PREPARATION OF LEAD ZIRCONATE TITANATE FILM BY SOL-GEL METHOD AND ITS CHARACTERIZATION

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ABSTRACT

A ferroelectric material film of Lead Zirconate Titanate, Pb(Zr,Ti)O₃ (PZT), was produced by sol-gel method from alkoxide and acetate precursors in a normal propanol solvent system. The excess amount of Pb was 10 mole % more than stoichiometrically used for preparing the solution. The concentration of PZT in coating solution was 0.7 M, and pH of the solution was 4.5. The films was prepared by dip-coating onto slide glass, silica glass and Pt/Ti/SiO₂/Si substrate. In order to avoid cracking TiO₂ was coated on the glasses as a barrier layer. The as-dried PZT film was amorphous from X-ray diffraction. The amount of pyrochlore and perovskite phase depended on the heating temperature and kind of barrier layer. Single perovskite phase was found for coated films on TiO₂/SiO₂ and Pt/Ti/SiO₂/Si heated at 600°C or higher, but it was never found for coated films on SiO₂ substrate without barrier layers. Crystallization of perovskite PZT film was retarded when deposited on amorphous substrates as compared to crystalline substrate. The coated film on Pt/Ti/SiO₂/Si was thicker and smaller in particle size than that of coated film on TiO₂/SiO₂. A columnar structure with a diameter around 6.5 nm, was observed and no boundary was observed between layers in 9 time dip-coated film on Pt/Ti/SiO₂/Si.

INTRODUCTION

Lead zirconate titanate (PZT) is a useful ferroelectric material for a variety of electronic and electro-optic application [1]. In recent years, thin film devices of PZT and other such ferroelectric compositions have gained interest due to their versatility in micro-device application [2]. Electronic applications of PZT thin films may include NVRAM (nonvolatile random access memory) [3], DRAM(dynamic random access memory), capacitor, micro-actuator, and pyroelectric sensor [4]. Electro-optic applications, on the other hand, may include optical waveguide modulators, optical inter-connects, memories and displays [5].

Certainly one of the most technologically important aspects of sol-gel processing is that, prior to gelation, the fluid sol or solution is...
ideal for preparing thin films by such common processes as dipping, spinning, or spraying. Compared to conventional thin film forming processes such as chemical vapor deposition (CVD), evaporation, or sputtering, sol-gel film formation requires considerably less equipment and is potentially less expensive; however the most important advantage of sol-gel processing over conventional coating methods is the ability to control precisely the microstructure of the deposited film.

In recent years, fabrication of PZT thin films by sol-gel processes has been reported [6,7,8]. However, fabrication of thick crack-free PZT films by sol-gel processing technique still needs to be studied, keeping in view the available substrate materials and their crystallographic mismatch with the deposited film. This is significant since the thickness of PZT thin film strongly influences the film properties such as dielectric constant, remanence polarization, and coercive field [9].

The application of PZT thin films to semiconductor memory technology requires the development of a technique for deposition onto Si. The Pb and O ions are quite active and can easily oxidize the Si substrate, inducing the formation of an unintentional amorphous layer at the interface between the film and the substrate during deposition and post deposition annealing [10]. The formation of an amorphous SiO₂ layer containing Pb ions decreases the overall dielectric constant of the thin film capacitor [11]. Various kinds of barrier layers have been examined to prevent the interfacial reactions between PZT thin films and Si substrates [12,13]. One of the most widely used materials was Pt-Ti bilayer, because of the excellent chemical stability of Pt and its relatively good adhesion to oxidized Si wafers due to the Ti adhesion layer [14,15].

Control of heating temperature and the type of barrier layers are critical factors in developing a single phase perovskite material, e.g. ceramic oxides of the general formula A₂B₂O₇, where A is a large-sizes cation of low charge, such as Pb²⁺, and B is a small highly charge cation, such as Zr⁴⁺. In the present study, PZT films have been prepared on TiO₂ and Pt/Ti barrier layers and also onto slide glass and SiO₂ without barrier layers at low temperature by sol-gel processing. This novel method leads to complete crystallization of the perovskite structure of PZT films without any additonal phase (such as pyrochlore phase, e.g. ceramic oxides with general formula A₂B₂O₇) at relatively low temperature.

EXPERIMENTAL

Apparatus

Glass reaction vessel for hydrolysis and condensation reaction., X-ray Photoemission Spectroscopy(XPS, JPS-90SX, JOEL Ltd.), Fourier Transform Infra Red spectroscopy (FTIR, Digilab FT-65, BIO-RAD),, X-ray diffraction (RAD-C system, RPT 300, Rigaku Co.), Scanning Electron Microscopy (SEM, JMS-5200, JEOL Ltd.), and LCR meter (Ando electric Co, type AG-4301B)

Materials/Reagents

Lead Acetate Trihydrate (Pb(CH₃CÖO)₂ 3H₂O), Kanto Chemicals Co. INC., minimum assay, 99.5%. Titanium tetra-i-propoxide (Ti(iso-OC₃H₇)₄), Soekawa Chemicals, minimum assay, 99%. Zirconium tetra-n-butoxide (Zr(n-C₃H₇O)₄), Soekawa Chemicals. Normal propanol (CH₃CH₂CH₂OH), Junsei Chemical, minimum assay, 99.5%. Ethylene glycol (HOCH₂CH₂OH), Kanto Chemical Co. INC., minimum assay, 99.7%. Acetic Acid (CH₃COOH), Kanto Chemical Co. INC., minimum assay, 99.7%. SiO₂ glass, slide glass and (111) plane of Pt/Ti/SiO₂/Si (ASTM No. 4-0802) substrates, Matsu bara kagaku Co. INC. The thickness of multilayers Pt/Ti/SiO₂ deposit-ed on silicon substrates are 300, 100, and 300 nm, respectively.

Experimental procedure

The film samples with composition near morphotropic phase boundary were prepared by sol-gel process. This process is similar to the previous study [16]. The starting materials consisted of Pb(CH₃COO)₂ 3H₂O, Ti(iso-OC₃H₇)₄, and Zr(n-OC₃H₇)₄. The excess amount of Pb, was 10 mol % more than stoichiometrically needed, (in order to compensate for a possible lead loss at the heating temperature over than 600 °C) and was used for preparing the solution. The lead acetate trihydride was dissolved in acetic acid in the proportion of 2 g of lead acetate to 1 ml of acetic
RESULTS

FTIR analysis

The bands around 1500 cm$^{-1}$ is due to acetate ligands [17] for zirconium tetra-n-butoxide and titanium tetra-i-propoxide in acetic acid (Fig.1a and 1b). The broad bands around 3400 cm$^{-1}$ may result from free moisture or -OH groups. The band spectra around 2965-2879 cm$^{-1}$ is due to the (C-H) vibrations. The (CH) band at 1386 cm$^{-1}$ appears as a shoulder of the strong peak at 1458 cm$^{-1}$. Fig. 2 shows the most significant feature that is the presence of a set of bands assigned to the C=O stretching at 1715 cm$^{-1}$ and COO vibrations at 1558 cm$^{-1}$ as a group in acetate ligands. The spectrum at 619 cm$^{-1}$ showed the bands due to the π(CH) or π(CO) [18]. Fig.3 shows the spectra of the PZT gel after heating at various temperatures in the range from 450 to 600°C. The spectra of residual organic weakens, and the broad band around 600 cm$^{-1}$ indicates the presence of metal-oxygen bonding appeared strong after heating at 600°C.

Crystallization behaviors of the films.

The crystallization behaviors were studied at room temperature by X-ray diffraction analysis. The PZT films have amorphous structures until heating at 450°C for 30 min. The amorphous structure will be transformed into perovskite phase through pyrochlore phase. The transformation of the pyrochlore to the perovskite can be monitored by X-ray diffraction. The relative amount (mol%) of perovskite phase could be calculated from [19].

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\text{Percent Perovskite} = \frac{I_{\text{perovskite}}}{I_{\text{perovskite}} + I_{\text{pyrochlore}}} \times 100 \quad (1)
\]

where $I_{\text{perovskite}}$ and $I_{\text{pyrochlore}}$ are the intensities of the major X-ray peaks (110) and (222) of the perovskite and pyrochlore phases, respectively. For coated films on TiO$_2$/glass and Pt/Ti/SiO$_2$/Si substrates after heating at 500°C for 30 min, the pyrochlore and perovskite phase started to appear. However, only perovskite phase appeared for coated films on glass substrate, which was stable until the heat treatment at 550°C. The percentage of perovskite and pyrochlore phase at various temperatures is shown in Fig. 4, 5 and 6. Single perovskite phase (ASTM No. 33-784) was found after heating at 600°C for coated
films on TiO$_2$/SiO$_2$ and Pt/Ti/SiO$_2$/Si, respectively. However single perovskite phase will never be found for coated films on SiO$_2$ substrate.

![Figure 1. Infrared spectra of (a) Zr(n-OC$_2$H$_4$), (b) Ti(i-OCH)$_4$ in acetic acid.](image1)

![Figure 2. Infrared spectra of PZT sol after aging at room temperature for several days.](image2)
Figure 3. Infrared spectra of PZT gel derived powders at various heating temperatures: (a) 450 °C, (b) 500 °C, (c) 550 °C and (d) 600 °C.

Figure 4. Percentage of perovskite and pyrochlore phase of PZT coated films on TiO$_2$/SiO$_2$ vs heating temperatures.
Figure 5. Percentage of perovskite and pyro-chlore phase of PZT coated films on Pt/Ti/SiO$_2$/Si vs heating temperatures.

Figure 6. Percentage of perovskite and pyro-chlore phase PZT coated films on SiO$_2$ vs temperatures heating.
Figure 7. X-ray diffraction patterns of the single (a) and triple (b) PZT coated films on (A) TiO$_2$/SiO$_2$, (B) Pt/Ti/SiO$_2$/Si substrates after heating at 600 °C for 30 min.

Figure 8. XPS depth profile of oriented 3 time dip-coated PZT film, crystallized at 600 °C for 30 min on a Pt/Ti/SiO$_2$/Si substrate.
Microstructure of the films.

Heating of coated film on SiO$_2$ at 600°C for 30 min. had resulted in a film crack as shown in Fig. 9A. The crack free PZT film was observed with grain size of approximately 0.3 μm (Fig. 9B) for coated film on TiO$_2$/SiO$_2$. The grain size (0.1 μm) of the crack free film coated on Pt/Ti/SiO$_2$/Si (Fig. 9C) was smaller than that coated on TiO$_2$/SiO$_2$ (Fig. 9B). The 9 time dip-coated films on Pt/Ti/SiO$_2$/Si indicate column structure of diameter around 6.5 nm. Fig. 10 shows that the thickness of film increases linearly with the number of dipping for both TiO$_2$/SiO$_2$ and Pt/Ti/ SiO$_2$/Si substrates. The thickness films on Pt/Ti/ SiO$_2$/Si is thicker than that on TiO$_2$/SiO$_2$.

Dielectric properties of the films.

Fig. 11 shows the plots of dielectric constant versus temperature for PZT films, where the Curie temperature and dielectric constant were approximately 360°C and 1615, respectively.
Figure 10. Films thickness vs number of dipping of PZT coated films on TiO$_2$/SiO$_2$ and Pt/Ti/SiO$_2$/Si substrates, after heating at 600°C.

Figure 11. Dielectric constant vs temperature of PZT film after heating at 600 °C.
DISCUSSION

The presence of acetic acid effected the acetate anion (\(\text{ac}^-\)) coordination to metal. The metal alkoxides was added into the solution and then reacted with acetic acid to form a bridging (bound to two metal) or a chelating (bonded to one metal) solution, which would be difficult to hydrolyze. The separation \(\Delta \nu (\text{COO}^-)\) between the \(\Delta \nu (\text{COO}^-)_{\text{sym}}\) and the \(\Delta \nu (\text{COO}^-)_{\text{asym}}\) frequency is generally taken as an indication of the nature of coordination of the carboxylate ion to metals [21]. The frequency separation \(\Delta \nu <130 \text{ cm}^{-1}\) suggests that \(\text{CH}_3\text{COO}^-\) acts as a bidentate ligand [22]. Two pairs of absorption peaks, those are: at 1558 and 1456 \text{ cm}^{-1} for \(\text{Zr(O-nBut)}_4\) in acetic acid (Fig. 1a) and at 1561 and 1451 \text{ cm}^{-1} for \(\text{Ti (O-iPr)}_4\) in acetic acid (Fig. 1, arrows) are \(\nu (\text{COO}^-)_{\text{asym}}\) and \(\nu (\text{COO}^-)_{\text{sym}}\), respectively. All of those peaks showed \(\Delta \nu <130 \text{ cm}^{-1}\) which suggested that bidentate chelating occurred. The PZT sol showed that a pair of absorption at 1557 and 1457 \text{ cm}^{-1} (arrows) are \(\nu (\text{COO}^-)_{\text{asym}}\) and \(\nu (\text{COO}^-)_{\text{sym}}\), respectively (Fig. 2). It indicated that band of COO- with coordinate to metals become chelated solution. The band around 600 \text{ cm}^{-1} in Figure 3 indicates the metal-oxygen bonding of Ti-O and Zr-O [22]. The crystallization behavior of PZT indicate that single perovskite phase of coated film on TiO\(_2\)/SiO\(_2\) and Pt/Ti/SiO\(_2\)/Si can occur at temperature lower than that of coated films on SiO\(_2\) (Fig. 4, 5 and 6). This is due to the presence of crystalline Pt/Ti and TiO\(_2\) which may thus accelerate the crystal-lization of perovskite phase PZT. The 9 time coated film on the Pt/Ti/SiO\(_2\)/Si substrates showed a columnar structure with a diameter around 6.5 nm regardless of the film thickness.

REFERENCES


CONCLUSIONS

The following conclusion could be drawn from the present observations:

1. Single perovskite phase of PZT crack free films were found for the coated films on TiO\(_2\)/SiO\(_2\) and Pt/Ti/SiO\(_2\)/Si substrates, heated at 600 °C or higher temperature.
2. Crystallization of perovskite film PZT was retarded when deposited on amorphous substrates compared to crystalline substrates. Single perovskite phase of PZT coated films on SiO\(_2\) substrates will never be found. The amounts of pyrochlore and perovskite phase depended on the heating temperature and kind of substrates.
3. The 9 time coated films onto Pt/Ti/SiO\(_2\)/Si showed a columnar structure with a diameter around 6.5 nm regardless of the film thickness.
4. The film thickness increases linearly with the number of dipping for coated films on TiO\(_2\)/SiO\(_2\) and Pt/Ti/SiO\(_2\)/Si substrates.
5. The PZT film after heating at 600 °C has a Curie temperature and a dielectric constant approximately 360 °C and 1615, respectively.

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