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, $Pb(Zr,Ti)O_3$ (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 $Pt/Ti/SiO_2/Si$ substrate. In order to avoid cracking TiO_2 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 TiO_2/SiO_2 and $Pt/Ti/SiO_2/Si$ heated at 600° C or higher, but it was never found for coated films on SiO_2 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 $Pt/Ti/SiO_2/Si$ was thicker and smaller in particle size than that of coated film on TiO_2/SiO_2. 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 $Pt/Ti/SiO_2/Si$.

INTISARI

Suatu film material ferroelektrik dari oksida timbal zirkonat titanat (PZT) telah dibuat dengan metoda sol-gel dari bahan-bahan alkoxida dan asetat dalam sistim pelarut normal propanol. Kelebihan Pb 10 mol% dari stoikiometri, telah digunakan dalam penyediaan larutan. Konsentrasi PZT dalam larutan pelapis adalah 0.7 M, dengan pH 4.5. Film dibuat dengan cara pelapisan celup pada substrat gelas *slide*, gelas silika dan $Pt/Ti/SiO_2/Si$. Untuk menghidari terjadinya retakan pada film, gelas dilapisi dengan TiO_2 sebagai lapisan penahan. Film PZT yang dikeringkan berfasa amorf dari hasil pengamatan difraksi sinar X. Kandungan fasa *pyrochlore* dan fasa *perovskite* ter-gantung pada suhu pemanasan dan macam lapisan penahan. Fasa tunggal perovskite telah diketemukan pada film yang dilapiskan pada substrat TiO_2/SiO_2 dan subtrat $Pt/Ti/SiO_2/Si$ pada suhu pemanasan 600°C atau lebih, sedangkan fasa tunggal tersebut tidak diketemukan pada film yang dilapiskan pada substrat SiO_2 tanpa lapisan penahan. Kristalisasi perovskite PZT terhambat ketika film dilapiskan pada substrat amorf dibandingkan pada substrat kristal. Film yang dilapiskan pada $Pt/Ti/SiO_2/Si$ lebih tebal dengan ukuran partikel yang lebih kecil dari pada film yang dilapiskan pada TiO_2/SiO_2. Struktur film yang berbentuk kolom dengan diameter sekitar 6.5 nm, dan tidak teramati adanya lapisan pembatas antara lapisan-lapisan film yang dilapiskan pada substrat $Pt/Ti/SiO_2/Si$ sebanyak 9 kali pengulangan.

INTRODUCTION

Lead zirconate titanate (PZT) is a useful ferroelectric material for a variety of electronic and electro-optic appli-cation [1]. In recent years, thin film devices of PZT and other such ferroelectric compositions have gained interest due to their versatility in micro-device applica-tion [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 crystallo-graphic 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 polariza-tion, and coercive field [9].

The application of PZT thin films to semiconductor memory techno-logy 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 for-mation 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 SiO_2 layer containing Pb ions decreases the overall dielec-tric 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 ABO_3, where A is a large-sizes cation of low charge, such as Pb^{2+}, and B is a small highly charge cation, such as Zr^{4+} . In the present study, PZT films have been prepared on TiO_2 and Pt/Ti barrier layers and also onto slide glass and SiO_2 without barrier layers at low tempera-ture by sol-gel processing. This novel method leads to complete crystallization of the perov-skite structure of PZT films without any additi-onal phase (such as pyrochlore phase, e.g. ceramic oxides with general formula $A_2B_2O_7$) at relatively low temperature.

EXPERIMENTAL

Apparatus

Glass reaction vessel for hydroly-sis and condensation reaction., X-ray Photoemis-sion Spectroscopy(XPS, JPS-90SX, JOEL Ltd)., Fourier Transform Infra Red spectrosco-py (FTIR, Digilab FTS-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 ($Pb(CH_3COO)_2$ $3H_2O$), Kanto Chemicals Co. INC., minimum assay, 99.5%. Titanium tetra-i-propoxide ($Ti(i\text{-}C_3H_7O)_4$), Soekawa Chemicals, minimum assay, 99%. Zirconium tetra-n-butoxide ($Zr(n\text{-}C_4H_9O)_4$), Soekawa Chemicals. Normal propanol ($CH_3CH_2CH_2OH$), Junsei Chemical, minimum assay, 99.5%. Acetic Acid (CH_3COOH), Kanto Chemical Co. INC., minimum assay, 99.7%. Ethylene glycol ($HOCH_2CH_2OH$), Kanto Chemical Co. INC., minimum assay, 99.5%. SiO_2 glass, slide glass and (111) plane of $Pt/Ti/SiO_2/Si$ (ASTM No. 4-0802) substrates, Matsu bara kagaku Co. INC. The thickness of multilayers $Pt/Ti/SiO_2$ 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 $Pb(CH_3COO)_2$ $3H_2O$, $Ti(iso\text{-}OC_3H_7)_4$ and $Zr(n\text{-}OC_4H_9)_4$. The excess amount of Pb, was 10 mole % more than stoichiometrically needed, (in order to compen-sate for a possible lead loss at the heating tem-perature over than 600 °C) and was used for preparing the solution. The lead acetate tri-hydrate was dissolved in acetic acid in the proportion of 2 g of lead acetate to 1 ml of acetic

acid. The solution was heated to 105 °C for 2 h to remove water. The dehydrated solution was cooled to below 80° C before the required quantity of zirconium tetra-n-butoxide was added. After adding zirconium tetra-n-butoxide the solution is stirred at room temperature for 1h and titanium (IV) tetra-i-propoxide in normal propanol was then added. After that, water, normal propanol and ethylene-glycol were added to the solution and stirred at room tem-perature for 2h. Ethylene-glycol was used as an additive in order to prevent cracking and to im-prove the surface smoothness of the films. The solution concentration was kept 0.7 M, pH around 4.5, and water was added 4 times of the theoretically required amount for hydrolysis. By dip-coating with a withdrawal speed of 10 cm/min, PZT films were prepared on slide glass substrates for heating under 600 °C, on silica glass substrates for heating above 550 °C, and on $Pt/Ti/SiO_2/Si$ for all experimental heating temperatures. In the preparation of multilayer films, each dip-coating and heating process was repeated. In order to avoid cracks of the films, TiO_2 was dip-coated onto glass substrates as barrier layer located between substrate and films. Dip-coated TiO_2 films were prepared by hydrolysis of $Ti(iso\text{-}OC_3H_7)_4$ in normal propa-nol solution using HCl as a catalyst, and were heat-treated at temperature up to 900 °C. The films were characterized by X-ray diffraction and SEM. The loss of the residual organics, formation of chelate and metal-oxygen bonds were followed using FTIR spectroscopy. IR absorption spectra were obtained for the solutions by placing them between glass KRS-5 disks and for the gel derived powders by mixing them with crystal KBr and then disks formatted. The chemical composi-tion of the film was determined by XPS, using Mg k_α X-ray radia-tion at room temperature in a vacuum range of $5x10^{-3}$ Pa. The dielectric constant measurements were done using an LCR meter at frequency 1 kHz in the temperature range of 25 to 400 °C. In this case, the films were dip-coated onto $Pt/Ti/SiO_2/Si$ substrates. This procedure was repeated 9 times to obtained thick films, and gold was sputtered on the films as top electrodes. The 2-terminal arrangement was employed.

RESULTS

FTIR analysis

The bands around 1500 cm^{-1} is due to acetate ligands [17] for zirconium tetra-n-butox-ide 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(COO) [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 residu-al 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 diffrac-tion 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 diffrac-tion. The relative amount (mol%) of perovskite phase could be calculated from [19].

Percent Perovskite =

$$I_{perov}/(I_{perov}+I_{pyro}) \text{ X } 100 \quad (1)$$

where I_{perov} and I_{pyro} are the intensities of the mayor 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 perochlore phase appear-ed 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.

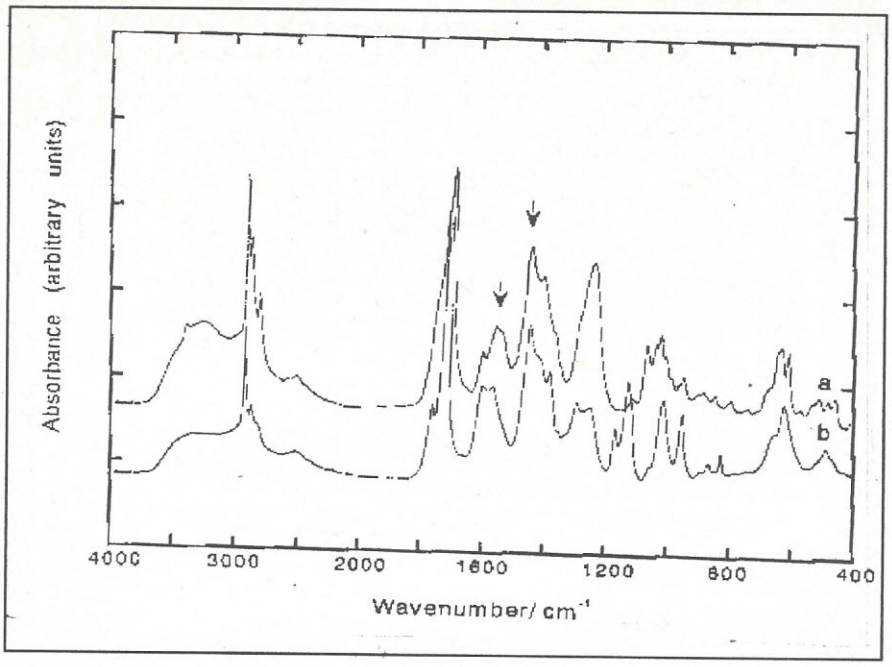

Figure 1. Infrared spectra of (a) $Zr(n\text{-}OC\ H)_4$, (b) Ti(i-OCH)4 in acetic acid.

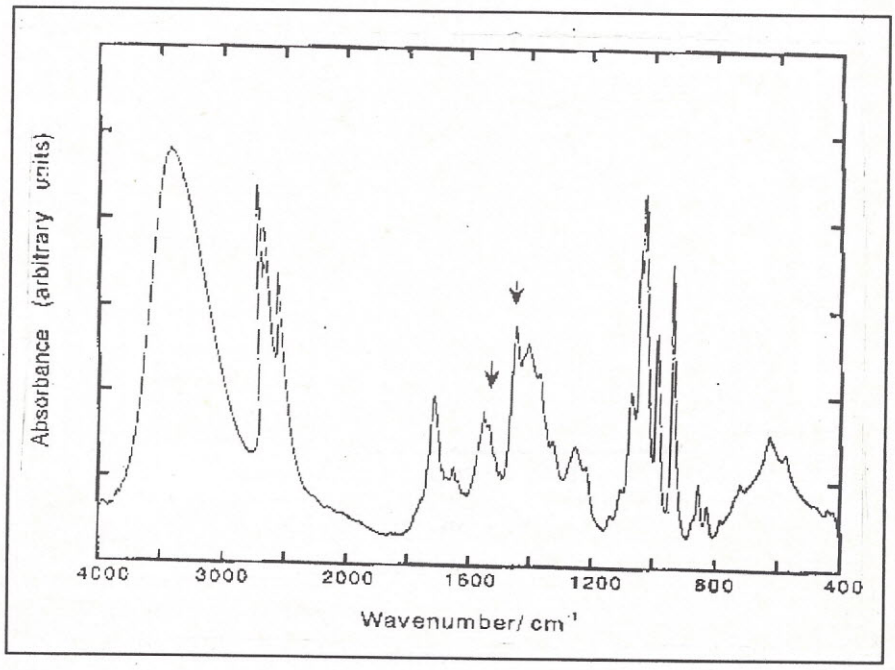

Figure 2. Infrared spectra of PZT sol after aging at room temperature for several days.

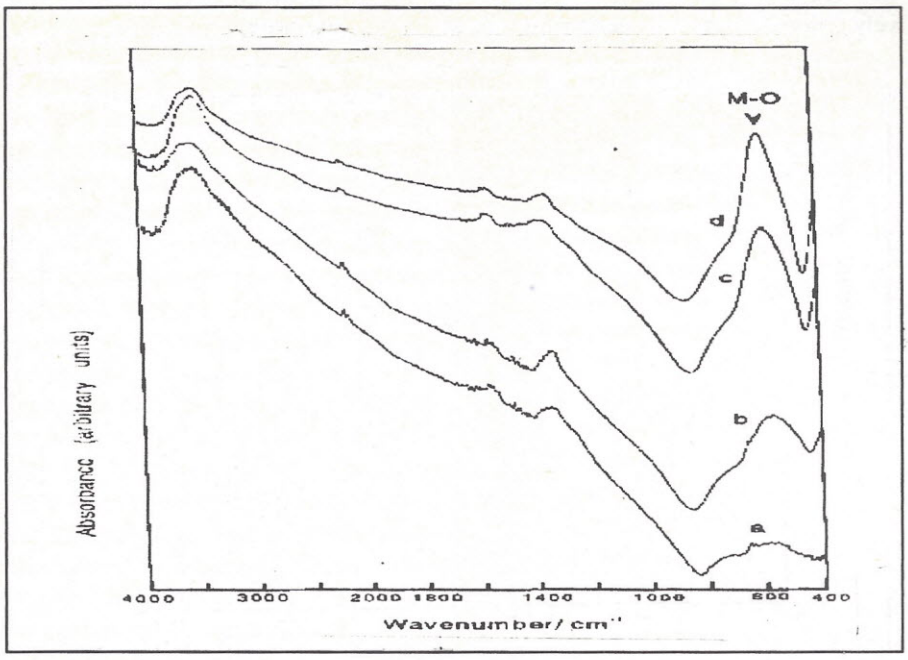

Figure 3. Infrared spectra of PZT gel derived powders at various heating tempera-tures : (a) 450 °C, (b) 500 °C, (c) 550 °C and (d) 600 °C.

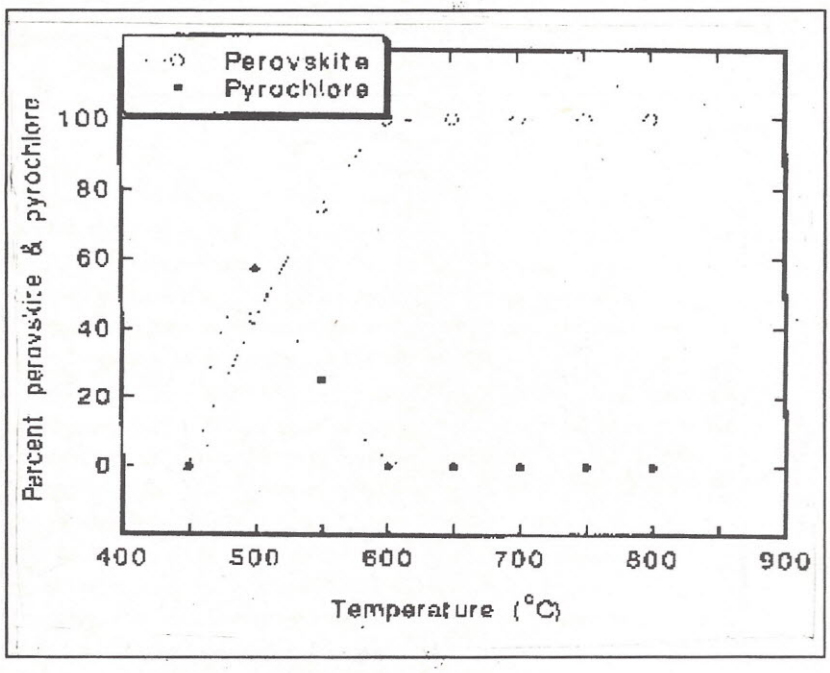

Figure 4. Percentage of perovskite and pyrochlore phase of PZT coated films on TiO_2/SiO_2 vs heating temperatures.

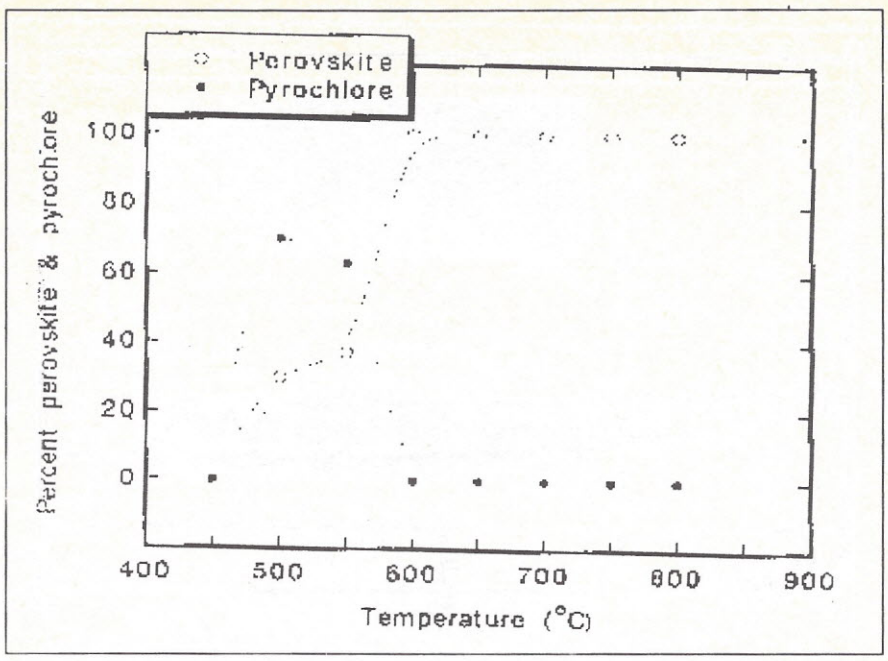

Figure 5. Percentage of perovskite and pyro-chlore phase of PZT coated films on $Pt/Ti/SiO_2/Si$ vs heating temperatures.

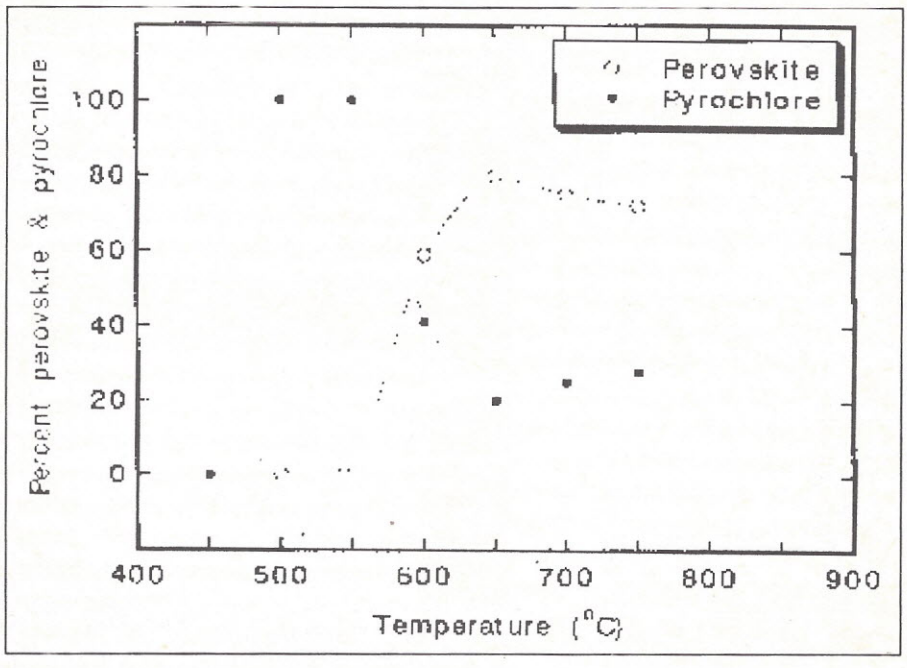

Figure 6. Percentage of perovskite and pyro-chlore phase PZT coated films on SiO_2 vs temperatures heating.

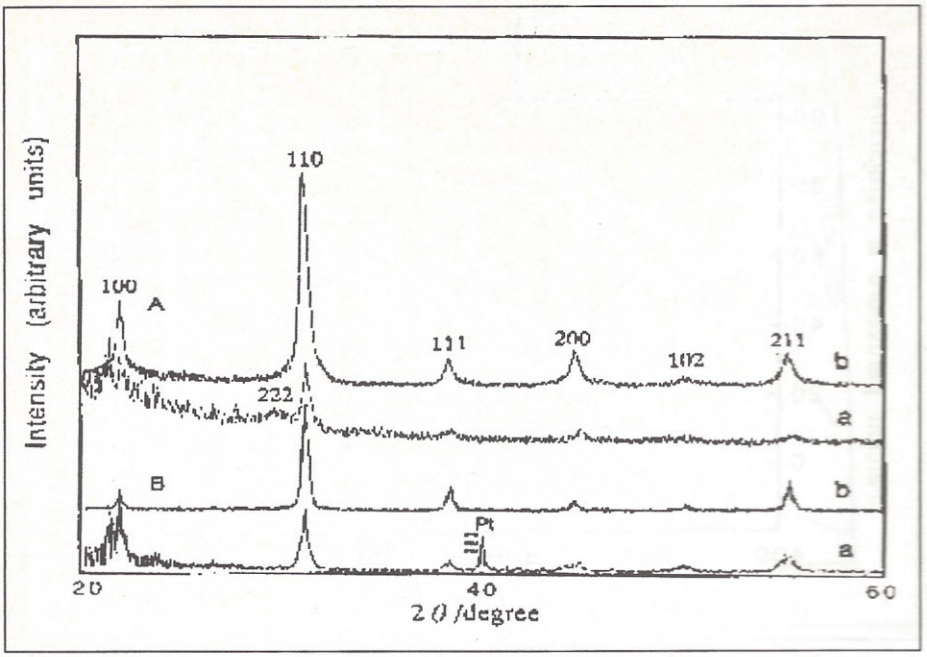

Figure 7. X-ray diffraction patterns of the single (a) and triple (b) PZT coated films on (A) TiO_2/SiO_2 , (B) $Pt/Ti/SiO_2$ /Si substrates after heating at 600 °C for 30 min.

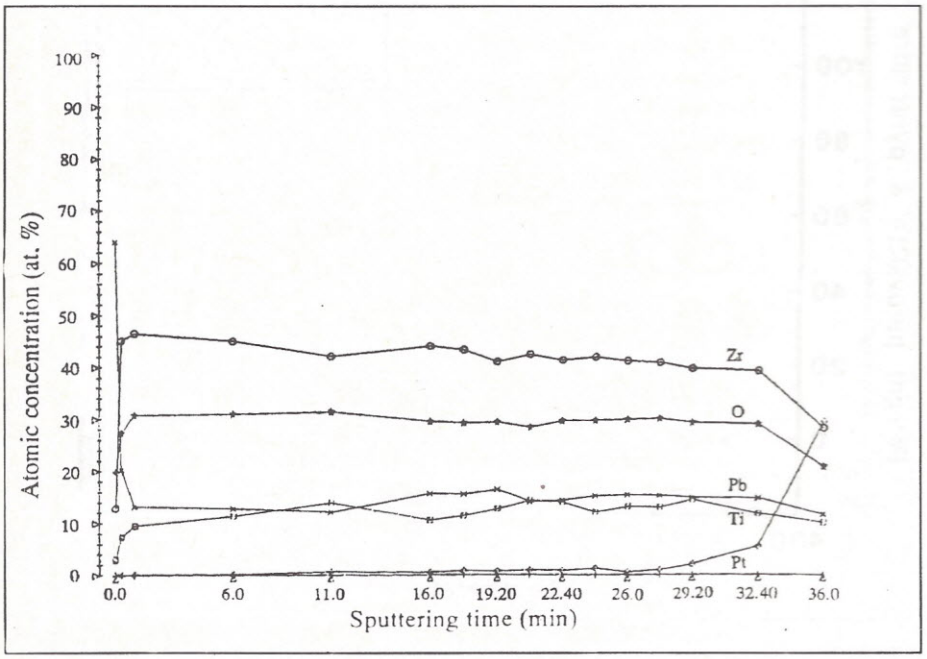

Figure 8. XPS depth profile of oriented 3 time dip-coated PZT film, crystallized at 600 °C for 30 min on a $Pt/Ti/SiO_2/Si$ substrate.

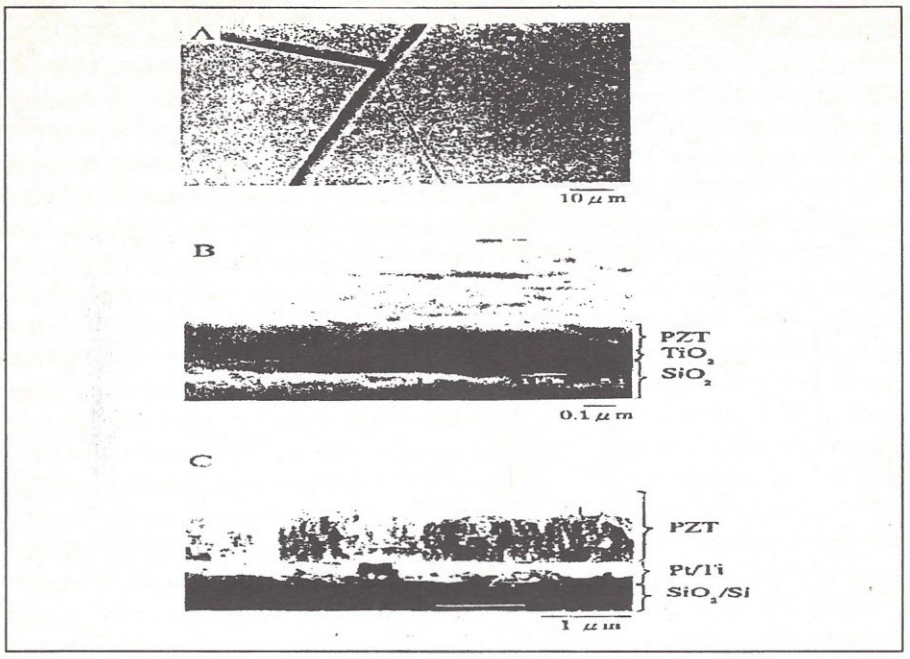

Figure 9. SEM image of the PZT films coated (A) 3 times on SiO_2 , (B) 3 times on TiO_2/SiO_2 and (C) 9 times on $Pt/Ti/SiO_2/Si$, after heating at 600°C for 30 min. (B and C is cross section)

Fig. 7A and 7B shows the x-ray diffraction patterns of the single coated films and the triple coated films on TiO_2/SiO_2 and $Pt/Ti/SiO_2/Si$ substrates, respectively. The XRD pattern of the single coated films on $Pt/Ti/SiO_2$/ Si shows only a perovskite phase. However the single coated films on TiO_2/SiO_2 shows perov-skite and pyrochlore phase.

Fig. 8 shows the depth profiles of an XPS for 3 times dip-coated PZT film (film thickness about 0.6 μm) crystallized at 600 °C on $Pt/Ti/SiO_2/Si$ substrate. When it was sputtered for 1 min (depth film about 0.02 μm) the Pb decreased drastically. This was not due to a lot of Pb content on the films surface, but because Pb was easily evaporated when sputtering hap-pened (20). Minor Pt diffusion into the PZT film during 26 min sputtering (depth film about 0.5 μm) was observed. The constant distribution of Pb, Zr and Ti after more than 1 min. sputtering confirmed the homogeneity.

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.

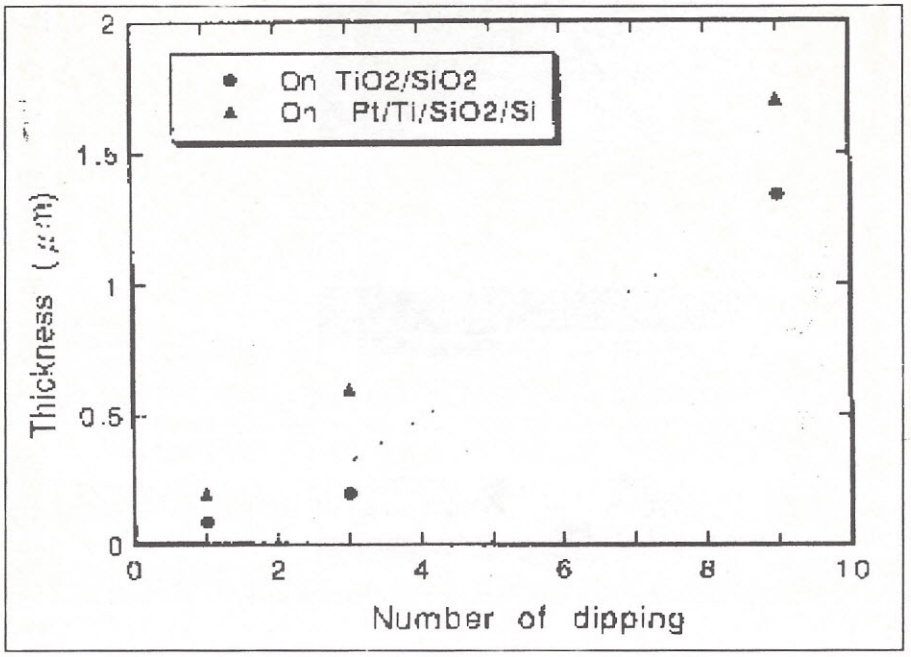

Figure 10. Films thickness vs number of dipping of PZT coated films on TiO_2/SiO_2 , and $Pt/Ti/SiO_2/Si$ substrates, after heating at 600°C.

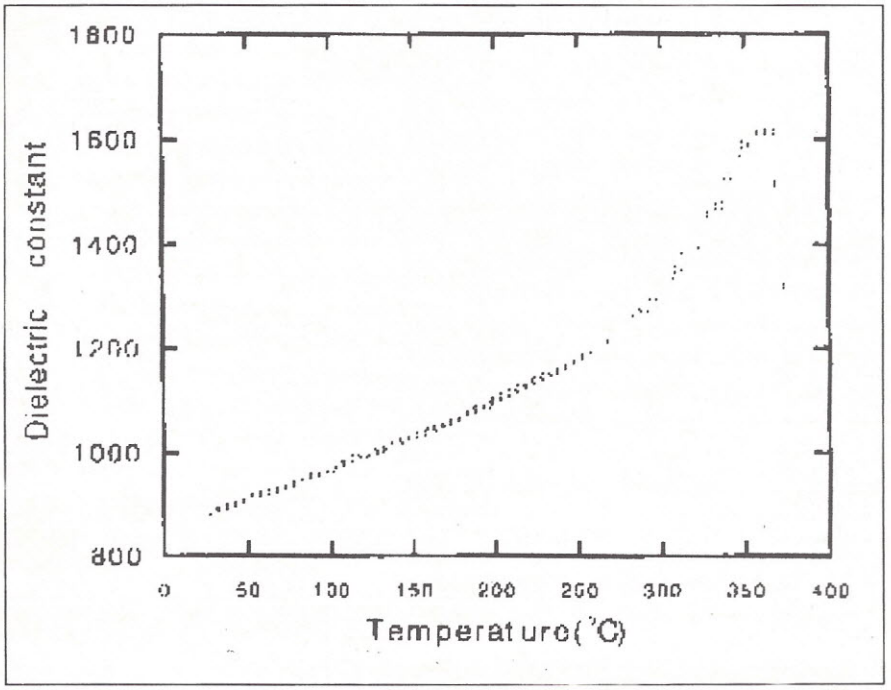

Figure 11. Dielectric constant vs temperature of PZT film after heating at 600 °C.

DISCUSSION

The presence of acetic acid effected the acetate anion ($(ac)^-$) 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 $\Delta\nu$ (COO^-) between the $\Delta\nu$ $(COO^-)_{asym}$ and the $\Delta\nu$ $(COO^-)_{sym}$ 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 cm^{-1}) suggests that CH_3COO^- acts as a bidentate ligand [22]. Two pairs of absorption peaks, those are : at 1558 and 1456 cm^{-1} for $Zr(O\text{-}nBut)_4$ in acetic acid(Fig. 1a) and at 1561 and 1451cm^{-1} for Ti $(O\text{-}iPr)_4$ in acetic acid (Fig.1, arrows) are ν $(COO^-)_{asym}$ and $\nu(COO^-)_{sym}$, respectively. All of those peaks showed $\Delta\nu$ <130 cm^{-1} which suggested that bidentate chelating occurred. The PZT sol showed that a pair of absorption at 1557 and 1457 cm^{-1} (arrows) are $\nu(COO^-)_{asym}$ and $\nu(COO^-)_{sym}$, respectively (Fig. 2). It indicated that band of COO^- with coordinate to metals become chelated solution. The band around 600 cm^{-1} in Figure 3 indicates the metal-oxygen bonding of Ti-O and Zr-O [22]. The crystalliza-tion behavior of PZT indicate that single perov-skite 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 have columnar structure (Fig. 9C). While each coated layer crystallizes during heating (Fig.7B), no boundary between these layers can be observed. These results indicate that the coated film crys-tallizes from the surface of the underlying film. The grain size of single perovskite phase coated films on Pt/Ti/SiO_2/Si is about 3 time smaller than that of coated films on TiO_2/SiO_2 , as indi-cated by the crystallographi c and d-spacings matching of (111) plane of polycrys-talline PZT to Pt (111), so there is more direct nucleation on (111) plane of platinum than on the TiO_2/SiO_2 substrate.

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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