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Compositional control of $PbTiO_3$ thin films by plasma enhanced metalorganic chemical vapor deposition

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$PbTiO_3$ thin films on the Si substrates were prepared by plasma enhanced chemical vapor deposition (PECVD) using $Ti(O\text{-}i\text{-}C_3H_7)_4$, $Pb(C_2H_5)_4$, and oxygen. The composition of PECVD $PbTiO_3$ thin films was intensively influenced by the input flow rate ratio of precursors while it was independent of the deposition temperatures. As-deposited PECVD $PbTiO_3$ thin film showed a uniform distribution of the Pb, Ti, and C component throughout the bulk of film. When an annealing process was performed at 750 °C under the O_2 ambient for 1 h, the Pb/(Pb+Ti) ratio of thin films was reduced from 0.567 to 0.509.

Ferroelectric materials such as $PbTiO_3$, $Pb(Zr_xTi_{(1-x)})O_3$, and La-doped $Pb(Zr_xTi_{1-x})O_3$ have been applied to many useful electronic and optical devices utilizing their excellent dielectric, piezoelectric, and optical properties. High quality ferroelectric films with reproducible ferroelectric properties should be required for fabrication of these application devices. Sputtering,[1] chemical vapor deposition (CVD),[2-4] sol-gel,[5] and laser ablation[6,7] have been studied as the deposition methods for ferroelectric thin films. Low pressure, metalorganic, and plasma enhanced chemical vapor deposition (LPCVD, MOCVD, and PECVD) methods are now developing because preliminary results are very promising due to high deposition rates, pinhole-free films, and stoichiometry control. Among these, plasma enhanced chemical vapor deposition (PECVD) of ferroelectric thin films using metalorganic precursors have been scarcely reported in spite of its potential usefulness.

Reproducible fabrication of stoichiometric ferroelectric thin films such as $PbTiO_3$ is difficult due to the high volatility of PbO with respect to TiO_2. The stoichiometry control of $PbTiO_3$ thin films is very important in that the crystal structure of $PbTiO_3$ thin films is changed from the pyrochlore phase, to a perovskite one, and to a PbO phase subsequently with increasing Pb/Ti atomic ratio.[8] Therefore, the composition control of thin films should be considered as a matter of primary importance. In this letter, we report the compositional control of novel PECVD $PbTiO_3$ thin films.

$PbTiO_3$ thin films on Si substrates were deposited by PECVD using $Ti(O\text{-}i\text{-}C_3H_7)_4$ (TTIP, 5N purity), $Pb(C_2H_5)_4$ (TEL, 5N purity), and oxygen. The PECVD apparatus mainly consisted of a source delivery system with bubblers for the metalorganic precursors, a vacuum system and cold-wall reaction chamber equipped with parallel electrodes. The bubblers for TTIP and TEL were controlled to 40 and 23 °C, respectively. Vapors of the metalorganic precursors were carried out by argon with 5N purity through the electropolished stainless steel tubing heated up to 70 °C to prevent the condensation of TTIP vapor during transfer. The vapors and oxygen were mixed before flowing into the reaction chamber. Gas mixtures were distributed through the upper electrode having a shower head type structure. The total flow rate of carrier gas was 80 sccm and oxygen flow rate was 8 sccm. The chamber pressure was 300 mTorr and substrate temperature was fixed at 250 °C unless otherwise indicated in the text. rf power of 20 W at 13.56 MHz was delivered to the upper electrode.

The susceptor electrode was heated with a shell-shaped resistive heating element with a PID controller prior to the deposition process. *p*-type Si substrates. (100) oriented, 4–5 Ω cm, were cleaned in a hydrogen-peroxide-sulphuric acid mixture, dipped in hydrofluoric acid, rinsed in deionized water, and blown with nitrogen sequentially. Post-deposition annealing of PECVD $PbTiO_3$ thin films was performed using a horizontal furnace in the range of temperature between 450 and 750 °C under O_2 ambient for 1 h. Other experimental details are described elsewhere.[9]

The elemental component distribution of as-deposited PECVD $PbTiO_3$ thin films using an input flow rate ratio of precursors, $V_{TEL}/(V_{TEL}+V_{TTIP})$, of 0.038 was obtained using Auger electron spectroscopy (AES, Perkin–Elmer PHI 610) as shown in Fig. 1. Pb, Ti, O, and C elements were detected by using the AES spectrum as shown in Fig. 1(a). Carbon as a contaminant originated from the metalorganic precursors of TEL and TTIP. The AES signals for each element were located at 93 eV for Pb ($N_{6,7}O_{4,5}O_{4,5}$) 383 eV for Ti ($L_3M_{2,3}M_{2,3}$), 417 eV for Ti ($L_3M_{2,3}M_{4,5}$), 510 eV for O ($KL_{2,3}L_{2,3}$), and 272 eV for C. The depth profile as shown in Fig. 1(b) yields a uniform distribution of the components throughout the bulk of the film. Calculating composition using formalism[10] with relative sensitivity factors gives a Pb/(Pb+Ti) ratio of about 0.6 which is in agreement with the result of energy dispersive x-ray (EDX) measurements. The composition of $PbTiO_3$ thin films was usually analyzed using EDX.

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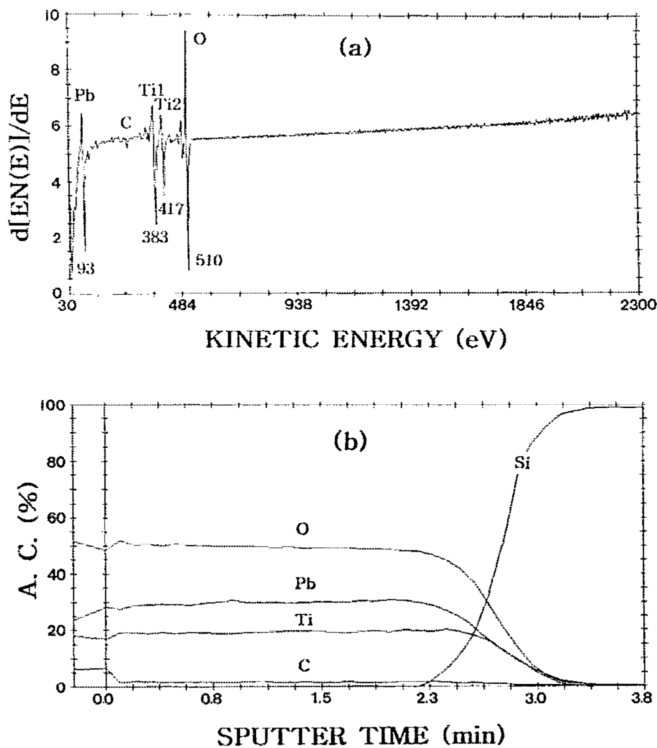

FIG. 1. (a) Surface survey AES spectrum and (b) depth profile spectrum of as-deposited PECVD $PbTiO_3$ thin film on silicon substrate.

Figure 2 shows the compositional variations of PECVD $PbTiO_3$ thin films as a function of the $V_{TEL}/(V_{TEL}+V_{TTIP})$ ratio. The composition ratio, Pb/(Pb+Ti), for the thin film deposited at a $V_{TEL}/(V_{TEL}+V_{TTIP})$ ratio of 0.034 was equal to 0.5. Pb content rapidly increases until the $V_{TEL}/(V_{TEL}+V_{TTIP})$ ratio of 0.23. The bonding strengths of Pb-C_2H_5 of TEL and Ti-O of TTIP are 230 kJ/mol[11] and 440 kJ/mol,[12] respectively, indicating that TEL can be dissociated more easily than the TTIP in a plasma. Because PECVD is a thermally nonequilibrium process and the degree of participation of reactive species into the thin film is controlled by the dissociation rate of reactants, it is believed that Pb species of TEL have more opportunities to participate in the formation of PECVD $PbTiO_3$ films than Ti species. On the contrary, it has been known that TiO_2 was produced by the pyrolysis of TTIP and PbO by the oxidation of TEL for the formation of $PbTiO_3$ by LPCVD.[3] The apparent activation energy for the surface reaction controlling step was estimated as 53.1 kJ/mol for TTIP pyrolysis and 77.8 kJ/mol for TEL oxidation. Because pyrolysis of TTIP can take place more easily than oxidation of TEL in LPCVD, participation of Ti species in the LPCVD of $PbTiO_3$ thin films is preferable.

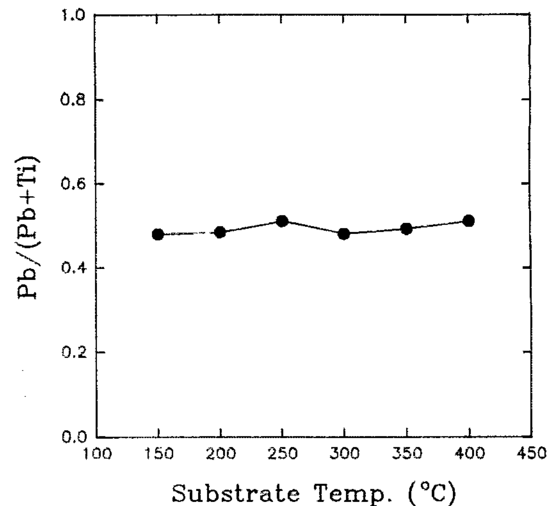

FIG. 3. Compositions of PECVD $PbTiO_3$ thin films as a function of substrate temperatures. ($V_{TEL}/(V_{TEL}+V_{TTIP})$ ratio=0.035, chamber pressure=300 mTorr, total gas flow rate=88 sccm and rf power=20 W).

Figure 3 shows the composition of PECVD $PbTiO_3$

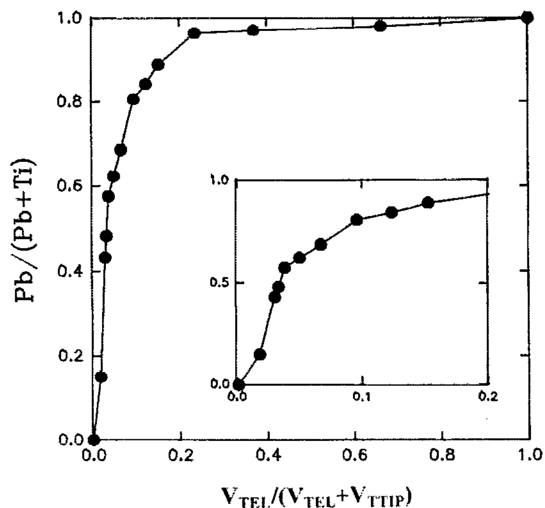

FIG. 2. Compositions of PECVD $PbTiO_3$ thin films as a function of precursors input flow ratio. (Chamber pressure=300 mTorr, substrate temperature=250 °C, total gas flow rate=88 sccm and rf power=20 W).

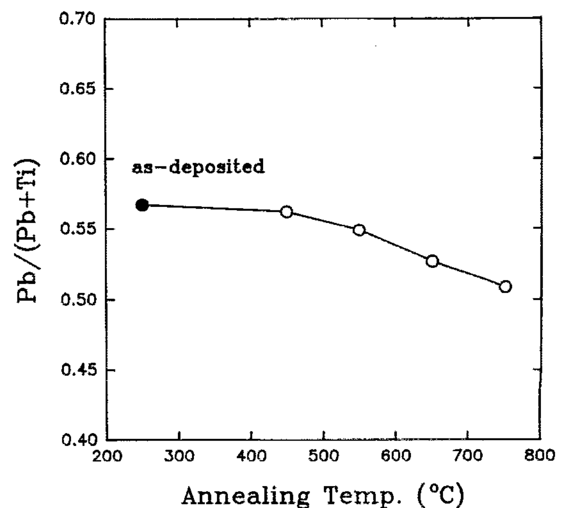

FIG. 4. The dependence of compositions of PECVD $PbTiO_3$ thin film on annealing temperature. (●) and (○) show the composition of as-deposited and annealed PECVD $PbTiO_3$ thin films, respectively. Annealing was performed under O_2 ambient for 1 h.

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thin films as a function of substrate temperatures. $V_{TEL}/(V_{TEL}+V_{TTIP})$ ratio was kept constant at 0.035 while substrate temperature was varied in the range between 150 and 400 °C. The composition of thin films was nearly independent of the substrate temperature.

The composition of $PbTiO_3$ thin films subjected to post-deposition annealing varied as shown in Fig. 4. Annealing was performed in the range of temperature between 450 and 750 °C under O_2 ambient for 1 h. The Pb/(Pb+Ti) ratio of an as-deposited $PbTiO_3$ thin film was reduced from 0.567 to 0.509 after annealing at 750 °C due to the high volatility of Pb compounds at high temperature.[7]

In summary, $PbTiO_3$ thin films on Si substrates were deposited by PECVD using TTIP, TEL, and oxygen and had the uniform distribution of Pb, Ti, and O elements throughout the bulk of the film. The composition of $PbTiO_3$ thin films was highly influenced by the input flow ratio of precursors. The composition of PECVD $PbTiO_3$ thin films was nearly independent of the deposition temperature. Annealing at 750 °C under O_2 ambient for 1 h reduced the Pb/(Pb+Ti) ratio of $PbTiO_3$ thin film from 0.567 to 0.509.

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