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Effects of Excess Lead Oxide Addition and Substrates on Crystallization and Electrical Properties of $Pb(Zr_{0.53}Ti_{0.47})O_3$ Thin Films from Stable Precursor Sol

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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 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 film was deposited at 550℃. As a result, ferroelectric PZT thin films were successfully deposited at above 550℃. The crystallization behavior was also affected by the substrates with electrodes. The PZT films deposited on the ITO/glass substrate has random orientation whereas the PZT thin films on the $Pt/Ti/SiO_2/Si$ substrate exhibited (111) orientation at above 550℃. The low-temperature processed PZT thin films with thickness about 500nm exhibited relatively good dielectric and ferroelectric properties (ε_r: 550 - 840, P_r:39 - 63 $\mu C/cm^2$).
Key words : PZT thin film, electrical properties, stable precusor sol, excess lead oxide

1. INTRODUCTION

Ferroelectric thin films with a perovskite structure have been attracting attention to apply nonvolatile memories, an infrared sensor, micro actuators and electrooptic devices. Especially, lead zirconate titanate (PZT) thin films with different compositions have been widely studied because of their high dielectric constant and remanent polarization as well as the superior pyroelectric and piezoelectric properties.

A physical method such as sputtering and laser ablation, chemical vapor deposition and wet chemical processing such as a sol-gel process have been used for the formation of ferroelectric PZT thin films[1)-3)]. Among them, a sol-gel process is one of the most promising method because it offers precise control of a composition at molecule level as well as the lower processing temperature, production of large film area with homogeneous composition. However, an alkoxide precursor solution reacts sensitively with the water in the atmosphere.

On the other hand, low-temperature processing is very important for the PZT thin films because high temperature annealing above 700℃ degrades the silicon transistor. In addition, interdiffusion of the atoms between a PZT film and a substrate causes a serious problem, leading to the fatigue of the resultant films. Therefore, low-temperature processing of the PZT films is indispensable for the memory application with high density integration. Moreover, various substrates with low-melting temperatures such as glass and aluminum could be available, leading to the wide application areas. In the previous paper[4),5)], low-temperature processing of PZT thin films have been successfully attained through single- or multi-seeding process from alkoxide precursor solution, in which a lead titanate (PT) seeding layers are inserted between PZT layers.

In this paper, effects of the excess lead oxide addition and substrates on the crystallization and electrical properties of the PZT thin films deposited from stable precursor sols were investigated, as well as the effect of the stacking structure of the precursor films including seeding layer. In this process, acetic acid was used as a chelating agent to stabilize the sols. In this study, single seeding process was used. Excess addition of lead oxide will compensate the depletion of a lead oxide by the evaporation and diffusion during annealing, leading to the low-temperature processing. This paper described the optimum conditions of these parameters for low-temperature processing of PZT thin film from stable precursor sol.

2. EXPERIMENTAL PROCEDURE

PZT (Zr/Ti=53/47) precursor sol of 0.3M was prepared from lead acetate trihydrate ($Pb(OCOCH_3)_2 \cdot 3H_2O$), titanium iso-propoxide ($Ti[(CH_3)_2CHO]_4$), zirconium n- propoxide ($Zr(C_3H_7)_4$) acetic acid, water and ethanol. At first, lead acetate trihydrated was dehydrated and then dissolved in acetic acid at 80℃. On the other hand, titanium iso-propoxide or zirconium n- propoxide was mixed and reacted with an acetic acid in ethanol, respectively. Ti-precursor solution was mixed and reacted with Pb solution and then reacted with the Zr-precursor solution to prepare the PZT precursor solution. PZT precursor solution was hydrolyzed with stoichiometric amount of water

to form a stable sol. Finally, acetylacetone was added to the sol as a stabilizing agent.

A PZT precursor film was deposited by dip-coating method on a Pt(111)/Ti/SiO_2/Si or ITO/glass substrates, in this study. The film thickness was about 500nm with 9 and 11times of coatings for silicon wafer and ITO/glass, respectively. After each precursor layers were deposited, precursor films were pre-annealed at 350℃ for 1 hour in an ambient atmosphere to pyrolyze the residual organic compound. Finally, these amorphous precursor films were annealed in the range from 450℃ to 600℃ for 2 hours in an ambient atmosphere using muffle furnace.

Crystalline phases in the PZT thin films were identified by X-ray diffraction (XRD). For electrical measurement, Au top electrodes with a diameter of 0.2 mm were sputtered. Dielectric property of the thin film was measured by LCR meter (HP-4284A). P-E hysteresis loops of the resultant thin films were measured by RT6600S (Radiant Technology Inc.).

3. RESULTS AND DISCUSSION

3.1 Crystallization behavior

PZT precursor sol or films with a stoichiometric composition, 30 and 50 mol % of excess lead oxide were abbreviated as PZT(100/53/47), PZT(130/53/47) and PZT(150/53/47), respectively. Lead titanate layer with a stoichiometric composition (PT(100)) or 50 mol % of excess lead oxide (PT(150)) was used as a seeding layer. Figure 1 shows three types of the stacking structures for the PZT thin films.

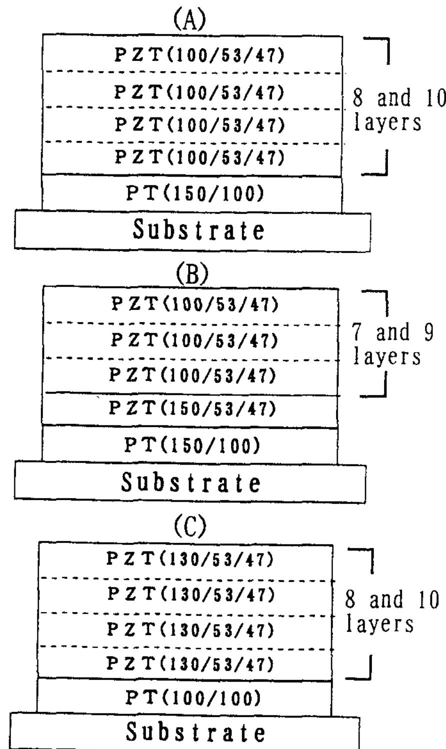

Fig. 1 Stacking structures of PZT thin films.

Figure 2 shows the XRD patterns for the PZT films deposited on a Pt/Ti/SiO_2/Si substrate, annealed at 550℃ to investigate the effect of the stacking structure on the crystallization behavior. The difference between stacking (A) and (B) is the composition of a PZT layer just above the seeding layer. (A) structure promoted the crystallization of a perovskite phase but still exhibited residual pyrochlore phase in the film. On the other hand, PZT films with stacking structures of (B) and (C) showed the single-phase perovskite structure. These results indicates that the lead element diffused into substrate during annealing and at least two layers (about 100 nm thick) with excess lead were indispensable for low-temperature processing of PZT thin films on a Pt/Ti/SiO_2/Si substrate through this process. As a result, single-phase perovskite PZT thin films with different stacking structures were successfully deposited on a Pt/Ti/SiO_2/Si substrate at low temperature of 550℃ by the insertion of PT seeding layer and the addition of excess lead oxide. In this case, PZT films showed (111) orientation.

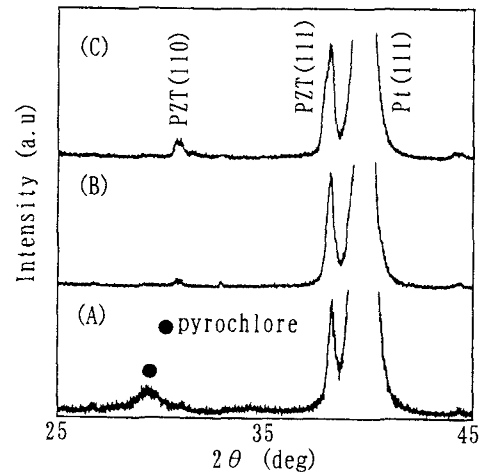

Fig. 2 XRD patterns for PZT thin films on Pt/Ti/SiO_2/Si substrates annealed at 550℃.

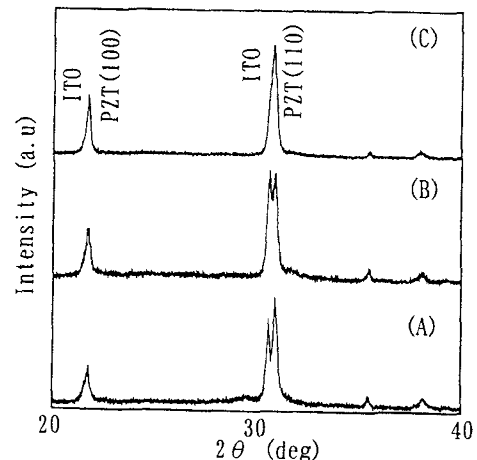

Fig. 3 XRD patterns for PZT thin films on ITO/glass substrates annealed at 550℃.

Figure 3 shows the XRD patterns for the PZT films on ITO/glass substrate annealed at 550℃. Only the single-phase perovskite with random orientation was identified for the films on ITO/glass substrate. However, the main peak shifted toward the lower angle by the 0.06° for the case of the PZT film with excess amount of a lead oxide (Fig. 3(C)). The reason was not clear.

3.2 Electrical properties

Figure 4 exhibits the change in the relative permittivity of the resultant film on ITO/glass and $Pt/Ti/SiO_2/Si$ substrate with the amount of excess lead oxide in the PZT precursor film. The amount of the excess lead oxide was calculated from the stacking structures. This figure shows that the PZT films on a $Pt/Ti/SiO_2/Si$ substrate had superior dielectric property than those on the ITO/glass substrate. Furthermore, relative permittivity of the resultant PZT films tends to be leveled off at above 30 mol % excess addition of a lead oxide. In addition, high temperature annealing improved the dielectric property of the resultant films, especially for the films on a $Pt/Ti/SiO_2/Si$ substrate. For the PZT film with a (C) stacking structure annealed at 600 ℃, highest permittivity of about 840 was obtained.

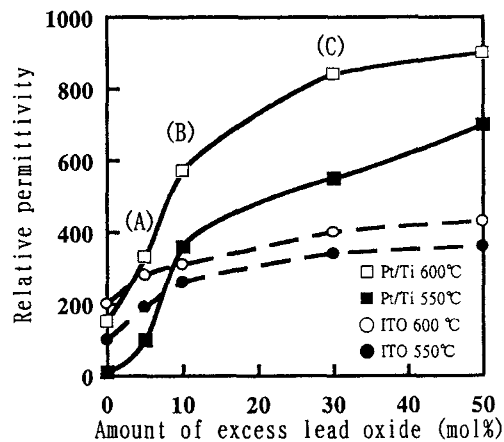

Fig.4 A relation between relative permittivity and amount of excess lead oxide.

As already described, relatively good PZT films were deposited both on the $Pt/Ti/SiO_2/Si$ and ITO/glass substrates at low temperature of 550℃. Therefore, ferroelectric property of the PZT films on $Pt/Ti/SiO_2/Si$ and ITO/glass substrates was estimated and shown in figure 5. From this figure, it is concluded that the PZT films with a single-phase perovskite structure and different stacking structures of (B) and (C) on a $Pt/Ti/SiO_2/Si$ substrate exhibited relatively high remanent polarization of 36 and 39 $\mu C/cm^2$, respectively. Coercive field of these films exhibited similar values (Fig. 5 (a)). On the other hand, PZT thin films with stacking structures of (A), (B) and (C) on ITO/glass substrate, annealed at 550 ℃, exhibited the remanent polarization of 19, 42 and 50 $\mu C/cm^2$, respectively. The PZT films on ITO/glass substrate showed relatively good ferroelectricity although the relative permittivity of these films was not so good. This suggests the formation of the amorphous reaction phase with low relative permittivity for the films on ITO/glass substrate. In addition, PZT films with larger amount of excess lead oxide tends to have higher remanent polarization and lower coercive field independent of the substrates.

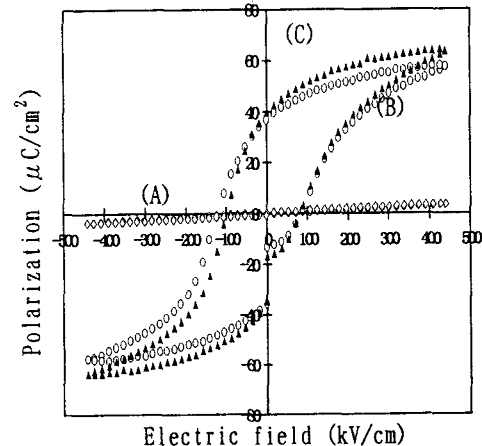

Fig.5 (a) P-E Hysteresis loops of PZT thin films on $Pt/Ti/SiO_2/Si$ substrates with different stacking structures of (A), (B) and (C) in Fig.1 annealed at 550℃.

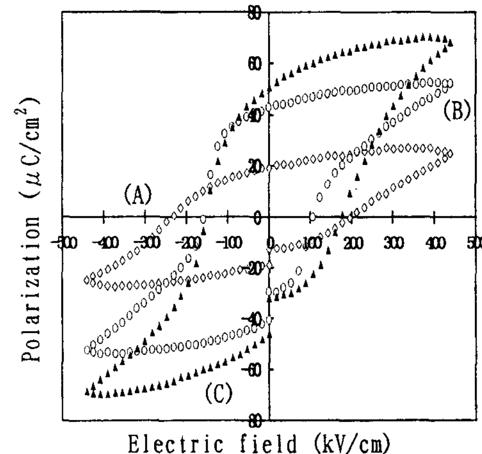

Fig.5 (b) P-E Hysteresis loops of PZT thin films on ITO/glass substrates with different stacking structures of (A), (B) and (C) in Fig.1 annealed at 550℃.

4. CONCLUSIONS

In this paper, effects of the excess lead oxide addition and the substrate on the crystallization and

electrical properties of the resultant PZT thin films were investigated in details. As a result, followings are concluded:

(1) Crystallization behavior of the PZT thin film was significantly affected by the amount of the excess lead oxide addition. Insertion of two layers with excess lead addition of 50 mol % was sufficient to obtain single-phase perovskite PZT thin film at relatively low temperature of 550℃, independent of the substrate.

(2) Dielectric property of the resultant PZT film was affected by the amount of the excess lead oxide addition and substrate. Addition of 30 mol % excess lead oxide was estimated to be enough to obtain the saturated dielectric property. In addition, a $Pt/Ti/SiO_2/Si$ substrate was better to obtain a PZT film with a good dielectric property at low temperature.

(3) PZT thin films with relatively good ferroelectricity were successfully deposited at low temperature of 550 ℃, independent of the substrate by the insertion of PT seeding layer with excess lead oxide addition of 50 mol % or 30 mol % of excess addition for the PZT films.

REFERENCES

1) H.Fujisawa, M.Yoshida, M.Shimizu and H.Niu, Jpn.J.Appl.Phys.,**37**, 5132 (1998)

2) Yi.G and M.Sayer, J.Sol-Gel Sci. and Tech., **6**, 65 (1996)

3) Yi.G and M.Sayer, J.Sol-Gel Sci. and Tech., **6**, 75 (1996)

4) H.Suzuki, M.B.Othman, K.Murakami, S.Kaneko and T.Hayashi, Jpn.J.Appl.Phys.,**35**, 4896 (1996)

5) H.Suzuki, M.B.Othman, K.Murakami, S.Kaneko and T.Hayashi, Jpn.J.Appl.Phys.,**36**, 5803 (1997)

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