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Role of Interface Reaction at High Temperature in Electrical Characteristics of $Bi_{3.25}La_{0.75}Ti_3O_{12}/Al_2O_3/Si$ Capacitors

Chia-Liang Sun and San-Yuan Chen[z]

Department of Materials Science and Engineering, National Chiao-Tung University, Hsinchu, 300 Taiwan

A novel face-to-face annealing process was used to investigate the enhanced electrical characteristics in $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT)/Al_2O_3/Si capacitors annealed at high temperatures. The low leakage current of BLT/Al_2O_3/Si capacitors can be obtained after high temperature annealing and the mechanism has been clarified and attributed to the formation of Si-rich aluminum oxide. The surface composition of aluminum oxide after annealing was further analyzed by X-ray photoelectron spectrometer (XPS) and XPS spectra revealed that the aluminum oxide would react with both Si substrate and BLT thin films to form Si-rich aluminum oxide. Because the aluminum oxide has weaker bonding than that of silicon oxide, Si composition can quench the electrical defects in aluminum oxide so as to reduce the leakage current of BLT/Al_2O_3/Si capacitors.
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In comparison with the existing one-transistor (1T) one-capacitor or 1T two-capacitor ferroelectric memory technology, one-transistor ferroelectric memory has attracted much attention due to the unique merits including small size, high speed, and nondestructive reading-out operation.[1-3] Among many issues in 1T ferroelectric memory fabrication, the manufacture of gate dielectric is always viewed as the key point because it is very difficult to integrate ferroelectric materials as the gate dielectric. Metal-ferroelectric-insulator-semiconductor (MFIS) structure is one of the proposed gate dielectric solutions and has been studied by many researchers.[4,5] Recently, we reported that $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) ferroelectric material with nonfatigue behavior can be integrated in an MFIS capacitor with Al_2O_3 as the insulator.[6,7] Furthermore, the effect of annealing temperatures on the electrical properties of BLT/Al_2O_3/Si capacitors has been also studied.[8] It was found that large BLT grain size, small leakage current, and a large memory window can be obtained with increasing annealing temperatures in the range of 700 to 950°C. In contrast, Noda *et al.* reported that the reduced leakage current in $Sr_xBi_{2+y}Ta_2O_9$ (SBT)/SiO_2/Si capacitors would be related to the decreased grain size of SBT thin films in the SBT/SiO_2/Si capacitors, in which SBT films were deposited by pulsed laser deposition at 400°C.[9] This conclusion is obviously opposite to our results in the high temperature annealed BLT/Al_2O_3/Si capacitors because these capacitors annealed in higher temperatures have lower leakage current but larger BLT grain size. Therefore, it is interesting to investigate these controversial phenomena. Because the interface reaction of stack gate dielectrics at high temperatures could be much more severe than that at low temperatures, the reaction of aluminum oxide with BLT and Si is believed to be correlated with this controversy. Thus, the electrical and physical characteristics of aluminum oxide after high temperature annealing should be characterized directly regardless of BLT. However, it is very difficult to etch BLT without damaging the aluminum oxide and defining the exact interface position between them. Therefore, in this study, a face-to-face annealing method is proposed to analyze the characteristics of aluminum oxide regardless of BLT in the stack dielectrics.

Experimental

Figure 1 illustrates the flow chart of the face-to-face annealing method for preparing aluminum oxide capacitors after high temperature reactions. Four-inch (100) Si wafers with ~10 Ω cm resistivity were used in this study. As shown in Fig. 1a, a 10 nm thick Al_2O_3 gate dielectric was first formed on Si.[10,11] Then BLT film was deposited on Al_2O_3/Si by chemical solution deposition using spin coating at 4000 revolutions per minute for 30 s in Fig. 1b.[7,8] Excess 10% Bi precursor was added to compensate for Bi loss during annealing. After each coating, the as-deposited films were pyrolyzed for several minutes so as to get the wet multilayer films. As shown in Fig. 1c and d, the wet multilayer films were placed upside down on the other Al_2O_3/Si substrates without BLT film coating so that upper BLT wet films contacted the bottom aluminum oxide. As shown in Fig. 1e and f, these face-to-face samples were annealed at high temperatures of 700, 850, and 950°C under oxygen ambient simultaneously and separated after furnace cooling to room temperature. Al was used as upper and bottom electrodes for the aluminum oxide capacitors as shown in Fig. 1g and the capacitor area was 5×10^{-4} cm^2. The electrical and physical properties were characterized by current density-voltage (J-V) measurements and X-ray photoelectron spectrometer (XPS), respectively.

Results and Discussion

Figure 2 shows the J-V characteristics of aluminum oxide capacitors after reaction with BLT and Si at 700, 850, and 950°C. The leakage current of aluminum oxide capacitors annealed at 700°C was the largest one among three conditions. In contrast, the leakage current dramatically decreased as much as several orders of magnitude after annealing at 950°C. It demonstrated that the leakage current of aluminum oxide capacitors after annealing would present almost the same decreasing trend as compared with the J-V curves of BLT/Al_2O_3/Si capacitors shown in inset figure.[8] Although the leakage current of aluminum oxide capacitors may be higher than that of BLT/Al_2O_3/Si capacitors at the same applied voltage, it could be attributed to the fact that the some voltage would drop across BLT films in BLT/Al_2O_3/Si capacitors. Therefore, it indicated that the reduced leakage current of BLT/Al_2O_3/Si capacitors would be related to the aluminum oxides but not to the microstructures of BLT films. On the other hand, high temperature annealed BLT films with large grain size provided lower trap density than those annealed at low temperatures because the grain boundaries were the sources of trapping centers.[12] Thus, the microstructures of BLT did contribute to the large memory window of high temperature annealed BLT/Al_2O_3/Si capacitors but it may not have been the major reason resulting in the reduced leakage current as compared to the aluminum oxide with large bandgap.[5]

Because the aluminum oxide is believed to be responsible for the reduced leakage current of capacitors, it is necessary to study the material properties after annealing. By means of the face-to-face annealing, XPS was used to detect the surface composition of aluminum oxide regardless of the etching problems. Figure 3 summarized the XPS spectra of aluminum oxide surface annealed at different temperatures. Take the reaction between aluminum oxide and BLT into account so that the results of Bi and Ti were first displayed in Fig. 3a and b, respectively. Figure 3a shows the Bi 4f spectra of

[z] E-mail: sychen@cc.nctu.edu.tw

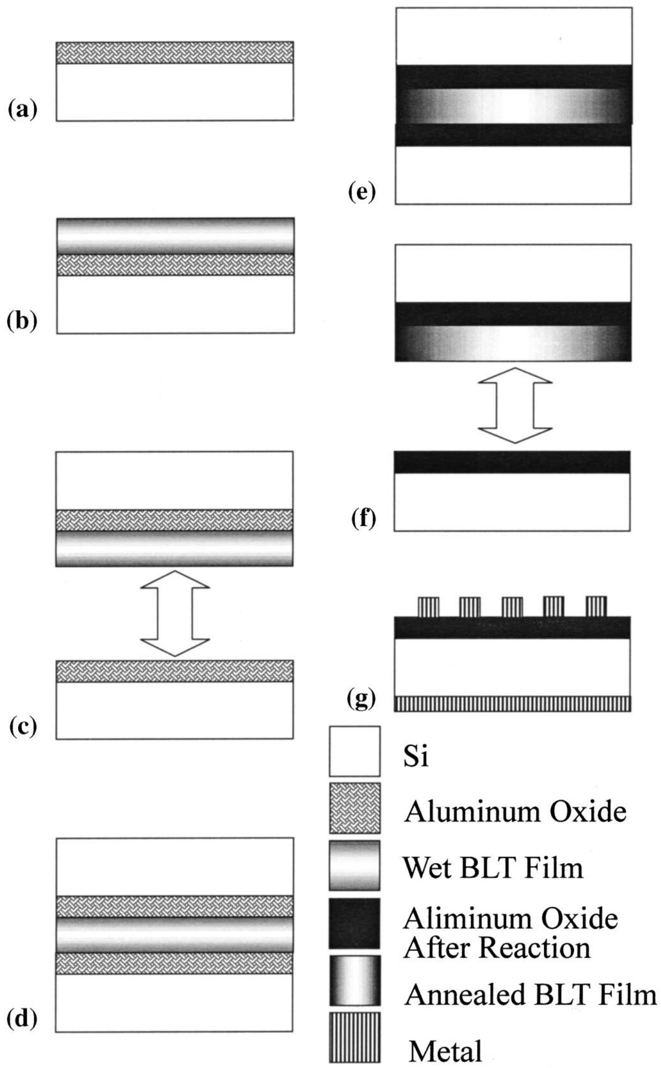

Figure 1. Schematic diagram of sample preparation for the aluminum oxide reacting with BLT and Si at 700, 850, and 950°C.

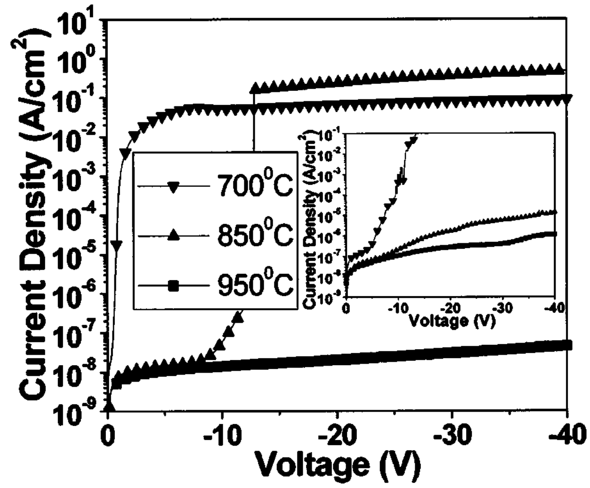

Figure 2. J-V characteristics of aluminum oxide capacitors reacting with BLT and Si at 700, 850, and 950°C. The inset figure is the J-V characteristics of BLT/Al_2O_3/Si capacitors annealed at 700, 850, and 950°C.[8]

aluminum oxide annealed at 700, 850, and 950°C. It was noted that Bi diffused into the aluminum oxide even annealed at 700°C. Figure 3b illustrates the Ti 2p and Bi 4d spectra. The Ti 2p signal cannot be found as compared to the results of BLT surface shown in the inset figure, in which Ti $2p_{1/2}$ peak superposes with Bi $4d_{3/2}$ to form a broad envelope. Also, La cannot be found. Thus it was suggested that Bi would react with aluminum oxide more easily than La and Ti. Figure 3c displays the Si 2p spectra. The increasing Si intensity is believed to be the evidence that aluminum oxide will react with Si substrate. Moreover, Al 2p spectra were shown in Fig. 3d and the low intensity at high temperature suggested that Al would diffuse into BLT. O 1s spectra of aluminum oxide were also shown in Fig. 3e and the shifted spectra at different temperatures depicted the ionic binding nature in aluminum oxide annealed at high temperatures.

Al 2p, O 1s, Si 2p, and Bi 4f core-level peaks measured by XPS can be further used to determine the surface compositions of aluminum oxide after annealing. The surface compositions were identified as the atomic ratios χ_{Al}, χ_{O}, χ_{Si}, and χ_{Bi}, where each atomic ratio χ was defined as the relations

$$\chi_{Al} = I^*_{Al}/I^*_{Al} + I^*_{O} + I^*_{Si} + I^*_{Bi}$$

$$\chi_{O} = I^*_{O}/I^*_{Al} + I^*_{O} + I^*_{Si} + I^*_{Bi}$$

$$\chi_{Si} = I^*_{Si}/I^*_{Al} + I^*_{O} + I^*_{Si} + I^*_{Bi}$$

and

$$\chi_{Bi} = I^*_{Bi}/I^*_{Al} + I^*_{O} + I^*_{Si} + I^*_{Bi}.$$

In the above relations, each I^* follows the definition represented as

$$I^*_{Al} = I_{Al}/S_{Al}$$

$$I^*_{O} = I_{O}/S_{O}$$

$$I^*_{Si} = I_{Si}/S_{Si}$$

and

$$I^*_{Bi} = I_{Bi}/S_{Bi}$$

where I_{Al}, I_{O}, I_{Si}, and I_{Bi} are the integrated intensities of Al 2p, O 1s, Si 2p, and Bi 4f peaks, respectively. S_{Al}, S_{O}, S_{Si}, and S_{Bi} are the individual atomic sensitivity factors referred to the analyzer. Figure 4 shows the surface atomic composition ratios of aluminum oxide. It was observed that the ratio of Al component decreased but the ratio of Si component increased at high temperatures. The lower Al content was due to the Al diffusion into BLT that has been evidenced by secondary ion mass spectrometry spectrum reported before.[8] Besides, it was suggested that the Si substrate would react with aluminum oxide, in which the Bi content was derived from BLT. Because silicon oxide has the lower formation enthalpy and large bond strength than those of aluminum oxide,[13] the low leakage current of BLT/Al_2O_3/Si capacitors would be attributed to Si-doped aluminum oxide after high temperature reaction.

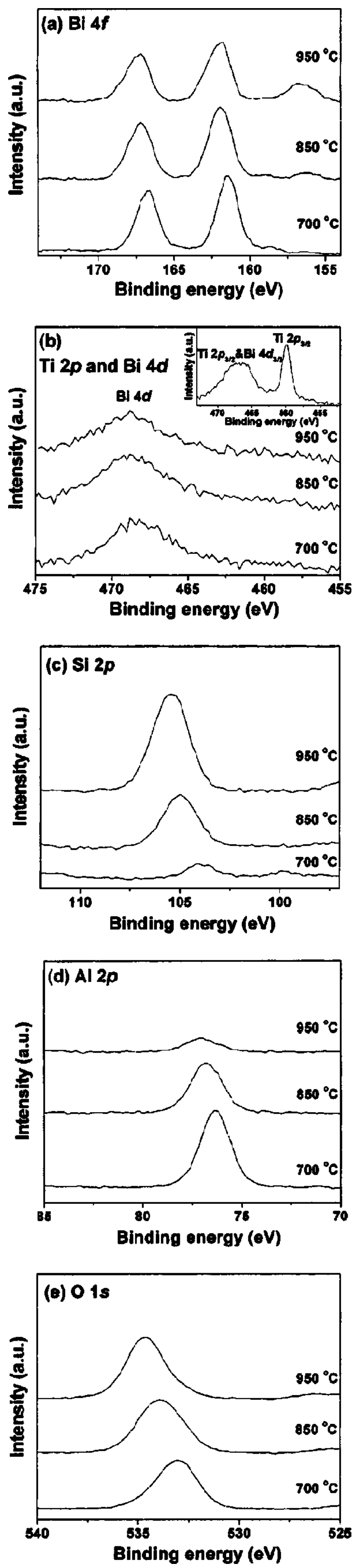

Figure 3. XPS spectra of aluminum oxide interface facing to BLT in the BLT/Al_2O_3/Si capacitors of (a) Bi 4f, (b) Ti 2p and Bi 4d, (c) Si 2p, (d) Al 2p, and (e) O 1s. The inset figure in Fig. 3(b) is the XPS spectra of Ti 2p and Bi 4d of BLT surface.

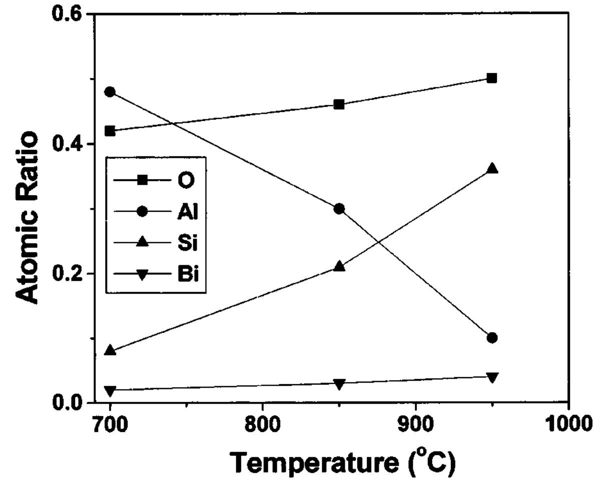

Figure 4. Surface atomic ratios of aluminum oxide interface facing to BLT in the BLT/Al_2O_3/Si capacitors.

Conclusions

In summary, the ambiguity of explanations for enhanced electrical properties of BLT/Al_2O_3/Si capacitors after high temperature annealing has been clarified. Because the characteristics of aluminum oxide can be measured regardless of BLT films using the face-to-face annealing process, the high temperature reaction of aluminum oxide was suggested to be responsible for the reduced leakage current of BLT/Al_2O_3/Si capacitors. Because of the larger bonding energy of silicon oxide than that of aluminum oxide, the electrical defects in aluminum oxide can be quenched so that aluminum oxide with high Si composition would have low leakage current.

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