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Low-temperature Processing of $Pb(Zr_{0.53}Ti_{0.47})O_3$ Thin Film from Stable Precursor Sol

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Abstract

A stable sol was prepared from a lead acetate trihydrate, zirconium and titanium alkoxides for a low–temperature processing of a lead zirconate titanate ($Pb(Zr_{0.53}Ti_{0.47})O_3$;PZT) thin film. The process involves the addition of an excess lead oxide and the insertion of a seeding layer of a perovskite lead titanate (PT) between PZT precursor layer and substrate. A perovskite ratio in the thin films increased with increasing amount of excess lead oxide and a single phase perovskite was deposited at 500°C with 50% excess lead oxide. As a result, ferroelectric PZT thin films were successfully deposited. The crystallization behavior was also affected by the substrates with electrodes. The PZT films deposited on the glass substrates has random orientation whereas the PZT thin film on the silicon water with platinum electrode exhibited (111) orientation at 500°C. The low-temperature processed PZT thin films with thickness of about 0·5 μm exhibited relatively good dielectric and ferroelectric properties (ε_r. 300–700, Pr: 21–44 $\mu C\,cm^{-2}$). © *1999 Elsevier Science Limited. All rights reserved*

Keywords: films, sol–gel processes, dielectric properties, ferroelectric properties, PZT.

1 Introduction

Ferroelectric $Pb(Zr_xTi_{1-x})O_3$ thin films show excellent piezoelectric, pyroelectric and dielectric properties, and have been used in many applications such as actuators and infrared sensors. However, relatively high processing temperatures above 600°C for the ferroelectric PZT thin films restricts the use of various substrates such as glass or aluminum. Recently, we developed novel sol–gel methods for low-temperature processing of PZT thin films with single- or multi-seeding layers.[1,2] These processes are very promising for applying PZT thin films in optical applications. For the low-temperature processing, we used the molecular-designed alkoxide precursor solution. This precursor solution is sensitive to humidity. Therefore, it is better to prepare the stable precursor solution for commercial use. Yi and Sayer[3,4] reported a new preparation method for a stable precursor sol from a lead acetate and the alkoxides by using an acetic acid as a solvent and a chelating reagent. However, the details of the experimental procedure and the properties of the PZT thin films deposited from the precursor sols are not clear.[5,6] In addition relatively high temperature above 650°C was essential to obtain the single phase perovskite for the precursor developed by Yi and Sayer.[5,6]

This paper describes a new preparation method for the stable precursor sol of PZT and the electrical properties of the resultant PZT thin films deposited from the stable precursor sol. This new process involves the addition of an excess lead oxide, which leads to low-temperature processing, and the effect of substrates on the crystallization behavior of the PZT thin film.

2 Experimental

Lead acetate [$Pb(CH_3COO)_2$], Zirconium n-propoxide [$Zr(OC_3H_7)_4$] and titanium iso-propoxide, {$Ti[(CH_3)_2CHO]_4$} were used as raw materials. Figure 1 shows the flow chart for preparation of a stable PZT precursor sol. Lead acetate tri-hydrate was refluxed in acetic acid for dehydration to prepare Pb–precursor solution. Then titanium and/or zirconium alkoxides, which were dissolved in ethyl alcohol with acetic acid, were mixed and reacted with a Pb-precursor solution to form a

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PT or a PZT precursor solution. PZT and PT precursor solutions were hydrolyzed with a stoichiometric amount of water to form a stable sol. Acetyl acetone was added to the precursor sol for further stabilization.

PT seeding layers and PZT layers were dip-coated onto a Corning 7059 class (glass), a Corning 7059 glass with an tin dioxide electrode (SnO_2/glass), a commercial soda lime glass with an indium tin oxide electrode and SiO_2 diffusion barrier (ITO/glass), or a silicon wafer with a (111) oriented Pt electrode, Ti buffer layer and SiO_2 diffusion barrier (Pt/Si). After each precursor layers were deposited, specimens were dried at 15°C for 10 min and then pre-annealed at 350°C for 1 h to remove the residual organic compounds from the precursor films. A PT precursor film was deposited between PZT film and substrate as a seeding layer. After multiple coating of PZT precursor films, specimens were annealed up to 600°C for 2 h in an air. The composition of the PZT with $X = 0{\cdot}53$, corresponding to the morphotoropic phase boundary, was chosen to compare the results of the films prepared from the molecular-designed alkoxide precursor solution.[1,2]

The crystalline phases developed during annealing were identified by X-ray diffraction (XRD). Thin films on a glass substrate were used to study the phase development. On the other hand, the electrical properties of the resultant films on the various substrates with different electrodes were measured as a function of the annealing temperature, using an HP-4284A impedance analyzer and a Radiant RT-6000 S. The upper electrode used in this study was a circle of gold with diameter of 0·2 mm. Microstructure of the resultant film was observed by a field emission type scanning electron microscope (FE-SEM).

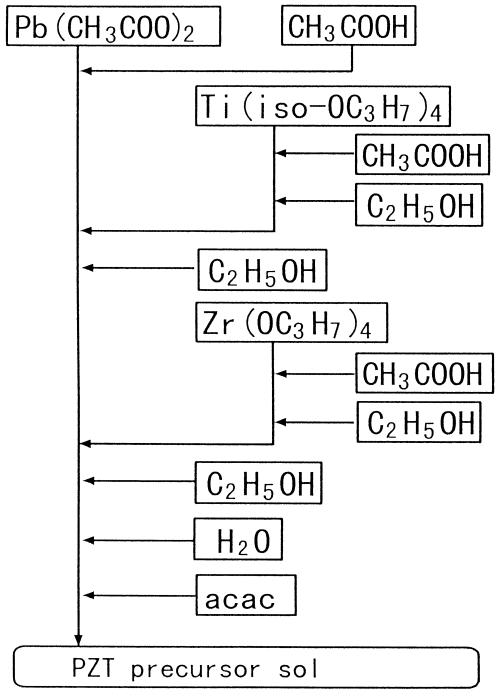

Fig. 1. Flow chart for preparation of PZT precursor sol.

3 Results

3.1 Phase development

The phase development during annealing was affected by many factors such as the homogeneity of the precursor solution or sol, selection of a seeding layer, annealing rate and temperature, substrate and/or electrode and the amount of excess lead oxide.[7] Therefore, the effect of excess addition of a lead oxide on the crystallization of the resultant film on glass was investigated and shown in Fig. 2 Relatively high temperatures above 650°C were indispensable to obtain a single phase perovskite the same as the result of the precursor film derived from stable sol.[3,4] However in this study, perovskite ratio in the low-temperature annealed PZT film increased with increasing amount of excess lead oxide. Single-phase perovskite film was obtained at 500°C with 50 mol% excess lead oxide.

Therefore, the properties of the PZT thin films with 50 mol% of excess lead oxide were investigated in this study. No lead oxide peak was identified in the XRD pattern of the annealed film above 500°C. In addition, the analysis by SEM with EDX exhibited only 10% excess lead at 500°C. This suggested that almost all excess lead oxide was vaporized during processing.

3.2 Effect of substrate

The substrate and/or electrode have a large effect not only on the crystallization behavior, but also

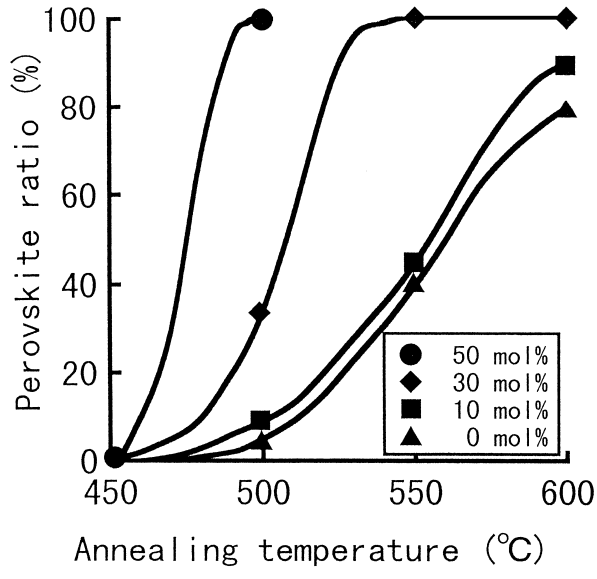

Fig. 2. Relationship between annealing temperature and perovskite ratio at different excess lead oxide addition (on Coming 7059 glass).

on the orientation and microstructure of the resultant film. The microstructure of the sol–gel derived PZT thin film commonly consists of ultra-fine grains with a diameter ranging from 20 to 80 nm.[8] On the other hand, highly oriented PZT film showed columnar structures.[2,9] In this study, the microstructure of the resultant PZT film exhibited a columnar structure independent of the substrate and/or electrode. The thickness of the PZT films prepared in this study was about 500 nm and that of the PT seeding layer was considered to be about 50 nm. However, only the PZT thin film with a Pt/Si substrate showed (111) orientation (Fig. 3). The PZT thin films on the glass substrates did not show any preferred orientation. This result suggested that the orientation of the sol–gel derived PZT thin film pre-annealed at 350°C and annealed at 500°C was controlled by the substrate.

3.3 Electrical properties

The electrical properties of a ferroelectric thin film with a perovskite structure largely depend upon the microstructure and orientation of the resultant film as well as the electrode on the substrate.[10] Fig. 4 exhibits the change in the relative permittivity of the resultant film on the different substrate and an electrode. The relative permittivity tends to increase with increasing annealing temperature and leveled off at 550°C. Saturated values of the permittivity depended upon the electrode used. PZT thin films on the Pt/Si substrate and SnO_2/glass substrate exhibited relatively high permittivity at above 550°C. On the other hand, PZT thin film on the ITO/glass substrate had a lower relative permittivity. This result showed that the dielectric property of the resultant PZT film depends upon the electrode used.

Ferroelectric property of the sol–gel derived PZT films on the different substrates was also investigated and is shown in Fig. 5. Low-temperature processed PZT films exhibited a P–E hysteresis loop, showing the relatively good ferroelectricity of the resultant films independent of the substrate. However, the remanent polarization of the resultant film decreased and the coercive field increased if the glass substrates were used. A PZT film on a Pt/Si substrate exhibited the high remanent polarization of 43 $\mu C\,cm^{-2}$ at 500°C.

Typical electrical properties of the resultant films were summarized in a Table 1. These data are the average of five points for each sample. Both relatively good results for dielectric and ferroelectric properties were obtained in the case of the PZT film deposited on the Pt/Si substrate. However, the coercive field of the resultant PZT films prepared in this study was relatively high, especially in the case of the films on the glass substrates. This may be ascribed to the amorphous phase formed between electrode and the PZT film and/or at the grain boundary. Further investigation is indispensable to reduce the coercive field of the resultant PZT film. The remanent polarization of the films showed relatively high values even for the PZT film on the ITO/glass substrate if an annealing was carried out at above 550°C. Dissipation factor of the resultant film was relatively high, however, below 0·1. This result also suggested the existence of the amorphous phase with low relative permittivity and high coercive field between PZT film and electrode, and/or at the grain boundary.

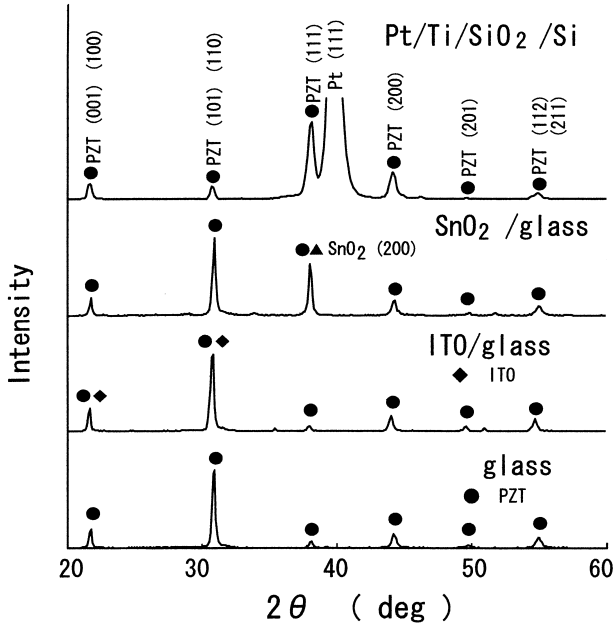

Fig. 3. XRD patterns for PZT thin films on Pt/Ti/SiO_2/Si, SnO_2/Corning 7059 glass and ITO/commercial soda lime glass (50 mol% excess lead oxide, annealing at 500°C).

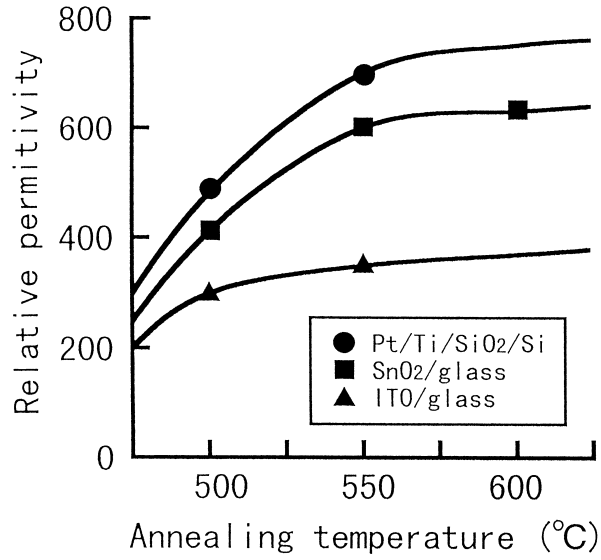

Fig. 4. Relationship between annealing temperature and relative permittivity of PZT thin films on Pt/Ti/SiO_2/Si, SnO_2/Corning 7059 glass and ITO/commercial soda lime glass (50 mol% excess lead oxide).

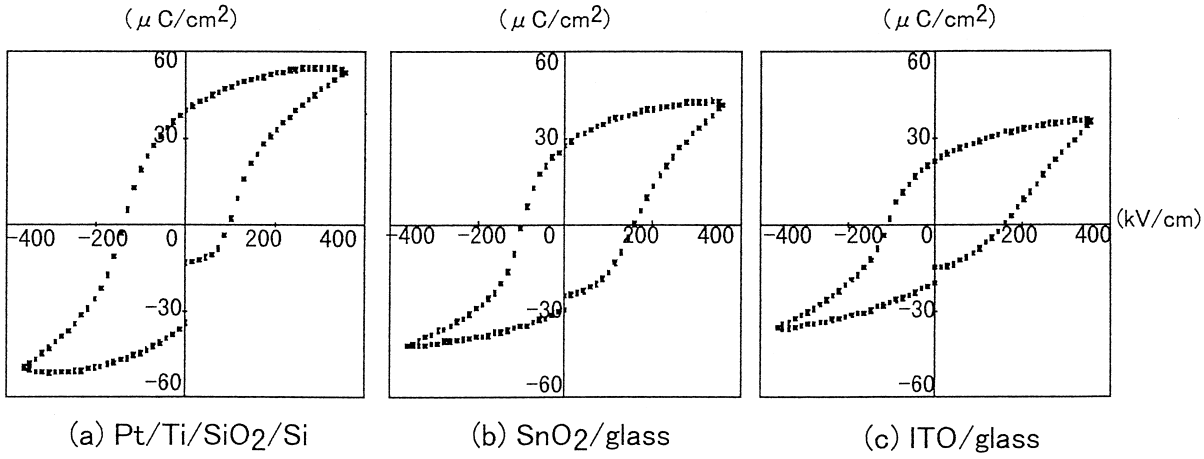

Fig. 5. P–E hysteresis loops of PZT thin films on Pt/Ti/SiO_2/Si, SnO_2/Corning 7059 glass and ITO/commercial soda lime glass (50 mol% excess lead oxide, annealing at 500°C).

Table 1. Typical electrical properties of the resultant PZT films on the different substrates

Electrode	*Annealing Temperature (°C)*	*Coercive field ($kv\,cm^{-1}$)*	*Remanent polarization ($\mu c/cm^{-2}$)*	*Relative permittivity*	*Dissipation factor ($tan\delta$)*
Pt	500	91	43	480	0·068
Pt	550	115	41	700	0·051
SnO_2	500	125	29	410	0·049
SnO_2	550	145	39	600	0·066
ITO	500	142	21	300	0·073
ITO	550	144	33	350	0·095

4 Discussion

4.1 Phase development

In this study, the stable precursor sols with the same Zr/Ti ratio as that of the MPB composition were prepared by chlating the acetic acid to the alkoxide followed by the hydrolysis with stoichiometric amount of hydrolysis water. The precursor sols were stable in an ambient atmosphere. However, the annealing temperature for a single phase perovskite was above 650°C in the case of PZT thin film deposited from precursor sol of a MPB composition without excess lead. This may be due to the compositional inhomogeneity on an molecular scale because the precursor thin film derived from molecular-designed alkoxide solution crystallized into single phase perovskite at 600°C.[1] Therefore, the effect of the amount of an excess lead oxide on the crystallization behavior of the PZT precursor thin film was investigated. As a result, an increasing amount of an excess lead oxide lowered the temperature for the single phase perovskite and reached 500°C when the amount of an excess lead oxide was more than 50 mol%. This confirmed the above discussion. The lead oxide precursor also easily evaporates during annealing, especially for the alkoxide-derived thin film. However, it was impossible to estimate the amount of evaporation during annealing because the amount of the evaporation depends on the chemical bonding, microstructure of the precursor film including thickness and the atmosphere during annealing. Although the amount of the residual lead oxide was not so large, FE-SEM analysis suggested the existence of the residual amorphous phase at 500°C. Further investigation will be performed in the near future.

On the other hand, phase development during annealing was affected not only by the amount of the excess lead oxide but also by the substrates. This suggests that the conversion of pyrochlore phase into perovskite was affected not only by the compositional inhomogeneity but also the impurity diffusion from substrate. The reaction between PT precursor layers and glass substrate may result in the formation of an amorphous layer with low permittivity and high coercive field at the interface between electrode and PT seeding layer, which should contain the lead oxide. This interfacial reaction will lead to reduced electrical properties of the resultant film.

4.2 Electrical properties

Dielectric and ferroelectric properties of the sol–gel derived PZT thin films are controlled by several factors. Compensation of the lead oxide depletion commonly improves the ferroelectric properties of the PZT thin film. From the FE-SEM observation the microstructure of the resultant PZT films

derived from stable precursor sol had dense and columnar structures. Therefore, the factors that affect the electrical properties of the resultant films are the orientation and amorphous phase remaining in the films after annealing. A relatively large dissipation factor of the resultant films listed in a Table 1 suggested the existence of the residual amorphous phase due to excess lead oxide. This type of amorphous phase is typical for the PZT thin film derived from astable precursor sol because the segregation of the lead precursor is easily achieved compared with the PZT precursor derived from a molecular-designed precursor solution in which all the cation is chemically bonded with the other cation through oxygen, homogeneously.

The amorphous phase in the annealed PZT film is also formed by the reaction between precursor film and the substrate during annealing. This type of amorphous phase should be typical for the film deposited on the ITO/glass substrate. Ohya *et al.*[11] reported that the sol–gel derived PZT thin film did not react with ITO on the Corning 7059 glass substrate. However in this study, commercial soda lime glass substrate with a 100 nm thick SiO_2 diffusion barrier was used. Comparison of the electrical properties of the PZT film on the SnO_2/glass substrate with that of the film on the ITO/glass substrate clearly shows the formation of the reaction phase between an electrode and the resultant thin film in the case of the commercial soda lime glass. The alkaline and alkaline-earth metals or cations in the soda lime glass easily diffuse during annealing even at lower temperatures. However, the remanent polarization of the low-temperature processed PZT thin film on the ITO/glass is not so bad. Therefore, the expected method is to apply the low-temperature processed PZT thin film to the optical devices. The amount of excess lead should be optimized for improving the electrical properties.

5 Conclusions

This paper focused on the phase development and the electrical properties of the PZT films on the various substrates deposited from a stable precursor sol. As a result, single-seeding process and the addition of excess lead oxide precursor were essential to attain the low-temperature processing for the PZT thin film. From the comparison of the films with different electrode/substrate structure and annealed at 500°C or 550°C, the following is concluded:

1. Low-temperature processing of the PZT thin film was successfully attained by adding the excess amount of lead oxide in the precursor sol and the insertion of a PT seeding layer between electrode and the PZT film.
2. Low-temperature processed PZT thin films have sufficient dielectric and ferroelectric properties for industrial use even for the films deposited on the glass substrates.
3. PZT thin film on the $Pt/Ti/SiO_2/Si$ substrate exhibits superior electrical properties probably due to the reduced amount of amorphous phase.

PZT thin film on the SnO_2/Corning 7059 glass substrate also exhibits superior electrical properties compared with the PZT film on the ITO/commercial soda lime glass substrate because of the reduced interaction between substrate and the PZT film during processing.

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