Extended Abstracts of the 1997 International Conference on Solid State Devices and Materials, Hamamatsu, 1997, pp. 28-29

Mechanisms of Synchrotron X-Ray Irradiation-Induced Damage in (Ba,Sr)TiO_3 Capacitors

Masayoshi Tarutani, Junji Tanimura, Tsuyoshi Horikawa, Muneyoshi Suita,
Takaaki Kawahara, Mikio Yamamuka, Hiroaki Sumitani and Kouichi Ono
Advanced Technology R&D Center, Mitsubishi Electric Corporation,
8-1-1 Tsukaguchi-Honmachi, Amagasaki, Hyogo 661, Japan
Phone: +81-6-497-7099, Fax:+81-6-497-7288, E-mail: tarutani@apr.crl.melco.co.jp

1. Introduction

It is widely appreciated that new types of capacitors with high-ε dielectrics are necessary for Gbit-scale DRAMs to be fabricated. We consider that stacked capacitors with (Ba,Sr)TiO_3 [BST] thin films prepared by chemical vapor deposition (CVD) are the most promising owing to their superior properties [1]. We have already reported that 25-nm-thick BST films deposited on Pt or Ru electrodes have a high permittivity ($\varepsilon > 150$), small equivalent SiO_2 thickness ($t_{eq} \sim 0.5$ nm), uniform film structure (polycrystalline fine grains), and low leakage current ($< 1.2\text{x}10^{-8}$ A/cm^2 at 1.1 V). A step coverage as high as 80 % can be obtained on a graded structure with an aspect ratio ~ 1.4, which enables a thick stacked structure to be applied for BST capacitors [1,2].

These properties meet the requirements for Gbit-scale DRAMs, if they remain through back-end processes for DRAM fabrication, such as lithography, plasma etching, and thermal processes. To evaluate the applicability of BST capacitors for DRAMs, it should be an important issue to examine the stability of BST capacitor properties for these back-end processes, and also to find a process for their recovery.

Extensive works have been concerned with hydrogen sintering damage for Pt/Pb(Zr,Ti)TiO_3/Pt capacitors [3] and high temperature annealing effects on BST capacitors [4]. In these papers, it has been shown that the properties of the high-ε dielectrics are affected severely by these processes. However, there have been few reports dealing with the other back-end processes.

In the present paper, we evaluate synchrotron X-ray radiation effects on current leakage property of BST capacitors. Due to its short wave length, synchrotron X-ray lithography [5] is considered to be a promising technique for Gbit-scale DRAM fabrication. We used flat BST film capacitors deposited on Pt electrodes for the experiments. The internal structures of BST films were observed with a transmission electron microscope (TEM). Based on these results, we discuss about mechanisms of radiation damage in the BST capacitors and the applicability of the BST capacitors for future DRAMs.

2. Experimental

Pt/BST/Pt capacitors were prepared as samples for SR irradiation experiments. The bottom Pt electrode on SiO_2/Si substrates and top Pt electrodes were deposited by RF magnetron sputtering. The BST films in thickness ~ 30 nm were deposited by liquid-source CVD using two-step deposition technique [2]. Ba(dipivaloylmethanato: $DPM)_2$, $Sr(DPM)_2$ and $TiO(DPM)_2$ dissolved in tetrahydrofuran were used as liquid source materials.

We used the Mitsubishi Electric synchrotron radiation (SR) facility for X-ray irradiation experiments. The BST capacitors were irradiated by ~ 1.65 keV photons from the normal to the substrates. The total X-ray energy density was varied as 10, 50, 130 mJ/cm^2, to investigate X-ray dose dependence of the degradation of BST capacitors. In addition, post annealing at 400℃ for 20 min in oxygen ambiance was performed to examine recovery of the X-ray irradiation damage.

The leakage current density (J) versus applied voltage (V) characteristics of BST capacitors were measured with an HP-4140B picoammeter/voltage-source. We also examined the internal structure of BST films with a JEOL-4000EX II TEM, operating at 400kV.

3. Results and Discussion

Figure 1 is a dark-field cross-sectional TEM image of a Pt/BST/Pt flat film capacitor, showing that two-step CVD-BST film consists of many fine grains 10 ~ 20 nm in size and few amorphous regions, where no enormously grown hillock is formed. Typical properties of the films used in the present experiments were as follows: a dielectric constant $\varepsilon > 150$, leakage current density ~ $2\text{x}10^{-8}$ A/cm^2, at 1.1 V of bias voltage, and equivalent SiO_2 thickness $t_{eq} \sim 0.6$ nm.

Figure 2 shows J-V characteristics of the Pt/BST/Pt capacitor measured (a) before and after the X-ray irradiation with X-ray energy densities of (b) 10 mJ/cm^2, (c) 50 mJ/cm^2, and (d) 130 mJ/cm^2, respectively. After the X-ray irradiation, the leakage current density has been found to increase at lower voltages. In this paper, we define the voltage at which the leakage current starts to increase as a turn-on voltage (V_{to}), and also the separation between (a) and the other data as a V_{to} shift. For example, the V_{to} shift of the sample after the X-ray irradiation of 130 mJ/cm^2 is estimated as ~ 0.35 V.

Figure 3 shows J-V characteristics of the Pt/BST/Pt capacitor measured (a) before and (b) after the X-ray irradiation, and (c) after the X-ray irradiation and the following annealing at 400℃ for 20 min in O_2. It is clear that the damage was easily recovered by annealing.

These results lead to a speculation that the degradation by X-ray irradiation is simply ascribed to charge damage. Figure 4 schematically shows the mechanisms of X-ray irradiation-induced damage. When a material is irradiated by high energy X-rays, it is well-known that reaction between X-rays and the material causes photoelectric effects, including charge damage and electron and photon emission. After the photoelectric reaction, electrons are scattered and lost, but some of positive charges are considered to be captured by charge traps such as impurities, point defects and grain boundaries. These charge damages are considered to induce degradation in J-V characteristics. Intensive works concerning to X-ray damage have been carried out for metal/SiO_2/Si capacitors [6], reporting that X-ray irradiation creates positive charge traps and they affect the device properties similar to the present results. Nevertheless, BST films comprise polycrystalline grains, unlike to amorphous SiO_2, as shown in Fig. 1, hence the internal structures is considered to reflect on the charge damages. We have also examined some other Pt/BST/Pt and Ru/BST/Ru capacitors, and similar tendencies of the charge damage with slight structural dependence were found (not shown).

The observed damage is thermally unstable or non-permanent, and easily recovered by relatively low-temperature annealing, indicating that it is not due to structural change or deoxidization. It may be concluded that the X-ray irradiation-induced damage is not a serious matter at the SR lithography process for the DRAM fabrication. Further investigations on the reliability of the BST capacitors are now under way.

4. Conclusions

We have shown degradation properties of the BST capacitor by X-ray irradiation. It was revealed that the X-ray irradiation causes small degradation, lowering of the turn-on voltage in J-V characteristics of the capacitor. The degree of the damage has been revealed to depend on the X-ray dose. However, the damage can be relieved by 400℃ annealing in O_2. The degradation appears to be caused by metastably trapped charges. These results indicate that the BST capacitors and SR lithography are applicable to the DRAM fabrication.

References

1) A. Yuuki, M. Yamamuka, T. Makita, T. Horikawa, T. Shibano, N, Hirano, H, Maeda, N. Mikami, K. Ono, H. Ogata and H. Abe: *Tech. Dig. IEDM*, (1995) p.115.
2) T. Kawahara, M. Yamamuka, A. Yuuki and K. Ono: Jpn. J. Appl. Phys., **33** (1995) p.5077.
3) K. Kushida-Abdelghafar, H. Miki, K.Torii and Y. Fujisaki: Appl. Phys. Lett., **69** (1996) p.3188.
4) T. Horikawa, T. Makita, M. Yamamuka, T. Kawahara, T. Kuroiwa, T. Shibano, N. Mikami and K. Ono: *Proc. 9th Int. Symp. Integrated Ferroelectrics*, (1997) to be published.
5) H. Sumitani, K. Itoga, M. Inoue, H. Watanabe, N. Yamamoto, K. Marumoto and Y. Matsui: *SPIE, Int. Symp. Microlithography*, (1995) p.2437.
6) L. C. Hsia and I. Magdo: J. Vac. Sci. Techol.: **B6** (1989) p.1667.

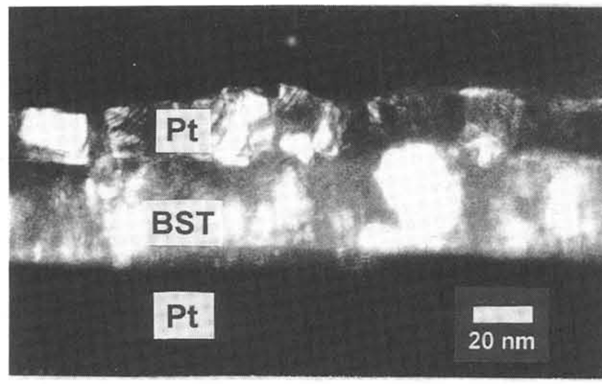

Figure 1. Dark-field cross-sectional TEM image of Pt/BST/Pt.

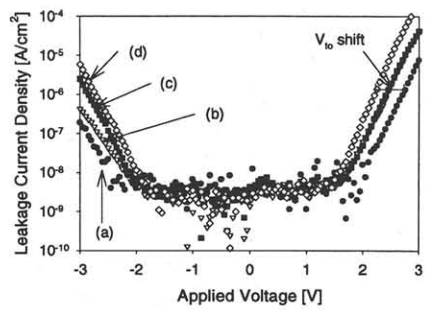

Figure 2. J-V characteristics of a Pt/BST/Pt capacitor: (a) as deposited BST, and after X-ray irradiation with X-ray energy densities (b) 10 mJ/cm^2, (c) 50 mJ/cm^2, and (d) 130 mJ/cm^2.

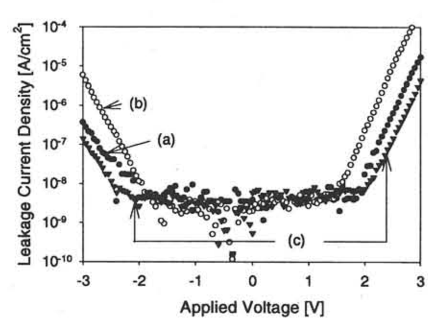

Figure 3. J-V characteristics of a Pt/BST/Pt capacitor: (a) as deposited, (b) after SR irradiation, and (c) after the subsequent annealing at 400℃ for 20min in O_2.

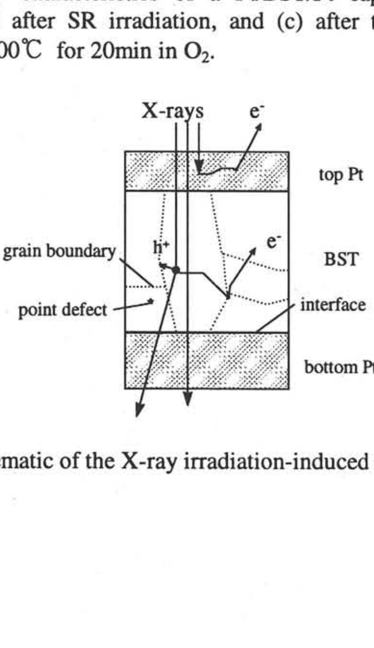

Figure 4. Schematic of the X-ray irradiation-induced damage.