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Effects of O_2 plasma treatment on the electric and dielectric characteristics of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films

Ching-Chich Leu [a,*], Shih-Hsiung Chan [a], Haur-Ywh Chen [b], Ray-Hua Horng [c], Dong-Sing Wuu [c], Luh-Huei Wu [c], Tiao-Yuan Huang [a], Chun-Yen Chang [b], Simon Min Sze [a]

[a] *National Nano Device Laboratory, Hsinchu 300, Taiwan, ROC*
[b] *Institute of Electrical Engineering, Chiao-Tung University, Hsinchu 300, Taiwan, ROC*
[c] *Institute of Electrical Engineering, Da-Yeh University, Hsinchu 515, Taiwan, ROC*

Abstract

The effects of the O_2 plasma treatment on the electric and dielectric characteristics of $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) thin films were investigated. As a result of the exposure of the as-deposited or the annealed BST films to the O_2 plasma, the leakage current density of the BST films can be improved. Typically, the leakage current density can decrease by three orders of magnitude as compared that of the non-plasma treated sample at an applied voltage of 1.5 V. It is found that the plasma treatment changes the surface morphology. The capacitance of the BST films was reduced by 10%~30%. The improvement of the leakage current density and the reduction of a dielectric constant for the plasma treated samples could be attributed to the reduction of carbon contaminations of BST thin films. The 10 year life time of the time-dependent dielectric breakdown (TDDB) studies indicates that all the samples have a life time of over 10 years of operation at a voltage bias of 1 V. © 2000 Elsevier Science Ltd. All rights reserved.

1. Introduction

Ferroelectric thin films have been extensively studied in the recent years for use as capacitors of nonvolatile random access memory (NVRAM) and dynamic random access memory (DRAM) [1,2]. Among them, (Ba,Sr)TiO_3 (BST) is expected to be a good candidate material for the storage capacitors of gigabit-scale DRAMs due to its high dielectric constant and good insulating properties. Although the electric and dielectric properties of the BST films have been proven to be excellent, they are highly thickness dependent [3,4]. The leakage current of a BST film has been reported to drastically increase, when film thickness is reduced to less than 20 nm. However, high-quality ultra-thin gate oxides will be required for future scaled ULSI devices. In this article, the O_2 plasma effects on the electric and dielectric properties of the BST films are investigated.

2. Experimental

The BST films were deposited on a Pt(200 nm)/Ti(20 nm)/SiO_2(250 nm)/Si substrate with (1 0 0) orientation using a spin-on MOD process. The coated films were dried at 150°C for 5 min and prebaked at 400°C for 20 min. This procedure was performed four times and the 100 nm thick BST thin films were obtained. These as-deposited films were subjected to three kinds of processes. One set of samples was directly treated by thermal annealing, and they were considered as the "reference" samples. The second set of samples first annealed and then treated by O_2 plasma was assigned to the "ann-plasma" process. The other set of samples was assigned to the "plasma-ann" process. The detail process flowchart was shown in Fig. 1. The thermal annealing for these BST films was carried out in a purified O_2 atmosphere at 700°C for 1 h. For the plasma

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[*] Corresponding author.
E-mail address: lcc@.ndl.gov.tw (C.-C. Leu).

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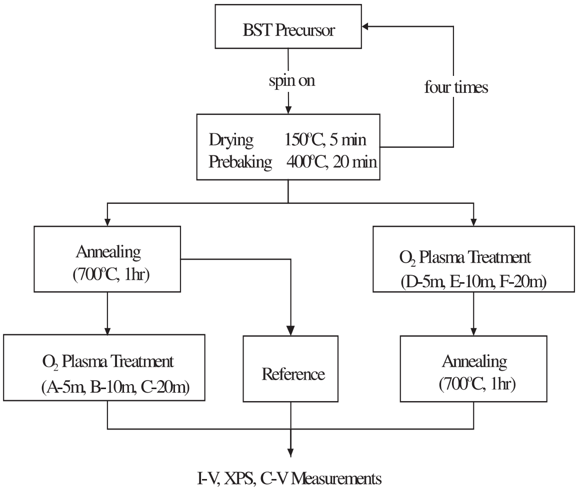

Fig. 1. Process flowchart of the BST thin films.

treatment, the substrate temperature, total gas pressure and RF power were maintained at 250°C, 650 mTorr and 300 W, respectively.

All the electric and dielectric characteristics were measured in the metal–insulator–metal configuration with Pt metal as the top and bottom electrodes. The 100 nm thick top electrodes with diameter of 0.3 mm were formed by electron beam evaporation and then patterned by the shadow mask process. The capacitance versus dc voltage (*C–V*) was measured at 100 kHz using a Keithley CV analyzer with an oscillation voltage at 50 mV. The leakage current density versus dc voltage (*J–V*) was measured using a HP 4145B semiconductor parameter analyzer. The voltage was applied with a step of 50 mV. Surface morphology of a BST film was observed using an atomic force microscope (AFM). The X-ray photoelectron spectroscopy (XPS) was used to identify the compositions and carbon concentration of the BST films. The time-dependent dielectric breakdown (TDDB) measurements were performed by measuring the current–time (*I–t*) with a constant voltage through the sample with the HP4145B semiconductor parameter analyzer.

3. Results and discussion

Fig. 2 shows the *J–V* curves of the three kinds of BST films. For the reference sample, the leakage current density is too high to act as the DRAM capacitor device, but it is suitable to evaluate the plasma effects on the electrical and dielectric properties of the BST thin films. It was found that the plasma treated BST films (before or after annealing) show higher current level than the reference sample in a shorter plasma time (samples A, D, E). For the plasma treated samples, whether ann-plasma or plasma-ann samples, the leakage density decreases as the plasma treated time increases. Typically, the leakage current density of sample C (ann-plasma sample, 20 min) decreases by three orders of magnitude as compared to that of the reference sample at an applied voltage of 1.5 V. Notably, the leakage current behaviors of the samples B and C under a negative bias are lightly different from that under a positive bias. It implies that the effect of the plasma on the interfaces of the BST/top electrode and BST/bottom electrode are also slightly different. Moreover, it is worth mentioning that the leakage current density of the ann-plasma samples is lower than that of the plasma-ann samples. The effects of an O_2 plasma treatment and an O-radical annealing of the BST films on the leakage current characteristic were studied by Matsui et al. [5]. They found that the O_2 plasma treatment and the O-radical annealing resulted in the reduction of the carbon contamination as the leakage current density of the BST capacitor decreased. The same phenomenon was also investigated in our experiment. The change in concentration of carbon in reference and plasma-ann (Sample F) samples are analyzed by XPS and shown in Fig. 3. After the plasma treatment, the peak intensity of carbon decreased significantly and resulted in the reduction of leakage current density.

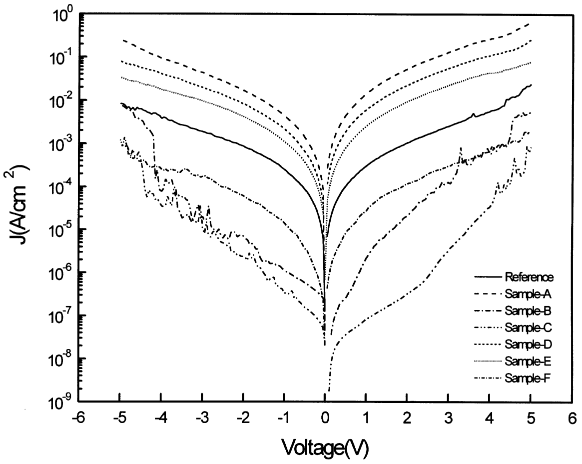

Fig. 2. *J–V* curves of the three kinds of BST films.

The surface roughness can be obtained using an AFM image measurement (not shown). Since the as-deposited sample reveal amorphous (examined by X-ray diffraction), the film exhibited a smooth surface with 0.18 nm roughness. For the reference sample, the AFM revealed that the grains merged together, results in an increase in roughness. The average surface roughness is about 1.041 nm over the relatively wide area 3 × 3 μm. Correspondingly, for the plasma treated samples, the

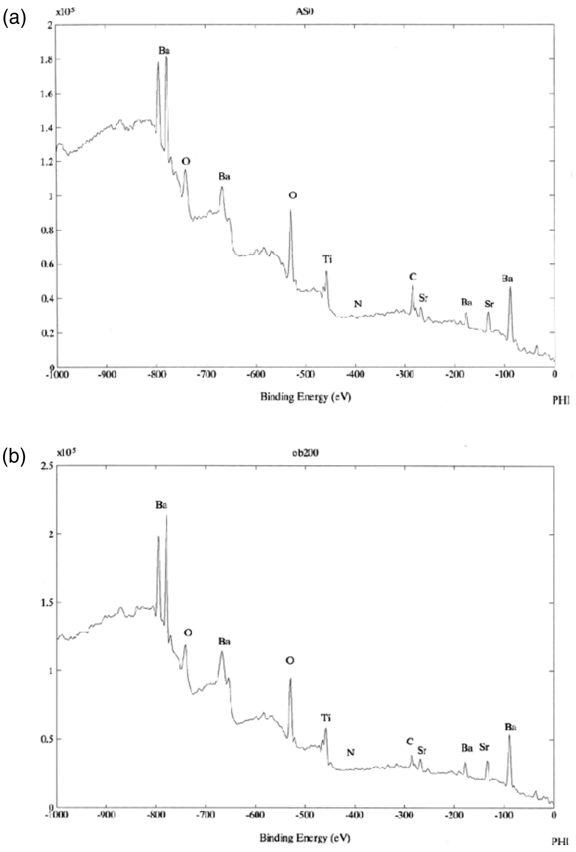

Fig. 3. The XPS patterns of (a) reference and (b) plasma-ann (Sample F) samples.

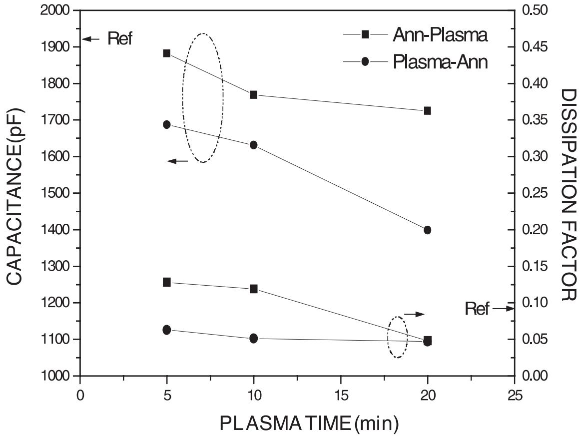

Fig. 4. Capacitance (at 1.5 V) and dissipation factor as the function of plasma treated time for the ann-plasma and plasma-ann samples and compared with the reference samples.

surface morphology present is hill-like. The average surface roughness of the ann-plasma and the plasma-ann is 0.966 and 0.787 nm, respectively. It is interesting to note that the surfaces of the plasma treated films are smoother than the reference sample. These results are different with the NH_3 plasma treated samples in our other studies [6]. For the NH_3 plasma treated samples, the surface of BST films were attacked by plasma bombardment and had larger roughness. One research on the BST growth during plasma bombardment generated by sputter has been proposed [7]. They found that the plasma bombardment with a mixture of O_2 and Ar gases suppress the outgrowth and/or enlargement of the island during the sputtering process. This suggests that the plasma bombardment with different gases have different effects on the surface morphology of the BST films. As concerning this point, further demonstration is in progress. The hill-like structure can be rounded by post-annealing, so that the sample (plasma-ann) has the smallest roughness among the three sets of samples.

Fig. 4 presents the capacitance (at 1.5 V) and dissipation factor as the function of plasma treated time for the ann-plasma and plasma-ann samples and is compared with the reference samples. The reference samples present the largest capacitance and the corresponding dielectric constant is about 300. It was found that the capacitances are reduced by 10%–30% for the sample treated by an O_2 plasma. For the plasma-ann samples, the capacitance decreases as the plasma treated time increases. Correspondingly, for the plasma-ann samples, the capacitances of the ann-plasma samples decrease first and then do not vary significantly as the treated time increases. From the surface morphology observation, it was found that the plasma makes the surface roughness decrease, especially for the plasma-ann samples. It should decrease the area of the capacitors. The smaller capacitor would be obtained for the plasma treated samples as compared with the reference samples. For the plasma-ann samples, the BST structure is amorphous and it is easily attacked by plasma so the plasma damage for the plasma-ann samples is more obvious than that for the ann-plasma samples. Thus, for the dielectric behavior, it could be attributed to damage by the exposure of the films to the plasma. They should suppress the spontaneous polarization of the films. In Fig. 5, we can find that the dissipation factor also decreased with increasing plasma time, while samples A and B (ann-plasma) are larger than reference. The change of dissipation factor in the BST films seems to be caused by several factors such as defect and contamination. It implies that the plasma damage effects of samples A and B are greater than carbon reduction. However, the carbon reduction effect is larger with increasing plasma time. Thus, plasma treatment could improve the leakage current, but decrease the capacitance.

The TDDB is an important consideration for the long term reliability of the device. The time to breakdown (t_{BD}) is measured by applying a voltage from 10 to

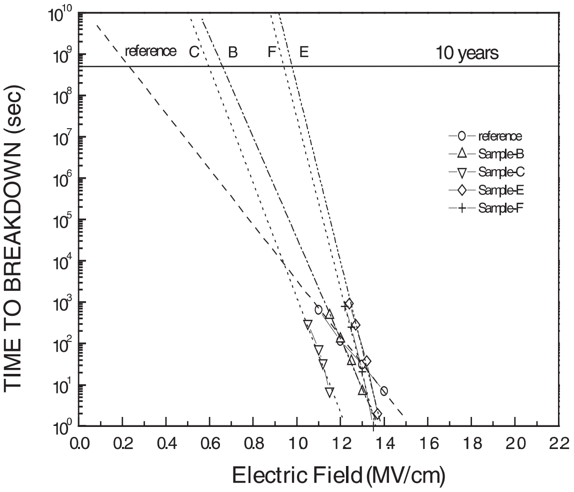

Fig. 5. Time-to-breakdown of the O_2 plasma treated BST films.

14 V (in Fig. 5). The dependence of $\log(t_{\mathrm{BD}})$ on the applied electrical stress E is linear. The studies indicate that plasma treated BST films have a longer life time at 1 V operation voltage than reference. The TDDB is characteristic of the intrinsic materials, the procedures and quality of the processing, and electrode material [8]. The 10 year life time of the TDDB studies indicates that all the samples have a life time over 10 years of operation at a voltage bias of 1 V.

4. Conclusion

The BST films with 100 nm thickness were prepared by spin coating onto $Pt/Ti/SiO_2/Si$ substrate. Both as-deposited and after annealed BST films were then exposed to the RF plasma using O_2 as the source gas. It was found that the O_2 plasma treatment results in the reduction of leakage current of the BST films. The AFM shows that the surface morphology of the BST films were changed by plasma treatment and the ann-plasma samples have larger roughness. For the samples treated by an O_2 plasma, the dielectric constant was reduced by 10%–30%. Plasma bombardment damage may be the main effect that resulted in the reduction of dielectric constant. The TDDB is an important consideration for long term reliability of the device. The studies indicate that the plasma treated BST films have a longer life time at 1 V operation voltage than reference.

References

[1] Paz de Araujo CA, McMillan LD, Melnick BM, Cuchiaro JD, Scott JF. Ferroelectrics 1990;104:241.
[2] Evans JT, Womack R. IEEE Solid-State Circuits 1998;23:1171.
[3] Hwang CS, Park SO, Cho H-J, Kang CS, Kang H-K, Lee SI, Lee MY. Appl Phys Lett 1995;67:2819.
[4] Park SO, Hwang CS, Cho H-J, Kang CS, Kang H-K, Lee SI, Lee MY. Jpn J Appl Phys Part 1 1996;35:233.
[5] Matsui Y, Torii K, Hirayama M, Fujisaki Y, Iijima S, Ohji Y. IEEE EDL 1996;17:431.
[6] Chen HY, Leu CC, Chan SH, Horng RH, Wuu DS, Wu LH, Huang TY, Chang CY, Sze SM. Jpn J Appl Phys, submitted.
[7] Tsai WC, Tseng TY. J Am Ceram Soc 1998;81:768.
[8] Parker LH, Tasch AF. IEEE Circuits Devices Mag, January 1990:17.