150	120	180	140
Carrier gas flow rate (sccm)	100 ~ 200	50	50	50
Substrate temp. (°C)	500 ~ 750			
Total gas flow rate (sccm)	400 ~ 500			
Reaction gas pressure (Torr)	10 ~ 30			

has been selected by some researchers^{4, 5)}, because high vapor pressure can be generated easily. However the material is toxic and must be handled under strict regulation.

In this study, harmless dipivaloylmethane (DPM) metal-organic precursors, Pb(DPM)₂, can be used as the starting material for PZN-PT thin films from viewpoints of applications to electronic devices. It is ideal that starting materials of almost equal reaction speed and diffusion coefficients be used for making stoichiometrically uniform compounds⁶⁾.

2. EXPERIMENTAL

We selected Pb(DPM)₂, Zn(DPM)₂, Nb(OⁿBu)₅, Ti(OPrⁱ)₂(DPM)₂, as starting materials because they are stable and harmless at room temperature and have relatively high vapor pressure at low temperature. PZN-PT thin films were prepared at reduced pressure (10 ~ 30 Torr) by a rotary pump.

Each source material was set in each separate vessel tube. Their

vapors were supplied into the main chamber using nitrogen (N₂) gas as the carrier gas. The flow rate of carrier gas for each material was 50 ~ 100 sccm. Oxygen (O₂) gas employed to produce an oxidative atmosphere was supplied from another vessel tube. The gas flow rate was 150 ~ 250 sccm. The mixed vapor of the source materials was guided by N₂ carrier gas into the reaction chamber and was blown out of the tip of a nozzle onto the heated substrate. Harmful materials were removed from waste gas by means of trap equipment with liquid nitrogen. Mirror-polished Pt/Ti/SiO₂/Si or MgO poly-crystals were used as the substrate.

The evaluation of the thin films was carried out as follows⁷⁾: the surface conditions were observed by scanning electron microscope (SEM), composition analysis was performed using the energy dispersive X-ray microanalyzer (EDX), determination of crystal structure was by means of the X-ray diffractometer, capacitance and dielectric loss tangent by multifrequency LCR meter, leakage current by DC voltage source and picoammeter, and

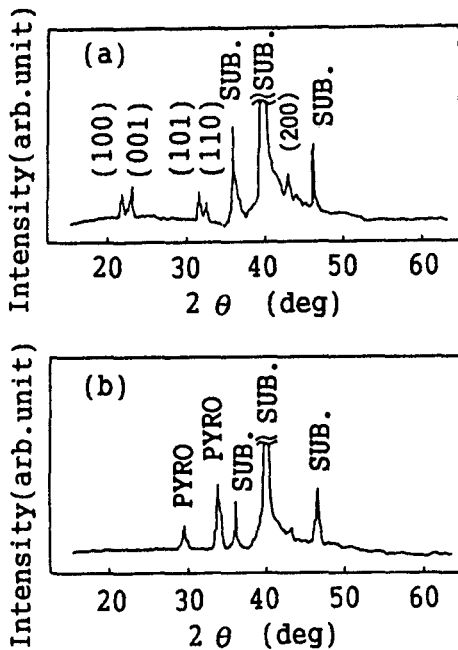


Figure 1. X-ray diffraction patterns of (a)PZN-PT38 and (b)PZN-PT7.

D-E hysteresis loop by Sawyer-Tower circuit.

3. RESULTS AND DISCUSSION

Figure 1 shows X-ray diffraction (XRD) patterns of the films grown on Pt/Ti/SiO₂/Si substrates under reduced pressure (10 ~ 30 Torr). The PT-rich side of the PZN-PT film (PZN-PT38) shows the perovskite structure, but a single phase of perovskite structure in PZN side (PZN-PT7) could not be prepared. The lattice constants of PZN-PT38 film were $a=3.91 \text{ \AA}$ and $c=4.08 \text{ \AA}$. Up to now, we can not obtain the film near the MPB composition.

Figure 2 shows a D-E hysteresis loop observed at frequency of 50 Hz. Remanent polarization, P_r , of the obtained film (PZN-PT50) was $6.3 \mu\text{C}/\text{cm}^2$ and coercive field, E_c , was $2.2 \text{ kV}/\text{cm}$, respectively. The typical grain sizes of PZN-PT

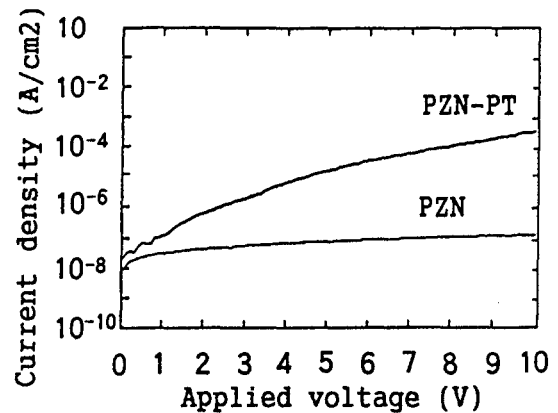


Figure 2. Leakage current-voltage characteristics of PZN and PZN-PT

films are $0.2 \sim 1.0 \mu\text{m}$. These values depend on substrate temperature and cooling speed. It was confirmed the tendency that the distribution of film thickness was improved by blowing oxygen gas after film-deposition.

Figure 3 shows leakage current-voltage characteristics of PZN film and PZN-PT38 film. The film thickness was about $2 \mu\text{m}$. The grain sizes of PZN-PT films was smaller than that of PZN film. As shown in this figure, pyrochlore type PZN film has high resistivity, on the other hand, that of perovskite type PZN-PT film was smaller by two orders at applied voltage of 5 V.

Figure 4 shows temperature dependence of dielectric constant ϵ_s and loss tangent $\tan \delta$ for PZN-PT50. The Curie temperature T_c of this film was about $360 \text{ }^\circ\text{C}$. This almost agrees with that of the single crystal or the ceramic^(8,9). It seems that the film was sufficiently reacted as a solid solution. The typical values of ϵ_s and $\tan \delta$ are $700 \sim 1000$ and $8 \sim 12 \%$, respectively.

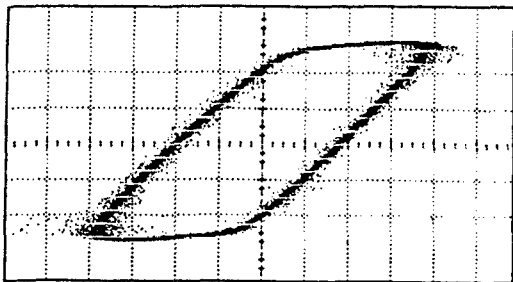


Figure 3. D-E hysteresis loop of PZN-PT50 film at 50 Hz

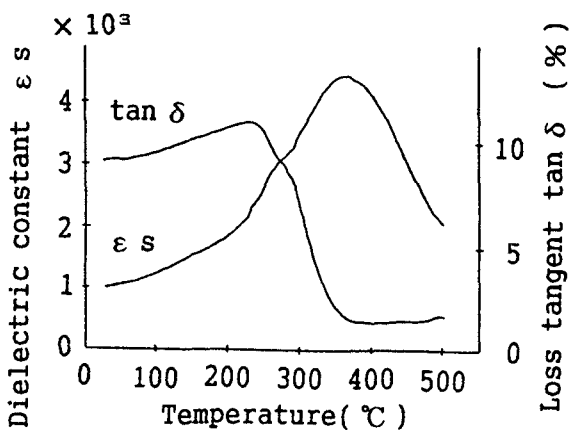


Figure 4. Temperature dependence of dielectric constant ϵ_s and loss tangent $\tan \delta$ for PZN-PT50 at 1 MHz

4. CONCLUSIONS

Stoichiometric PZN-PT thin films were prepared by the MOCVD method under reduced pressure using DPM metalorganic precursors as the starting materials. Thin films of the PT-rich side in the PZN-PT system show the perovskite structure. The resistivity ρ of PZN

film was sufficiently high, but that of PZN-PT films were rather low.

Obtained values, $Pr=6.3 \mu C/cm^2$ and $Ec=2.2 kV/cm$, from D-E hysteresis loop were slightly low. The Curie temperature T_c of PZN-PT50 film was about $360^\circ C$ and the lattice constants were $a=3.91 \text{ \AA}$ and $c=4.08 \text{ \AA}$, which almost agree with those of single crystal or the ceramic.

It is desirable to establish the MOCVD process to obtain perovskite-type PZN-PT thin films near the MPB composition for the applications to electronic devices.

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