Integrated Ferroelectrics, 59: 1483–1489, 2003

ISSN: 1058-4587 print/ 1607-8489 online
DOI: 10.1080/10584580390273375

Atomic Layer Deposition (ALD) of Bismuth Titanium Oxide Thin Films Using Direct Liquid Injection (DLI) Method

YOUNG JIN CHO,[1] YO-SEP MIN,[1] JUNG-HYUN LEE,[1]
BUM-SEOK SEO,[1] JUNE KEY LEE,[1] YOUNG SOO PARK,[1]
and JIN-HAK CHOI[2]

[1]*Materials and Devices Lab., Samsung Advanced Institute of Technology, San #24, Nongseo-Ri, Kiheung-Eup, Yongin-City, Kyungi-Do 449-900, Korea*
[2]*Analytical Engineering Center, Samsung Advanced Institute of Technology, San #24, Nongseo-Ri, Kiheung-Eup, Yongin-City, Kyungi-Do 449-900, Korea*

(Received April 20, 2003)

We report on atomic layer deposition of bismuth titanium oxide thin films for use in ferroelectric random access memory (FRAM). Bismuth titanium oxide thin films were grown on ruthenium and platinium coated silicon substrates respectively. We used tris(1-methoxy-2-methyl-2-propoxy)bismuth, $Bi(mmp)_3$ and tetrakis(1-methoxy-2-methyl-2-propoxy)titanium, $Ti(mmp)_4$ as metal organic precursors, which were mixed together in organic solvent, ethyl cyclo hexane (ECH), and then put through the vaporizer.

The variations of the composition and growth rate with wafer temperature over 350∼450 and 250∼500C was investigated. The process window for ALD is below 350C and bismuth content in films starts to decrease above 425C.

The as-grown films at 300C were amorphous. After post deposition annealing at 700C for 5 minitues we had well-cystallised $Bi_4Ti_3O_{12}$ thin films. However, we didn't have well-saturated hysterisis curve, which the remenant polization is 8.9 uC/cm^2 at 7 V.

The dielectric constant is about 320 and the leakage current is below 10^{-8} A/cm^2 at 0.8 MV/cm.

Keywords: ALD; vaporizer; FRAM, hysteresis loop; dielectric constant; leakage current; bismuth titanium oxide

1. INTRODUCTION

Ferroelectirc random access memory (FRAM) is one of promising candidates for future memory devices due to its ideal properties such as non-volatility, high edurance, fast write/read time and low power consumption. Recently, 32Mb FRAM was developed using 1T1C COB cell structure and 0.25 um technology [1].

Futher, a high density of FRAM will require processes compatible to above 200 mm wafer, to produce high quality ferroelectric materials and conformality over 3 dimensional capacitor storage node. We need a new deposition method like metal organic chemical vapor depositon (MOCVD) [4].

However, it is diffcult to get high quality ferroelectic thin films and good conformality over storage node with high aspect ratio simultaniously using MOCVD. In order to get high quality films, the deposition tempature have to be high, but improving step coverage, the deposition temperature need to be low because of difference of growth mechanisms between the low and high temperature MOCVD.

Lately, there are many reports about oxide materials grown by the atomic layer depositon method, which are high quality and good step coverage over 3 dimensioal tophologies at relatively low deposition temperature [3].

So, we report on atomic layer deposition of bismuth titanium oxide thin films in use for ferroelectric random access memory (FRAM) using direct liquid injection (DLI) method.

2. EXPERIMENTAL

The bismuth titanium oxide thin films were prepared on ruthenium and platinium coated silicon substrates by atomic layer deposition (ALD). The tris(1-methoxy-2-methyl-2-propoxy)bismuth, $Bi(mmp)_3$ and the tetrakis(1-methoxy-2-methyl-2-propoxy)titanium, $Ti(mmp)_4$ (Ashai Denka Kogyo K.K., Japan) were chosen as the metal organic precursors, where these precursors were mixed together in ethyl cyclo hexane (ECH) and put through vaporizer heated at 230C. Oxyzen and ozone gas were used as the oxidizing gas. A summary of growth condition is given in Table I.

The composition of a bismuth titanium oxide was measured by inductively coupled plasma-atomic emmision spectroscopy (ICP-AES) and X-ray photoelectron spectroscopy (XPS).

We fabricated planar metal-ferroelectrics-metal capacitor, which we used platinium as metal electrodes. The top electrode was formed by dc magnetron sputter at room temperature using stainless steel shadow-mask, diameter 300 um.

To investigate the electrical properties, we use RT66A, HP 4156 semiconductor parameter analyzer, and HP 4284 LCR meter.

TABLE I The deposition condition for bismuth titanium oxide thin films

Substrate temperature	250~500C
Vaporizer temperature	230C
Working pressure	1 torr
Precursors	$Bi(mmp)_3$: $Ti(mmp)_4$ = 0.1 mole/liter : 0.1 mole/liter and 0.04 mole/liter : 0.12 mole/liter in ethyl cyclo hexane
Reaction gas	Oxyzen and ozone
Source feed rate	0.01~0.03 cc/cycle
Substrate	Ru(1000A)/SiO_2(1000A)/Si and Pt(1000A)/Ti(100A)/ SiO_2(2000A)/Si

3. RESULTS AND DISCUSSIONS

As shown in Fig. 1, the growth characteristics of bismuth titanium oxide thin films are different between below and above 350C. The former is independent of thermal energy, the latter is highly dependant. The atomic layer deposition defines self-limiting film growth via alternate saturative surface reaction [3]. Thus, we found that the process window for ALD is below 350C.

In general, many reports said that the control of bismuth content in films is difficult in growing the bismuth related oxide system at low deposition temperature, due to the low incoporation efficiency of bismuth [4, 5]. But using newly suggested precursor, $Bi(mmp)_3$, we could get the bismuth rich titanium oxide at low temperature [6]. Figure 2 shows that the bismuth

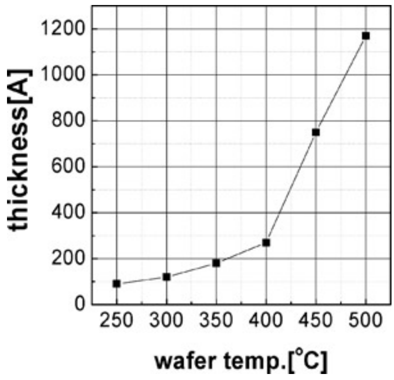

FIGURE 1 The variation of films' thickness with wafer temperature. One cycle consists of four steps such as, argon purging, source feeding, argon purging and oxidizing gas feeding. (The number of cycle: 200, substrate: Ru/SiO_2/Si.)

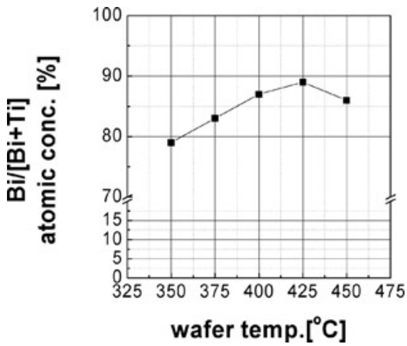

FIGURE 2 The variation of the bismuth content in films with wafer temperature, measured by ICP-AES. ($Bi(mmp)_3$: $Ti(mmp)_4$ = 0.1 mole/liter : 0.1 mole/liter in ECH.)

content in films starts to decrease above 425C due to the volatile bismuth species [4].

In order to get stoichiometric $Bi_4Ti_3O_{12}$ thin films, we try to change the composition in cocktail solution, $Bi(mmp)_3$: $Ti(mmp)_4$ = 0.04 mole/liter : 0.12 mole/liter. Figure 3 shows that XRD patterns of as-grown and

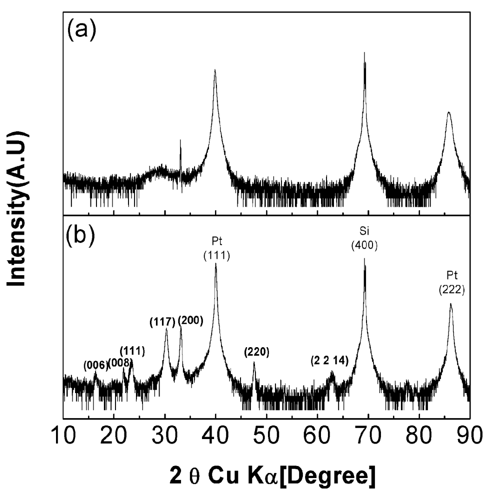

FIGURE 3 XRD patterns of (a) as-grown (300C) and (b) annealed (700C, 5 min, oxidizing ambient). (Substrate: $Pt/Ti/SiO_2/Si$, $Bi(mmp)_3$: $Ti(mmp)_4$ = 0.04 mole/liter : 0.12 mole/liter in ECH.)

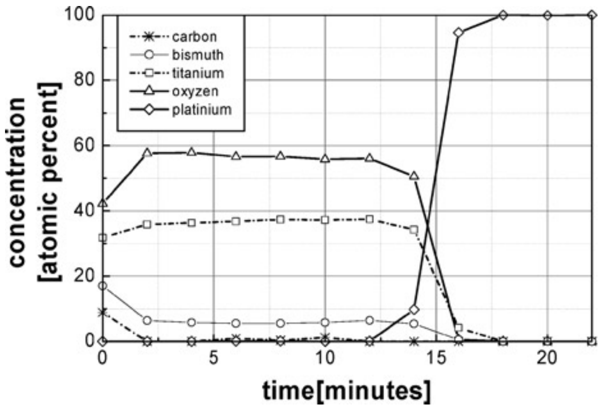

FIGURE 4 The depth profiles of $Bi_4Ti_3O_{12}$ thin films, measured by XPS, sputtering condition: Ar 2 kV.

annealed bismuth titanium oxide thin fims. As-grown films are amorpous but $Bi_4Ti_3O_{12}$ formed after annealing at 700C for 5 minutes. And as shown in Fig. 4, although the deposition temperature is as low as 300C, the carbon impurity originated from precursors is very low, below 1 atomic percent.

To investigate electrical properties, we fabricated Pt/(annealed)-$Bi_4Ti_3O_{12}$/Pt MFM planar capacitor. Figure 5(a) shows that their P-E

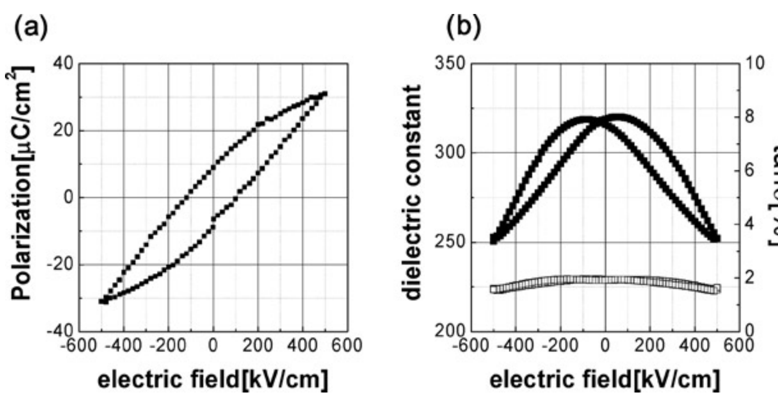

FIGURE 5 (a) Polarization—electric field hysteresis loop of a Pt/(annealed)-$Bi_4Ti_3O_{12}$/Pt planar capacitor, remnant polarization(Pr): 8.9 uC/cm^2, coecive field(Ec): 109.7 kV/cm at applied voltage: 7 V, (b) dieletric constant—electric field curves for a Pt/(annealed)$Bi_4Ti_3O_{12}$/Pt planar capacitor. (thickness: 1400 A, frequency: 10 kHz, oscilation amplitude: 50 mV, measured by HP 4284 LCR meter.)

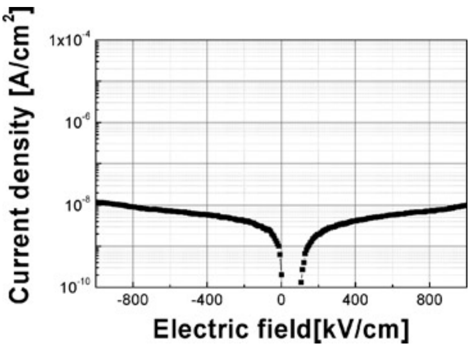

FIGURE 6 The current density—electric field characteristics of a Pt/(annealed) $Bi_4Ti_3O_{12}$/Pt planar capacitor.

hysteresis loop. Even if a well-crystallised $Bi_4Ti_3O_{12}$, we didn't get a well-saturated hysteresis loop, which the remnant polarization is 8.9 uC/cm^2, the coercive field 109.7 kV/cm.

Figure 5(b) shows the dielectric properties, which the dielectric constant was around 320 and the loss factor (tangent delta) was below 2%. And as shown in Fig. 6, the leakage current was low, below 10^{-8} A/cm^2 at 0.8 MV/cm.

4. CONCLUSIONS

In summary, bismuth titanium oxide thin films were grown on platinium and ruthenium coated silicon substrate by atomic layer deposition (ALD), which we were used direct liquid injection (DLI) method as a source delivery system. The process window for ALD is below 350C, which we didn't get troubled with control of bismuth content in thin films, since bismuth content in films starts to decrease above 425C due to the volatile bismuth oxide.

As-grown bismuth titanium oxide thin films at 300C were amorpous, but after post-deposition annealing we had a well-crytallise $Bi_4Ti_3O_{12}$, which the dielectirc constant was about 320 and the leakage current was 10^{-8} A/cm^2. However, we didn't get a well-saturated hysteresis loop of Pt/annealed $Bi_4Ti_3O_{12}$/Pt planar MFM capacitor, which the remnant polarization was 8.9 uC/cm^2 and the coercive field 109.7 kV/cm.

REFERENCES

[1] S. Y. Lee and K. Kim, *IEDM* 547 (2002).
[2] A. Nitayama, Y. Kohyama, and K. Hieda, *IDEM* 355 (1998).
[3] M. Ritala and M. Leskela, *Handbook of Thin Film Materials* **1**, 103, Academic Press (2002).
[4] J. F. Roeder, B. C. Hendrix, F. Hintermaier, D. A. Desrochers, T. H. Naum, G. Bhandari, M. Chappuis, P. C. Van Buskirk, C. Dehm, E. Fritsch, N. Nagel, H. Cerva, W. Honlein, and C. Mazure, *Journal of the European Ceramic Society* **19**, 1463 (1999).
[5] M. Schuisky, K. Kukli, M. Ritala, A. Harsta, and M. Leskela, *Chemical Vapor Deposition* **6**, 139 (2000).
[6] P. A. Williams, A. C. Jones, M. J. Crosbie, P. J. Wright, J. F. Bickley, A. Steiner, H. O. Davies, T. J. Leedham, and G. W. Critchlow, *Chemical Vapor Deposition* **7**, 205 (2001).