

# Preparation of $\text{PbTiO}_3$ thin films using an alkoxide–alkanolamine sol–gel system

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The stable range of  $\text{PbTiO}_3$  sol and the processing conditions of uniform thin films were investigated using a solution of titanium isopropoxide, three kinds of alkanolamines (monoethanolamine, diethanolamine, triethanolamine), lead acetate trihydrate and isopropanol. Depending on the sol state with various alkanolamine/alkoxide molar ratios, diethanolamine (DEA) was very effective in preparing uniform and dense oxide films through room-temperature reaction, owing to its superior stability during the hydrolysis and condensation reaction. Perovskite  $\text{PbTiO}_3$  thin films were obtained on oxidized silicon wafer above  $550^\circ\text{C}$  and completely pure films were obtained at  $650^\circ\text{C}$  using DEA as a complexing agent. The dielectric constant and loss tangent of these thin films fired at  $650^\circ\text{C}$  for 30 min were found to be  $\sim 240$  and  $\sim 0.01$  at 1 kHz, respectively.

## 1. Introduction

The potential applications of ferroelectric  $\text{PbTiO}_3$  and PZT thin films in a wide range of devices, such as non-volatile memories, sensors and actuators, have recently provided strong motivation for investigating their modification and microstructure [1–8]. Because modifications and microstructures of the films directly affect their characteristics, it is very important to ascertain whether or not the modifications and microstructures can be effectively controlled in the deposition process.

The alkoxide–alkanolamine system has an excellent dissolving power for many inorganic salts and a long-term stability to hydrolysis and condensation [9]. Lead acetate trihydrate can be easily dissolved in a solution of alkanolamine–alcohol to give a clear and stable solution, but it is insoluble in the alcohol without the addition of alkanolamine.

So far, only a few alkoxide–alkanolamine systems have been reported. The preparation methods of  $\text{PbTiO}_3$  sol and films in this study are very simple and also suitable for the fabrication of other types of lead-based ferroelectric thin films. The details of the experimental results on the complexed sol–gel solution used for ferroelectric  $\text{PbTiO}_3$  thin films are reported.

## 2. Experimental procedure

The reagents used during this work were titanium isopropoxide (TIP), isopropanol (IPA), various alkanolamines (i.e. monoethanolamine (MEA), di-

ethanolamine (DEA), triethanolamine (TEA)) as a complexing agent, lead acetate trihydrate and nitric acid as a catalyst.

In order to ensure a clear and homogeneous range of the sol, various molar ratios of alkanolamine (MEA, DEA, TEA) were mixed with the isopropanol solution of the titanium isopropoxide under a nitrogen atmosphere. The complexed solution was stirred well for 1 h at room temperature, and then lead acetate trihydrate was directly added to the complexed solution without removal of the water of the lead acetate trihydrate. Lead acetate trihydrate dissolved in the solution within 1 h at room temperature to give a clear and homogeneous solution, but it is insoluble in the alcohol without the addition of alkanolamine.

The substrate used in this experiment was an oxidized silicon wafer. The substrate was cleaned with acetone and nitrogen gas before being used. Typical dimensions of the substrate were  $20 \times 20 \text{ mm}^2$ . In order to prepare the thin films, the complexed solution was dropped on to the oxidized silicon substrate, spun at a constant speed ( $\sim 3000$  r.p.m.) for 30 s and dried in air at  $400^\circ\text{C}$  for 5 min. Then the dried gel films were fired from  $450$ – $650^\circ\text{C}$  for 30 min in a nitrogen atmosphere.

The resultant films were investigated by X-ray diffractometry (XRD), viscometry, ellipsometry, scanning electron microscopy (SEM), and impedance analysis. For dielectric measurement, a top electrode, 1 mm diameter, was deposited on  $0.8 \mu\text{m}$  thick  $\text{PbTiO}_3$  films by d.c. sputtering. Platinum and aluminium were used as the bottom and top electrodes, respectively.

### 3. Results and discussion

Because the titanium atom has a low electronegativity, high partial charge ( $\delta(\text{Ti}) = +0.60$ ) and large ionic radius ( $r = 0.064 \text{ nm}$ ), TIP has a tendency to react easily with  $\text{H}_2\text{O}$  containing  $\text{OH}^-$  ligands [10, 11]. To prepare a stable and clear sol for spin coating, the hydrolysis and condensation rate of the sol must be controlled. For this reason, studies of complexing agents such as  $\beta$ -diketone and alkanolamine have been performed. Generally, a complexing agent induces two effects [12]: the steric hindrance effect where complexing agents substitute for the alkoxy group ( $-\text{OR}$ ) of the alkoxide and complicate the surrounding titanium atoms, thus decreasing the hydrolysis and condensation rate, and the inductive effect which changes the partial charge in the titanium complex, lowering its reactivity.

In this study, it was found that alkanolamine has not only the complexing agent effect but also excellent dissolving power for the acetate used as the lead source. Therefore, the room-temperature reaction for preparing the stable coating solution could be achieved easily without a further distillation process. Table I shows three kinds of alkanolamine used as complexing agents and the variation of the sol state as a function of alkanolamine/alkoxide molar ratio. For MEA, the clear sol was only formed above  $R = 5$  ( $R = \text{alkanolamine/TIP molar ratio}$ ) and precipitated below  $R = 5$ . This was thought to be insufficient to represent the complexing agent effect, because the molecular weight of MEA is too small for it to be a complexing agent. Therefore, excess addition of the complexing agent (above  $R = 5$ ) will induce undesirable properties in the sol and the thin films because of the presence of excess organics. For DEA, gelation was observed at  $R = 0.5$ , but the clear sol was obtained above  $R = 1$ . The clear sol range of DEA-modified sol was larger than for any other alkanolamine, and the solution with DEA had a higher stability. However, when a small amount of DEA (below  $R = 1$ ) was added to the sol, it did not show many complexing agent effects because of the fast hydrolysis and condensation reaction with the  $3\text{H}_2\text{O}$  in the lead acetate trihydrate. In the case of TEA, a clear solution was obtained below  $R = 1$ , but it precipitated even before the addition of lead acetate trihydrate in the range above  $R = 1$ . From Table I, DEA can be seen to retard the precipitation of the oxides or hydroxides from the mixture of TIP. DEA has a larger range of clear sol compared to TEA and MEA. In this work, therefore,  $\text{PbTiO}_3$  thin films were prepared with DEA

as a complexing agent. Figs 1 and 2 show the ranges required to form the clear solution. The former indicates the dependency of TIP at  $R = 1$  and the latter explains the relationship between DEA/TIP molar

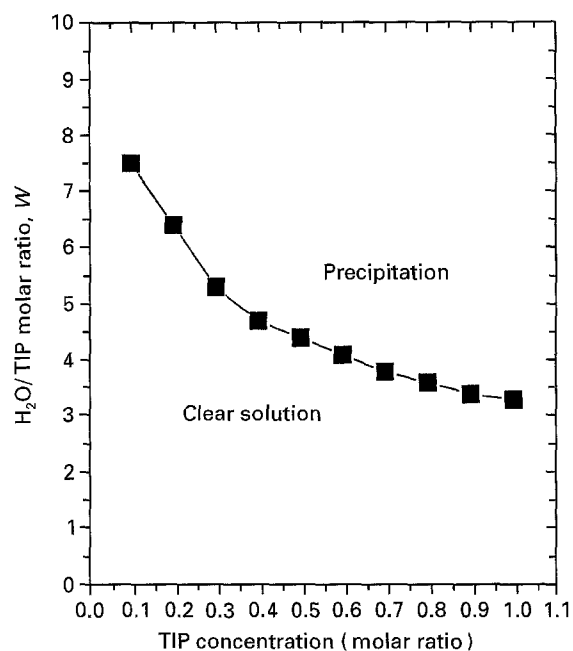


Figure 1 The range of clear solution formation between TIP and  $\text{H}_2\text{O}/\text{TIP}$  molar ratio at  $R = 1$ .

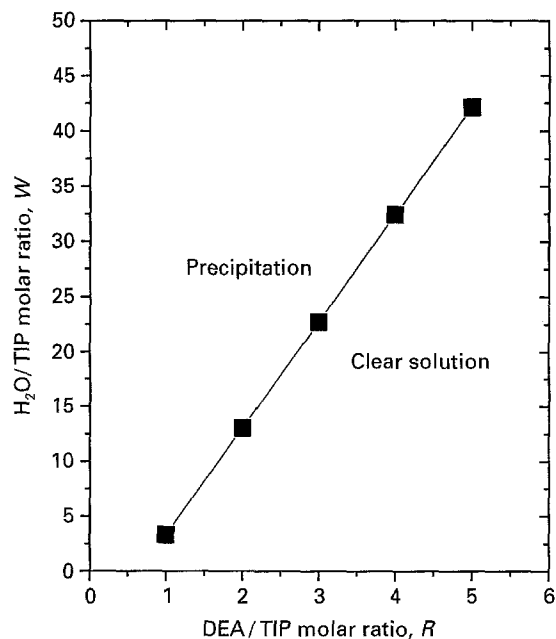


Figure 2 The range of clear solution formation between DEA/TIP and  $\text{H}_2\text{O}/\text{TIP}$  molar ratio at 1 M TIP.

TABLE I Variation of the sol state with the alkanolamine/alkoxide molar ratio,  $R$  (alkanolamine/titanium isopropoxide (TIP) molar ratio)

Alkanolamine	$R$				
	0.5	1	2	3	5
Triethanolamine (TEA)	← Clear solution →		← Precipitation →		
Diethanolamine (DEA)	Precipitation	← Clear solution →			Precipitation
Monoethanolamine (MEA)	← Precipitation →			← Clear solution →	

ratio,  $R$ , and  $H_2O/TIP$  molar ratio,  $W$ , at 1 M TIP. It is very obvious from the figures that excess water can be added to the solution in the presence of DEA. Lead acetate trihydrate used as the lead source contained 3 mol  $H_2O$ . Therefore, when 1 M TIP and 1 M DEA are used,  $W$  in the solution can be fixed at 3 without further addition of excess water. Therefore, lead acetate trihydrate can be used in the hydrolysis reaction directly, without the addition or removal of water at room temperature, in order to simplify the preparation method. This solution can be stored for as long as 2 years without appreciable change in the transparency and the viscosity of the solution.

The flow diagram for the preparation of  $PbTiO_3$  sol and thin films is shown in Fig. 3.  $PbTiO_3$  thin films were spun-cast on to oxidized silicon substrates by a spin coater at 3000 r.p.m. for 30 s. The thin layer was formed by controlling the concentration and the viscosity of the  $PbTiO_3$  precursor solution. Generally, the lower the concentration, the smoother was the film surface. In the case of multiple layers, the final top layer was of lowest concentration.

Successful preparation of thin film requires that the film should be free from cracks and defects. However, a large internal stress causes cracking owing to the volume change during the firing process of a wet-coated film. This internal stress can be partially relaxed by control of the drying process, related with the selection of complexing agents. Therefore, the drying process accompanied by pyrolysis of organometallic compounds is the most important step in preparation. This process is complicated, because the film undergoes a series of physicochemical reactions as follows [13, 14].

(a) Lead precursor as a starting material is dehydrated, melted and mixed in the  $TiO_2$  complexed solution at room temperature and the resultant solution is coated on to the substrate. Then the coated film is dried on a hot plate.

(b) With increasing temperature, the consequent large volume change and the generation of internal stress accompanies the evaporation of the solvent. Generally, these occur in the range from room temperature to 400 °C. In this stage, the organic compounds begin to decompose and the volume change of the film continues. At the end of this stage, the organic film changes to a fine mixture of oxides of lead, titanium and free carbon.

(c) At higher temperatures, the free carbon oxidizes and the mixture of oxides is converted to a transparent amorphous  $PbTiO_3$  film.

The investigation and control of these physicochemical reactions are very important in preparation of the thin films. The high boiling point (217 °C) and latent heat of vaporization of the DEA complexing agent raise the solution evaporation temperature towards the "decomposition" temperature in stage (b). This suppresses atomic mobility in the films and significantly reduces the tendency to crack. So, this method is more effective than any other method in the preparation of crack-free films.

Fig. 4 shows the change in the X-ray diffraction patterns as a function of the heat-treatment temper-

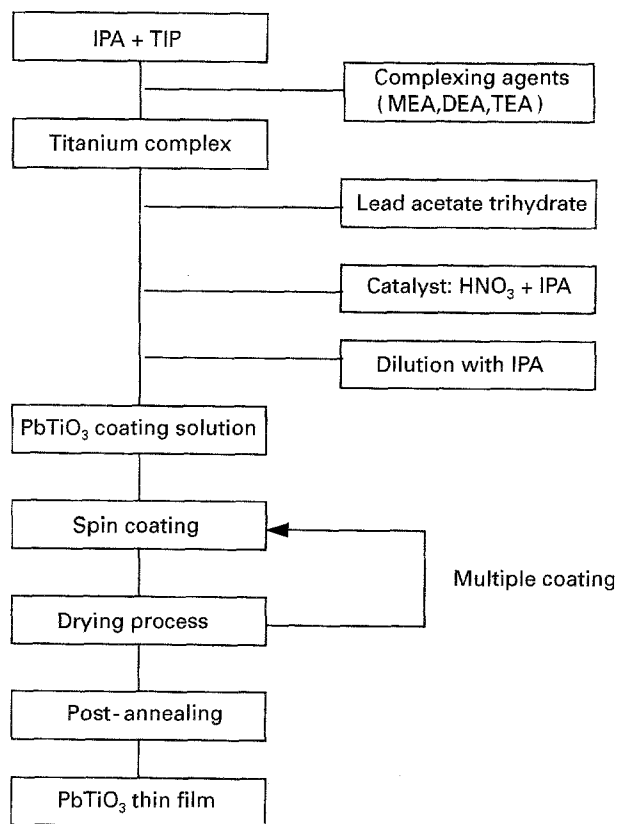


Figure 3 Flow diagram of the  $PbTiO_3$  precursor solution and films.

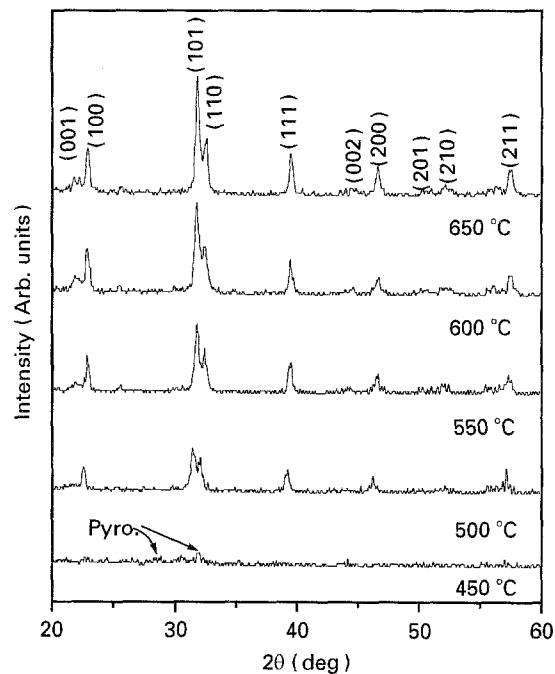


Figure 4 X-ray diffraction patterns of the  $PbTiO_3$  films heat treated at various temperatures for 30 min.

ature of the films. Amorphous  $PbTiO_3$  films could be obtained up to 450 °C, while crystalline films were formed from 500–650 °C. It is obvious that the pyrochlore peak grew together with the perovskite peak at 500 °C heat treatment. At this temperature, the (001) diffraction peak of the perovskite phase is absent and the (101) and (110) diffraction peaks have nearly equal intensities, implying partial orientation to the

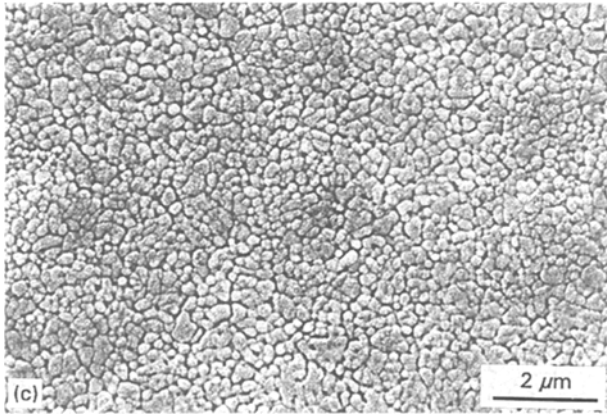
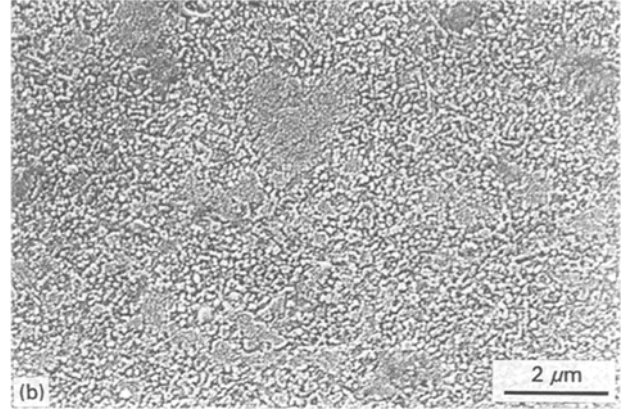
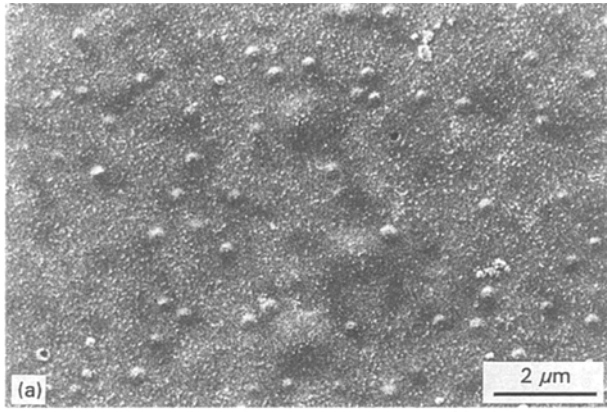


Figure 5 Scanning electron micrographs of the  $\text{PbTiO}_3$  films heat treated at (a) 450, (b) 550, and (c) 650 °C for 30 min.

$a$ -axis. At 550 °C, the pyrochlore phase disappeared, and only the perovskite phase was formed without (110) perovskite peak development. At higher temperature, the diffraction peaks were sharp owing to complete crystallinity. Pyrochlore phase could be readily converted to perovskite phase to a great extent when heated above 550 °C for 30 min, and was completely converted at 650 °C for 30 min. However, no preferred orientation was observed at 650 °C.

Fig. 5 shows scanning electron micrographs of the  $\text{PbTiO}_3$  film surfaces fired at 450, 550 and 650 °C. The films are about 0.8  $\mu\text{m}$  thick, crack-free and transparent with smooth surfaces. At 450 °C heat treatment, the morphologies of the surfaces were found to be very non-uniform with localized bloating and precipitation, and no grains could be grown successfully. At 550 °C, bloating and precipitation were not observed, but the grains were of non-uniform size due to insufficient growth. After firing at 650 °C for 30 min, the surfaces of these films were smooth and dense, and showed uniform microstructures. The major parts of the grains were of uniform size, 0.1–0.3  $\mu\text{m}$ , and no second phase was found. These indicated that the microstructures changed in shape with the firing temperature, and the film could have spherical surfaces and rounder boundaries at higher temperature.

Fig. 6 shows the frequency dependence of the dielectric constant and the loss tangent from 1–500 kHz of the  $\text{PbTiO}_3$  films on platinum/oxidized silicon substrates. The dielectric constants of the films increased with increasing heat-treatment temperature and showed a maximum ( $\sim 240$ ) at 650 °C. However, no remarkable change in the dielectric constants was

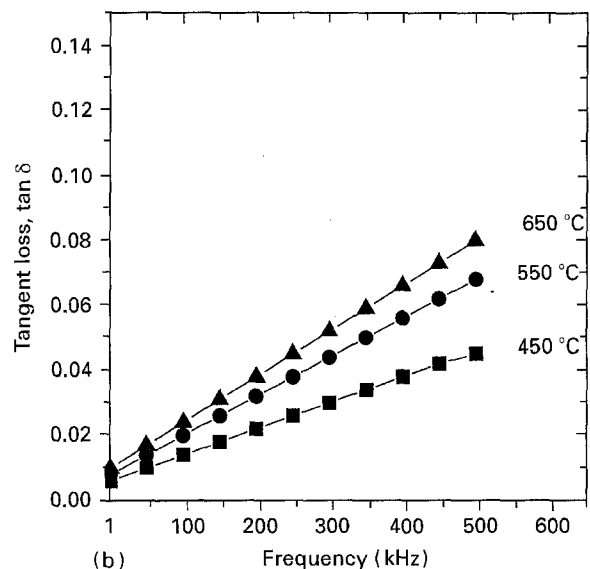
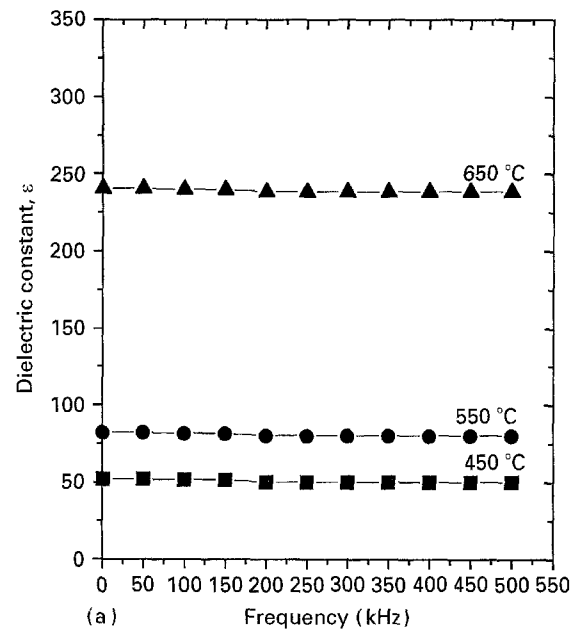


Figure 6 (a) Dielectric constants, and (b) tangent loss of the  $\text{PbTiO}_3$  films heat treated at 450, 550, and 650 °C for 30 min.

found as a function of frequency. On the other hand, the loss tangent of the films had a tendency to increase with increasing heat-treatment temperature and frequency. The loss tangent of all specimens was about 0.01 at 1 kHz.

From the results described above, DEA complexing agent can be concluded to be an effective agent in the sol-gel process in which alkoxides are used as the starting materials, because of its ability to extend the region of the clear solution, especially the water content. In addition, DEA has a rather positive effect on the formation of crack-free films and their densification. Using this DEA-modified sol-gel system, other lead-based ferroelectric films can be prepared much easier from the alkoxides, because other inorganic compounds soluble in DEA and solvent can be added to the mother composition at room temperature without the formation of precipitate despite the excess water content.

#### 4. Conclusions

1. The solution mixed with 1 M DEA/TIP and 3 M water/TIP at room temperature was a stable solution that could be stored for 2 years without appreciable change in viscosity.

2. Of MEA, DEA and TEA alkanolamines, DEA complexing agent had excellent dissolving power for inorganic salts and could effectively suppress precipitation from the alcoholic solution during hydrolysis of TIP.

3. The crystal structure of  $\text{PbTiO}_3$  films strongly depends on the post-annealing temperature. Perovskite phase was dominant above  $550^\circ\text{C}$  and the films were completely pure at  $650^\circ\text{C}$  when using DEA as a complexing agent.

4. The dielectric constants increased with increasing annealing temperature but there was no remarkable change with frequency; however, the loss

tangent of the films increased with annealing temperature and frequency. The measured dielectric constant and loss tangent of the  $\text{PbTiO}_3$  thin film fired at  $650^\circ\text{C}$  for 30 min were 239 and 0.01 at 1 kHz, respectively.

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