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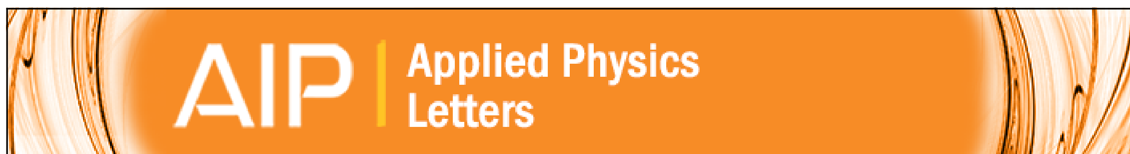

Lowtemperature metalorganic chemical vapor deposition of perovskite Pb(Zr x Ti1x)O3 thin films

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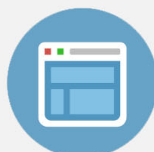

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Low-temperature metalorganic chemical vapor deposition of perovskite $Pb(Zr_xTi_{1-x})O_3$ thin films

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$Pb(Zr_xTi_{1-x})O_3$ thin films with perovskite structure were successfully prepared on sapphire disks, $Pt/Ti/SiO_2/Si$, and $RuO_x/SiO_2/Si$ substrates at temperatures as low as 550 °C by hot-wall metalorganic chemical vapor deposition. Safe and stable precursors were used, namely: lead tetramethylheptadione [$Pb(thd)_2$], zirconium tetramethylheptadione [$Zr(thd)_4$], and titanium ethoxide. The deposition rates were in the range of 10.0 to 20.0 nm/min. The Auger electron spectroscopy (AES) depth profile showed good uniformity across the bulk of the films. The AES spectra also showed no carbon contamination in the bulk of the films. Zr/Ti ratio were easily controlled by the precursor temperatures and the flow rate of diluent gas. Optical constants were measured by a UV-VIS-NIR spectrophotometer. As-deposited films were dense and showed uniform and fine grain size. The 600 °C annealed film (Pb/Zr/Ti=50/41/9) showed a spontaneous polarization of 23.3 $\mu C/cm^3$ and a coercive field of 64.5 kV/cm.

Perovskite lead zirconate titanate, $Pb(Zr_xTi_{1-x})O_3$ or PZT, ceramics are well-known materials which have very interesting ferroelectric properties for nonvolatile memory applications. The reported methods to form PZT films include: sputtering,[1] electron beam deposition,[2] ion beam deposition,[3] pulsed laser deposition,[4] sol-gel process,[5] metalorganic decomposition (MOD),[6] and metalorganic chemical vapor deposition (MOCVD).[7,8] Of all the reported techniques, the MOCVD technique appears to be most promising because it offers the advantages of simplified apparatus, excellent film uniformity, composition control, high film densities, high deposition rates, excellent step coverage, and amenability to large scale processing. However, very few reports are available on MOCVD PZT films at this time.[7,8] These reported MOCVD PZT films were fabricated at a relatively high temperature (>600 °C) by a cold-wall-type reactor. To incorporate into large scale processing and mass production, a low-processing temperature and a hot-wall-type reactor are desirable.

MOCVD is a mature technique for the deposition of complex oxide thin films. The most critical step for a successful deposition is the selection of the precursors. A large effort has been made on the selection of precursors for PZT deposition. For example, zirconium acetylacetonate [$Zr(C_5H_7O_2)_4$] and zirconium trifluoroacetylacetonate [$Zr(C_5H_4F_3O_2)_4$] were used for ZrO_2 deposition and lead hexafluoroacetylacetonate [$Pb(C_5HF_6O_2)_2$], tetraethyl lead [$Pb(C_2H_5)_4$], and lead bis-heptafluorodimethyloctadione [$Pb(fod)_2$] for PbO deposition. Several difficulties were encountered in using the above zirconium and lead precursors. Zirconium acetylacetonates resulted in cubic ZrO_2 films with carbon contaminations up to 15 at. %.[9] All the precursors containing fluorine resulted in fluorine contaminations. The fluorine contamination problem may be solved by introducing water vapor into the reactor during deposition. However, it is not easy to control the appropriate flow rate of water vapor under a reduced pressure condition. On the other hand, although good quality PbO films were obtained from tetraethyl lead, the extremely toxic nature of this precursor may prevent its use in large scale applications. After intensive studies, searching for the most suitable precursors for ZrO_2 and PbO thin-films deposition, zirconium tetramethylheptadione [$Zr(thd)_4$ which has a chemical formula of $Zr(C_{11}H_{19}O_2)_4$] and lead tetramethylheptadione [$Pb(thd)_2$ which has a chemical formula of $Pb(C_{11}H_{19}O_2)_2$], were found to be the best.

In this letter, we present the structure, composition, optical, and ferroelectric properties of hot-wall MOCVD PZT thin films using $Pb(thd)_2$, $Zr(thd)_4$, and Ti ethoxide as precursors. As far as we know, this is the first report of the hot-wall MOCVD PZT thin films by using the precursor combination of reagent grade $Pb(thd)_2$, $Zr(thd)_4$, and Ti ethoxide. Furthermore, we were able to deposit perovskite films at relatively low temperatures ($\cong$550 °C). Pure oxygen was used as a diluent gas. The substrates used were sapphire disks, $Pt/Ti/SiO_2/Si$, and $RuO_x/SiO_2/Si$ wafers. Typical deposition conditions are listed in Table I. Detailed experimental procedure can be found elsewhere.[10]

The identification of PZT phases was carried out by an x-ray diffractometer with Cu$K\alpha$ radiation. The composition of the films was investigated by using Auger electron spectroscopy (AES) and energy dispersive spectroscopy (EDS). Scanning electron microscopy (SEM) was used to study the surface morphology of the films. Film thickness,

TABLE I. Typical deposition conditions for MOCVD PZT thin films.

Precursors	$Pb(thd)_2$	$Zr(thd)_4$	$Ti(C_2H_5O)_4$
Precursor temp.	150 °C	215–230 °C	107–115 °C
Carrier gas (sccm, N_2)	20–30	15–30	5
Substrate	Sapphire and $Pt/Ti/SiO_2/Si$		
Substrate temperature	550 °C		
Dilute gas (sccm, O_2)	500–1000		
Total pressure	6 Torr		
Deposition rate (nm/min)	10.0–20.0		

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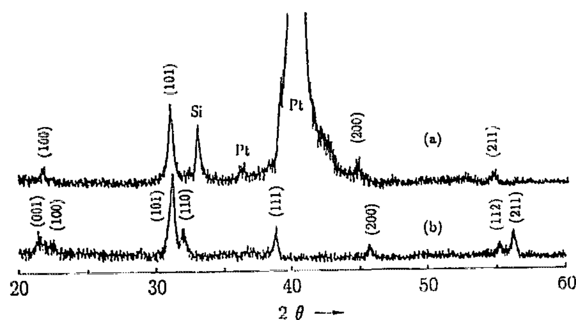

FIG. 1. XRD patterns of as-deposited PZT films (a) with Zr/Ti=60/40 on $Pt/Ti/SiO_2/Si$ substrate and (b) with Zr/Ti=40/60 on sapphire disk.

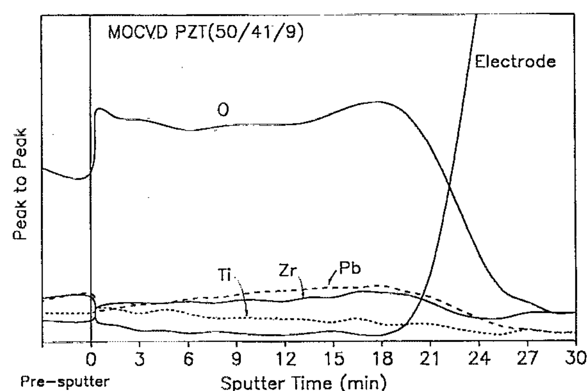

FIG. 2. AES depth profile of as-deposited MOCVD PZT films.

refractive index (n), and extinction coefficient (k) were obtained from UV-VIS-NIR transmission measurements. Ferroelectric properties were measured by a Sawyer–Tower circuit at 60 Hz. The top electrodes were e-beam evaporated palladium.

As-deposited MOCVD PZT films were specular, crack-free, uniform, and adhered well on all substrates used and were highly transparent on sapphire substrates. These films also showed very smooth surfaces as viewed by means of both optical microscopy and scanning electron microscopy. For the conditions described in Table I, film growth rates were typically in the range of 10.0 to 20.0 nm/min.

Typical XRD patterns of as-deposited PZT films on sapphire and $Pt/Ti/SiO_2/Si$ substrates are shown in Fig. 1. The XRD patterns show that the films with Zr/Ti=60/40 have rhombohedral perovskite structure [Fig. 1(a)] and the films with Zr/Ti=40/60 have tetragonal perovskite structure [Fig. 1(b)]. No preferred orientation was found under the deposition conditions described in Table I.

The stoichiometry of the films can be mainly controlled by varying the individual precursor temperatures and the diluent gas-flow rate. The variation of the Zr/Ti ratio under different deposition conditions is illustrated in Table II. As can be seen from Table II, the desired Zr/Ti ratio can be easily obtained across the entire PZT solid-solution range.

Auger electron spectroscopy (AES) was used to examine the carbon contamination and the composition uniformity across the thickness of the film. The AES depth profile of the as-deposited PZT film on $RuO_x/SiO_2/Si$ is shown in Fig. 2. The dilute gas-flow rate used for this sample was 1000 sccm O_2. The composition of as-deposited PZT films was uniform, as can be seen in Fig. 2. No carbon contamination was observed in the films except the carbon adsorption on the sample surface. For the annealed sample, the AES profile behaved similar to that of the as-deposited sample except the Pb content decreased at the surface.

TABLE II. Variation of Zr/Ti ratio at different deposition conditions (substrate temperature: 550 °C, total pressure: 6 Torr).

Zr/Ti ratio	Precursor temp. and carrier gas (N_2)		Dilute gas (sccm, O^2)
	$Zr(thd)_4$	$Ti(C_2H_5O)_4$	
26/74	220 °C/20 sccm	115 °C/5 sccm	1000
40/60	231 °C/20 sccm	114 °C/5 sccm	1000
42/58	226 °C/15 sccm	114 °C/5 sccm	750
45/55	225 °C/30 sccm	112 °C/5 sccm	1000
48/52	231 °C/30 sccm	112 °C/5 sccm	500
52/48	231 °C/30 sccm	113 °C/5 sccm	500
65/35	231 °C/20 sccm	109 °C/5 sccm	750
78/22	231 °C/20 sccm	107 °C/5 sccm	500

The UV-VIS-NIR transmission spectrum of the as-deposited PZT ($x=0.6$) film on the sapphire substrate is shown in Fig. 3. The spectrum illustrates that the transmittance drops down to 0% (the absorption edge) at wavelength 302 nm and has a value of 85% at wavelength 2000 nm. An envelope method[11] was used to calculate the film thickness as well as the refractive index and extinction coefficient of the film as a function of wavelength. The film thickness calculated using this method is 510 nm. The n and k values are 2.413 and 0.0008, respectively, at $\lambda=633$ nm for the film with Zr/Ti=60/40. The high refractive index value, compared to the value of 2.239 from MOD PZT films,[6] indicates that the MOCVD PZT film is dense. The very low extinction coefficient illustrates the nature of the specular and highly transparent films. The band-gap energy of the PZT film was calculated from the absorption coefficients near the absorption edge under the assumption

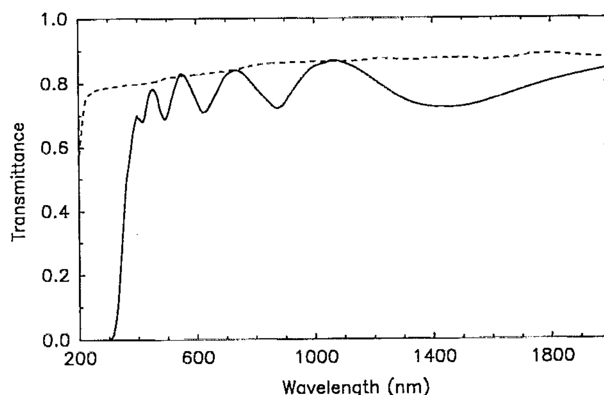

FIG. 3. Optical transmission spectrum of MOCVD $Pb(Zr_{0.6}Ti_{0.4})O_3$ film on sapphire substrate. Dashed line shows the transmittance of the uncoated sapphire substrate.

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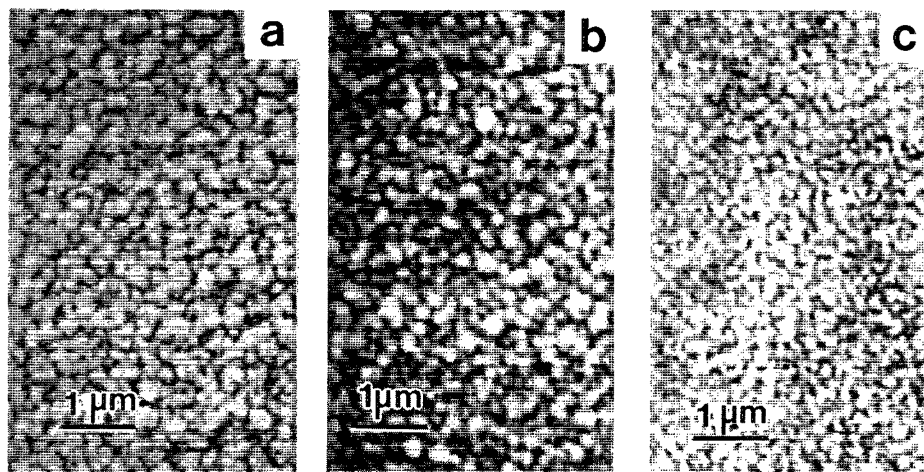

FIG. 4. SEM micrographs of as-deposited MOCVD PZT films: (a) on $Pt/Ti/SiO_2/Si$, (b) on $RuO_x/SiO_2/Si$, and (c) on sapphire. The diluent gas used was 1000 sccm O_2.

of a direct band transition and found to be 3.65 eV. This value agrees well with the earlier reported value for the MOD films with Zr/Ti=60/40.[6]

The surface morphology of the as-deposited PZT films was investigated by SEM and is shown in Fig. 4. The SEM micrographs showed that the films were dense and smooth on all three different substrates used. The grains were very fine and uniformly distributed. The average grain size was estimated to be 0.15 μm for the film on $Pt/Ti/SiO_2/Si$ and $RuO_x/SiO_2/Si$ substrates and less than 0.1 μm for the film on the sapphire substrate.

Figure 5 shows the typical *D-E* hysteresis loop of MOCVD PZT film. The film had the composition of Pb/Ar/Ti=50/41/9 and was annealed at 600 °C for 30 min in air. The thickness of the film was 200 nm. The spontaneous polarization P_s, remanent polarization P_r, and coercive field E_c had values of 23.3 $\mu C/cm^2$, 12.3 $\mu C/cm^2$, and 64.5 kV/cm, respectively.

In summary, PZT thin films were successfully and reproducibly fabricated at low temperature (550 °C) on sapphire disks, $Pt/Ti/SiO_2/Si$, and $RuO_x/SiO_2/Si$ substrates by a MOCVD technique. The films had the pure perovskite phase in the as-deposited state. The stoichiometry of the films was controlled by varying the precursor temperatures and the flow rate of the dilute gas. The AES spectrum showed no carbon contamination in the bulk of the film. The AES depth profile indicated that Pb, Zr, and Ti were uniformly distributed across the film thickness. A high refractive index (2.413) and low extinction coefficient (0.0008) were obtained at $\lambda=633$ nm in the as-deposited PZT films. Very fine grains ($\cong$0.1 μm) were observed for the films on all three different substrates used. The well-defined *D-E* hysteresis loop was observed with the ferroelectric properties of $P_s=23.3$ $\mu C/cm^2$, $P_r=12.3$ $\mu C/cm^2$, and $E_c=64.5$ kV/cm.

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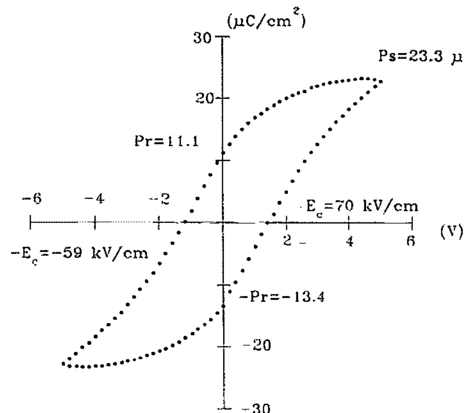

FIG. 5. Typical *D-E* hysteresis loop of MOCVD PZT film. The composition and the thickness of the film were Pb/Zr/Ti=50/41/9 and 200 nm, respectively.

[1] R. Takayama and Y. Tomita, J. Appl. Phys. **65**, 1666 (1989).
[2] M. Oikawa and K. Toda, Appl. Phys. Lett. **29**, 491 (1976).
[3] R. N. Castellano and L. G. Feinstein, J. Appl. Phys. **50**, 4406 (1979).
[4] J. S. Horwitz, K. S. Grabowski, D. S. Chrisey, and R. E. Leuchtner, Appl. Phys. Lett. **59**, 1565 (1991).
[5] K. D. Budd, S. K. Dey, and D. A. Payne, Proc. Br. Ceram. Soc. **36**, 107 (1985).
[6] C. H. Peng, S. W. Park, and S. B. Desu, Ceram. Tran. **25**, 169 (1992).
[7] Y. Sakashita, T. Ono, H. Segawa, K. Tominaga, and M. Okada, J. Appl. Phys. **69**, 8352 (1991).
[8] K. Kashihara, H. Itoh, K. Tsukamoto, and Y. Akasaka, *Extended Abstracts of the 1991 International Conference on Solid State Development and Materials* (Business Center for Academic Societies Japan, Tokyo, 1991), pp. 192–194.
[9] S. B. Desu, S. Tain, and C. Kwok, Mater. Res. Soc. Symp. Proc. **168**, 349 (1990).
[10] C. H. Peng and S. B. Desu, Proceedings of the 4th International Symposium on Integrated Ferroelectrics, Monterey, CA, 1992, (in press).
[11] J. C. Manifacier, J. Gasiot, and J. P. Fillard, J. Phys. E **9**, 1002 (1976).