

Low Temperature CVD of $Pb(Zr,Ti)O_3$ Using $Pb(tmhd)_2$, $Zr(dmae)_4$, and $Ti(dmae)_4$

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Pb(Zr,Ti)O₃ (PZT) thin films were deposited at low temperatures by direct liquid injection metallorganic chemical vapor deposition (MOCVD) process using Pb 2,2,6,6,-tetramethyl 3,5-heptanedionate $(tmhd)_2$, Zr dimethyl aminoethoxide $(dmae)_4$, and Ti(dmae)₄, and Ti(dmae)₄, and Ti(dmae)₄ were found to be less sensitive to moisture and air but their dissociation temperature was about the same as alkoxides. Two separate solution of Pb(tmhd)₂ and of Zr(dmae)₄ and Ti(dmae)₄ were used and the growth rate of PZT films was around 11 nm/min at substrate temperatures of 380-440°C. Because decomposition temperatures of Pb(tmhd)₂, Ti(dmae)₄ are in the same range, control of the film composition was comparatively easy. PZT films deposited below 450°C had negligible carbon and nitrogen content. Pure perovskite PZT films were obtained at temperatures as low as 440°C on Pt/Ti/SiO₂/Si substrate and 425°C on Ir/Ti/SiO₂/Si substrate was 21 μ C/cm² and the leakage current density at 100 kV/cm was less than 10⁻⁶ A/cm².

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Lead zirconate titanate, Pb(Zr,Ti)O₂ (PZT) thin films were deposited by metallorganic chemical vapor deposition (MOCVD) us-Pb(2,2,6,6,-tetramethyl 3,5-heptanedionate)₂ $(\text{tmhd})_2$. ing $Zr(dimethyl aminoethoxide)_4$ (dmae)₄, and Ti(dmae)₄. PZT film has been investigated for the application in nonvolatile ferroelectric random access memory (NVFeRAM), dynamic random access memory (DRAM), electro-optic devices, and microactuators because of its superior ferroelectricity and piezoelectricity.¹ In highdensity NVFeRAM, three-dimensional (3-D) capacitor cells will be required and continued downscaling dictates the needs to shift to a deposition method such as MOCVD (metallorganic chemical deposition) with better step coverage. MOCVD is one of the most important techniques for practical applications because of its conformal coverage, high deposition rate, large area uniformity and high throughput. Also, with the introduction of a direct liquid injection (DLI) system, there is a great improvement in the delivery of precursors.

In the DLI-MOCVD process used in this study, precursors are dissolved in a solvent and a controlled amount of the solution is injected into the flash evaporator. Evaporated gas mixture is introduced into the deposition chamber and film is deposited on the substrate as in an ordinary CVD process. It is an attractive method to inject exact amount of solid precursors and schematic diagram of the DLI-MOCVD apparatus was shown elsewhere.^{2,3} Vaporization characteristics of the precursor is important in DLI-MOCVD as in other CVD process and also the solubility of the precursor in a solvent and the stability of the solution is important.

There is much interest in low temperature MOCVD process to realize good surface roughness, good step coverage, and a low chemical interaction with a substrate. Low temperature fabrications of PZT films using a $PbTiO_3$ seed⁴ and a pulse-CVD⁵ have already been reported.

Various precursors such as metal alkoxide, β -diketonates, fluorinated β -diketonates, and anhydrous nitrates have been used for the MOCVD of TiO₂ and ZrO₂. But there are few precursors that satisfy both high reactivity at low temperature and long-term stability in the solution-based process. Though zirconium tetrakis(t-butoxide) [Zr(O^tBu)₄] and titanium tetrakis(i-propoxide) [Ti(OⁱPr)₄] are effective in low temperature growth, they are inadequate at solutionbased DLI process due to their high sensitivity to air and moisture. On the other hand, zirconium tetrakis [Zr(tmhd)₄], a homoleptic zirconium β -diketonate, or $[Zr(tmhd)(O^iPr)_3]^{6,7}$ has high thermal stability and allows the optimized growth of ZrO_2 but is not suitable for the low temperature CVD processing.

In order to lower the growth temperature of PZT thin films in DLI-MOCVD processes, a new approach was pursued by using new precursors having donor-functionalized alkoxy ligand such as dimethylaminoethoxide (dmae). In the previous study, titanium tetrakis dmae [Ti(dmae)₄]⁸ and Zr(dmae)₄ (zirconium tetrakis dmae)⁹ were used to deposit metal oxides such as (Ba,Sr)TiO₃ and ZrO₂ using DLI-MOCVD. Since the dmae ligand has an additional Lewis base site that is able to form chelate rings, $M(dmae)_4$ (M = Zr, Ti) is more stable to air and moisture than Ti(OⁱPr)₄ and Zr(OⁱBu)₄. due to their more saturated metal center, and are more favorable to solution-based processes.

In this study, low temperature MOCVD process for PZT films with lead bis(tmhd) [Pb(tmhd)₂], Ti(dmae)₄, and Zr(dmae)₄, was studied. It was shown that the newly adopted PZT precursors were effective in lowering the fabrication temperature of PZT films in the solution-based DLI system.

Experimental

Preparation and characterization of $Ti(dmae)_4$ and $Zr(dmae)_4$.—Zr(dmae)_4 was synthesized with zirconium tetradiethylamine [Zr(NEt₂)₄] and dimethyl-aminoethanol. Zr(NEt₂)₄ (24.68 g, 65 mmol) was added to 150 mL of dry toluene and N,Ndimethylaminoethanol (26 mL, 260 mmol) was then added slowly to that solution. The mixture was refluxed for 20 h and then cooled. The solvent was removed under a reduced pressure to obtain Zr(dmae)₄ as a viscous liquid (yield > 90%). ¹H nuclear magnetic resonance (NMR, C₆D₆, 300 MHz): δ 4.35 (s, OCH₂, 8H), 2.61 (s, NCH₂, 8H), 2.30 (s, CH₃, 24H), ¹³C NMR (C₆D₆, 300 MHz): δ 68.11 (s, OCH₂), 64.95 (s, NCH₂), 47.34 (s, CH₃).

Ti(dmae)₄ was synthesized with titanium (NEt₂)₄ [Ti(NEt₂)₄] and dimethyl-aminoethanol. Ti(NEt₂)₄ (21.87 g, 65 mmol) was added to 150 ml of dry hexane and N,N-dimethylaminoethanol (26 ml, 260 mmol) was then added slowly to that solution. The mixture was refluxed for 20 h and then cooled. The solvent was removed under a reduced pressure to obtain Ti(dmae)₄ as a viscous liquid (yield > 90%). ¹H NMR (C₆D₆, 300 MHz): δ 4.55 (s, CH₂, 8H), 2.58 (s, CH₂, 8H), 2.23 (s, CH₃, 24H).

To investigate the stability of the precursor solution with respect to shelf time, ¹H NMR (300 MHz Varian, Unity Plus) studies were performed. Precursor solutions were made in a glove box with C_6D_6 solvent. NMR tubes, filled with solution sample, were sealed to

C516

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Table I. Parameters for the deposition of PZT films by DLI-MOCVD.

Bottom electrode	Pt(150 nm)/TiO ₂ (20 nm)/SiO ₂ (300 nm)/Si
	Ir(150 nm)/Ti(5 nm)/SiO ₂ (200 nm)/Si
Precursors	$Pb(tmhd)_2$, $Ti(dmae)_4$, $Zr(dmae)_4$
Substrate temperature	300-480°C
Deposition pressure	1.4 Torr
Deposition time	5-30 min
Gas flow rate	Ar 50 sccm ^a (vaporizer)
	Ar 200 sccm, O ₂ 300 sccm (under vaporizer)
Solvent	<i>n</i> -octane
Vaporizer pressure	7 Torr
Vaporizer temperature	240°C

^a Sccm is standard cubic centimeters per minute.

prevent oxygen and moisture penetration and were stored at room temperature. There was no precipitant in all precursor solutions for up to 10 days.

MOCVD of PZT thin films.—A cold wall, low pressure DLI CVD reactor with solution delivery system was fabricated. A schematic diagram of the MOCVD apparatus used in this study was shown elsewhere.^{2,3} PZT thin films were prepared using Pb(tmhd)₂, Ti(dmae)₄, Zr(dmae)₄, and O₂ as source materials. The total pressure in the reactor was adjusted to 1.4 Torr. PZT films were deposited on a Pt/TiO₂/SiO₂/Si and Ir/Ti/SiO₂/Si layered substrate. The vaporizer temperature and the feed line temperature after the vaporizer were held at 240°C. The experimental conditions of PZT preparation are summarized in Table I.

The composition of the film was analyzed using inductively coupled plasma-atomic emission spectrometry (ICP-AES, Jobin-Yvon, JY 38 plus) and the deposition rate was measured by scanning electron microscopy (SEM, Hitachi S-4200). The surface morphology and roughness were investigated using SEM, (Hitachi S-4200) and atomic force microscopy (AFM, PSIA XE-100). The crystal structure was analyzed by X-ray diffractometer (XRD, MAC Science M18XHF) with Cu Kα radiation operating at 30 kV and 40 mA and the depth profile and film composition were investigated by X-ray photoelectron spectroscopy (XPS, PHI 5400 ESCA) with Al Ka radiation. For electrical characterizations, the metal-insulatormetal (MIM) capacitors were fabricated and platinum dot electrode was deposited by the thermal evaporation through a metallic mask. Polarization-electric field (P-E) and leakage current-voltage (I-V) characteristics of MIM structure were measured using an RT6000 ferroelectric tester (Radiant Technologies) and HP4140B semiconductor parameter analyzer, respectively.

Results and Discussion

Characterization of PZT precursors.—Dmae group precursors are slightly viscous liquid at room temperature. The ¹H NMR and ¹³C NMR spectra of $M(dmae)_4$ show three distinct proton and carbon environments. There is no evidence in the ¹H and ¹³C NMR spectra to suggests a presence of dimeric species of $M(dmae)_4$. Similar results supporting that $M(dmae)_4$ exists as a monomeric state were obtained in the previous studies on the mass spectra of $M(dmae)_4$. ^{8,9} Only mass peaks lower than the parent molecular mass of Ti(dmae)_4 and Zr(dmae)_4 were observed. Consequently, $M(dmae)_4$ seems to exist as a monomer in solution and in gas phase without forming aggregated species such as dimer and trimer which may deteriorate vaporization efficiency of precursor solutions.

In the liquid delivery system, one of the key problems is the solution stability. For example, $Zr(O^{i}Pr)_{2}(tmhd)_{2}$, which has two different ligands, disproportionates to $Zr(O^{i}Pr)_{4}$, $Zr_{2}(O^{i}Pr)_{6}(tmhd)_{2}$ and $Zr(tmhd)_{4}$ on dissolution.¹⁰ Also, $Ti(O^{i}Pr)_{4}$ and $Zr(O^{i}Bu)_{4}$ are not suitable for DLI process due to their low solution stability. Stability of M(dmae)_4 solutions with respect to

storage time was studied using ¹H NMR. The solution of Ti(dmae)₄ and C_6D_6 and that of Zr(dmae)₄ and C_6D_6 showed no significant change in chemical shift ($\delta = 4.56$, 2.58, and 2.24 ppm) for Ti(dmae)₄ and $\delta = 4.37$, 2.62, and 2.31 ppm for Zr(dmae)₄ and no precipitation even after ten days. These results indicate that M(dmae)₄ are stable enough in the solution state.

Further investigation was performed with the single mixture solution of Pb(tmhd)₂, Ti(dmae)₄, and Zr(dmae)₄ to find out the precursor interaction in the mixed solution. From NMR analysis, it was found out that there was a serious cross interactions such as ligand exchange reactions between Pb precursors and M(dmae)₄. Thus one should use a solution of Pb precursor and a solution of M(dmae)₄ mixture injected separately into the evaporator.

To investigate the oxidation temperature of the precursors, differential scanning calorimetry (DSC) measurements were performed at a heating rate of 10° C/min. Initial decomposition temperatures are 270° C for Pb(tmhd)₂ and Ti(dmae)₄ and 310° C for Zr(dmae)₄. Note that the major exothermic peak of Zr(tmhd)₄ appears at 410° C. These results suggest that precursors in this study are oxidized at lower temperature. The decomposition temperature of Pb(tmhd)₂ on a heated surface is known to be 350° C at vacuum and 260° C at the presence of oxygen.¹¹ It seems that the increased saturation of the metal center with the introduction of the dmae ligand is not related closely to the oxidation temperature of Ti and Zr precursor. Ti(dmae)₄ and Zr(dmae)₄ have low oxidation temperatures like simple metal alkoxides such as Ti(OⁱPr)₄ and Zr(OⁱBu)₄.

MOCVD of PbO, TiO₂, ZrO₂ and PZT films.—The PbO, TiO₂, ZrO₂, and PZT thin films were deposited on Pt/TiO₂/SiO₂/Si substrate using flash-vaporized metalorganic precursor solutions with $Pb(tmhd)_2$, $Ti(dmae)_4$, and $Zr(dmae)_4$ dissolved in an *n*-octane solvent (bp = 126° C). Prior to PZT deposition, the growth rate of single oxide with each precursor was studied as a function the substrate temperature. For compariof son, $Pb(methoxytetramethylheptanedionate)_2[Pb(methd)_2]$, $Ti(methylpentanedioxy)(methd)_{2}[Ti(mpd)(methd_{2})]$ and $Zr(methd)_{4}$ were also used to deposit each single oxide. Methd compound of barium and strontium were used to deposited barium strontium titanate films.² Figure 1 shows deposition rate of PbO, ZrO₂, and TiO₂ films as a function of the substrate temperature at a fixed vaporizer temperature of 240°C. As shown in Fig. 1a, the deposition rate of PbO shows a sharp increase reaching a maximum value at around 400°C and decrease at higher temperature. It was pointed out that the decrease of the growth rate at high temperature was due to the short residence time of Pb oxide molecules especially on Pt substrate.¹¹ The deposition characteristic of $Pb(tmhd)_2$ is similar to that of Pb(methd)₂. It seems that the modification of the tmhd ligand to the "lariat" method ligand does not influence significantly the decomposition temperature range of precursor molecules.

The deposition rate of ZrO₂ using Zr(dmae)₄ shows a high value of above 10 nm/min even at 375°C. The decrease of the growth rate at high temperatures above 450°C is probably due to the predecomposition of precursor molecules in the gas phase with oxygen.¹² The deposition rate with Zr(methd)₄ shows a lower value of 5 nm/min at 425°C and the maximum deposition rate was observed at 500°C. The deposition rate of TiO₂ using Ti(dmae)₄ is 12 nm/min even at 330°C and reaches a maximum value of 16 nm/min at 410°C while the deposition rate with Ti(mpd)(methd)₂ reaches a maximum value of 12 nm/min at 440°C. It is apparent that two dmae group precursors have high deposition rate at lower temperatures, which is consistent with DSC measurement. Also, Pb(tmhd)₂ shows adequate reactivity at low temperature. Thus M(dmae)₄ and Pb(tmhd)₂ are possible candidates for the low temperature (< 450°C) deposition of PZT.

To investigate optimum vaporizer temperature, the growth rate of PbO, TiO_2 , and ZrO_2 as a function of the vaporizer temperature was investigated at a fixed substrate temperature of 410°C. 0.05 M so-



Figure 1. Deposition rate of (a) PbO, (b) ZrO_2 , and (c) TiO_2 films as a function of the substrate temperature at a fixed vaporizer temperature of 240°C. 0.05 M solution was injected with a rate of 0.15 mL/min.

lution was injected at a rate of 0.15 mL/min. For the Ti precursor, the growth rate increased with increasing vaporizer temperature and the highest growth rate appeared at 240°C. For the Zr precursor, the highest growth rate appeared at 230°C. For Pb precursor, the growth rate remained constant apparently with vaporizer temperatures of



Figure 2. Pb/(Zr + Ti) and Zr/(Zr + Ti) concentration ratio in the PZT film as a function of $(A/B)_{solution} \cdot (A/B)_{solution}$ values are (a) 0.6, (b) 0.8, and (c) 1. Deposition temperature was 410°C.

200-260°C. We have selected a vaporizer temperature of 240°C for PZT depositions in this study.

PZT films were deposited using Pb(tmhd)₂, Ti(dmae)₄, and Zr(dmae)₄. To avoid chemical interaction in the mixed solution, we used two individual solutions, i.e., A site (=Pb) solution and B site (=Zr + Ti) solution. Three precursor solutions of 0.07 M (cation mole/liter) were prepared with *n*-octane solvent. Then, Ti(dmae)₄ and Zr(dmae)₄ precursor solutions were mixed to make B site solution having a particular molar ratio of Zr:Ti = 3:7 or 4:6.

Figure 2 shows A site to B site ratio in the films, $(A/B)_{\text{film}}$, and Zr to B site ratio in the films, $[Zr/(Zr + Ti)]_{\text{film}}$, as a function of the A site to B site ratio in solutions, $(A/B)_{\text{solution}}$. PZT films were deposited at 410°C. Because the total solution injection rate was fixed at 0.1 mL/min, an increase in the amount of A site solution was accompanied by a decrease in amount of B site solution. With increasing $(A/B)_{\text{solution}}$, $(A/B)_{\text{film}}$ increased linearly and $[Zr/(Zr + Ti)]_{\text{film}}$ slightly increased. We found there exists a linear response of $(A/B)_{\text{film}}$ to $(A/B)_{\text{solution}}$ at 410°C. Generally the "selfregulating phenomenon" that $(A/B)_{\text{film}}$ stays unchanged with the different $(A/B)_{\text{solution}}$, frequently appears at high temperatures above 550°C.¹² There is no self-regulating phenomenon in this study, because the volatilization of PbO is not significant at low



Figure 3. Pb/(Zr + Ti) and Zr/(Zr + Ti) concentration ratio in the PZT film as a function of the substrate temperature when $(A/B)_{solution}$ values are 0.6, 0.8, and 1.



Figure 4. XRD patterns of as-deposited PZT films as a function of the substrate temperature when $(A/B)_{\text{solution}} = 1$.

temperatures. Thus, various PZT films having different $(A/B)_{\text{film}}$ values can be prepared easily by adjusting the solution composition precisely at low temperature.

Further experiments were performed under different substrate temperatures when $(A/B)_{solution}$ are 0.6, 0.8, and 1 (Fig. 3). At temperatures between 340°C and 465°C, the $(A/B)_{film}$ shows a gradual increase reaching a maximum value at around 410°C and a gradual decrease at higher temperature in case of $(A/B)_{solution} = 0.8-1$. Practically, $(A/B)_{film}$ and $[Zr/(Zr + Ti)]_{film}$ are not varied much at temperatures between 375 and 440°C, which is probably due to the



Figure 5. XRD pattern of PZT film as a function of the annealing temperature. Films were deposited at 410° C with $(A/B)_{solution} = 1$.



Figure 6. XRD patterns of as-deposited and furnace annealed (700°C, 30 min, O_2 ambient) PZT/Pt films as a function of $(A/B)_{solution}$.

sufficient reactivity of three precursors at low temperatures. Based on Fig. 3, the required $(A/B)_{solution}$ is 0.8 to obtain 1.0 of $(A/B)_{film}$ at around 410°C. The growth rate of PZT films near stoichiometry is 11 nm/min. In the case of the Pb(tmhd)₂, Zr(tmhd)₄, and Ti(OⁱPr)₂(tmhd)₂ precursor set,¹² the difference between the $(A/B)_{film}$ and the $(A/B)_{solution}$ is large and the required $(A/B)_{solution}$ is below 0.5 to obtain stoichiometric PZT films at temperatures below 475°C. This means that more B site solution should be injected to compensate the high reactivity of Pb precursor due to the mismatch of thermal decomposition temperature of different precursors. With M(dmae)₄, we found that the difference between the $(A/B)_{film}$



Figure 7. XRD patterns of as-deposited and furnace annealed (700°C, 30 min, O_2 ambient) PZT/Ir films as a function of $(A/B)_{solution}$.



Figure 8. SEM images of PZT films deposited on Ir substrate with various $(A/B)_{\text{solution}}$. $(A/B)_{\text{solution}}$ values are (a) 0.7, (b) 0.8, and (c) 0.9.

and the $(A/B)_{\text{solution}}$ is 0.2 for 410°C and there exists a linear response of $(A/B)_{\text{film}}$ to $(A/B)_{\text{solution}}$. These results imply that chemical reactivity of three precursors matches well and the composition control can be achieved easily with changing $(A/B)_{\text{solution}}$.

Figure 4 shows XRD patterns of as-deposited PZT films as a function of the substrate temperature when $(A/B)_{\text{solution}} = 1$. Figure 5 shows XRD patterns of PZT films, deposited at 410°C with $(A/B)_{\text{solution}} = 1$, as a function of annealing temperature. For $(A/B)_{\text{solution}} = 0.6$, films show an amorphous phase below 410°C and only show a Pb-deficient pyrochlore phase at 440°C. For $(A/B)_{\text{solution}} = 1.0$, films show a perovskite phase with a strong Pt₅₋₇Pb intermetallic phase at 410°C [$(A/B)_{\text{film}} = 1.2$] and a pure perovskite phase at 440°C [$(A/B)_{\text{film}} = 1.1$]. We believe that the evolution of a Pt₅₋₇Pb intermetallic phase is closely related with



Figure 9. I-V characteristics of PZT films deposited on (a) Pt substrate and (b) Ir substrate with various $(A/B)_{\text{solution}}$ values. Thickness of PZT samples ranges from 320 to 330 nm.

substrate temperature and concentration of Pb species. In this study, the Pt₅₋₇Pb phase appeared at temperatures of 375-430°C when $(A/B)_{\rm film}$ exceeded 0.8. The Pt₅₋₇Pb intermetallic phase disappeared after 500°C annealing. Chen *et al.* reported that Pt₅₋₇Pb can provide template for the growth of (111)-oriented PZT.¹³ However, the Pt₅₋₇Pb phase, in this study, has no relation with (111) PZT probably due to the low substrate temperature. More studies on the phase evolutions of PZT films deposited at low temperature are required.

Further experiments were performed under narrower $(A/B)_{solution}$ range of 0.7-0.9 on different substrates $(Pt/TiO_2/SiO_2/Si \text{ and } Ir/Ti/SiO_2/Si)$ at a fixed substrate temperature of 425°C. The composition and the growth rate of PZT/Pt were similar to those of PZT/Ir. Also, the composition ratios in the PZT films $[(A/B)_{film}]$ are 0.83 for $(A/B)_{solution} = 0.7$, 1.0 for $(A/B)_{solution} = 0.8$ and 1.12 for $(A/B)_{solution} = 0.9$, respectively.

Figure 6 shows XRD patterns of as-deposited and furnace annealed (700°C, O_2) PZT/Pt films as a function of $(A/B)_{solution}$. The Pb-deficient PZT film $[(A/B)_{solution} = 0.7]$ shows a perovskite phase with traces of pyrochlore and Pt₅₋₇Pb. The pyrochlore phase was not removed after furnace annealing due to the lead deficiency. The stoichiometric PZT film shows mixed phases of perovskite, pyrochlore, and Pt₅₋₇Pb. Even though the film stoichiometry is satisfied to unity, the film shows mixed perovskite and second phase due to the low processing temperature. A pure perovskite PZT phase was obtained after annealing. The Pb-rich PZT film $[(A/B)_{solution}$



Figure 10. I-V characteristics of stoichiometric PZT thin films deposited on (a) Pt substrate and (b) Ir substrate with various annealing temperatures. Thickness of PZT samples ranges from 210 to 220 nm.

= 0.9] shows a perovskite phase and $Pt_{5-7}Pb$ with the trace of pyrochlore and shows single perovskite in annealed film.

XRD patterns of as-deposited and furnace-annealed PZT films on Ir electrode are also shown in Fig. 7. The surface microstructures of PZT/Ir thin films are also shown in Fig. 8. PZT films show welldeveloped grains with a dense and smooth morphology. With the increase of the $(A/B)_{solution}$ from 0.7 to 0.8, the grain size gradually increased. However, the Pb-rich PZT film shows unknown irregular PbO-like second phase. In XRD spectrums, the Pb-deficient PZT/Ir film shows only the perovskite phase without nonferroelectric phases in appearance. However, lead-deficient pyrochlore and IrO₂ phases appear in annealed film. In this study, IrO₂ phase appears at annealing temperatures above 650°C. Unlike the PZT/Pt film, the stoichiometric PZT/Ir film deposited at 425°C shows a single perovskite phase. The Pb-rich PZT film shows a perovskite phase with the trace of PbO. The pyrochlore phase, which may be attributed to the excess lead, appears after annealing.

We investigated the fundamental electrical properties, such as P-E hysteresis loop and the I-V characteristics of PZT thin film capacitors. Leakage current characteristics of the PZT capacitors with different $(A/B)_{solution}$ are shown in Fig. 9. Before constructing the PZT capacitor, furnace annealing was carried out at 700°C for 30 min in oxygen ambient. Thickness of PZT samples ranged from 320 to 330 nm and root-mean-square roughness ranged from 26 to 28 nm. For lead deficient and stoichiometric PZT films, the leakage



Figure 11. P-E hysteresis loops of (a) Pt(top)/PZT/Pt and (b) Pt(top)/PZT/Ir capacitors formed at various annealing temperatures.

current densities were below 7×10^{-7} A/cm² up to 100 kV/cm, irrespective of the bottom electrode. However, the 12% lead-rich Pt(top)/PZT/Ir capacitor shows high leakage current density. High leakage current density in Pb-rich PZT films on Ir substrate may be caused by unknown electrically leaky phases such as amorphous Pb-Ir-O phase.¹⁴ It seems that excess Pb (or PbO) promotes the reaction between Pb (or PbO) and Ir during furnace annealing. Consequently, more precise composition control may be needed for the PZT/Ir system to avoid high leakage current after annealing.

Leakage current characteristics of the stoichiometric PZT capacitors with different annealing temperatures are shown in Fig 10. Thickness of PZT samples ranges from 210 to 220 nm. Above annealing temperatures of 650°C, Pt(top)/PZT/Ir capacitors show high leakage current density. From the XRD patterns of these samples, not shown in this paper, we find that IrO₂ phase appears above 650°C.

Figure 11 shows P-E hysteresis loops of Pt/PZT/Pt and Pt/PZT/Ir capacitors formed at various annealing temperatures. PZT samples are identical with samples in Fig. 10. Well-saturated P-E hysteresis loops were obtained when PZT films were prepared on Ir electrode. The remanant polarization (P_r) values of Pt/PZT/Pt capacitors are 5.2 μ C/cm² (as-deposited), 7 μ C/cm² (annealed at 550°C), 8.3 μ C/cm² (650°C), and 21 μ C/cm² (750°C), respectively. Also P_r values of Pt/PZT/Ir capacitors are 21 μ C/cm² (as-deposited), 23 μ C/cm² (550°C), 34 μ C/cm² (650°C), and 37 μ C/cm² (750°C),

respectively. The increase of P_r with the annealing temperature on Pt/PZT/Ir capacitor is partially ascribed to the increase of leakage current density. The Pt/PZT/Pt capacitor prepared at 425°C shows poor ferroelectric property due to the imperfect crystallinity, as shown in Fig. 10. On the contrary, since PZT films prepared on Ir substrate at 425°C shows a single perovskite phase, Pt/PZT/Ir capacitor prepared at 425°C shows a single perovskite phase, Pt/PZT/Ir capacitor prepared at 425°C shows P_r of 21 μ C/cm² and coercive electric field (E_c) of 62 kV/cm. From these results on the electrical properties, it was found that PZT films on Ir electrode prepared by low temperature DLI-MOCVD, even below 425°C, showed good ferroelectric properties. This is one of the lowest deposition temperatures reported at which a PZT film with large P_r value was obtained. We also found from XPS depth profiles of PZT films that percentage order nitrogen and carbon are not incorporated even at 375°C.

Conclusions

Dmae group precursors are moderately stable with air and moisture and have low oxidation temperature, indicating that they are favorable to low temperature process. It was found that separate solution should be prepared for direct injection CVD of PZT because there is a serious cross interaction between Pb(tmhd)₂ precursor and M(dmae)₄. With Zr and Ti dmae group precursors we have developed a low temperature MOCVD process for the deposition of PZT with Pb(tmhd)₂. The growth rate was around 11 nm/min at 410°C. Because there exists a linear response of $(A/B)_{film}$ to $(A/B)_{solution}$ at low temperatures, we could easily prepare PZT films with various $(A/B)_{film}$ values by adjusting the solution composition. We obtained single perovskite PZT film at substrate temperatures as low as 425°C. The remanant polarization of PZT films prepared at 425°C on Ir substrate was 21 μ C/cm² and the leakage current density at 100 kV/cm was less than 10^{-6} A/cm². It is believed that this precursor set is a useful candidate for DLI-MOCVD of PZT thin films at the temperature range between 350 and 460°C.

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