Low-Pressure Deposition of Pb(Zr,Ti)O$_3$ Films by MOCVD at Low-Temperature

Gouji Asano[1], Takahiro Oikawa[2], Kouji Tokita[2], Kiyoshi Okada[3], and Hiroshi Funakubo[2]

[1]Department of Inorganic Materials, Tokyo Institute of Technology
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan
[2]Department of Innovative and Engineered Materials, Tokyo Institute of Technology
4259 Nagatsuta-cho, Midori-ku, Yokohama 226-8502, Japan
[3]Department Metallurgy and Ceramics Science, Tokyo Institute of Technology
2-12-1 O-okayama, Meguro-ku, Tokyo 152-8552, Japan
Fax: +81-45-924-5446, e-mail: asano@iem.titech.ac.jp, funakubo@iem.titech.ac.jp

Polycrystalline PZT films were prepared on (111)Pt/TiO$_2$/SiO$_2$/Si substrates by source-gas-pulsed-introduced MOCVD (pulsed-MOCVD) under the reactor pressure of 670 and 67 Pa. When the deposition temperature decreased from 580 to 395 °C, the region of input gas flow rate of lead source to obtain PZT single phase, "process window", was decreased to one-tenth. This was owing to diminishment of reevaporation of excess lead element from the surface of the substrate. The width of "process window" increased by the decrease of the reactor pressure because of the acceleration of the reevaporation of the lead element. The width of "process window" at 395 °C under 67 Pa by pulsed-MOCVD was almost the same as the width at 580 °C under 670 Pa by conventional source-gas-introduced MOCVD (continuous-MOCVD). Moreover, almost the same deposition rate and ferroelectric properties with remnant polarization of 29 μC/cm^2 were obtained by this low pressure deposition. As a result, it is found that preparation under lower pressure is effective to obtain a PZT film with high reproduciblity even at low temperature.
Key words: Pb(Zr,Ti)O$_3$, MOCVD, low pressure, low temperature, pulsed-MOCVD

1. INTRODUCTION

Pb(Zr,Ti)O$_3$ (PZT) films have been widely investigated for ferroelectric random-access memory (FeRAM) [1]. Metalorganic chemical vapor deposition (MOCVD) is one of the most promising deposition methods because of high step coverage, high deposition rate, and large area uniformity of film quality [2-3]. Lowering the preparation temperature of PZT films retaining large ferroelectricity is the essential point to realize the high-density FeRAMs. Moreover, reproducibility of the film composition is severe problem because the ferroelectricity of PZT film is widely known to be strongly depended on the film composition [4]. Especially, lead content is the most important because it is known to be strongly affected the leakage character and the ferroelectricity of the film [5]. However, the film composition reproducibility dramatically decreased with decreasing the deposition temperature for MOCVD process as M. De Keijser *et al.* pointed out [6]. In the previous study, polycrystalline PZT film with epitaxial-grade ferroelectricity was obtained even at 415 °C by source-gas-pulsed-introduced-MOCVD (pulsed-MOCVD) [7]. In the present study, high-reproducible preparation to get the lead content corresponding to PZT single phase was achieved by pulsed-MOCVD combined with low pressure of the reactor from 670 to 67 Pa. As a result, 50% fraction of

the concentration of the input Pb source gas was accepted to get the film having good ferroelectricity.

2. EXPERIMENTAL

250-nm-thick polycrystalline PZT films were prepared on (111)Pt/TiO$_2$/SiO$_2$/Si substrates by MOCVD using Pb(C$_{11}$H$_{19}$O$_2$)$_2$, Zr(O · *t*-C$_4$H$_9$)$_4$, Ti(O · *i*-C$_3$H$_7$)$_4$ and O$_2$ gas as the source materials. Figure 1 shows schematic diagram of the MOCVD apparatus used in the present study. A horizontal cold-wall-type reactor kept at 670 and 67 Pa in pressure was used for the preparation. In pulsed-MOCVD, mixture of the source gases were introduced for 10s with a 5s interval while O$_2$ gas was continuously introduced into the reactor. PZT films were also prepared by conventional MOCVD with a continuous introduction of the source gases, continuous-MOCVD. Table I summarizes the deposition conditions of the films. Theoretical gas concentration of each gas was defined as R[source] [8]. In the present study, only the concentration of Pb source, R[Pb(C$_{11}$H$_{19}$O$_2$)$_2$], was changed under the fixed concentrations of Zr and Ti sources, R[Zr(O·*t*-C$_4$H$_9$)$_4$] and R[Ti(O · *i*-C$_3$H$_7$)$_4$], at 0.067 and 0.11 cm^3/min, respectively together with O$_2$ gas.

The composition of the films and the deposition rate of each constituent metal element were measured by X-ray fluorescence (XRF) spectroscopy calibrated using standard samples. Electrical property was measured
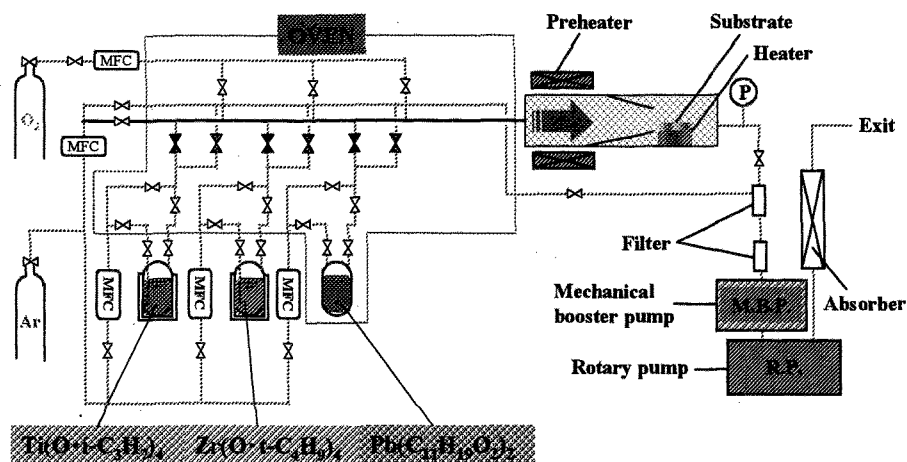
Fig. 1. Schematic diagram of the MOCVD apparatus.

Table I. Deposition conditions of PZT film

Temperature of the vessel	$Pb(C_{11}H_{19}O_2)_2$	140 °C
	$Zr(O \cdot t\text{-}C_4H_9)_4$	35 °C
	$Ti(O \cdot i\text{-}C_3H_7)_4$	41 °C
Pressure of the Vessel	$Pb(C_{11}H_{19}O_2)_2$	24-30 kPa
	$Zr(O \cdot t\text{-}C_4H_9)_4$	27 kPa
	$Ti(O \cdot i\text{-}C_3H_7)_4$	24 kPa
Deposition temperature	395-580°C	
Substrate	$(111)Pt/TiO_2/SiO_2/Si$	
Film thickness	250 nm	

Reactor pressure	67 Pa	670 Pa
Total gas Flow rate	300 cm³/min	1000 cm³/min
Flow rate of O_2 gas	150 cm³/min	500 cm³/min

by preparing 100 μφ diameter Pt top electrode.

3. RESULTS AND DISCUSSION

3.1 Film composition

Figure 2 shows $R[Pb(C_{11}H_{19}O_2)_2]$ dependence of the Pb/(Pb+Zr+Ti) ratio of the film deposited at 395 and 580 °C under 670 Pa by pulsed-MOCVD. When the $R[Pb(C_{11}H_{19}O_2)_2]$ increased, the Pb/(Pb+Zr+Ti) ratio increased and became 0.5, corresponding to PZT single phase composition. This value, 0.5, was kept when $R[Pb(C_{11}H_{19}O_2)_2]$ was between 0.22 and 0.33 cm³/min and between 0.077 and 0.088 cm³/min at 580 and 395 °C, respectively. This-constant-value region can be explained by the reevaporation of excess lead element from the surface of the substrate. Pb/(Pb+Zr+Ti) ratio again increased with increasing $R[Pb(C_{11}H_{19}O_2)_2]$ for excess Pb element. This region to get the single phase is defined as "process window" because PZT single phase was obtained even though the $R[Pb(C_{11}H_{19}O_2)_2]$ of the input gas was fractuated. This means that the wide process window shows easy high
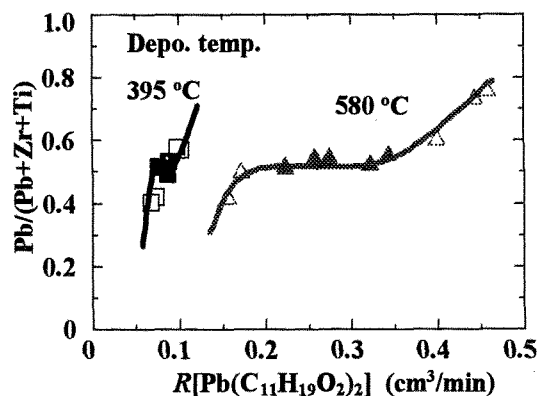

Fig. 2. Pb/(Pb+Zr+Ti) ratio of the film deposited by pulsed-MOCVD as a function of $R[Pb(C_{11}H_{19}O_2)_2]$.
Deposition temperature, (■, □) : 395 °C, (▲, △) : 580 °C
Constituent phase, (■, ▲) : Single phase of PZT, (□, △) : Mixture phase of PZT and the contamination phase

reproducible preparation of the film consisting of PZT single phase. The width of "process window" at 395 °C was about one-tenth wider than that prepared at 580 °C as shown in Fig. 2. Thus, the reproducibility to get PZT single phase was dramatically decreased when the deposition temperature decreased from 580 to 395 °C. Therefore, wide "process window" to get PZT single phase is required even at low temperature for high reproducibility.

Figure 3 shows a schematic diagram of the deposition mechanism of PZT film by MOCVD. When the deposition temperature decreased, reevaporation of the excess lead element was diminished by the decrease of the vapor pressure in the case of continuous-MOCVD as shown in Fig. 3(a). However, this reevaporation accelerated by making an interval time of the gas supply, pulsed-MOCVD, as shown in Fig. 3(b). In fact, PZT single phase films were obtained in a wider $R[Pb(C_{11}H_{19}O_2)_2]$ region by pulsed-MOCVD than that
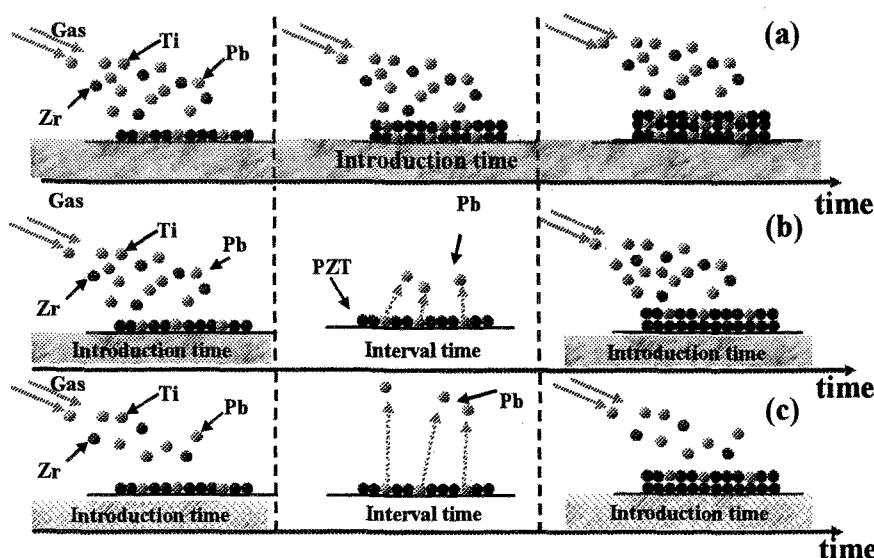
Fig. 3.   Schematic diagram of the deposition model of (a) continuous-MOCVD under conventional pressure, (b) pulsed-MOCVD under conventional pressure and (c) pulsed-MOCVD under low pressure.

by continuous-MOCVD [9]. Therefore, the acceleration of reevaporation of excess lead element is a key point to get wider "process window". Low pressure preparation combined with pulsed-MOCVD is considered to be also accelerated the reevaporation of lead element even at low temperature, because the reevaporation rate of lead element increased by the decrease of atmospheric pressure.

Figure 4 shows the Pb/(Pb+Zr+Ti) ratio of the film as a function of $R[Pb(C_{11}H_{19}O_2)_2]$ prepared at 395 °C under 67 Pa by pulsed-MOCVD together with that prepared at 580 °C under 670 Pa by continuous-MOCVD. The Pb/(Pb+Zr+Ti) ratio of 0.5 was kept at $R[Pb(C_{11}H_{19}O_2)_2]$ between 0.067 and 0.098
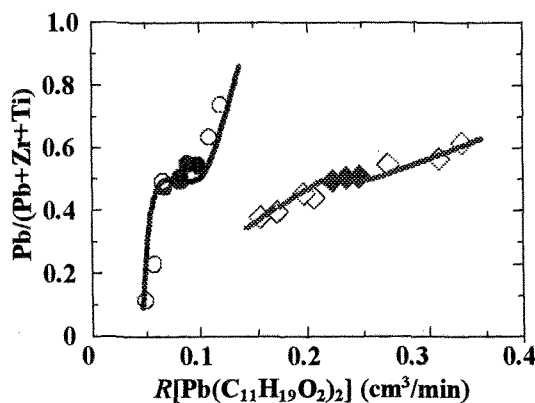

Fig. 4.   Pb/(Pb+Zr+Ti) ratio of the film as a function of $R[Pb(C_{11}H_{19}O_2)_2]$.

Preparation condition; (●, ○) : 580 °C, 670 Pa by continuous-MOCVD, (◆, ◇) : 395 °C, 67 Pa by pulsed-MOCVD, Constituent phase; (●, ◆) : Single phase of PZT, (○, ◇) : Mixture phase of PZT and the contamination phase

cm^3/min, about 50 % fractuation of $R[Pb(C_{11}H_{19}O_2)_2]$, which was three times wider than that prepared at same temperature under 670 Pa by pulsed-MOCVD as shown in Fig. 2. This width was almost the same as that prepared by conventional-MOCVD at 185 °C-higher-temperature, 580 °C, under 670 Pa as shown in Fig. 4, $R[Pb(C_{11}H_{19}O_2)_2]$ between 0.212 and 0.245 cm^3/min. This reveals that same fractuation of $R[Pb(C_{11}H_{19}O_2)_2]$ for the preparation of films consisting of PZT single phase in case of widely used MOCVD condition was accepted even at 395 °C. This is owing to the fact that the reevaporation of excess Pb element was accelerated by pulsed-MOCVD combined with low reactor pressure as shown in Fig. 3(c).

3.2 Deposition rate

Figure 5 shows the change of the deposition rates of the constituent Pb, Zr, and Ti elements of the films as a function of $R[Pb(C_{11}H_{19}O_2)_2]$ for the films deposited under 67 and 670 Pa at 395 °C. The deposition rates of each constituent element of the films were almost independent of the reactor pressure even though the concentration of each source gas was 10 times different. This is because that rate limiting step is not mass transport but surface reaction.

3.3 Ferroelectricity

Figure 6 shows the P-E hysteresis loops of PZT film prepared by pulsed-MOCVD at 395 °C under 67 Pa. Well saturated hysteresis loops having the remnant polarization (P_r) and the coercive field (E_c) of 29 $\mu C/cm^2$ and 132kV/cm, respectively were observed. As a result, the film having good ferroelectricity was
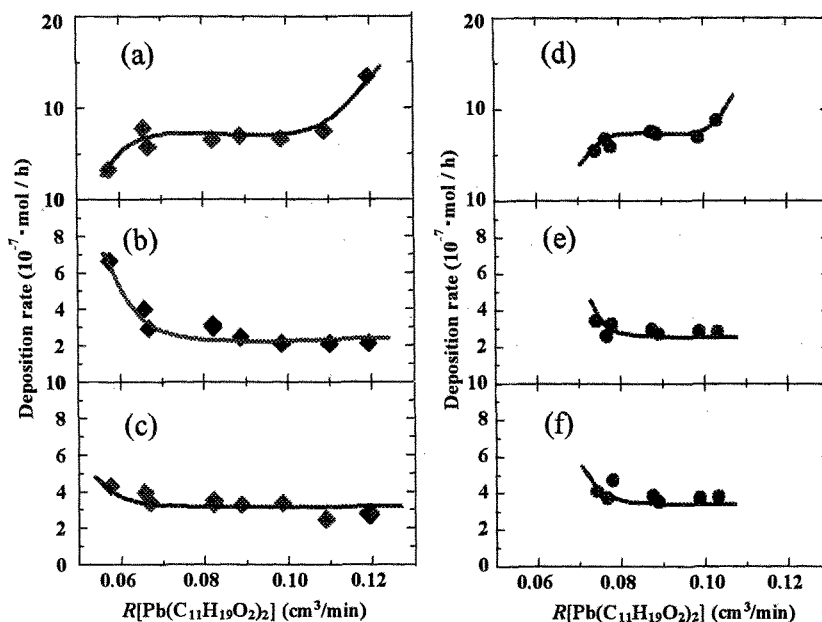
Fig. 5. The deposition rates of the constituent Pb [(a), (d)], Zr [(b), (e)] and Ti [(c), (f)] elements of the films prepared under 67 (◆) and 670 Pa (●) as a function of $R[Pb(C_{11}H_{19}O_2)_2]$.
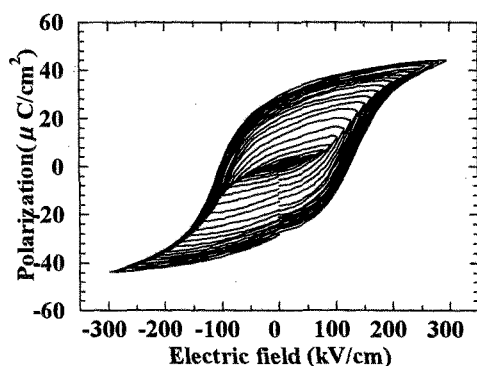

Fig. 6. *P-E* hysteresis loops of PZT films prepared at 395 °C under 67 Pa.

prepared with high reproducibility by pulsed-MOCVD combined with low reactor pressure retaining same deposition rate.

4. CONCLUSION

PZT films were prepared with good composition-reproducibility even at 395 °C by pulsed-MOCVD under low pressure. The width of "process window" to get PZT single phase by pulsed-MOCVD under 67 Pa was wider than that under 670 Pa at 395 °C, which was almost the same with that by continuous-MOCVD at 580 °C under 670 Pa, widely used MOCVD condition. The deposition rate of PZT film prepared under 67 Pa were almost the same with that under 670 Pa nevertheless the concentrations of source gases under 67 Pa were one-tenth lower than that under 670 Pa for the films prepared at 395 °C by

pulsed-MOCVD. The P_r value of 29 μC/cm² was obtained for the films prepared by pulsed-MOCVD at 395 °C under 67 Pa. As a result, the film having good ferroelectricity was prepared with high reproducibility by pulsed-MOCVD combined with low reactor pressure retaining same deposition rate.

5. REFERENCES

[1] A. Manish, Ferroelectrics 102, 69 (1990).

[2] M. Okada, Y. Tominaga, T. Araki, S. Katayama and Y. Sakashita, Jpn. J. Appl. Phys. 29, 718 (1990).

[3] T. Li, P. Zawadzki and R. Stall, Integ. Ferro., 18, 155 (1997).

[4] C. M. Foster, G. R. Bai, R. Csencsits, J. Vetrone, R. Jammy, L. A. Wills, and J. Amano, J .Appl. Phys. 8, 2349 (1997).

[5] Gwo-Chin Chao and Jenn-Ming Wu, Jpn. J. Appl. Phys. 40, 2417 (2001).

[6] M.De Keijser, P.J. Van Veldhoven, and G. J. M. Dormans, Mat. Res. Soc. Symp. Proc. 310, 234 (1993).

[7] M. Aratani, T. Oikawa, T. Ozeki, and H. Funakubo, Appl. Phys. Lett. 79, 1000 (2001).

[8] T. Matsuzaki, N. Okuda, K. Shinozaki, N. Mizutani, and H. Funakubo, Jpn. J. Appl. Phys. 37, 6229 (1998).

[9] M. Aratani, K. Nagashima, and H. Funakubo, Jpn. J. Appl. Phys. 40, 4126 (2001).