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Characterization of NH_3 plasma-treated $Ba_{0.7}Sr_{0.3}TiO_3$ thin films

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Abstract

The effects of plasma surface treatment, using NH_3 gas, of $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) films on the leakage and dielectric characteristics of a Pt/BST/Pt capacitor were investigated. As a result of the exposure of BST to the plasma, the leakage current density of the BST capacitor can be improved by three orders of magnitude as compared to that of the non-plasma-treated sample at an applied voltage of 1.5 V. Nevertheless, the surface morphology of BST was also changed by the NH_3 plasma, as explored by atomic force microscopy. From the X-ray photoelectron spectroscopy examination, the existence of the N 1 s peak was observed in the plasma-treated sample. It induces the additional space charge and results in the reduction of the dielectric constant.

1. Introduction

The advancement of dynamic random access memories (DRAMs) has significantly decreased the available area per cell. Especially, Gbit-scale DRAMs require a very small SiO_2 equivalent thickness of less than 1 nm to provide a sufficient capacitance of 25 fF/cell in a cell size smaller than 0.1 μm^2 [1]. The effort to shrink charge storage devices has stimulated interest in high-dielectric-constant materials. Among the numerous ferroelectric materials, $(Ba,Sr)TiO_3$ (BST) thin films have attracted considerable attention, because of its high dielectric constant, low leakage current density, high dielectric breakdown strength, paraelectric perovskite phase that does not exhibit fatigue, and the ease of composition control due to the absence of a volatile lead oxide [2–4]. Although the leakage and dielectric properties of BST films have been proven to be excellent, they are highly thickness dependent [5,6]. The leakage current of BST has been reported to drastically increase, when the film thickness is reduced to less than 20 nm. It has been reported that an additional oxidation of a nitrided silicon dioxide can achieve the reduction of both electron trapping and interface-state generation [7–9]. The improvement of interfacial quality has been attributed to nitrogen incorporation at the Si/SiO_2 interface. Nitridation of gate oxide films with NH_3 or N_2O is an effective process in blocking impurity penetration and in reducing interface trap states. N_2O-annealing and plasma treatments have been employed to improve the properties of Ta_2O_5 and BST [10,11]. In this article, the NH_3 plasma effects on the leakage and dielectric properties of the BST films were investigated. The material properties of BST modified by the NH_3 plasma will also be described.

2. Experimental

The BST thin films with a Ba/Sr ratio of 70/30 were deposited on Pt(200 nm)/Ti(20 nm)/SiO_2(250 nm)/Si substrates using a spin-on sol–gel process. The coated films were dried at 150°C for 5 min and pre-baked at

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400°C for 20 min. This procedure was repeated four times and the 100-nm-thick BST thin film was obtained. The as-deposited BST films were subjected to three kinds of process treatment. One set of samples was directly treated by thermal annealing without plasma treatment. They were used as the "reference" samples for the aim of measurement comparison. The second set of samples was first annealed and followed by NH_3 plasma treatment (anneal before plasma, ABP) for 30, 60 and 120 s. They were correspondingly denoted by NH_3-30, NH_3-60 and NH_3-120, respectively. The third set of samples was exposed to the NH_3 plasma for 30, 60 and 120 s and then thermal annealed (anneal after plasma, AAP). They were correspondingly denoted by NH_3-B30, NH_3-B60 and NH_3-B120. The anneal for these BST films was carried out in a purified O_2 atmosphere at 700°C for 1 h. During the plasma treatment, the substrate temperature, chamber pressure and RF power were maintained at 250°C, 300 mTorr and 200 W, respectively.

All the leakage and dielectric characteristics were measured using the metal–insulator–metal structure with Pt as the top and bottom electrodes. The top electrodes with diameter of 300 μm were formed by sputtering and patterned by the shadow mask process. The leakage current density versus dc voltage (*J–V*) was measured by HP 4145B. The capacitance versus dc voltage (*C–V*) was measured at 100 kHz using a Keithley *CV* 82 analyzer with an oscillation voltage at 50 mV. The chemical compositions of samples were examined by X-ray photoelectron spectroscopy (XPS). The surface morphology of the BST film was observed by an atomic force microscope (AFM).

3. Results and discussion

Fig. 1(a) and (b) shows the *J–V* curves of the BST films treated by AAP and ABP processes, respectively. The data taken from the reference sample are also depicted for comparison. It was found that the plasma-treated BST films (AAP or ABP) showed lower leakage levels than the reference sample, except for the NH_3-30 sample. Further, the leakage current density of the AAP sample is lower than that of ABP sample. The leakage current density was found to decrease as the plasma-treated duration increased. Notably, except for the reference and NH_3-30 samples, the leakage current density of the BST film under a negative bias is slightly higher than that under a positive bias. Fig. 2 shows the dielectric constant (ε) as a function of voltage for the plasma-treated and reference samples. It was found that the dielectric constants for these samples are as follows: $\varepsilon(\text{referencesample}) > \varepsilon(\text{ABPsample}) > \varepsilon(\text{AAPsample})$. The lower dielectric constants of the plasma-treated films imply that the BST films are damaged by the exposure of the BST surface to the plasma. For the AAP samples, the film structure of BST was amorphous as exposed to the plasma. Thus, they are more easily attacked by plasma as compared with the ABP samples. This results in a lower ε value of the AAP sample. Nevertheless, the dissipation factors are obviously reduced by 50–70% by the plasma treatment, as shown in the Fig. 3. For the AAP samples, the dissipation factor

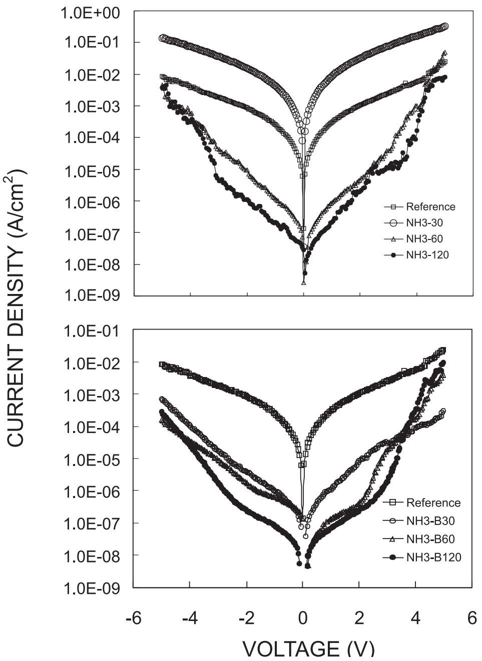

Fig. 1. *J–V* curves of the reference samples and compared with the BST films treated by (a) thermal annealing before NH_3 plasma, and (b) thermal annealing after NH_3 plasma.

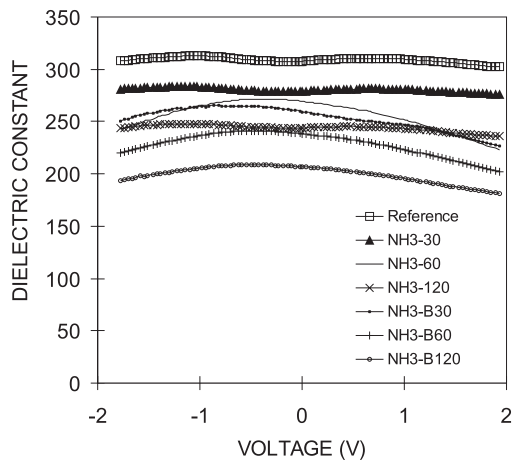

Fig. 2. Dielectric constant as a function of applied voltage for the reference and NH_3 plasma-treated samples.

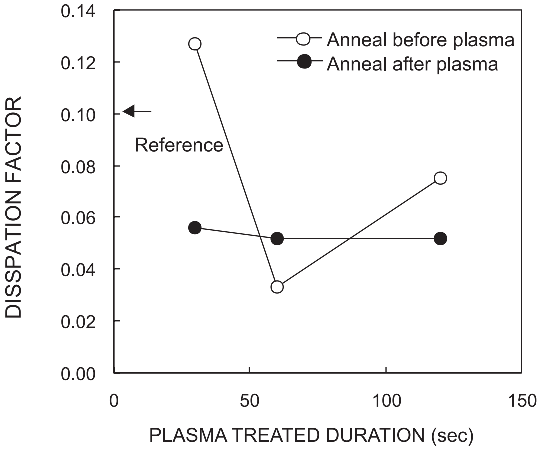

Fig. 3. Dissipation factor as a function of plasma-treated duration for the BST samples. The arrow indicates the dissipation factor of the reference sample.

decreases slowly as the plasma-treated duration increases. It could be due to the fact that the thermal annealing can rearrange the surface morphology after the plasma treatment.

The surface morphology of BST is an important factor in consideration of the conduction mechanism. The AFM topographies of the reference, ABP (NH_3-120) and AAP (NH_3-B120) samples are shown in Fig. 4. The corresponding surface roughness for these samples is 1.041, 1.398 and 1.428 nm, respectively. For the reference sample, AFM revealed that grains merged together. However, for the plasma-treated samples, the surface presents needle-like morphology due to the plasma bombardment. During the AAP treatment, the film structure of BST was amorphous as exposed to the plasma. Although the needle-like structure can be smoothed by post-annealing, the AAP sample still has the greatest roughness among three sets of samples. Thus, the plasma effect for the AAP samples is larger than that for the ABP samples. Nevertheless, the annealing process will benefit the surface morphology and make it smoother. The rounded surface morphology for the AAP samples may also result in the reduction of leakage current density. Moreover, the surface roughness also enlarges the capacitor electrode area, which could be one of the factors affecting the properties of the films. The roughness for the AAP sample is more than that of the ABP sample; however, the ε value for the AAP sample is lower than that of ABP samples. The effect of surface roughness seems to be negligible in this study. The plasma-treated BST films with lower ε values may be due to the nitrogen space charge accumulation (this point will be further discussed by XPS observation). This suggests that nitrogen incorporation into the BST thin films is more obvious for the AAP samples.

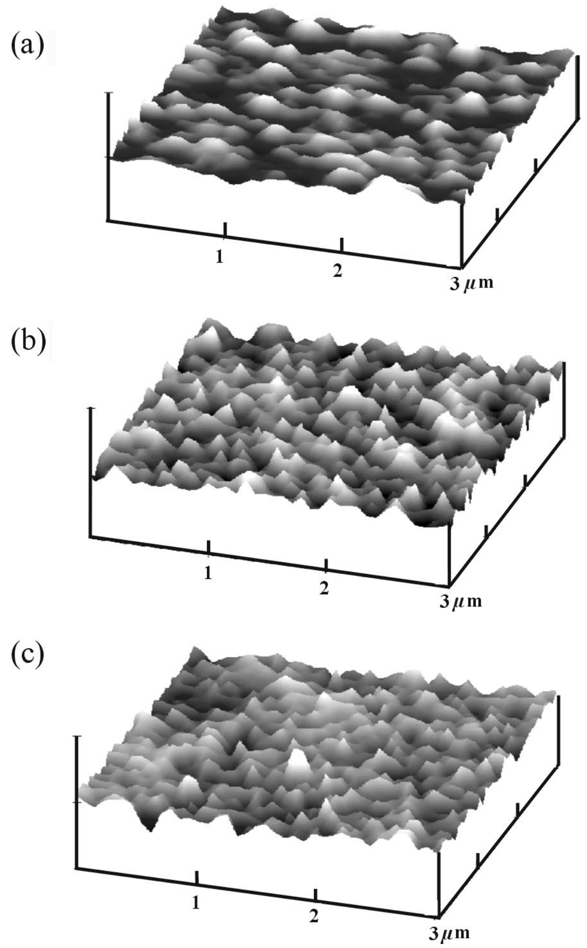

Fig. 4. AFM topographies of the (a) reference sample, (b) NH_3-120 sample and (c) NH_3-B120 sample.

The result is consistent with the leakage behavior as described in Fig. 2.

The nitrogen incorporation into the BST films can be confirmed by the XPS measurement, as shown in Fig. 5. No nitrogen signal can be detected in the reference sample. It was found that the N 1 s peak obviously existed in the plasma-treated BST films. The nitrogen incorporation into the AAP samples is expected to be easier than that into the ABP samples. Note that the AAP treatment will activate and redistribute the nitrogen into the BST thin films. It would result in the surface nitrogen concentration lower than that of the ABP sample. The nitrogen incorporation will reduce the electron traps and interface states, and it will improve the leakage current performance. This can be supported by the evident reduction of leakage current density in the AAP samples. Typically, the leakage current density of the NH_3-B120 sample decreases by three orders of magnitude as compared with that of the reference

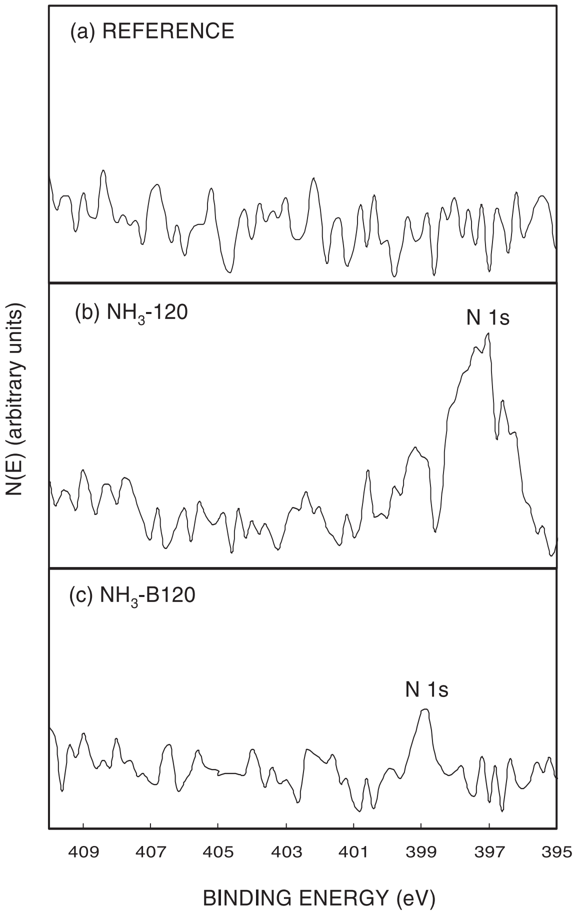

Fig. 5. XPS spectra of the (a) reference sample, (b) NH_3-120 sample and (c) NH_3-B120 sample.

sample at an applied voltage of 1.5V. But the annealing process for the AAP samples would make the space charge range widen, which results in lowering the dielectric constant.

4. Conclusions

The BST films with a 100 nm thickness were prepared by spin coating onto Pt(150 nm)/Ti(20 nm)/SiO_2(200 nm)/Si substrate. Both BST films before and after thermal anneal were then exposed to RF plasma using NH_3 as the source gas. It is found that the NH_3 plasma treatment results in the reduction of leakage current of BST films. When the plasma-treated duration increases, the leakage current density decreases. 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 1.5V. The AFM shows that the surface morphology of BST films was changed by plasma treatment and the AAP samples have greater roughness. For the samples treated by NH_3 plasma, the dielectric constant were reduced by 10–40%. Nitrogen accumulation induced by plasma bombardment may be the main effect, which results in the reduction of dielectric constant. It is necessary to trade off the capacitance property for leakage current property.

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