Effects of Ti Buffer Layer on Retention and Electrical Characteristics of Cu-Based Conductive-Bridge Random Access Memory (CBRAM)

Behnoush Attarimashalkoubeh, Amit Prakash, Sangheon Lee, Jeonghwan Song, Jiyong Woo, Saiful Haque Misha, Nusrat Tamanna, and Hyunsang Hwang*

Department of Materials Science and Engineering, Pohang University of Science and Technology, Pohang 790-784, South Korea

We propose an ultrathin Ti buffer layer in the Cu/Al2O3 interface to overcome the high temperature retention failure and switching non-uniformity of conductive-bridge random access memory (CBRAM) device. The sacrificial effect of Ti resulted significant improvement in retention by minimizing Cu oxidation. A novel mechanism for this improvement on the basis of the difference in the electrode potentials of the Cu and Ti layers was also proposed. The Ti atoms help in retaining the copper filament with higher electrode potential by donating electrons to it. Moreover, device with a Ti buffer layer exhibits better uniformity that can be explained by the controlled diffusion of Cu ions through the buffer layer.

Results and Discussion

The Al2O3 was selected as an oxide layer because of its superior performance comparing to ALD-deposited TiO2 and HfO2. In the Al2O3 electrolyte, the cell leakage and forming voltage (Vf) varied with the thickness of the oxide layer. Al2O3 with a thickness of 2.5 nm exhibited the best trade-off between Vf and the cell leakage current. Excellent results with buffering role of Ti for Cu ion diffusion have been reported previously. Therefore, to have an insight into this effect, a layer of Ti at Cu/Al2O3 interface was inserted in this work. To clearly understand the filament properties in the device with Ti buffer layer, we have studied different behavior of this device by comparing the switching properties of the sample without Ti buffer layer as well as samples with various thicknesses of Ti buffer layer. After forming, the sample without Ti buffer layer exhibited unstable switching with large variations and small on/off ratio (Fig. 1c) due to uncontrolled Cu diffusion in the switching layer (the forming cycle is shown in black). On the other hand, the sample having the Ti buffer layer thickness of >3 nm showed no switching upto 20 V and leakage current remained very low (data not shown). The best results were found for the sample with the Ti buffer layer thickness of 2–3 nm [Figs. 1b, 1d and 1e]. Fig. 1b shows the typical I-V characteristics of the device under an external bias (the forming bias is shown in black). A sudden current drop in reset region under applying negative bias is observed in Fig. 1b, then the current followed in the same level with the forming cycle in further set cycles. This means the formed thin filaments completely dissolved under negative biasing as reset bias. Increasing compliance current (e.g., 1 mA) led to the formation of thicker filaments and results in degraded on/off ratio (to 10^3). This is assumed to be due to the noticeable amount of Cu injected into the Cu/Al2O3 interface, which could not be removed completely after the reset bias and acts as a duplicate Cu electrode. From the above understanding, we have concluded that Ti buffer layer controls the Cu diffusion and results good switching characteristics with high On/Off ratio (∼10^6) and good uniformity. It is noticeable that Ti is deposited thin enough not to participate in the formation of metallic filaments under positive biasing.

The chemical properties and state of Cu and Ti buffer layer were examined by X-ray photoelectron spectroscopy (XPS). We deconvoluted the Ti 2p core level spectra as shown in Figure 2a where we have obtained 8 different peaks which are ascribed to Ti2p1/2, Ti2p3/2, TiO2, TiO, Ti2O3, TiO2 and well matched with previous reported values. By considering these oxide peaks together with Ti metallic peaks with high intensity, it can be concluded that Ti and TiO2 co-exist within Ti buffer layer. Similar results are also reported in the

Experimental

We fabricated a W/Cu/Ti/Al2O3/Pt device having 250 nm via-hole in Pt/Ti/SiO2/Si substrate with Pt bottom electrode (BE). At first Pt (∼50 nm) as a BE was deposited on Ti/SiO2/Si substrate by dc sputtering. Next, 100 nm SiO2 layer was deposited by PECVD followed by the patterning and etching of 250 nm via-holes by conventional lithography and reactive ion etching systems. Then, 2.5 nm thick Al2O3 layer as a solid electrolyte was deposited by an atomic layer deposition system using Tri Methyl Aluminum (TMA) as a precursor at 200°C. Subsequently a Ti buffer layer of 2–3 nm was deposited by dc sputtering with Ar flow rate of 30 sccm and dc power of 100 W. Finally, 80 nm thick Cu as active top electrode and W (∼50 nm) as a capping layer were deposited by sputtering system and patterned using shadow mask. The dc power for Cu and W deposition was 100 W and working pressure was 5 mTorr. The bias was applied on top electrode and BE was grounded during measurements. The device schematic is shown in Figure 1a.

E-mail: hwangs@postech.ac.kr
The oxidation of Ti is by absorbing oxygen from Al₂O₃ at the Ti/Al₂O₃ interface.

In the de-convoluted XPS spectra for Cu in Fig. 2b, only two peaks are observed near the Cu/Ti interface. This indicates that the Cu layer remained in the metallic state because of the presence of a Ti buffer layer that protected the Cu layer against oxidation.

Next, we verified the retention properties at high temperatures (175, 200, and 225 °C) for both devices (with and without the Ti layer). When the external bias removed in LRS condition, the copper conductive filaments tend to break by oxidizing even at room temperature and results Cu⁺⁺ ions or retreat back to top electrode. However, when Ti buffer layer will be present, it will prevent the oxidation of Cu filament by donating the electrons to Cu⁺⁺ ions to form metallic state again as Ti has lower electrode potential and higher electronegativity than the Cu. The measurements results are shown in Figure 3a and 3b. The device with a Ti buffer layer exhibited a failure time that was approximately ten times higher which is easier to understand in Fig. 3c. It is clear that adding a Ti layer increased the stability of the copper filament, even at high temperatures. The XPS results show the presence of Ti and TiOₓ in the buffer layer. Therefore, a new device with TiOₓ as a buffer layer was fabricated to understand if the stabilized copper filaments originated from Ti metallic or oxide states. TiOₓ was deposited from a Ti target in the presence of oxygen by a DC sputtering system. This device exhibited a tight distribution of set/reset and LRS/HRS. The TiOₓ layer with buffering role, partially blocks copper ions to diffuse and controlled formation of filaments. When the device retention was studied at high temperatures, mean time to failure was worse than both of the other devices (with Ti buffer layer and without any buffer layer). Therefore, the effect of TiOₓ buffer layer is supposed to be limited just in improving uniformity by controlling Cu diffusion by formation of fine filaments. We assumed the early failure
seen in retention for this device could be explained by considering the higher possibility of breaking in fine filaments. So, in device with Ti layer (contained Ti and TiOx) the observed improvement in retention is expected to be mainly due to the Ti metallic state. This improvement can be explained by the difference in the standard electrode potentials for Ti (−1.63) and Cu (+0.34). In resistive random access memory (RRAM) devices, failures happen after removal of the bias owing to the filaments tendency to disintegrate into ions and react into the active electrode (Cu-> Cu^{2+} + 2e). However, when two metal layers with different standard potentials are in contact, the one with the lower potential (here Ti) tends to be reduced and release electrons (Ti->Ti^{2+} + 2e), therefore, electrons are injected from the sacrificial Ti layer to the copper filament to stabilize the conducting filaments and caused significant improvement in retention.

The suggested retention improvement mechanism is demonstrated in Fig. 3d. By applying an external bias, copper diffuses through the ultrathin buffer and oxide layers and forms a filament [see Fig. 3d]. A retention failure means that the Cu filament ruptured due to oxidation. In devices with a ~2-3 nm-thick Ti layer, Ti atoms near the TiAl2O3 interface donate electrons, minimizing the oxidation of copper atoms and protecting the copper filament. This leads to a significant improvement in retention, even at high temperature.

The increasingly need of high-density storage requires devices with the capability to store multiple levels in one cell. The multilevel cell (MLC) properties in CBRAM have been reported for different structures and shows to be a function of Vstop for reset (the maximum negative applied bias) and the compliance current.4,5,18,19 The MLC level cell (MLC) properties in CBRAM have been reported for different structures4,5,18,19 and shows to be a function of Vstop for reset (the maximum negative applied bias) and the compliance current.4,5,18,19

In devices with a Ti buffer layer, we assume that a copper filament is formed through the Al2O3 layer. The observed MLC properties are thought to be due to the thickening of the filament through the oxide layer, especially near the Al2O3/Ti interface which thought to be the thinnest part [shown with red circle in Fig. 4c], by increasing the compliance current [Fig. 4b, 4c]. Increased compliance current resulted in a controlled change in the filament thickness. In turn, this led to a lower resistance state for this device. Figure 4d shows retention characteristic of the corresponding MLC states of the device with Ti buffer layer which confirms the non-volatility of the obtained MLC levels.

In this study, a thin Ti layer was inserted between the active Cu electrode and the ALD Al2O3 solid electrolyte to enhance the switching uniformity and reliability of a CBRAM device. Partial oxidation of the Ti film and the metallic state of Cu were confirmed from the XPS analysis. The improvement in the switching cycle (>100 consecutive DC cycles) and the high on/off ratio (>10^6) of the devices with a Ti buffer layer were validated by comparison with a control sample without a Ti layer. The improvement can be attributed to the suppression of Cu diffusion into the Al2O3 switching layer owing to the presence of the Ti buffer layer. A stable data retention characteristic at temperatures >200 °C is achieved because of the lower electrode potential and higher electronegativity of Ti compared to Cu, which prevents the oxidation of the Cu metallic filament.

Acknowledgments

This work was supported by the Future Semiconductor Device Technology Development Program (100045085) funded by MOTIE (Ministry of Trade, Industry & Energy) and KSRC (Korea Semiconductor Research Consortium).

References