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Preparation of ferroelectric PZT films by thermal decomposition of organometallic compounds

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Transparent PZT thin films with perovskite structure were successfully obtained by thermal decomposition of organometallic compounds at the temperatures of 500 to 700° C. The films deposited on platinum substrates were smooth and uniform, but microcrackings were observed in the films deposited on fused silica substrates. The ratio of metal composition in the PZT film agreed with that in the mixture of starting materials. Films obtained at 700° C on platinum substrate showed a hysteresis loop. A spontaneous polarization was 35.65 $\mu C\,cm^{-2}$, a saturation remanent polarization was 30.56 $\mu C\,cm^{-2}$ and a coercive field was 45 kV cm^{-1}. Dielectric constant and dielectric loss angle were about 300 and 0.05, respectively.

1. Introduction

Lead–zirconate–titanate(PZT) is a typical ferroelectric ceramic with useful properties for piezoelectric devices. In recent years, works on PZT and PLZT thin films have been proposed for the purpose of more wider applications to electronic devices [1–3]. The thin films of PZT were prepared by r.f. sputtering [4–6], ion beam sputtering [7, 8], electron-beam evaporation [9] and liquid phase epitaxial [10] methods. Large scale and complicated apparatus for the preparation of the thin films were needed in the sputtering and evaporation methods. In the liquid phase epitaxial method, high temperatures above 1000° C are required. Further, the PbO loss during deposition of film is a major problem in these processes. The authors have reported on the fabrication and properties of SnO_2, ZnO, PbO and $BaTiO_3$ thin films by thermal decomposition of organometallic compounds [11–13].

In this paper, the preparation and properties of PZT thin films prepared by thermal decomposition of organometallic compounds are described. Crystal phase and composition of the films are also investigated.

2. Experimental details

Lead 2-ethylhexanoate(Pb:15.0 wt %), zirconium acetylacetonate(Zr:18.7 wt %) and titanium tetrabutoxide(Ti:14.1 wt %) were used as the source materials. The butanol solution which contains 30 wt % organometallic compounds (the composition: $Pb_{1.0}Zr_{0.5}Ti_{0.5}$) was prepared. Fused silica and platinum plates were used as substrates. The butanol solution applied to a substrate was dried at 110° C for 30 min in air to vaporize the butanol, and then calcined at 500 to 800° C for 30 min in an electric furnace. The successive deposition of the films was repeated up to ten times to prepare a thick film.

The thickness of the film deposited on a substrate was measured by ellipsometric and multiple beam interference methods. The microstructure and grain size of the films were observed by the scanning electron microscope.

Crystal phase and chemical composition of the films were determined by powder X-ray diffraction patterns and X-ray fluorescence analysis.

Ferroelectric and dielectric properties of the films deposited on platinum substrate were measured by using a Swyer–Tower circuit at a

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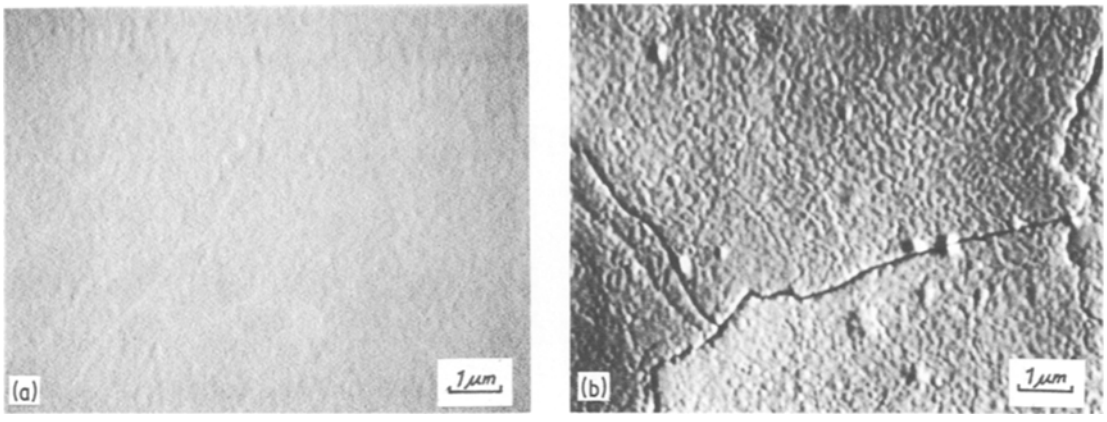

Figure 1 Scanning electron micrographs of the film (2 μm in thickness) deposited at 700° C on platinum substrate (a) and fused silica substrate (b).

frequency of 50 Hz. Vaccum evaporated gold (5 mm and 0.1 μm thick) was used as an electrode. The capacitance and dielectric loss angle of the films were measured by a Q-meter at 50 kHz. The dielectric constants were calculated from these values.

3. Results and discussion

3.1. Properties of the films

The films deposited on both fused silica and platinum substrates at the temperatures up to 700° C were transparent and slightly yellowish in colour. The films deposited at temperatures above 700° C became translucent owing to the reaction between the film and the substrate.

The thickness of the films obtained by the deposition for the first chosen time was about 0.2 μm. The thickness was proportional to the deposition times. A film of 2 μm in thickness was obtained by the depositions at ten times the initial period. Depositions over ten times caused the devitrification of the films and the lack of uniformity of the surface.

The electron micrographs of the film 2 μm in thickness and deposited at 700° C are shown in Fig. 1. The surface on platinum substrate was very smooth and uniform. The grain size of this film was about 50 nm. The size was approximately comparable to that of the film by Castellano and Feinstein [7]. On the other hand, the film on fused silica substrate had relatively large grains with about 100 nm compared with that on platinum substrate. A microcracking in the film on fused silica substrate was caused by the differences in the thermal expansion coefficients between PZT (2.5×10^{-6} °C^{-1}) and fused silica (5×10^{-7} °C^{-1}) [8].

3.2. Crystal phases and composition of the films

X-ray powder diffraction patterns of the film 2 μm in thickness are shown in Fig. 2. According to the r.f. sputtering method [5], the film crystallized in a pyrochlore type structure at substrate temperatures of 350 to 450° C. At temperatures above 450° C, the films crystallized in a perovskite structure. In the present work, the peaks at $d = 0.0405$, 0.288, 0.234, 0.202, 0.118, 0.166 and 0.144 nm corresponded to a perovskite structure as did those obtained by the sputtering method [5]. The position of diffraction patterns of the films deposited on both fused silica and platinum substrates at 500 to 700° C were the same. At temperatures above 700° C, small and diffuse diffraction peaks in the pattern were observed in addition to that of perovskite structure. The compound will be a reaction product between PZT film and fused silica substrate at high temperatures. In the PZT films deposited by the sputtering and evaporation methods, ferroelectric perovskite and para-electric pyrochlore type PZT films are deposited [6, 7]. In the present work, only the perovskite type films were obtained at 500 to 700° C. The lattice constants of the PZT films were $a = 0.40475$ and $c = 0.40823$ nm.

According to the studies of PZT films [4, 6], vaporization of lead can be caused during deposition of the film. At the thermal decomposition of organometallic compounds of lead,

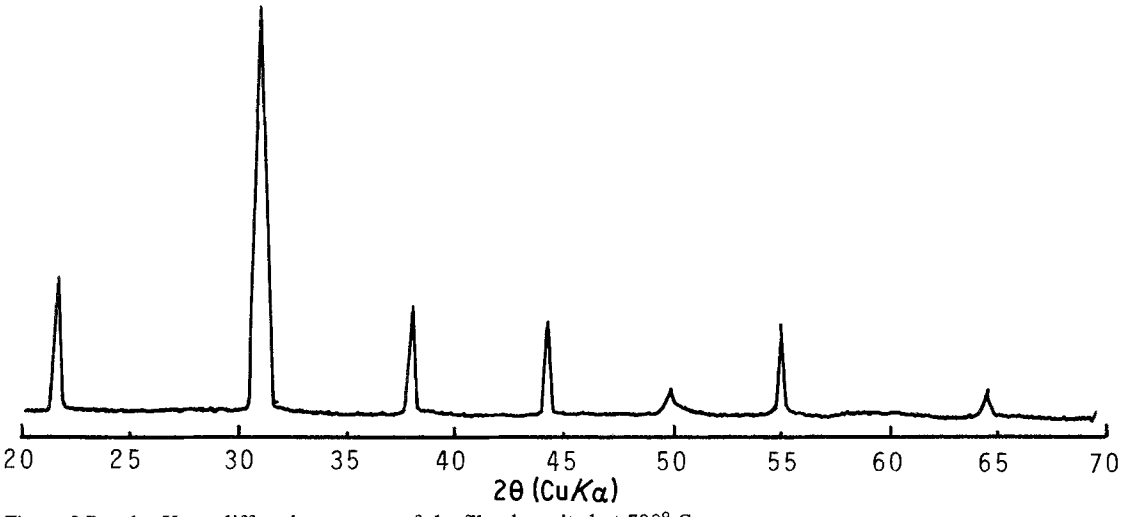

Figure 2 Powder X-ray diffraction pattern of the film deposited at 700° C.

the vaporization of lead metal often takes place. A deviation of metal components from starting composition gives an influence on the dielectric and ferroelectric properties. Therefore, the composition of metal component in both the starting mixture and the film was determined by X-ray fluorescence analysis. The results are indicated in Table I. As is evident from these values, the ratio of metal compositions in the PZT film agrees well with that in the starting mixture. It may be confirmed that the metal components in the films did not deviate from those of the starting mixtures through preparation of films by the present method.

3.3. Ferroelectric and dielectric properties

Fig. 3 shows a typical P–E hysteresis loop of the film deposited at 700° C on a platinum substrate. The thickness was about 2 μm. The remanent polarization (P_r) was 30.56 $\mu C\,cm^{-2}$, the spontaneous polarization (P_s) was 35.65 $\mu C\,cm^{-2}$ and the coercive force (E_c) was 45 $kV\,cm^{-1}$. Relatively high P_r, P_s and E_c values and a broad loop were obtained. These values were close to that of PZT films prepared by the other methods [5–8]. The reason is due to good crystallization of the films by heat treatment at a high temperature of 700° C in the present method.

Dielectric properties of the films prepared at 700° C on a platinum substrate were summarized in Table II. The value of dielectric constant is lower than that of Okada [5] and by Hamada *et al.* [6], but similar to the value by Castellano and Feinstein [7]. The differences of dielectric constants may due to a different ratio of the zirconium and titanium composition.

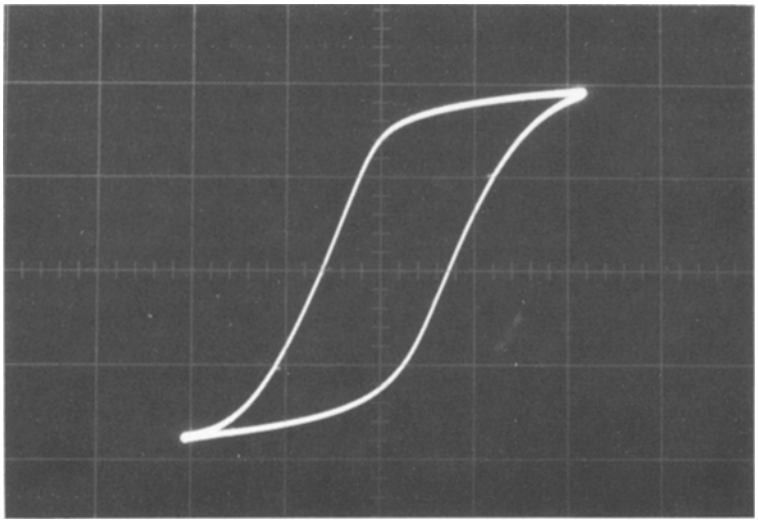

Figure 3 P–E hysteresis loop of the ferroelectric film (2 μm in thickness) deposited at 700° C on platinum substrate.

TABLE I Results of X-ray fluorescence analysis on PZT thin films

Metal	Mixture of source material	PZT thin film
Pb	0.996	0.982
Zr	0.498	0.506
Ti	0.506	0.510

4. Conclusions

Transparent thin films of lead–zirconate–titanate (PZT) with perovskite structure were successfully produced by thermal decomposition of organometallic compounds at the temperatures of 500 to 700° C on platinum and fused silica substrates. The ratio of metal composition in the PZT films agreed with that in the mixture of starting materials. Lead loss did not occur in this experiment.

Films obtained at 700° C on a platinum substrate showed a hysteresis loop. A spontaneous polarization was $35.65\,\mu C\,cm^{-2}$, a saturation remanent polarization was $30.56\,\mu C\,cm^{-2}$ and a coercive force was $45\,kV\,cm^{-1}$. Dielectric constant and dielectric loss angle were about 300 and 0.05, respectively.

TABLE II Dielectric properties of PZT thin film

Film thickness (μm)	Dielectric constant, ϵ	Dielectric loss angle, tan δ
2	300	0.05

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