電極/鐵電薄膜/結緣層/矽晶體結構之薄膜製程及特性劣化研究 (II)
Forming gas annealing on physical characteristics and property degradation of Pt/$Sr_{0.8}Bi_2Ta_2O_9$/Al_2O_3/Si capacitors

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主持人：陳三元 教授 交通大學材料科學與工程系

中文摘要

本研究主要是利用化學溶液法將 SBT 鐵電薄膜沉積在 Al_2O_3/Si 二種基材上，以研究還原氣氛退火對元件在微結構及電性上的影響。實驗發現經過還原氣氛退火後，會造成 MFIS 結構試片的電容值嚴重降低，但是對於記憶窗並沒有顯著的影響。根據 SIMS 結果可發現造成電性劣化的來源，來自於鐵電成分的變動。當 SBT 試片沉積上電極後，電性受還原氣氛退火的劣化程度會降低，此現象則出自於上電極抑制 SBT 鐵電成分的變動所致。在漏電流方面，實驗顯示 MFIS 結構的 SBT 試片經過還原氣氛退火後，會大幅降低漏電流密度，此應該是由於退火過程中，基板形成鋁-矽-氧非晶質所致。

關鍵詞: 電極/鐵電薄膜/結緣層/矽晶體、還原氣氛退火、鍶鉍鉭薄膜、記憶窗、特性劣化

Abstract

$Sr_{0.8}Bi_2Ta_2O_9$ (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 positive effect on the leakage current of MFIS in contrast to that of metal/ferroelectric/metal (MFM) 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.

Keywords:
Metal/Ferroelectric/Insulator/Si, forming gas annealing, $Sr_{0.8}Bi_2Ta_2O_9$, memory window, property degradation

1. Introduction

Ferroelectric thin films have been widely investigated for nonvolatile random access memory (NVRAM) 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 candidate 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 the literature shows that the treatment of forming gas annealing leads to the decrease of switch charge and fatigue resistance, and the increase of leakage current density [4]. 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 → 2H-M) and the generation of the hydrogen atoms by the catalytic activity of Pt(e.g., 2H-M→2H+2M) [5]. However, Kwon *et al*. 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 [6]. This will cause the increase in both leakage current and fatigue degradation [7]. These pinning centers of domain in the SBT films could be unlocked after oxygen recovery at 750^{o}C and the fatigue property of SBT thin films could be recovered to the original state before FGA.

In comparison with the existing MFM structure, metal-ferroelectric-semiconductor (MFS) ferroelectric memory has attracted much attention due to the unique performance and advantages including obeying the scaling rule, high switch speed and nondestructive reading [8]. Recently, we have reported that free-fatigue $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) ferroelectric films could be integrated in 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 could be obtained [9]. 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 MFIS structure is further discussed. For comparison, the MIM structure is also prepared.

2. Experimental

Four-inches Si p-type wafers were used in this study. A HF-vapor passivation was used to suppress the native oxide formation before other treatment. Al layer was thermally evaporated on wafers, oxidized at a temperature of 400 ^{o}C for 2 hours to form 5-nm~10-nm -thick Al_2O_3, and finally annealed at 900 ^{o}C for 30 min in 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 metal-organic precursors for SBT formula solution synthesis and xylene was used as the solvent. The solutions were spin-coated on the gate dielectrics and then followed by subsequent drying. After multiple coating, the as-deposited films were annealed at 800 ^{o}C for 30 min in the oxygen ambient. Pt top and backside electrodes with a hard mask size of 3.14×10^{-4} cm^2. The FGA is carried out at the temperature ranging from 200 to 500 ^{o}C for 15min under an atmosphere of 5%H_2 / 95%N_2. The crystal structure of SBT films was analyzed by X-ray diffractometer with Cu Kα radiation and the thickness of SBT films was measured using Alpha-stepper The capacitance-voltage (C-V) and current-voltage (I-V) were characterized and measured using HP4284 and HP4155B, respectively. Secondary ion mass spectrometer (SIMS, Cameca IMS-4f) was used for depth profiling of each element in the capacitors.

3. Results and Discussion

3.1 Crystal phase and microstructure

Figure 1 shows the x-ray diffraction patterns of SBT thin films annealed at 800 ^{o}C and then treated under FGA at 200 to 500 ^{o}C for 15 minutes 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. This indicated that the ferroelectric perovskite phase remains unchanged even after FGA treatment. In addition, the SEM images of the SBT film reveal no significant differences on the surface morphology of the films before and after 500 ^oC annealing as shown in Fig. 2. The microstructure of both SBT films present similar feature with round and smaller grains. Figure 3(a) demonstrates the cross-sectional TEM micrographs of SBT/Al_2O_3/Si structure without top electrode after FGA process. In comparison with the sample with top electrode, the sample without top electrode shows no apparent differences on TEM morphology. However, both images give different contrast, especially around grain boundaries of SBT and near the interface of SBT/Al_2O_3, indicating that some of H^+ has diffused into the SBT structure for the sample with FGA treatment as shown in Fig. 3(b).

Figure 4 shows the measurement of SIMS for the SBT thin films under annealed at 800^{o}C in the oxygen ambient and then treated with FGA process at 400 ^oC for 15 minutes. While the sample was treated with FGA, hydrogen atoms highly exist in 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 similar ion size and easily exchange during heat-treatment. On the other hand, after the sample was deposited with Pt top electrode and then treated under FGA, it was found that only Bi accumulation 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 become weaker compared to the sample without Pt top electrode coating. That indicates the importance of Pt top electrode in preventing the H^+ accumulation and Sr out-diffusion in comparison with that without Pt coated.

3.2 C-V and memory window characteristics

Several researches in the literature focused on the FGA degradation of MIM structure with different top electrodes and found that H_2 is easily catalyzed into H ions with Pt electrode and the electrical properties would be deteriorated. Especially, while the H ions penetrate into the ferroelectric thin film, the electric properties will become worse. However, the FGA treatment for the metal/ferroelectric /insulator/semiconductor field-effect transistors (MFIS-FET's) has been few reported. In this work, however, it was found that when the Pt/SBT/Al_2O_3/Si (MFIS) was post-annealed at various FGA temperatures, good ferroelectric characteristics was 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 make significant influence on memory window properties. However, the FGA can cause the shift of C-V to negative direction, indicating that positive charge has 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. For the sample without 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 ^oC. 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 dangling bond existed in the SBT/Al_2O_3/Si interface. In addition, the H ion tends to form space charge around the grain boundaries, which will lead to the reduction of dipole moment and the rapid drop of dielectric constant.

On the other hand, Figure 5(b) shows the C-V curve of Pt/SBT/Al_2O_3/Si (MFIS) structure with 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 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 to 200 ^{o}C. Apparently, the coated Pt electrode plays a passivation role in buffering the diffusion of H^+ and reduces the degradation of 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 ^{o}C, especially for the sample with Pt top electrode.[10] That is because while the sample was treated with FGA below Curie temperature (T_c), the accumulated H^+ ions and electrons around the grain boundaries of SBT film tend to induce 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 ^{o}C. However, with 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 MFM structure in which no ferroelectric properties was detected for the SBT thin film after FGA [6], this work demonstrates that the SBT film on MFIS still exhibits the ferroelectric properties in spite of the reduced capacitance. It implies that both 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.

3.3 Leakage current

Figure 7 shows the leakage current characteristics of SBT films on MFIS structure at different FGA temperatures. As shown in Fig. 7(a), for the sample without Pt top electrode, the leakage-current density of SBT films decreases. The leakage current density dropped directly from 1E-6 A/cm^2 to 1E-8 A/cm^2 at 2V. On the other hand, as the SBT films were coated with 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.[11] The leakage current in 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 in-diffused H^+ ion with the interface defects of SBT/Al_2O_3/Si.

In order to clarify the effect of SBT/Al_2O_3/Si interface on the leakage current of MFIS structure, Al_2O_3/Si sample was prepared and annealed at the similar condition (800 ^{o}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^{o}C, a decreased leakage current was observed for the Al_2O_3/Si sample under FGA treatment. Although a systematic study of forming gas annealing 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.

4. Conclusion

In summary, we have investigated that the effect of FGA treatment on the ferroeletric properties of $Sr_{0.8}Bi_2Ta_2O_9$ (SBT) ferroelectric film constructed on Al_2O_3/Si. After FGA treatment, the XRD 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 positive effect on the leakage current of MFIS in contrast to that of metal/ferroelectric/metal (MFM) structure. A rapid decrease as much as two orders of magnitude was obtained for SBT-based MFIS capacitors after FGA at 500^{o}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.

Acknowledgments

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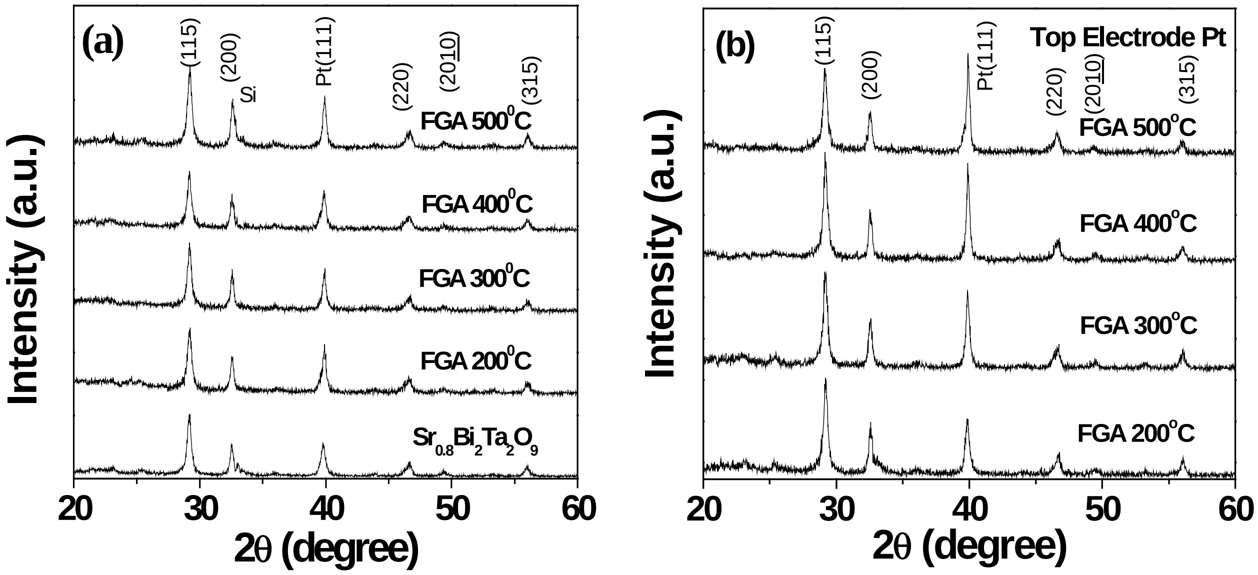

Fig. 1. X-ray diffraction patterns for SBT thin films (a) without top electrode and (b) with Pt top electrode after FGA at 200-500 ^{o}C.

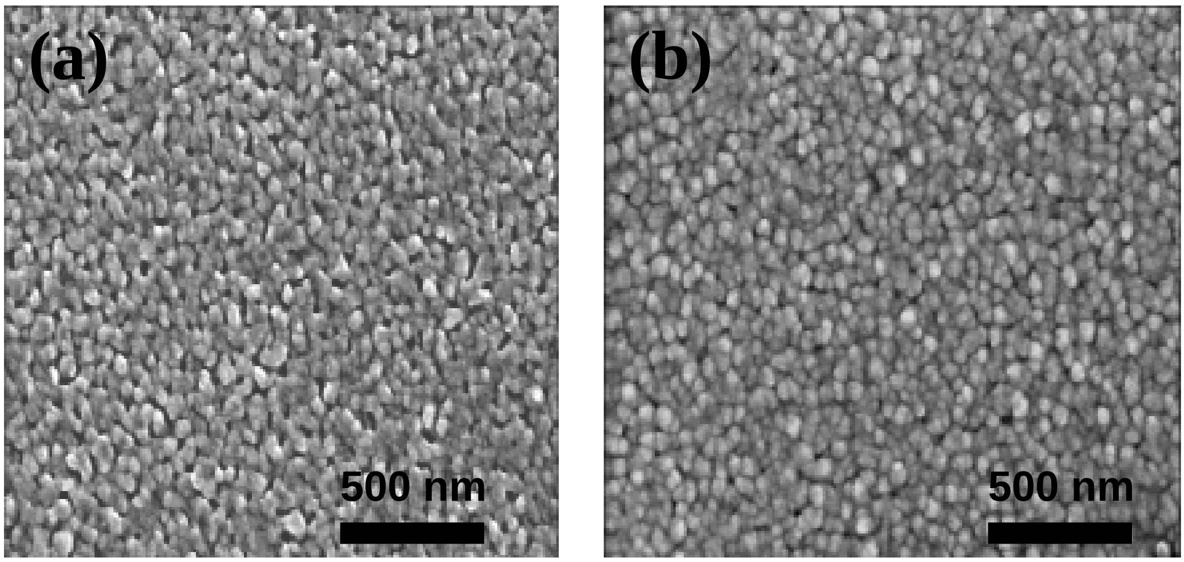

Fig. 2. Surface morphology of SBT thin films (a) before FGA and (b) after FGA at 500 ^{o}C.

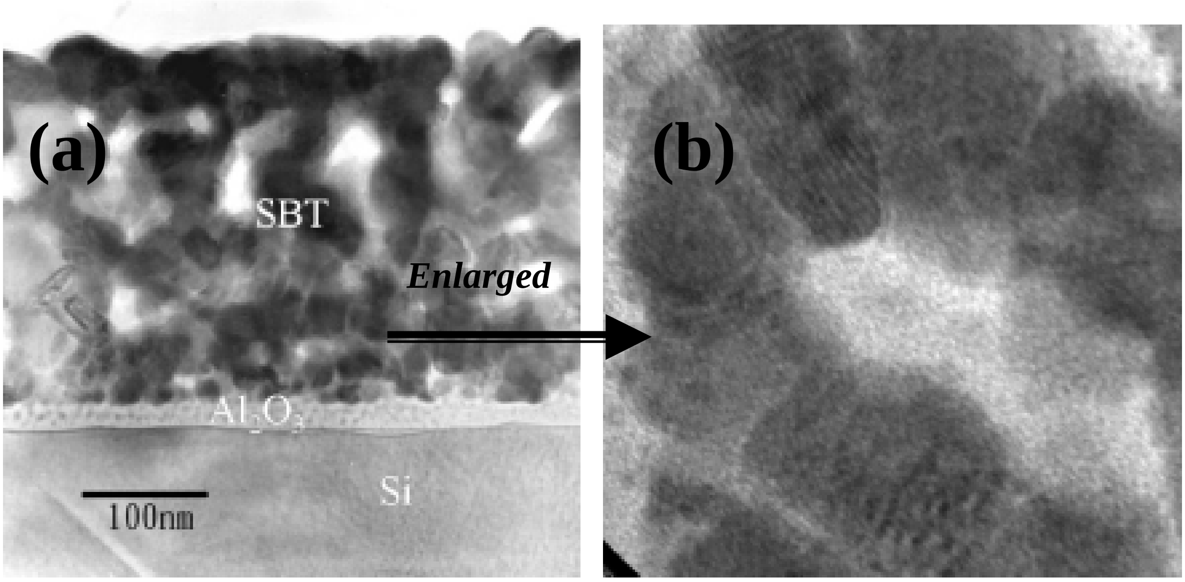

Fig. 3. (a) Cross-sectional TEM micrograph of SBT/Al_2O_3/Si structure without Pt top electrode after FGA process at 500 ^oC. (b) H-mapping of SBT/Al_2O_3 showing that H^+ has diffused into the SBT structure for the sample with FGA treatment.

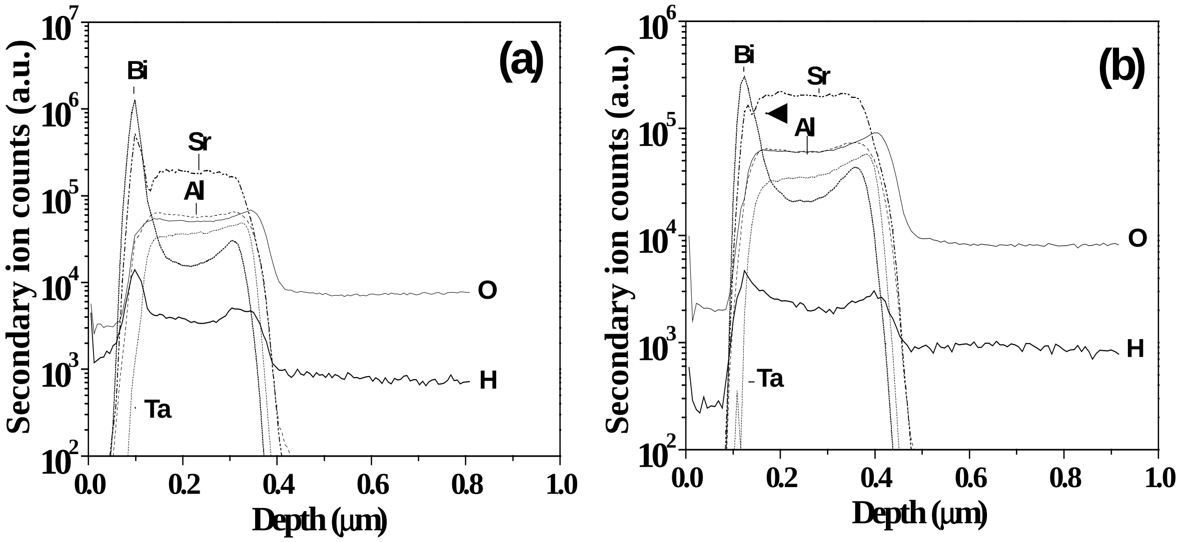

Fig. 4. SIMS spectra of SBT/Al_2O_3/Si capacitors (a) without top electrode and (b) with Pt top electrode after FGA at 400 ^oC.

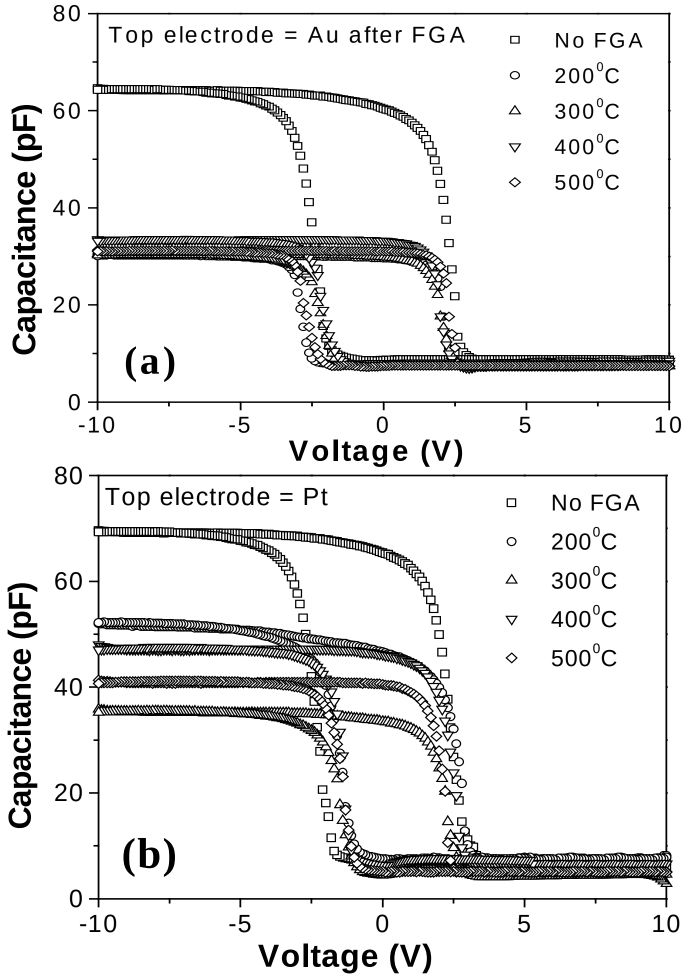

Fig. 5. C-V characteristics of SBT/Al_2O_3/Si capacitors (a) without top electrode, (b) with Pt top electrode after FGA at 200-500 ^oC.

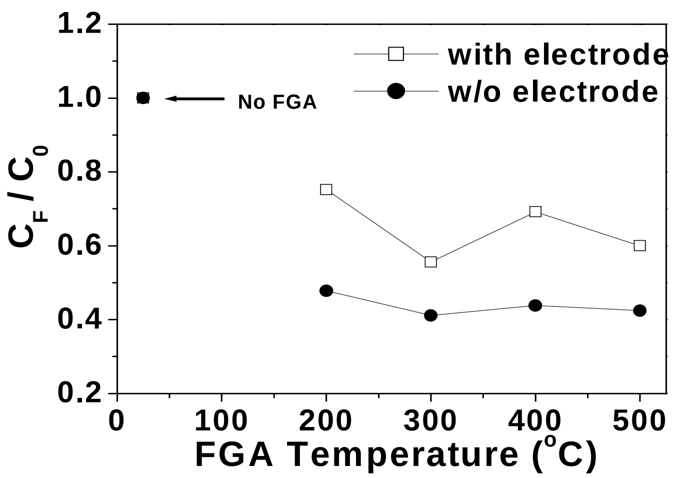

Fig. 6. Capacitance of SBT/Al_2O_3/Si with respect to the original value as a function of FGA temperatures.

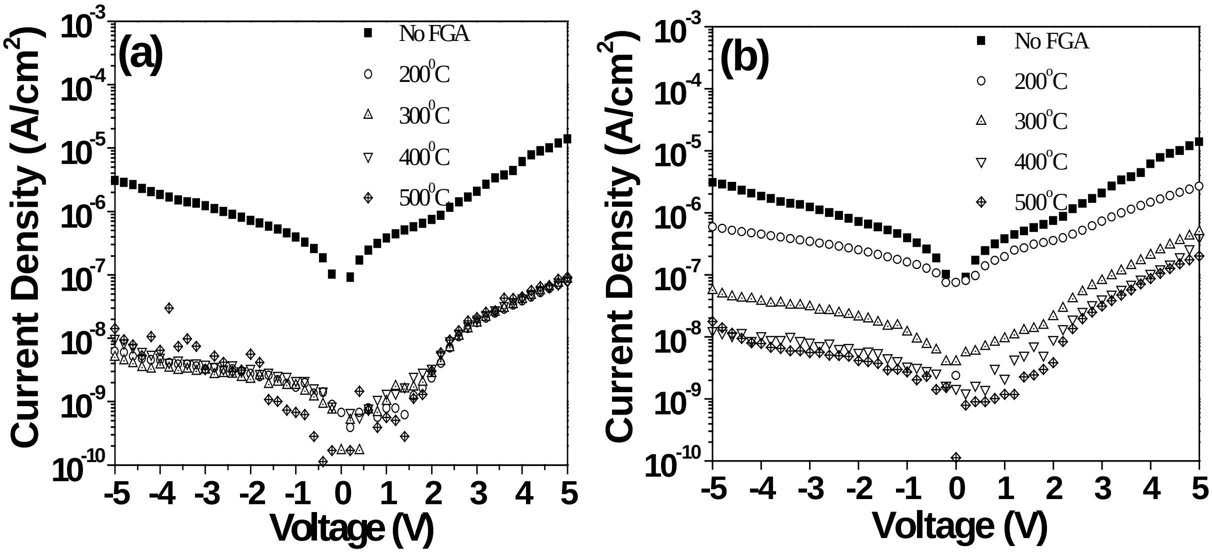

Fig. 7. J-V characteristics of SBT/Al_2O_3/Si capacitors (a) without top electrode and (b) with Pt top electrode after FGA at 200-500 °C.

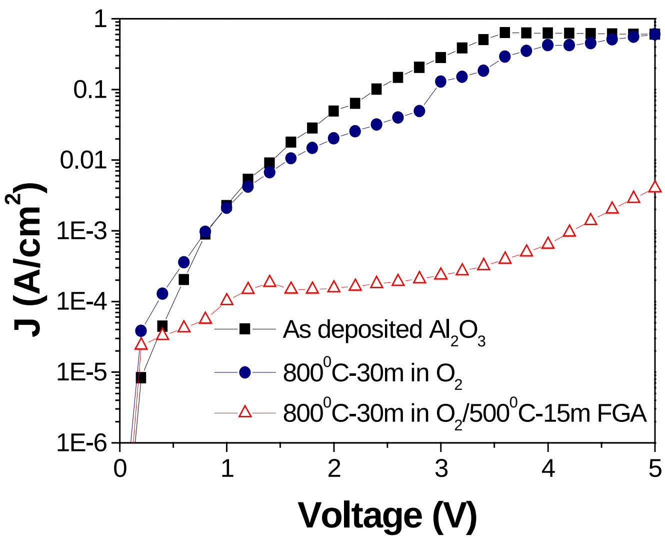

Fig. 8. I-V characteristics of annealed at 800 °C in O_2 and then FGA at 500 °C normalized with respect to the original value as a function of FGA temperatures.