

## Oxygen Enhanced Dissociation Effect on MOCVD PZT Thin Film

Shigeo Ohnishi, Masaya Komai, Kazuya Ishihara and Keizo Sakiyama  
 Masaru Shimizu\* and Tadashi Shiosaki\*

VLSI Development Laboratory, IC-Group, SHARP Corp.  
 2613-1 Ichinomoto-cho, Tenri-city, Nara 632, JAPAN

\*Department of Electronics, Faculty of Engineering, Kyoto University  
 Yoshidahonmachi, Sakyo-ku, Kyoto-city, Kyoto 606, JAPAN

This paper describes the oxygen enhanced dissociation effect of Pb precursors for high-quality MOCVD-PZT thin film. Bis(dipivaloyl)methanate lead for Pb source material is easily decomposed between Pb and oxygen bond, causing the poor PbO formation. This generates the Pb-poor phase at the initial stage of PZT deposition. By enough oxygen gas supply to form PbO sufficiently, the fine surface morphology and the excellent crystallinity are obtained. As a result, excellent polarization properties ( $P_r = 23.6 \mu\text{C}/\text{cm}^2$ ,  $k = 838$ ) are achieved and it enables the application for 16-64 Mbit FRAMs.

### INTRODUCTION

Ferroelectric thin films, such as PZT and PLZT, have attracted much attention for application to future non-volatile memories and high density DRAMs, because of the extremely high dielectric constant and polarization effects<sup>4)5)</sup>. MOCVD (Metal-Organic-Chemical-Vapor-Deposition) technology is expected to obtain the excellent step coverage and controllability of film composition<sup>1)3)</sup>, compared with the sputtering and sol-gel technologies. However, the sufficient properties for 64mega-bit FRAM have not been obtained at the thickness of around  $0.1 \mu\text{m}$ , with practical wafer size like 6 inches.

In this study, the high quality PZT films with excellent polarization properties are obtained at the thickness of  $0.12 \mu\text{m}$  on 6 inch wafer with excellent uniformity, by controlling the decomposition of Pb-precursors for MOCVD-PZT formation.

### EXPERIMENTAL

Fig.1 shows the schematic drawing of the apparatus and metalorganic source materials for MOCVD-PZT films.  $\text{Ti}(\text{O}-i-\text{C}_3\text{H}_7)_4$ ,  $\text{Zr}(\text{O}-t-\text{C}_4\text{H}_9)_4$ , and  $\text{Pb}(\text{DPM})_2$  are used for Ti, Zr and Pb sources. These precursors were evaporated by controlling the carrier Ar gas flow ratio and the temperature of reservoir and were supplied into the reactor through the mixing chamber. Oxygen gas was supplied at the flow ratio between 200 to 2000sccm to enhance the oxidation of each species. The 6 inch wafer was placed on the SiC susceptor and raised the temperature by controlling the carbon heater. In this experiment, wafer temperature was fixed at  $600^\circ\text{C}$ . The diffuser is installed in the reaction chamber to keep the uniformity for 6 inch wafers. The uniformity of the film thickness is  $\pm 2\%$  across a wafer. As shown in Fig.2, the uniformity of Ti, Zr, Pb compositional ratio is excellent across a wafer.

To evaluate surface morphology, X-ray diffraction and electrical properties, PZT films are deposited on Pt/Ti( $0.2/0.02 \mu\text{m}$ ) electrode.

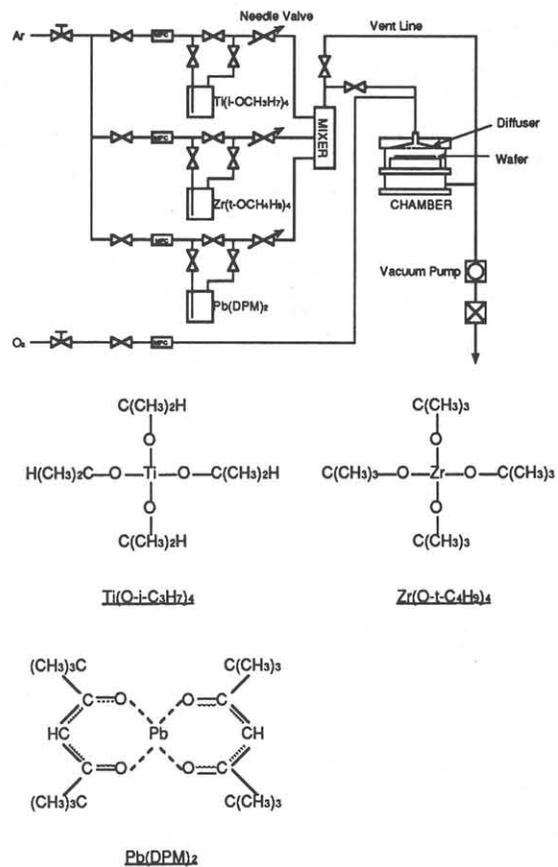


Fig.1 Schematic drawing of the apparatus and metalorganic materials for MOCVD-PZT

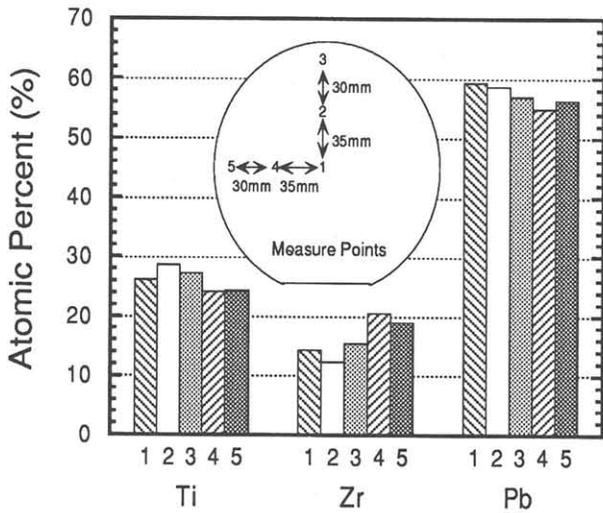


Fig.2 Compositional ratio of Ti, Zr, Pb into a wafer

### RESULTS AND DISCUSSION

Firstly, the deposition rate for  $TiO_2$ ,  $ZrO_2$  and  $PbO$  were evaluated as a function of  $O_2$  flow ratio. In the case of  $ZrO_2$  and  $TiO_2$  deposition, the deposition rate is independent of  $O_2$  flow ratio. However,  $PbO$  deposition rate is sensitive to  $O_2$  flow ratio and 1000sccm is needed to obtain enough deposition rate. Fig.3 shows the  $Pb/(Ti+Zr)$  compositional ratio for PZT film as a function of  $O_2$  flow ratio. By raising the  $O_2$  flow ratio from 200sccm to 1000sccm, Pb contents are gradually increased and stoichiometric atomic ratio is obtained above 1000sccm. For  $Ti(O-i-C_3H_7)_4$  and  $Zr(O-t-C_4H_9)_4$  materials, Zr-O and Ti-O have strong covalent bonds, so the  $TiO_2$  and  $ZrO_2$  are easily produced. However, oxygen atoms in DPM are weakly coordinated to Pb atom for  $Pb(DPM)_2$ , so Pb-O bond is easily decomposed instead of  $PbO$  formation. Increasing the wafer temperature above  $650^\circ C$  is also an important factor to enhance the  $PbO$  formation and to increase Pb content into the PZT film. However, the film deposition at the high temperature region degrades the interface properties between Pt and PZT, and grows the grains at  $0.5\mu m$  in size. So, it is essential to enhance the  $PbO$  formation at the lower temperature region.

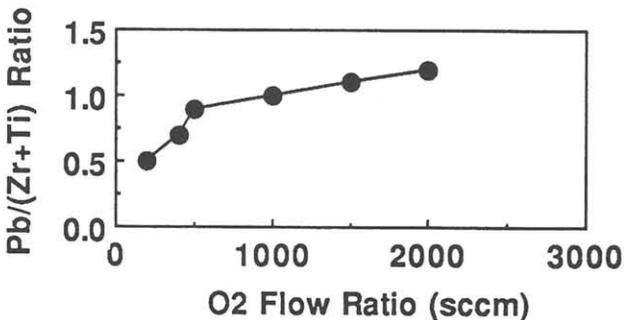


Fig.3  $Pb/(Ti+Zr)$  compositional ratio for PZT as a function of  $O_2$  flow ratio

Fig.4 shows the SEM micrograph of PZT/Pt/Ti structure, where the  $Pb/(Ti+Zr)$  compositional ratio is fixed to 1. For the  $O_2$  flow ratio of 500sccm, PZT film shows rough surface morphology. However, by increasing the  $O_2$  flow ratio to 1000sccm, the surface roughness is largely improved. Fig. 5 shows the X-ray diffraction of PZT/Pt/Ti structure. For the lower  $O_2$  flow ratio of 500sccm, the Pb poor phase such as  $PbTi_3O_7$  is observed. However, by increasing the  $O_2$  flow ratio to 1000sccm, the Pb poor phase is disappeared and only the perovskite structure is observed. When  $O_2$  flow ratio is lower, Pb precursors are easily decomposed to Pb instead of forming  $PbO$ . It is believed that Pb atoms are difficult to adsorb on Pt electrode because of high vapor pressure of Pb atoms (one order of magnitude higher than  $PbO$ ). Therefore, the non-uniform and poor  $PbO$  layer is formed at the initial deposition period. It causes the rough surface morphology and the Pb poor phase formation. However, by increasing  $O_2$  flow ratio, the uniform  $PbO$  layer is easily produced, so that it causes the uniform PZT deposition and results in the excellent surface morphology and the perovskite structure.

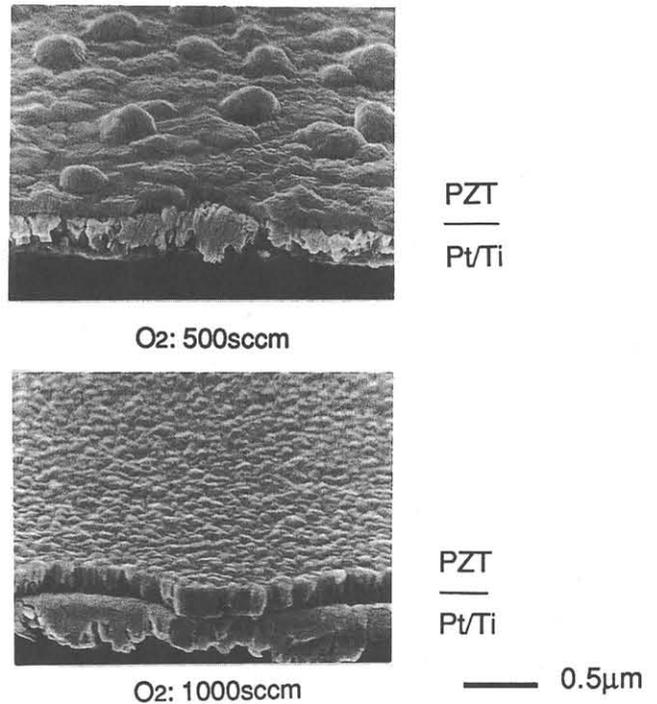


Fig.4 SEM micrograph of PZT/Pt/Ti structure ( $Pb/(Ti+Zr)$  compositional ratio = 1)

Fig.6 shows the polarization characteristics as a function of  $O_2$  flow ratio. With increase in the  $O_2$  flow ratio, the hysteresis window in the D-E curves are improved. For the sample with  $O_2$  flow ratio of 2000sccm, the excellent polarization properties ( $P_r=23.6\mu C/cm^2$ ,  $e = 838$ ) are obtained at the film thickness of  $0.12\mu m$ . The sensing charge (switched charge - non switched charge) for FRAM operation is  $34.7\mu C/cm^2$  at 1.5 V application and it enables the application for 16 - 64Mbit FRAMs. The equivalent silicon dioxide thickness of  $5.4\text{Å}$  may be used to realize 1Gbit DRAMs.

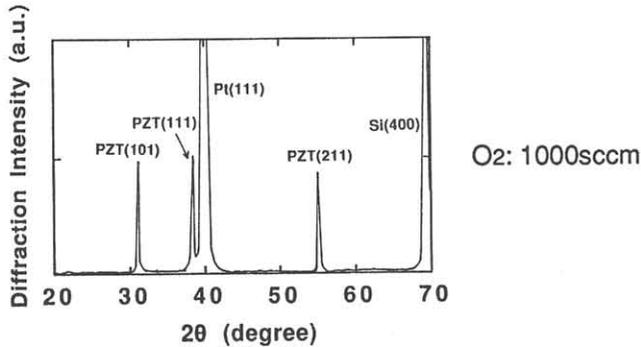
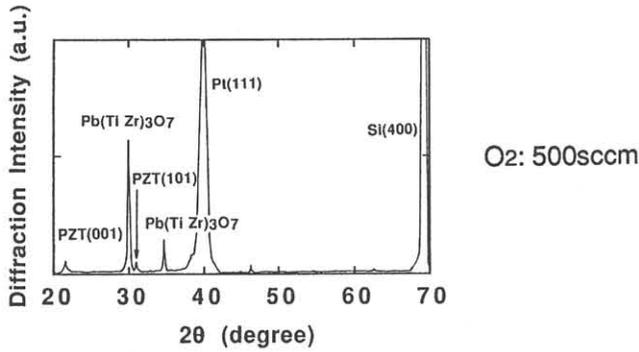
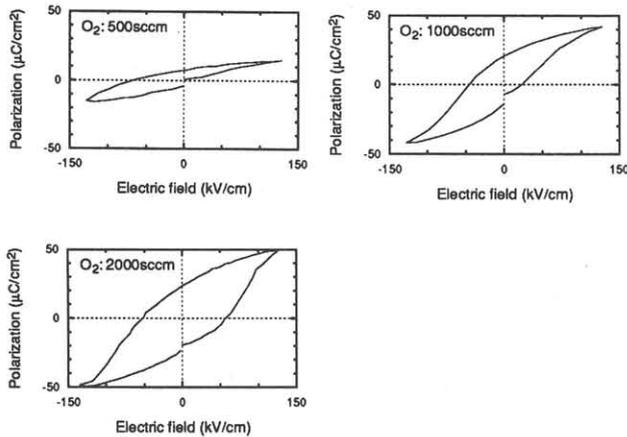


Fig.5 X-ray diffraction of PZT/Pt/Ti structure



	O <sub>2</sub> : 500sccm	O <sub>2</sub> : 1000sccm	O <sub>2</sub> : 2000sccm
Remanent polarization (μC/cm <sup>2</sup> )	3.9	17.5	23.6
Dielectric constant	427	1096	838
Sensing charge at 125kV/cm (μC/cm <sup>2</sup> )	6.8	15.8	34.7

Sensing charge=Switched charge - Non-switched charge

Fig.6 Polarization properties as a function of O<sub>2</sub> flow ratio

Fig.7 shows the SEM micrograph of PZT film at the fine contact hole patterns. For the sputtered PZT film, the bottom film thickness is about 30% of the top film thickness. However, the conformal step coverage is obtained for CVD-PZT film and it is a promising technology to fabricate high density Ferroelectric memory devices with a large step height.

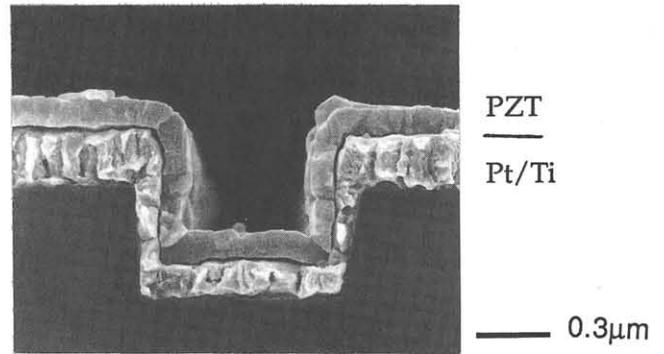


Fig.7 Step coverage of MOCVD-PZT film

## CONCLUSION

It has been demonstrated that, for the MOCVD-PZT formation, the sufficient PbO formation by enough O<sub>2</sub> gas supplement should be the key technology and it improves the surface morphology and crystallinity.

By controlling the oxygen concentration, high dielectric constant ( = 838) and high polarization ( Pr = 23.6μC/cm<sup>2</sup> ) are obtained at 0.12μm in thickness with excellent uniformity on 6 inch wafer.

As a result, the MOCVD-PZT formation, developed in this study, is suitable for 16-64 Mbit FRAMs fabrication.

## ACKNOWLEDGEMENT

We would like to thank Associate Professor Seshu B. Desu in Virginia Polytechnic Institute and State University for his helpful discussion.

## REFERENCE

- 1) H. Itoh, K. Kashiwara, T. Okudaira, K. Tsukamoto and Y. Akasaka, Tech. Dig. of IEDM 91 (1990) 831.
- 2) M. Okada, K. Tominaga, T. Araki, S. Katayama and Y. Sakashita, Jpn. J. Appl. Phys., 29 (1990) 718.
- 3) T. Katayama, M. Fujimoto, M. Simizu and T. Shiosaki, Jpn. J. Appl. Phys., 30 (1991) 2189.
- 4) R. Moazzami, C. Hu, and W.H. Shepherd, IEEE Electron Device Lett., 11(10) (1990) 454.
- 5) R. Womach and D. Toisch, Tech. Dig. of ISSCC (1989) 242.