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Formation of PZT Films by MOCVD

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PZT thin films were prepared by the MOCVD method. Bisdipivaloylmethanato lead, zirconium tetra-t-butoxide and titanium tetra-i-proxide and oxygen were used as source materials. A typical deposition rate was 50~200Å/min over a 6-inch diam. substrate. The physical and the electrical characteristics were evaluated. Polycrystallized films with the well developed perovskite phase were formed on Pt(111) substrate at 600~700°C. The dielectric constant and tanδ were 65~3000 and 0.009~0.133. A typical dielectric breakdown voltage of 2400Å thick PZT film was 21V, while the leakage current of 0.26μA/cm^2 at 5V was achieved. A film formed by this method showed the ferroelectric characteristic.

1. Introduction

With a recent increase in the integration density of DRAMs, the use of capacitor insulator with higher dielectric constant has attracted many attentions. PZT is expected as a capacitor insulator applicable to DRAMs beyond 64Mbits. As for the film formation, only sputtering or sol-gel coating methods have been reported so far[1)2)3)]. A three dimensional nature of the capacitor structure, however, demands a better step coverage of PZT films. Very few reports can be available on the CVD method to form PZT films[4)]. Here, we first propose an MOCVD method to form PZT films using novel metalorganic source materials, with easy handling, less toxicity, and better reproducibility, and the results of physical and electrical characterization of as-deposited CVD-PZT films will be shown.

2. Experimental

Figure1 shows the schematic diagram of apparatus used. A PZT film is deposited onto a radiantly heated substrate with 6-inch diameter under a reduced pressure of 1~2 Torr. The formation of PZT is done by the thermal oxidation of metalorganic source materials at the temperature ranging 600~700°C.

Bisdipivaloylmethanato lead {$Pb(DPM)_2$}, zirconium tetra-t-butoxide {$Zr(O\text{-}t\text{-}C_4H_9)_4$}, titanium tetra-i-propoxide {$Ti(O\text{-}i\text{-}C_3H_7)_4$} and oxygen are used as the most suitable Pb, Zr, Ti source and oxidant, respectively. Among these materials, only $Pb(DPM)_2$, which is a kind of β-diketone Pb complexes as shown in Fig.2, has a solid phase(white powder) at the temperature below 140°C. A high vapor pressure of these source materials at a relatively low temperature makes this CVD method practical for the LSI fabrication in conjunction with the non-toxic nature of each source material. A supply rate of each source material is controlled by the flow rate of N_2 carrier gas and the temperature of the reservoir tank. A film composition can easily be controlled by simply changing the supply rate of each source material. A typical deposition rate over a 6-inch diam. substrate is 50~200 Å/min as summarized in Table I.

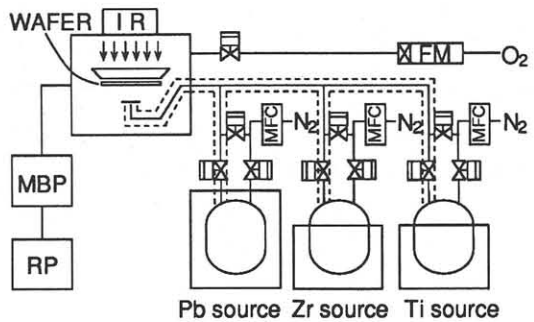

Fig.1 Schematic diagram of apparatus for CVD-PZT.

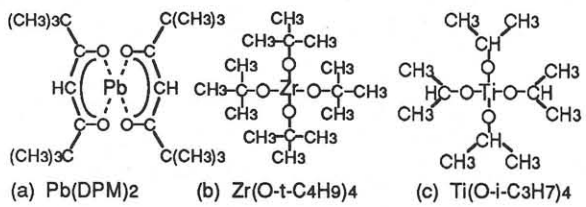

Fig.2 Metalorganic source materials for CVD-PZT.

3. Results and Discussion

Figure 3 shows the X-ray diffraction patterns of as-deposited CVD-PZT films on a Si(100) and a Pt(111) substrate. The perovskite crystalline

Table I Typical deposition condition for CVD-PZT.

Substrate	Si(100), Pt(111), 6-inchϕ	Temp. = 600~700°C	
Source	Pb(DPM)2	N2 carrier 100~200sccm	135°C
	Zr(O-t-C4H9)4	0~100sccm	30°C
	Ti(O-i-C3H7)4	0~100sccm	30°C
	O2	700sccm	
Pressure	1 ~ 2 Torr		
Depo. rate	50 ~ 200 Å/min		

structure oriented to the several crystallographic directions is observed only in the films on Pt(111), which is similar to the case of other film formation methods. In Figs.3(b) and 3(c), it is also shown that the deposition condition affects the crystallinity. In the case of deposition at 600°C, the perovskite crystal has a tetragonal unit cell with the lattice constants of 4.00Å(a-axis) and 4.14Å(c-axis), while a cubic unit cell with the lattice constant of 4.07Å for the deposition at 700°C.

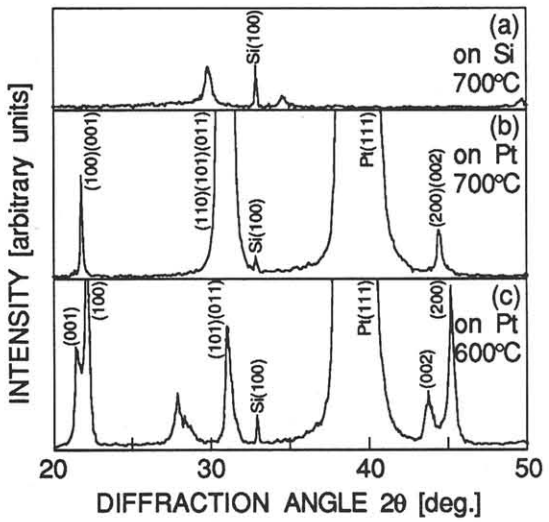

Fig.3 X-ray diffraction patterns of CVD-PZT on (a)Si(100) and (b)(c)Pt(111). The temperature of substrate is (a)700°C (b)700°C (c)600°C.

SIMS in-depth analysis reveals a diffusion of underlying Pt into the PZT films during deposition. It is shown that, in Fig.4, a remarkable Pt diffusion occurs, especially in the case of insufficient supply of oxygen. This anomalous diffusion implies an alloy formation between Pt and elementary metals of PZT and an optimization in flow ratio at the initial stage of deposition would be effective in obtaining a better insulating characteristics in PZT.

A possible incorporation of carbon from the organic source materials is also shown to be deniable in Fig.4.

To evaluate the morphological features of CVD-PZT, SEM observations are done. A coverage of CVD-PZT over a Pt step is shown in Fig.5. It is shown that this CVD system gives an excellent step coverage. The change of surface morphology for a variety of film thickness and composition are given in Fig.6 and Fig.7. The characteristic hilloks with a

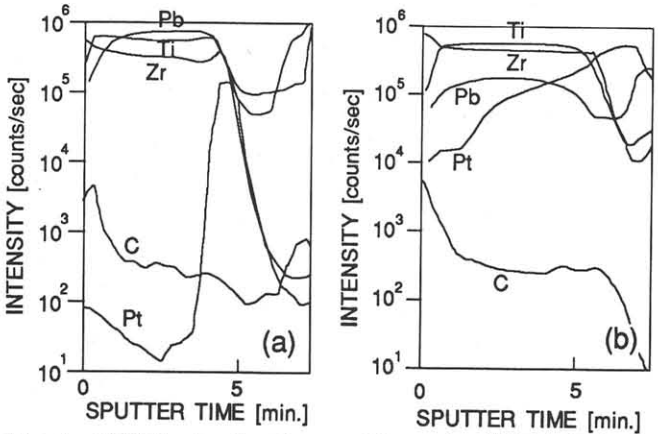

Fig.4 SIMS in-depth profile of CVD-PZT on Pt(111). The O2 gas flow rate is (a)1000sccm (b)300sccm.

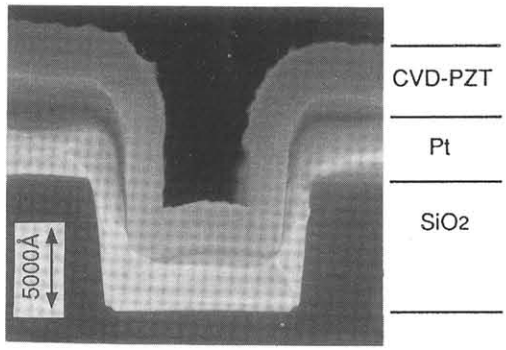

Fig.5 Cross sectional SEM photograph of step coverage of PZT over Pt step.

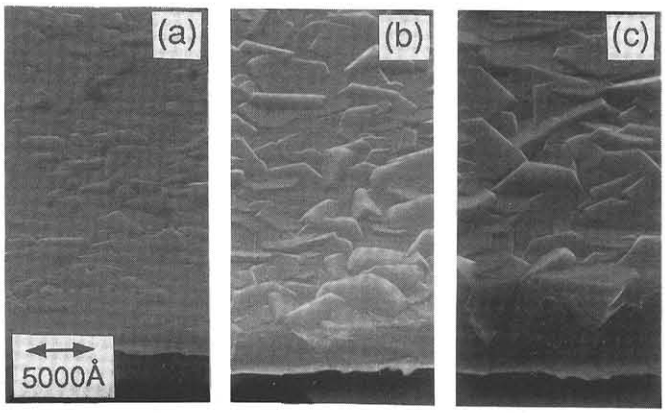

Fig.6 Surface morphology dependence on film thickness : (a)850Å (b)3500Å (c)7300Å. The deposition condition is fixed.

pyramidal shape, which would be a sign of well-grown crystal grains, are seen, especially in the case of thicker and Pb-rich films.

The electrical characteristics are measured at room temperature using Pt/PZT/Pt capacitor structures for a variety of composition of CVD-PZT. In Table II, the relative dielectric constant and the dissipation factor of various samples are shown, together with the source supply conditions. Note that the behavior of Zr content is distinctive. There seems to be a tendency that the content of Zr is strongly affected by that of other two elements. The

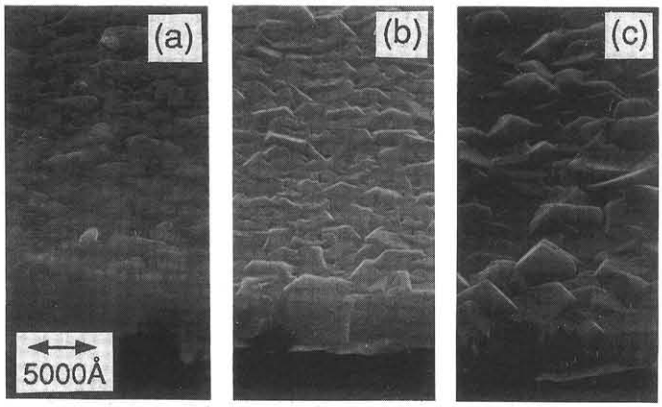

Fig.7 SEM observations of surface morphology as a function of Pb supply condition. (a)100sccm (b)150sccm (c)200sccm. Other conditions are same.

Table II Dielectric constant and tanδ for the different supply rate of source. O_2 flow rate : 700sccm, substrate temperature : 700°C.

No. of sample	N2 carrier flow rate Pb	Zr	Ti (sccm)	composition Pb / Zr / Ti (%)	dielectric constant	tanδ
#139	100	0	100	52 / 0 / 48	350	0.030
#145	100	50	100	47 / 22 / 31	1400	0.133
#146	100	100	100	22 / 59 / 19	500	0.031
#148	100	100	0	3 / 97 / 0	65	0.009
#240	100	100	100	31 / 34 / 35	1300	0.118
#248	150	100	100	38 / 28 / 34	1600	0.069
#249	200	100	100	43 / 25 / 32	1700	0.091

electrical characteristics varies widely depending upon the composition, and the relative dielectric constants as high as 1300~1700 are obtained for the samples with properly given composition.

Figure8 illustrates the dependence of the dielectric constant on the film thickness. Also, the oxide equivalent thickness(t_{eq}) are plotted in Fig.8.

Although a decreasing tendency can be seen for thinner films, the dielectric constant seems to be less dependent on the film thickness than that observed in other film formation methods. At a PZT film thickness of 850Å, a t_{eq} as thin as 2.1Å is realized.

An I-V characteristics of a 2400Å thick PZT film is shown in Fig.9. In this sample, the dielectric constant is ~170. It is shown that the dielectric breakdown voltage is around 21V(0.88MV/cm), while the leakage current is ~1nA(0.26μA/cm^2) at 5V.

Using a Sawer-Tower circuit with 1kHz sine wave oscillation, the ferroelectric characteristics is examined. Figure10 is a hysteresis loop of a typical Pt/PZT/Pt device, showing a remanent polarization(Pr) of 18μC/cm^2 and a coercive field of 55kV/cm.

4. Conclusion

For the first time, we demonstrated the MOCVD method to form PZT films using novel source materials, and evaluated the physical and the

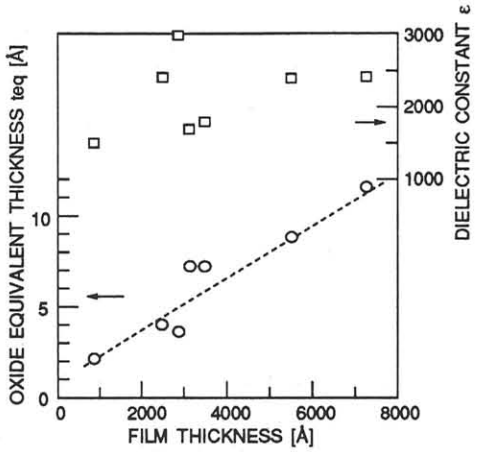

Fig.8 Oxide equivalent thickness(t_{eq}) and dielectric constant(ε) as a function of the film thickness of PZT. The capacitance of 850Å thick PZT corresponds to 2.1Å silicon dioxide.

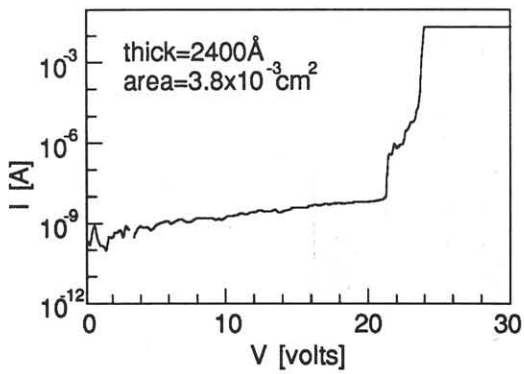

Fig.9 Leakage current(I) as a function of applied voltage(V). (2400Å thick and electrode area of 3.8x10^{-3}cm^2)

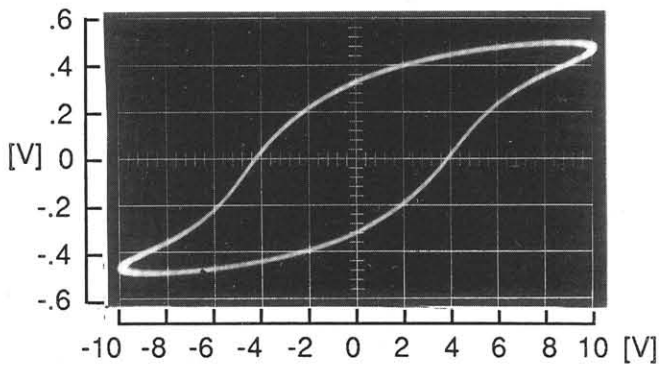

Fig.10 Characteristic P-E hysteresis loop generated using a 1kHz sine wave and an amplitude of 10V. Pr=18μC/cm^2, and E_c=55kV/cm. (7300Å thick, and electrode area of 3.8x10^{-3}cm^2, C_s=0.47μF)

electrical characteristics of those films. With process improvements, this method will be used to form PZT films in future memories.

References

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