Highly Oriented Pb(Zr, Ti)O₃ Films Prepared by Multi-step Process*

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Pb(Zr_{0.52}Ti_{0.48})O₃ films up to 1.5 μm thickness have been prepared by multi-step process to suppress the problem of crack formation due to the thermal stress. The thickness dependence of film structure, ferroelectric, dielectric properties have been investigated over the thickness range of 0.24–1.5 μm . A strong (111) orientation was obtained from all films deposited in the experiments. For a constant applied field of 170 kV/cm, remanent polarization, $2P_r$, developed from 14 $\mu\text{C}/\text{cm}^2$ to 30 $\mu\text{C}/\text{cm}^2$, as film thickness increased from 0.24 to 1.5 μm . Dielectric constant also increased with film thickness, and reached the maximum value of 1200 at 1.5 μm . These trends are interpreted in terms of the influence of interfacial effect on the electrical characteristics.

1. Introduction

In recent years, lead zirconate titanate, PZT, with the composition near the morphotropic phase boundary, Pb(Zr_{0.52}Ti_{0.48})O₃, has been extensively studied because of the excellent piezoelectric and ferroelectric properties. The research activities have been focused on two distinct areas: one is the exploitation of submicron films ($\sim 0.2 \mu\text{m}$) for ferroelectric memory applications¹⁾ and another is in the area of piezoelectric applications where PZT active layers are integrated on Si substrates and serve to convert between mechanical vibrations and electrical signals^{2,3)}. These require much thicker PZT films with thickness from 1 up to 10 μm with the geometries of μm^2 to cm^2 .

In the sensor applications, the need for thicker PZT films is desirable to maximize the sensor performance. For example, in an ultrasonic sensor with Si membrane structures, the optimal thickness of PZT is approximately one half of the silicon membrane thickness^{2,4)}.

Here, we have attempted to deposit thick PZT films using facing target sputtering system (FTS).

With our early experimental results⁵⁾, crack-free PZT films with preferred (111) orientation could be deposited up to 240 nm using our FTS system and post-annealing process, but beyond this thickness, the layer cannot resist the tensile stress that built up during the post annealing process. The existence of cracks causes much trouble in the electrical measurements and this reduces yields substantially^{6,7)}. To overcome the above problem, the multi-step process has been adopted, instead of growing a thick PZT film at once, thin PZT layers are deposited successively on the post-annealed PZT films as shown in Fig. 1(a). Even though cracks exist in the former layer, they will be compensated by the deposition of the later layer. In this article, we report the preparation of highly (111) oriented PZT thick films using multi-step process. The variations of film properties such as ferroelectric and dielectric properties are discussed as a function of film thickness.

2. Experimental procedures

The facing target sputtering system (Osaka Vacuum: FTS-1CB) was used in the experiments. The distance between targets was fixed at 100 mm and the distance between substrate and the central line

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Fig. 1 (a) schematic diagram of multi-step process and (b) the process flow used in the experiments.

of the two targets was controlled at 135 mm. In this study, PZT films were sputtered from a commercial hot-pressed ceramic $\text{Pb}_{1.2}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ targets. A 20 mol% excess of PbO in the targets was added to compensate the loss of Pb during thermal process. All PZT samples were prepared on platinized Si substrates, Pt(600 nm)/Ti(30 nm)/SiO₂(800 nm)/Si. Each PZT layer was deposited at 300°C, 0.8 Pa under rf power 700 W⁵⁾. The thickness of all layers was fixed at 240 nm. The sample was transferred to a tube furnace and heated to 600°C in air with a heating rate of 30°C/min, before depositing a further layer. The annealing time for each layer is discussed in the following section.

X-ray diffraction spectra of the multilayer PZT films were taken with a Rigaku diffractometer. The peak heights in x-ray pattern were used to calculate a preferred oriented parameter, e.g. $\alpha_{(111)} = I_{(111)} / I_{\text{Total}}$. To evaluate electrical properties, top Al electrodes with 0.5 mm in diameter were prepared by sputtered Al on PZT surface, and patterned using a lift-off technique. Ferroelectric properties of all films were evaluated at constant electric field of 170 kV/cm using a Radiant Technology ferroelectric tester, RT-6000, in the virtual ground mode. The low field dielectric constant, ϵ_r was measured using a LCR meter for a field of 1.25 kV/cm at a frequency of 1 kHz. The current-voltage characteristics were measured using an HP4155A semicon-

Fig. 2 X-ray spectra of 480, 960 and 1440 nm multilayer PZT films.

ductor parameter analyzer with a step voltage of 0.1 V and a delay time of 2 sec.

3. Results and Discussions

By considering the crystallization of PZT layers, the experimental process for deposit multilayer PZT films has been divided into two main parts as shown in Fig. 1(b). These are the crystallization of PZT films on Pt/Ti bottom electrodes, i.e. 1st layer and on PZT film itself (2nd, 3rd and further layers). The optimum annealing time for each layer was defined as the minimum required time to obtain the complete perovskite phase in our PZT films. This was determined from the peak heights of perovskite and pyrochlore phase in x-ray spectra. It was found experimentally that the optimum annealing time was 1 hr for the deposition of 1st layer and 10 min for 2nd, 3rd and further layers. The remarkable reduction in the annealing time for the further layers implied that the underlying PZT layer enhanced the crystallization of perovskite phase in the next layer. It should be noted that the optimum annealing time also varied with the thickness of PZT layers.

X-ray diffraction spectra for multilayer PZT films with different film thickness are shown in Fig. 2. All films exhibited strong textured of (111) perovskite orientation with $\alpha_{(111)} \sim 95\%$, independent on the film thickness. It is well known that PZT crystallization proceeds preferentially by heterogeneous nucleation and growth from the (111) Pt/Ti electrode. Therefore, one would expect a reduction of (111) orientation with film thickness. This was observed in our single-layer PZT films, however, in the case of multilayer PZT films, the surface of the preceding layer played an important role as a seed layer for the next layer.

Figure 3 compares the surface morphology of single and multilayer PZT films. The film thickness was 1.2 μm . The improvement of surface morphol-

Fig. 3 Comparison of surface morphology for 1.2 μm (a) single-layer PZT film, (b) multilayer PZT film.

ogy could be observed in multilayer PZT films, which showed relatively smooth and nearly crack-free surface. The improvement in surface roughness apparently resulted in a film with a better degree of orientation⁸⁾. The surface microstructure of the multilayer films showed the average grain size about 50–100 nm, and it tended to increase with thickness.

Ferroelectric and dielectric properties were evaluated for all films in the experiments. At least ten different capacitors were tested for each sample, the average values of these, together with their standard deviations are presented in the relevant experimental plots. The results of ferroelectric properties are shown in **Fig 4**. All P–E hysteresis loops were taken at constant electric field of 170 kV/cm.

The P–E hysteresis loops for the 0.24 μm films were broad, inclined and shifted along the positive electric field axis. The shift along the electric field axis is consistent with a significant internal bias field⁹⁾ in our samples. But as the thickness increased the shift became smaller, and loops became squarer and more saturated. Values of remanent polarization, $2P_r$ and coercive field, E_c are plotted

Fig. 4 (a) P–E hysteresis loop for multilayer PZT films and (b) variation of remanent polarization and coercive field with film thickness.

versus film thickness in **Fig. 4(b)**. The values of $2P_r$ improved with film thickness. The values of $2P_r$ varied from 14 $\mu\text{C}/\text{cm}^2$ for a 0.24 μm film to 30 $\mu\text{C}/\text{cm}^2$ for a 1.5 μm film. The coercive field, E_c also showed the strong dependence on the field thickness as shown in **Fig. 4(b)**. The values decreased with film thickness, and would reach the value of 30 kV/cm for thicker films. The weak field dielectric data are shown in **Fig. 5(a)**. With the increase of film thickness, dielectric constant increased from 700 to 1200.

The effects of PZT film thickness on dielectric and ferroelectric properties are interpreted as being due to the proportionately greater contribution from interfacial effect as sample thickness decreased^{10,11)}. To demonstrate the dependence of dielectric constant on film thickness, the reciprocal of small signal capacitance was plotted with film thickness as shown in **Fig. 5(b)**. A linear relation with a nonzero interception was obtained. A nonzero interception ($1/7.9 \text{ nF}^{-1}$) indicates the existence of non-ferroelectric capacitance at the interface between PZT film and electrode. We could model the equivalent circuit of our PZT film as a series connection of ferroelectric capacitance and

Fig. 5 (a) Dielectric constant and (b) reciprocal of capacitance as a function of film thickness.

non-ferroelectric capacitance. The mathematical model for this equivalent circuit could be described as follows:

$$\frac{1}{C_{\text{meas}}} = \frac{1}{C_0} + \frac{1}{C_{\text{ferro}}} = \frac{1}{C_0} + \frac{d}{A\epsilon_0\epsilon_r} \quad (1)$$

where d is the film thickness, A is the top electrode area and ϵ_0 and ϵ_r are the permittivity of free space and dielectric constant of PZT, respectively. From the slope in Fig. 5(b), we could calculate the dielectric constant of the pure ferroelectric phase to be about 1300. The variations of the dielectric constant with film thickness were calculated using this value with shown as the solid line in Fig. 5(a). The agreement between the calculated curve and the experimental data was fairly well.

The representative leakage current density-electric field (J - E) characteristic for a multilayer PZT films with the thickness of 480 nm are shown in Fig. 6. The magnitude of current flows showed a strong dependence of the bias direction, with a small current density in positive bias. This is due to the difference of materials used in the top and bottom electrodes¹²⁾. At low electric field region, a power law dependence of J on E ($J \propto E^2$) could be observed. At higher electric field, leakage current increased sharply with electric field, but with differ-

Fig. 6 Leakage current density-voltage characteristic of a 480 nm PZT films.

Fig. 7 Dependence of leakage current density on film thickness at a constant electric field of 200 kV/cm.

ent slopes under positive and negative bias. This is corresponding to the transition from space-charge limited conduction to trap-fill limited conduction. These J - E behaviors were similar to those of space-charge limited (SCL) current injection in which the currents were controlled by the trap located in the forbidden energy gap^{13,14)}. It should be noted that at constant electric field of 200 kV/cm, the reduction of leakage current density was observed with film thickness, as shown in Fig. 7.

4. Conclusions

Highly oriented (111) PZT films up to 1.5 μm thickness were prepared by multi-step process. Suppression of cracks could be accomplished in PZT films with multilayer structure. As the film thickness increased from 0.24 to 1.5 μm , $2P_r$ and dielectric constant improved and could reach 30 $\mu\text{C}/\text{cm}^2$ and 1200, respectively. Trends in these electrical properties were presumed to be the effect of interface between PZT film and electrode. Improvement of leakage current density with film thickness was also observed.

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