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Influence of purge gas on the characteristics of lead–zirconium–titanate thin films prepared by metalorganic chemical vapor deposition

June-Mo Koo [a], Sukpil Kim [a], Sangmin Shin [a], Youngsoo Park [a], June Key Lee [b,*]

[a] Devices Lab., Samsung Advanced Institute of Technology, Suwon 440-600, Republic of Korea
[b] School of Materials Science and Engineering, Chonnam National University, 300 Yongbong, Gwangju 500-757, Republic of Korea

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Abstract

In order to optimize the metalorganic chemical vapor deposition process for $PbZr_xTi_{1-x}O_3$ (PZT) thin films, the effect of purge gas species was investigated. Two steps of gas input process for stabilizing reaction chamber pressure, the gas flow prior to $PbTiO_3$ (PTO) seed layer deposition and PZT thin film deposition, were varied and their effect on structural and electrical properties were examined with regard to the memory device application. PZT film properties exhibited remarkable dependency on the gas species before PTO seed deposition, and insignificant dependency on the gas species before PZT film deposition. With the optimized pre-deposition gas flow, PZT thin film showed excellent properties such as high (1 1 1)-orientation (92.2%), high remnant polarization value of 71 $\mu C/cm^2$ at 3 V. Retention property also showed a heavy dependency on the pre-deposition gas flow that 91.1% of initial charge could be maintained after 100 h of baking at 150 °C.

Keywords: C. Ferroelectric properties; D. PZT; E. Capacitors; MOCVD

1. Introduction

The promising properties of ferroelectric materials for application as nonvolatile memory devices have driven the intensive investigation of ferroelectric thin film technology since 1960s. Recently the demand for portable equipment strongly requires the development of high-density ferroelectric random access memories (FRAM), because ferroelectric thin film can provide non-volatility, low power operation and high read/write speed [1]. Three materials, $PbZr_xTi_{1-x}O_3$ (PZT), $SrBi_2Ti_2O_9$ and $Bi_{4-x}La_xTi_3O_{12}$, have been investigated intensively for the realization of FRAM device. In this study, PZT was chosen as the ferroelectric material because it possesses a relatively lower crystallization temperature and a larger remnant polarization [2–4]. Various kinds of thin film deposition technology have been utilized to make PZT thin films such as chemical solution deposition, sputtering, pulsed laser deposition, and metalorganic chemical vapor deposition (MOCVD) [3–8]. Among them, MOCVD is the most promising technique for high-density FRAM integration from a practical point of view because MOCVD has advantages such as low deposition temperature, high growth rate, high uniformity, and high step coverage. According to an international technology roadmap for semiconductor, the semiconductor industry expects that the MOCVD technique should be utilized for the integration of 256 Mbit density and beyond after 2010 [9].

However, the PZT MOCVD process has a fundamental problem in that stable delivery of metalorganic precursors is hard to achieve with conventional bubbler technology because of the lack of suitable precursors [10]. In order to overcome the limitation of precursors, liquid source delivery MOCVD was suggested and has exhibited promising results recently, although it still requires high reproducibility for the mass production [3,11–13]. MOCVD is a quite complicated process because it has many process parameters to control. Process parameters such as deposition temperature and input amount precursors and their ratio, and creative ideas such as seed layer and pulse-MOCVD have been evaluated and displayed the improvement in structural and electrical properties of PZT thin films [3,14,15]. In order to achieve a reliable PZT MOCVD process, the effects of all possible process parameters should be fully understood. In this study, attention is focused on the purge

* Corresponding author. Tel.: +82 62 530 1692; fax: +82 62 530 1699.
E-mail address: junekey@chonnam.ac.kr (J.K. Lee).

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gas species that was supplied to reaction chamber prior to PZT thin film deposition to stabilize reaction chamber pressure. In general the effect of purge gas species has been ignored because chemically inert gas was previously utilized. On the other hand, if the purge gas interacts with the substrate, the initial state of the PZT MOCVD process could be seriously influenced, resulting in variations of PZT thin film properties. The effect of purge gas species was monitored in terms of the structural and electrical properties of PZT thin films.

2. Experimental procedure

PZT thin film deposition was carried out in a Nexcap 2000 CVD reactor (Sunic System Ltd.). The showerhead technique was employed for uniform deposition of a 6 in. wafer, and a liquid source delivery system was utilized in order to control the supply amount of precursor solutions to within ±1% accuracy. The metalorganic precursors were $Pb(tmhd)_2$, $Zr(tmhd)_2(^iOPr)_2$ and $Ti(tmhd)_2(^iOPr)_2$, all of which were dissolved in octane solvent and reserved separately in each ampoule. PZT thin films were grown on an Ir (100 nm)/Ti (5 nm) electrode, which was deposited on SiO_2 (200 nm)/Si(1 0 0) wafer at 200 °C by dc magnetron sputtering. The deposition temperature of PZT thin film was 530 °C and other major process parameters were described in Refs. [4,14]. The growth rate was about 6.0 nm/min, resulting in a PZT film thickness of about 100 nm after the deposition of 18 min. $PbTiO_3$ (PTO) was utilized as a seed layer with a thickness of 6 nm. As a purge gas, oxygen, nitrogen and their mixture was utilized with a total amount of 2000 sccm.

A top Ir (70 nm)/IrO_2 (30 nm) electrode was sputter-deposited, and etched off to pattern the capacitors with the size of 100 μm × 100 μm for the measurement of electrical properties. The etching process was accomplished by the inductively coupled plasma-reactive ion etcher (ICP-RIE). Electrical properties were measured using the Radiant Technologies Precision Pro system.

3. Results and discussion

The MOCVD process for PZT thin film deposition consisted of five steps as shown in Fig. 1 in this study. 6 nm thick PTO seed layer was introduced in order to reduce the deposition temperature of PZT thin films [14,16]. There are two purge gas steps for 1 min prior to PTO seed layer deposition and PZT thin film deposition. Generally chemically inert gas has been utilized as a purge gas for MOCVD. The main role of purge gas is to stabilize the reaction chamber pressure, which could be perturbed by the sudden supply of metalorganic precursors at the initial stage of film growth. Conventionally N_2 was utilized as a purge gas for the PZT MOCVD process, but it was replaced with O_2 in this work. Interestingly hysteretic property was greatly improved that remnant polarization ($2P_r$) value was drastically increased to 62 μC/cm^2 compared with the $2P_r$ = 34 μC/cm^2 when N_2 was used as purge gas as shown in Fig. 2. Since the Iridium (Ir) electrode can be oxidized in O_2 ambient, the initial stage of PTO seed growth might be seriously influenced by purge gas species during step (a). Once again, N_2 was added to O_2 purge gas and the effect was evaluated in terms of hesteretic property. $2P_r$ value was

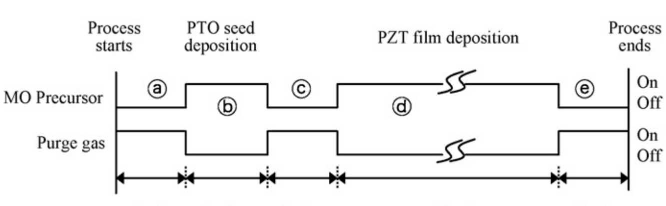

Fig. 1. Process sequence of MOCVD process for PZT thin film preparation. Step (b) corresponds to PTO seed layer deposition, and step (d) is assigned to PZT thin film deposition. Step (a) and (c) correspond to purge gas flow for 1 min in order to stabilize the pressure in the reaction chamber.

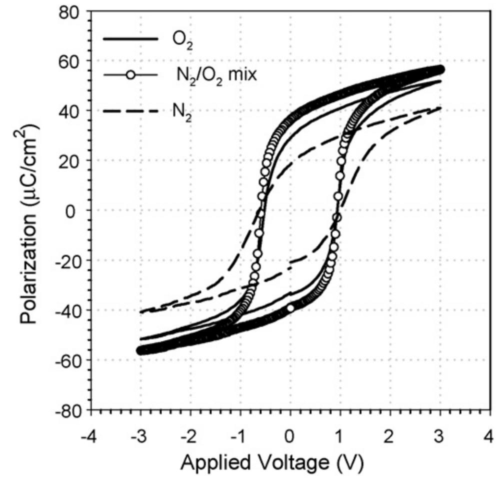

Fig. 2. Ferroelectric hysteresis loops for Ir/IrO_2/PZT/Ir capacitors fabricated using three different purging gases for PTO seed deposition (step (a)). Step (c) was fixed with N_2/O_2 = 0/2000 sccm. (—): O_2 2000 sccm; (– – –): N_2 2000 sccm; (○): N_2/O_2 = 500/1500 sccm. Remnant polarization values ($2P_r$) are 62 μC/cm^2 (—), 34 μC/cm^2 (– – –), and 71 μC/cm^2 (○), respectively.

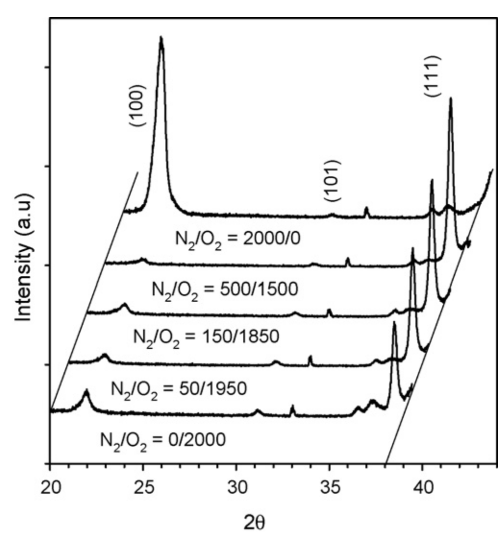

Fig. 3. X-ray diffraction θ–2θ pattern of PZT thin films deposited with a variation of purging gas mixture ratio prior to PTO seed layer deposition. Purge gas in step (c) was fixed with N_2/O_2 = 0/2000 sccm.

increased with added amount of N_2, and exhibited the optimized value (71 μC/cm^2) at the mixture ratio of N_2/O_2 = 500/1500 sccm. Fig. 3 shows an X-ray diffraction θ–2θ scan analysis, which indicates that crystal structure of PZT thin films is heavily dependent on the purge gas species. FRAM chip makers have endeavored to achieve highly (1 1 1)-oriented PZT thin films because they exhibit higher $2P_r$ and more improved retention properties [17]. However, unlike CSD-derived PZT thin film that is highly (1 1 1)-oriented, MOCVD PZT thin films usually show predominantly (1 0 0), (0 0 1)-textured structure with some (1 0 1), (1 1 0) and (1 1 1)-type orientation, or polycrystalline structures without any preferred orientation when the PZT films were deposited at low temperature [4,15,17]. MOCVD PZT could also demonstrate (1 1 1) preferred orientation but required high deposition temperature, greater than 590 °C [3,18]. It was revealed that PZT thin film orientation could be controlled by simply altering purge gas species as shown in Fig. 3. At optimized purge gas flow, that is N_2/O_2 = 500/1500 sccm, PZT thin film displayed 92.2% (1 1 1)-orientation with 5.1% (1 0 0) and 2.7% (1 0 1)-orientation as shown in Table 1. When the N_2 portion exceeded the optimized condition, XRD peak intensity I(1 1 1) and $2P_r$ values were gradually decreased and finally the PZT thin film had highly (1 0 0) preferred orientation.

After step (a) was ended in Fig. 1, the process was stopped and Ir electrodes were removed for surface analysis. XPS analysis was attempted in order to investigate the difference of surface state when Ir electrodes were exposed to O_2, N_2, and a mixture of these gases. However, differences were observed by XPS analysis. The PTO seed layer was also removed after step (b) was finished for further XPS analysis. In Fig. 4, the peak shift of Ti 2p peak to lower binding energy about 0.5 eV could be observed when purge gas was pure N_2. Peak synthesis indicated that about 60% of Ti was in partially oxidized Ti(+3) state. This observation could not directly explain the PZT crystal orientation hereafter, but proved that purge gases do affect the initial state for PZT thin film growth.

The influence of purge gas species during step (c) was examined with the same approach as conducted for step (a). On the basis of hysteresis shapes, the effect of purge gas species is not significant. PZT thin film capacitors exhibited $2P_r$ values within the range of 56–62 μC/cm^2 depending on the purge gas mixing ratio. Obviously there is systematic trend that (1 1 1)-orientation is growing as O_2 portion in purge gas is increasing (Table 2). In accordance with the previous results, highly (1 1 1)-oriented PZT thin film displayed bigger $2P_r$ values.

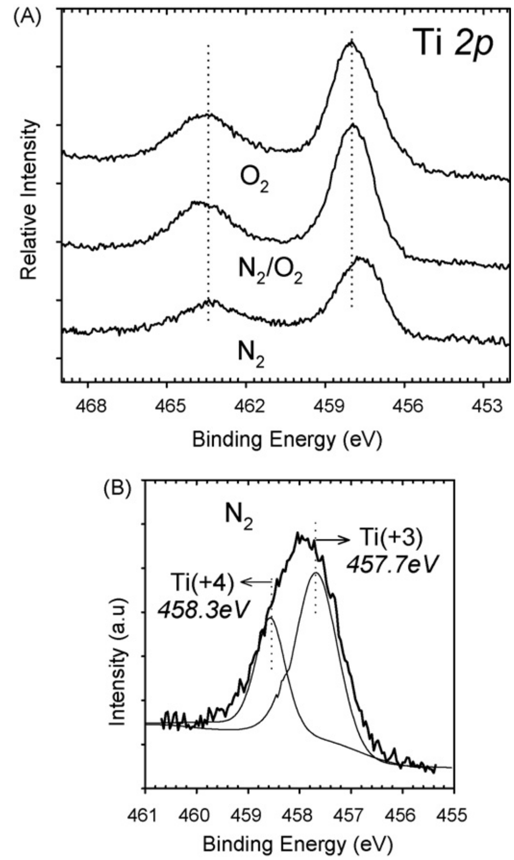

Fig. 4. XPS analysis of Ti elements in PTO seed layer deposited with three different purge gases in first purge step (a). In N_2 purge gas, Ti 2p peak was shifted to lower binding energy (A). Peak synthesis indicates that about 60% of Ti is in partially oxidized Ti(+3) state (B).

With the optimized purge gas conditions in step (a) and step (c), that is N_2/O_2 = 500/1500 sccm for PTO seed layer deposition and N_2/O_2 = 0/2000 sccm for PZT thin film deposition, a PZT thin film capacitor showed excellent resistance against retention test as shown in Fig. 5. After baking 100 h at 150 °C, the PZT thin film capacitor maintained about 91.1% of initial switching charge in the optimized condition, while the O_2 purged condition and the N_2 purged condition resulted in 83.6% and 54.9% of initial switching charge, respectively. This might be attributed to the fact that highly (1 1 1)-oriented PZT allows simple domain switching movement.

In this study, it turned out that purge gas species could significantly influence the structural and electrical properties of

Table 1
Ratio of XRD peak intensity as a function of purging gas (N_2/O_2) flow rate in step (a)

N_2/O_2 flow (sccm) (%)	0/2000	50/1950	150/1850	500/1500	2000/0
I(1 0 0)	19.9	13.2	9.5	5.1	90.9
I(1 0 1)	6.9	6.4	4.0	2.7	3.4
I(1 1 1)	73.2	80.4	86.5	92.2	5.7

Purge gas in step (c) was fixed with N_2/O_2 = 0/2000 sccm. $I(i\,j\,k)\,(\%) = I(i\,j\,k)/[I(1\,0\,0) + I(1\,0\,1) + I(1\,1\,1)] \times 100$.

Table 2
Ratio of XRD peak intensity as a function of purging gas (N_2/O_2) flow rate in step (c)

N_2/O_2 flow (sccm) (%)	0/2000	50/1950	150/1850	500/1500	2000/0
I(1 0 0)	19.9	21.7	28.2	32.3	36.5
I(1 0 1)	6.9	7.0	5.7	4.4	8.7
I(1 1 1)	73.2	71.3	66.1	63.3	54.8

Purge gas in step (a) was fixed with N_2/O_2 = 0/2000 sccm. $I(i\,j\,k)\,(\%) = I(i\,j\,k)/[I(1\,0\,0) + I(1\,0\,1) + I(1\,1\,1)] \times 100$.

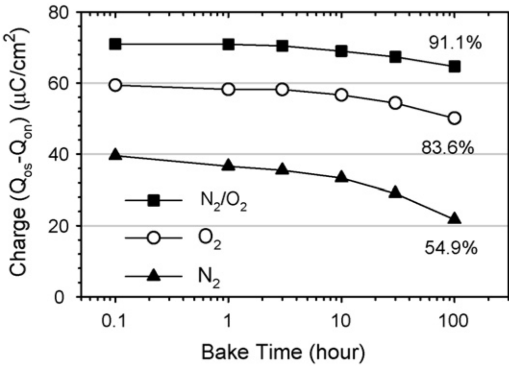

Fig. 5. Retention properties of Ir/IrO_2/PZT/Ir capacitors fabricated using three different purging gases for seed PTO deposition. Second purge step (c) was fixed with N_2/O_2 = 0/2000 sccm. Baking temperature is 150 °C and hysteresis properties were measured at 85 °C. (○): O_2 = 2000 sccm; (▲): N_2 = 2000 sccm; (■): N_2/O_2 = 500/1500 sccm.

PZT thin films in the MOCVD process. For the MOCVD of PZT thin films with high remnant polarization and (1 1 1)-orientation, it is recommended that optimized N_2 and O_2 mixture should be employed as a purge gas.

4. Conclusions

One hundred nanometer thick PZT thin films were prepared on an Ir electrode by MOCVD with a 6 nm thick PTO seed layer. The PZT films were deposited at 530 °C and the effect of purge gas was investigated in detail. For purge gas flow prior to PTO seed layer deposition, as the N_2 portion increased in purge gas, the crystal (1 1 1)-orientation and remnant polarization values were linearly increased. When only N_2 was employed, PZT film showed high (1 0 0)-orientation and small remnant polarization value. On the contrary, for purge gas flow prior to PZT film deposition, the effect was insignificant even though there was a linear trend that (1 1 1)-orientation was increased as the N_2 portion in the purge gas decreased. At the optimized condition, purge gas flow of N_2/O_2 = 500/1500 sccm before PTO seed layer, and N_2/O_2 = 0/2000 sccm before PZT film deposition, PZT thin film showed excellent properties such as high (1 1 1)-orientation (92.2%), remnant polarization value of 71 $\mu C/cm^2$ and coercive voltage of 0.72 V at 3 V. Retention property also showed a heavy dependency on the purge gas species such that 91.1% of initial charge was maintained after 100 h of baking at 150 °C.

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