Forming gas annealing on physical characteristics and electrical properties of Sr 0.8 Bi 2 Ta 2 O 9 / Al 2 O 3 / Si capacitors

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Forming gas annealing on physical characteristics and electrical properties of $Sr_{0.8}Bi_2Ta_2O_9/Al_2O_3/Si$ capacitors

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$Sr_{0.8}Bi_2Ta_2O_9$ (SBT) ferroelectric film constructed on Al_2O_3/Si to form metal–ferroelectric–insulator–semiconductor (MFIS) was prepared to study the degradation behavior of SBT films under forming gas annealing (FGA). Although the diffusion of hydrogen ions has been detected during FGA treatment, no significant differences in the microstructure and crystalline phase are observed for the SBT film compared to that without FGA treatment. However, the diffusion of hydrogen ions leads to the rapid decrease in the dielectric constant but shows no apparent influence on the memory window of $Sr_{0.8}Bi_2Ta_2O_9/Al_2O_3/Si$ capacitors. In addition, it was found that FGA shows a positive effect on the leakage current of MFIS in contrast to that of metal/ferroelectric/metal structure. The leakage current density of MFIS dramatically decreases as much as two orders of magnitude after FGA at 500 °C compared to that without FGA treatment that was attributed to the reduced defects at the interface of Al_2O_3/Si.
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I. INTRODUCTION

Ferroelectric thin films have been widely investigated for nonvolatile random access memory applications.[1] $SrBi_2Ta_2O_9$ (SBT) thin film has superior ferroelectric properties in retention endurance, fatigue, and leakage current and therefore appears to be one of the most favorable candidates for ferroelectric materials in ferroelectric memory device.[2] However, there are still several problems that impede the incorporation of the ferroelectric thin films in microelectronic devices. One of the problems is the degradation of ferroelectric properties after forming gas annealing (FGA) treatment because this FGA process is required in microchip fabrication to passivate the device and eliminate defects in the field effect transistor.[3] Several reports in literature show that the treatment of FGA leads to the decrease of switch charge and fatigue resistance, and the increase of leakage current density.[4–6] It was reported that the degradation on the ferroelectric properties of SBT thin films in metal/ferroelectric/metal (MFM) structure is related to the dissociative adsorption of the hydrogen molecule (e.g., $H_2+2M \rightarrow 2H-M$) and the generation of the hydrogen atoms by the catalytic activity of Pt (e.g., $2H-M \rightarrow 2H+2M$).[7] However, Kwon *et al.*[8] supposed that the H^+ ions and electrons produced by the dissociative adsorption of hydrogen molecules on the Pt surface are responsible for the suppressed Pr due to the pinning of the domains. With the increase of annealing temperature, the H^+ ions and electrons may diffuse into the SBT and accumulate around grain boundaries to form space charge and prohibit the domain motion, and thus result in the ferroelectric degradation in MFM structure. Wang *et al.*[9] studied the fatigue behavior of FGA-SBT samples and supposed that more weak pinning center of domain will be formed on SBT thin film after FGA process. This will cause the increase in both leakage current and fatigue degradation.[9] These pinning centers of domain in the SBT films could be unlocked after oxygen recovery at 750 °C and the fatigue property of SBT thin films could be recovered to the original state before FGA.[10] In addition, it was also reported that the forming gas atmosphere and deposited top electrode show a strong influence on the degradation behavior of the MFM structure.[8,11]

In comparison with the existing MFM structure, metal–ferroelectric–semiconductor ferroelectric memory has attracted much attention due to the unique performance and advantages including obeying the scaling rule, high switch speed, and nondestructive reading.[12] Furthermore, the metal–ferroelectric–insulator–semiconductor (MFIS) capacitor has been widely studied because it has not only the same small 1 T cell structure as flash memory but also the merits of ferroelectric random access memory mentioned herein.[13] Recently, we have reported that free-fatigue $Bi_{3.25}La_{0.75}Ti_3O_{12}$ ferroelectric films could be integrated in a MFIS capacitor with Al_2O_3 as the insulator and excellent ferroelectric properties can be obtained, such as smaller leakage current and larger memory window.[14,15] However, there have been few studies focused on the structural variation of the MFIS under FGA treatment. Therefore, in this work, the effect of forming gas annealing on the physical characteristics and electrical properties of $SBT/Al_2O_3/Si$ will be investigated. The role of top electrode in the passivation and electrical characterization in a MFIS structure is further

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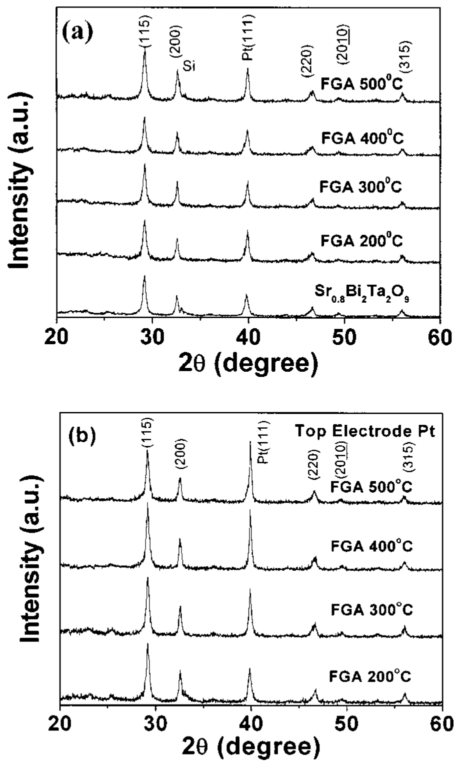

FIG. 1. X-ray diffraction patterns for SBT thin films (a) without top electrode and (b) with Pt top electrode after FGA at 200–500 °C.

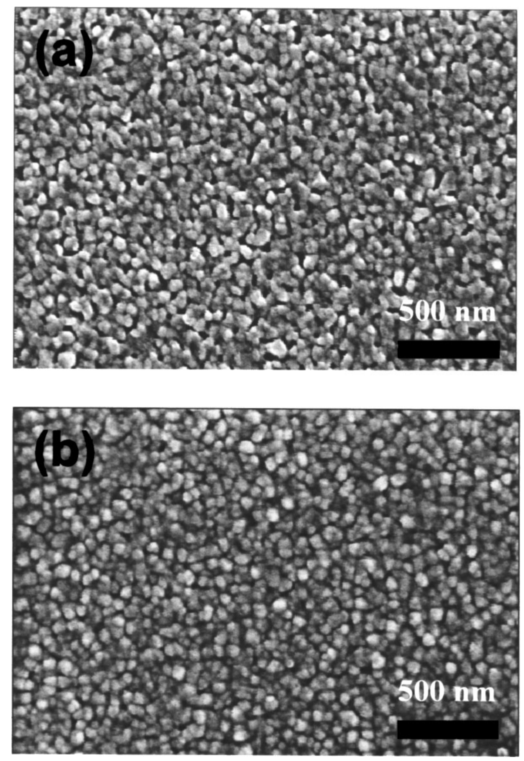

FIG. 2. Surface morphology of SBT thin films (a) before FGA and (b) after FGA at 500 °C.

discussed. For comparison, the MIM structure is also prepared.

II. EXPERIMENT

4-in.-Si *p*-type wafers were used in this study. A HF-vapor passivation was used to suppress the native oxide formation before other treatment. The Al layer was thermally evaporated on wafers, oxidized at a temperature of 400 °C for 2 h to form 5-nm-thick Al_2O_3, and finally annealed at 900 °C for 30 min in a nitrogen ambient. Strontium 2-ethylhexanotate $[Sr(C_8H_{15}O_2)_2]$, bismuth 2-ethylhexanoate $[Bi(C_8H_{15}O_2)_2]$, tantalum ethoxide $[Ta(OC_2H_5)_5]$ were used as the metalorganic precursors for the SBT formula solution synthesis and xylene was used as the solvent for adjusting the concentration of the solution following our previous works.[16] $Sr_{0.8}Bi_2Ta_2O_9$ composition was selected because a large memory window can be obtained with a smaller applied voltage in the MFIS structure according to our previous work and a related report in literature.[17] The solutions were spin coated on the gate dielectrics and then followed by subsequent drying. This procedure was repeated for several times to obtain the desired film thickness about 300 nm. Between each coating, the wet films were pyrolyzed at 400 °C for several minutes. After that, the as-deposited films were annealed at 800 °C for 30 min in the oxygen ambient. Pt top and back side electrodes were formed by sputtering. The hard mask size used for the fabrication of MFIS capacitor is $3.14\times10^{-4}\,cm^2$. In the work, the FGA is carried out at the temperature ranging from 200 to 500 °C for 15 min under an atmosphere of 5% H_2/95% N_2. The crystal structure of the SBT films was analyzed by an x-ray diffractometer (MAC Science M18XHF) with Cu $K\alpha$ radiation and the thickness of SBT films was measured using Alpha-stepper (Sloan Dektak). The capacitance–voltage $(C-V)$ and current–voltage $(I-V)$ were characterized and measured using HP4284 and HP4155B, respectively. A secondary ion mass spectrometer [(SIMS) Cameca IMS-4f] was used for depth profiling of each element in the capacitors.

III. RESULTS AND DISCUSSION

A. Crystal phase and microstructure

Figure 1 shows the x-ray diffraction patterns of SBT thin films annealed at 800 °C and then treated under FGA at 200 to 500 °C for 15 min using 5% H_2/95% N_2 for both samples without and with Pt top electrode coated. It revealed that neither major changes in the film crystallinity nor any noticeable second-phase formation after FGA were observed for SBT films on Al_2O_3/Si substrates.[16,18] This indicated that the ferroelectric perovskite phase remains unchanged even after FGA treatment. In addition, the scanning electron microscopy (SEM) images of the SBT film reveal no significant differences on the surface morphology of the films before and after 500 °C annealing as shown in Fig. 2. The microstructure of both SBT films present similar features with round and smaller grains. Figure 3(a) demonstrates the cross-section transmission electron microscopy (TEM) micrographs of the Pt/SBT/Al_2O_3/Si structure without a top electrode after FGA process, respectively. In comparison with the sample with a top electrode, the cross section of TEM of the sample without a top electrode shows no apparent differ-

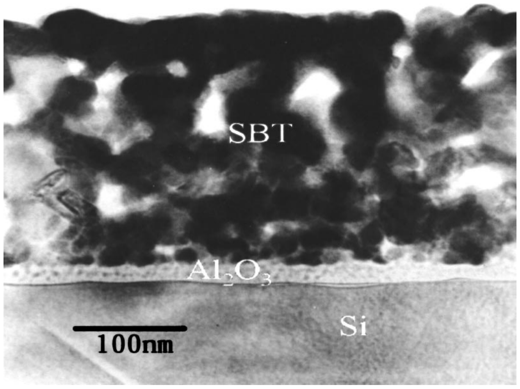

FIG. 3. Cross-sectional TEM micrograph of SBT/Al_2O_3/Si structure without Pt top electrode after FGA process.

ences on TEM morphology the SBT grains also become smaller near the interface of SBT/Al_2O. However, both images give a different contrast, especially around the grain boundary and near the interface of SBT/Al_2O_3, indicating that some H^+ has diffused into the SBT structure for the sample with FGA treatment.

Figure 4 shows the measurement of SIMS for the SBT thin films annealed at 800 °C in an oxygen ambient and then treated with a FGA process at 400 °C for 15 min. While the sample was treated with FGA, hydrogen atoms highly exist in a SBT thin film as shown in Fig. 4(a). In addition, Sr is also detected on the film surface along with a great amount of Bi. It was believed that the hydrogen ion would cause the reduction of bismuth oxide, and accelerates the volatilization of Bi and the formation of Bi vacancy. The formation of bismuth vacancies may cause the accumulation of Sr because both Sr^{+2} and Bi^{+3} have a similar ion size and easily exchange during heat treatment. On the other hand, after the sample was deposited with a Pt top electrode and then treated under FGA, it was found that only Bi accumulated on the film surface as shown in Fig. 4(b). In other words, little Sr was detected on the film surface. Furthermore, the H intensity at the film surface became weaker compared to the sample without Pt top electrode coating. That indicates the importance of a Pt top electrode in preventing the H^+ accumulation and Sr outdiffusion in comparison with that without Pt coating.

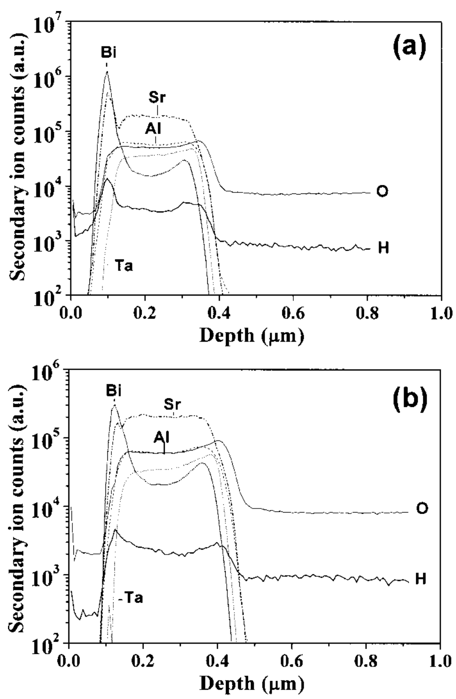

FIG. 4. SIMS spectra of SBT/Al_2O_3/Si capacitors (a) without top electrode and (b) with Pt top electrode after FGA at 400 °C.

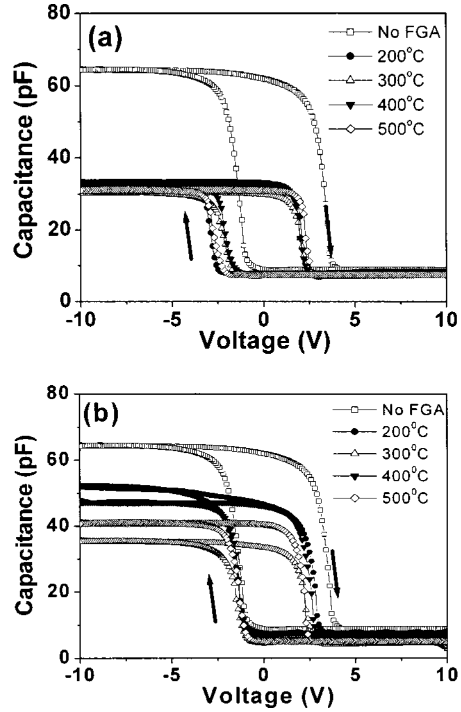

FIG. 5. $C-V$ characteristics of SBT/Al_2O_3/Si capacitors (a) without top electrode and (b) with Pt top electrode after FGA at 200–500 °C.

B. Capacitance–voltage and memory window characteristics

Some research in literature focused on the FGA degradation of a MFM structure with different top electrodes and found that H_2 is easily catalyzed into H ions with a Pt electrode and the electrical properties would deteriorate.[8,19] Specifically, while the H ions penetrate into the ferroelectric thin film, the electric properties will become worse. However, the FGA treatment for the MFIS field-effect transistors has been reported. In this work, however, it was found that when the Pt/SBT/Al_2O_3/Si (MFIS) was postannealed at various FGA temperatures, good ferroelectric characteristics were obtained. The Pt/SBT/Al_2O_3/Si shows the clockwise hysteresis loops of $C-V$ curves as observed in Fig. 5, indicating the switching of the ferroelectric polarization. In other words, the FGA temperature does not have a significant influence on memory window properties. However, the FGA can cause the shift of $C-V$ to a negative direction, indicating that positive charge has been inserted into SBT thin film.

Figure 5 also shows that a rapid decrease in the dielectric constant was detected for the sample after FGA treatment.

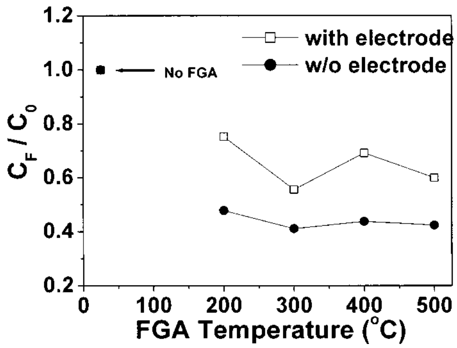

FIG. 6. Capacitance of $SBT/Al_2O_3/Si$ with respect to the original value as a function of FGA temperatures.

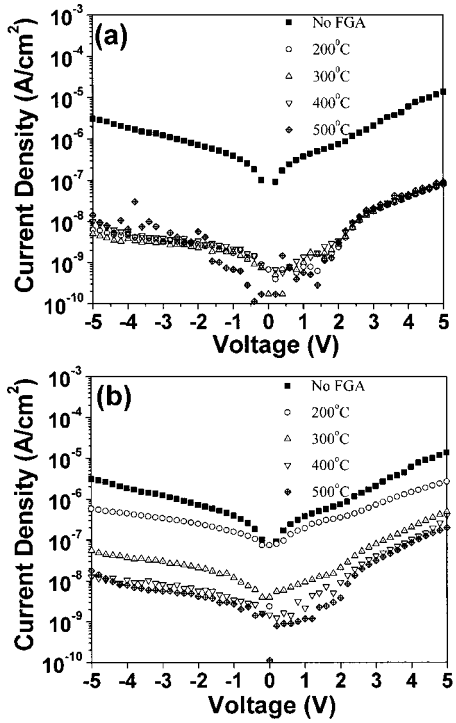

FIG. 7. Current density–voltage characteristics of $SBT/Al_2O_3/Si$ capacitors (a) without top electrode and (b) with Pt top electrode after FGA at 200–500 °C.

For the sample without a Pt electrode, a remarkable degradation of capacitance for the SBT thin films is observed in Fig. 5(a) and the capacitance decreases from 65 pF to 32 pF at 200 °C. Above that temperature, no further degradation is detected with increasing forming gas temperature. The decrease in the dielectric constant may be attributed to the diffusion of H^+ ions into the SBT thin films and change the dipole motion during FGA process. That is because the H^+ ions are probably bonded with a dangling bond in the $SBT/Al_2O_3/Si$ interface. In addition, the H ion tends to form a space charge around the grain boundaries, which will lead to the reduction of the dipole moment and the rapid drop of the dielectric constant.

On the other hand, Fig. 5(b) shows the $C-V$ curve of the $Pt/SBT/Al_2O_3/Si$ (MFIS) structure with a Pt top electrode under FGA treatment. No significant variation on the memory windows is discerned compared to that [Fig. 5(a)] of the sample without a Pt top electrode. However, the decrement of capacitance in Fig. 5(b) is strongly dependent on the annealing temperature of FGA, which is completely different from that in Fig. 5(a) where the capacitance rapidly drops to the lowest value as the annealing temperature reached 200 °C. Apparently, the coated Pt electrode plays a passivation role in buffering the diffusion of H^+ and reduces the degradation of a SBT thin film caused by FGA. The effect of FGA temperature on the dielectric constant of both samples can be summarized in Fig. 6. It was found that with increasing annealing temperature, a minimum dielectric constant in the SBT films appears at around 300 °C, especially for the sample with a Pt top electrode.[20] That is because while the sample was treated with FGA below the Curie temperature (T_C), the accumulated H^+ ions and electrons around the grain boundaries of the SBT film tend to induce an internal electric field and thus pin the domain motion. Therefore, a rapid decrease in the dielectric constant was obtained. On the other hand, as the FGA temperature was above T_C, the high-temperature effect may cause the dispersion of both hydrogen atoms and electrons more homogenously. In addition, the induced local electrical field will become weak due to the disappearance of spontaneous polarization. The two reasons are believed to be responsible for the increase of dielectric constant over 300 °C. However, by further raising the FGA temperature, the amount of hydrogen atoms diffusing into the SBT film keep increasing that will lead to the reduction in the dielectric constant again. As compared with the result on the MFM structure in which no ferroelectric properties were detected for the SBT thin film after FGA,[8] this work demonstrates that the SBT film on MFIS still exhibits the ferroelectric properties in spite of the reduced capacitance. It implies that both the distribution of hydrogen ions and electrons play different roles in the MFM and MFIS structures, which further reflect different physical characteristics and electrical properties in these two structures.

C. Leakage current

Figure 7 shows the leakage current characteristics of SBT films on a MFIS structure at different FGA temperatures. As shown in Fig. 7(a), for the sample without a Pt top electrode, the leakage-current density of the SBT films decreases. The leakage current density dropped directly from $1\times10^{-6}\ A/cm^2$ to $1\times10^{-8}\ A/cm^2$ at 2 V. On the other hand, as the SBT films were coated with a Pt top electrode, Fig. 6(b) shows that the leakage current is gradually reduced with the increase of FGA temperature, completely different from that in the MFM structures.[21,22] The leakage current in a MFM structure is highly increased after the FGA and that was attributed to the disappearance of the Schottky barrier caused by the neutralization of the depletion layer due to the production of the space charge at the interface of SBT/electrode. However, it was believed that the decreased leakage current of the SBT film in the MFIS structure is strongly correlated with the interaction of indiffused H^+ ion with the interface defects of $SBT/Al_2O_3/Si$.

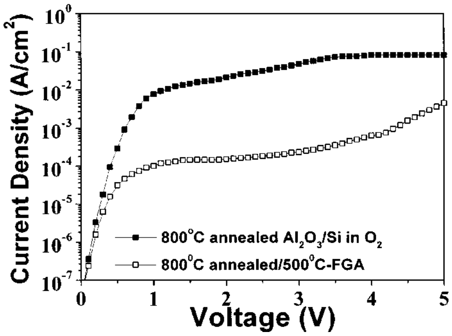

FIG. 8. $I-V$ characteristics of a sample annealed at 800 °C in O_2 and then FGA at 500 °C normalized with respect to the original value as a function of FGA temperatures.

In order to clarify the effect of the SBT/Al_2O_3/Si interface on the leakage current of a MFIS structure, Al_2O_3/Si sample was prepared and annealed at the similar condition (800 °C in O_2). The leakage current of Al_2O_3/Si without FGA was compared with the sample under FGA treatment and shown in Fig. 8. It was found that, after FGA at 500 °C, a decreased leakage current was observed for the Al_2O_3/Si sample under FGA treatment. Although a systematic study of FGA dependence of the reduced leakage current in the $Sr_{0.8}Bi_2Ta_2O_9$/Al_2O_3/Si remains to be further conducted, the result in Fig. 8 indicates that the reduced defects (or dangling bonds) in the Al_2O_3/Si interface are probably responsible for the decreased leakage current of SBT-based MFIS structure after FGA.

IV. CONCLUSION

In summary, we have investigated the effect of FGA treatment on the ferroelectric properties of SBT ferroelectric film constructed on Al_2O_3/Si. After FGA treatment, X-ray diffraction shows only perovskite SBT phase but TEM reveals the probable diffusion of H^+ ion into the SBT film. Due to the diffusion of hydrogen ions, a rapid decrease in the dielectric constant was observed but the memory window size of $Sr_{0.8}Bi_2Ta_2O_9$/Al_2O_3/Si capacitors was kept unchanged. In addition, it was found that FGA shows a positive effect on the leakage current of MFIS in contrast to that of a MFM structure. A rapid decrease as much as two orders of magnitude was obtained for SBT-based MFIS capacitors after FGA at 500 °C compared to that without FGA treatment. It was believed that the reduced defects at the interface of Al_2O_3/Si during FGA are responsible for the decreased leakage current density.

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