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Resistive Switching Property of Copper Sulfide and its Dependence on Electrode

Sang-Jun Choi[1], W.-Y. Yang[2,*], K.-H. Kim[2], Y.-K Kyoung[2], J.-G. Chung[2], H.-J. Bae[1], J.-C. Park[3], Koung-Kook Kim[4], Sangbin Lee[5], and Soohaeng Cho[5,*]

[1]System LSI, Samsung Electronics Co. Ltd., Yongin 446-712, Korea
[2]Corporate Technology Operations SAIT, Samsung Electronics Co. Ltd., Yongin 446-712, Korea
[3]Research Institute of Advanced Materials, Seoul National University, Seoul 151-742, Korea
[4]Department of Nano-Optical Engineering, Korea Polytechnic University, Siheung 429-793, Korea
[5]Department of Physics, Yonsei University, Wonju 220-710, Korea

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We investigated the effect of the electrode on the resistive switching property of (Cu, Zn, Pt)-Cu_2S-W structures to clarify the role of metallic ions and electrodes in forming conductive paths in solid-electrolytes and also to improve the switching property. Notably, Zn-Cu_2S-W and Pt-Cu_2S-W structures that lack of oxidizable metal electrodes exhibited bipolar switching characteristics, and practically preferable switching properties with appropriately higher a turn-ON voltage and resistance were achieved for Zn-Cu_2S-W in comparison to Cu-Cu_2S-W with too low turn-ON voltage. In contrast, the degrading evolution of switching was observed in Pt-Cu_2S-W. A simplified but convincing model is also suggested and discussed to explain the observations.

Keywords: resistive switching, solid-electrolyte, bipolar switching

1. INTRODUCTION

Resistive switching devices based on solid-electrolyte materials are highly interesting owing to the advantages of high endurance, low operation voltage and stable switching behavior[1] and the filament model has been adopted to explain these switching behaviors.[2,3] Among the solid-electrolyte materials (GeTe,[4] Ag_2S,[5] GeSeAg,[6] GeTeAg,[7] GeS,[8] and ZnCdS[9]), only a few reports on Cu_2S has been made. The resistive switching characteristics of the Cu_2S layer with a low turn-ON voltage (V_{ON}) of < ~0.1 V, which may cause practically incorrect switching was introduced[10] and it was clarified that the fast migration of Cu ions induced the low V_{ON} of the Cu-Cu_2S device.[11] Also, there was an attempt to replace Cu_2S with Ta_2O in order to enlarge V_{ON}.[12] The structural and electrical switching properties of copper sulfide layers with various material compositions by sulfurizing a Cu layer were reported.[13] The role of the electrode in the switching mechanism of oxide resistive switching devices should also be considered to properly understand and to optimize the switching property.[14] However, Cu (or Ag) has been employed as an active electrode in solid-electrolyte switching devices.[10,11] In this report, the effect of the electrode on the resistive switching property of Cu_2S layers with various bottom electrode (BE) materials, such as Zn, Pt and Cu, was investigated.

2. EXPERIMENTAL PROCEDURE

All samples were fabricated by RF sputtering (LA440) with a Cu_2S sputter target. Various metals (Cu, Zn, and Pt) were employed for BEs. SiO_2 (100 nm) layers thermally oxidized on 6 inch (100) silicon wafers were used as substrates. Particularly, during the Cu_2S deposition process, we intentionally applied a positive bias to the BE layer. The objective of this positive bias was to induce the diffusion of copper ions in the Cu_2S layer in order to produce an asymmetric Cu/S ratio distribution.[4] The substrate temperature was fixed at room temperature. Cu (30 nm), Zn (30 nm), and Pt (30 nm) BE layers were deposited on the different substrates as a BE, and copper sulfide (50 nm) films were grown as a switching layer. We employed a W (tungsten) probe with an area of 5×5 mm^2 as a top electrode (TE). The structural property of the Cu_2S layers was characterized by high-angle X-ray diffraction (HXRD) scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS). The XRD measurement was performed by the conventional 2θ scan at 2θ = 25° ~ 80° in a thin film mode (Philips Expert Pro) and the thickness and composition of the samples were determined

*Corresponding author: shcho@yonsei.ac.kr
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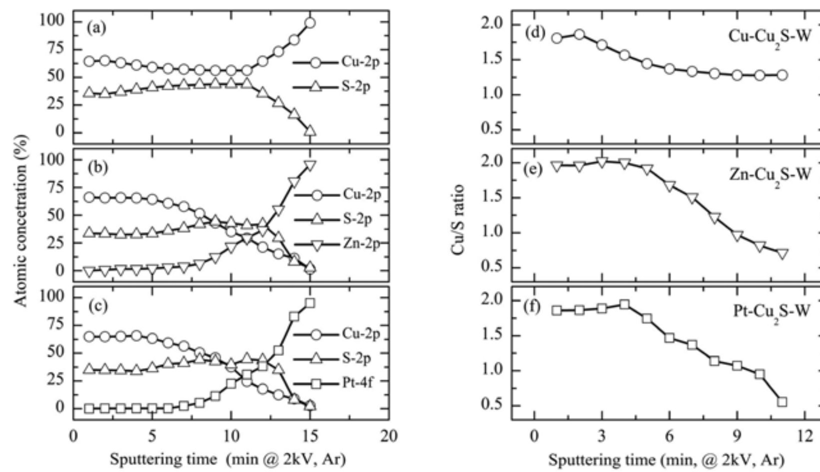

Fig. 1. XPS measurements of Cu_2S layers on (a) Cu, (b) Zn and (c) Pt BEs. (d)-(f) Cu/S ratio profiles of the devices along to the depth.

by SEM and energy dispersive spectrometry (EDS). The electrical properties were measured at room temperature using an HP 4156B precision semiconductor parameter analyzer.

3. RESULTS AND DISCUSSION

The XRD measurements revealed no differences among the Cu_2S films on the different electrodes. The EDS measurements of the prepared Cu_2S film revealed that the ratio of Cu to S was about 1.81 at the top. However, the XPS measurement of the prepared Cu_2S films shown in Fig. 1(a)-(f) revealed that the expected asymmetric distribution of the Cu to S ratio was induced by the bias during sputtering. Consequently, the Cu composition with regard to S has a negative compositional gradient along the depth to the BE. We recently reported that such an asymmetric distribution of metal atoms/ions in these types of device actually determines the switching polarity.[15]

Fig. 2 show the I-V curves of the samples without any pretreatments. Bias voltage was applied to the TE, whereas the BE was grounded. By applying a negative bias, it was possible to make the ionized Cu ions migrate to the BE in order to form the conductive filaments. In Fig. 2, there are two notable features. First, all the devices show the bipolar switching behavior and have the same switching polarity regardless of BE. Secondly, the Pt-Cu_2S-W structure exhibits non-Ohmic ON-state switching, which will be discussed later.

Note that the bipolar switching behaviors of Zn-Cu_2S-W and Pt-Cu_2S-W suggested that the excessive Cu ions in the Cu_2S lattices participate in the formation of the conductive filament even without the oxidizable electrode Cu. This indicates that an oxidizable electrode is not required when a Cu_2S layer is employed for a resistive switching material because the Cu_2S layer acts as a Cu source. Accordingly, Cu-Cu_2S-W with the additional Cu source demonstrated a lower

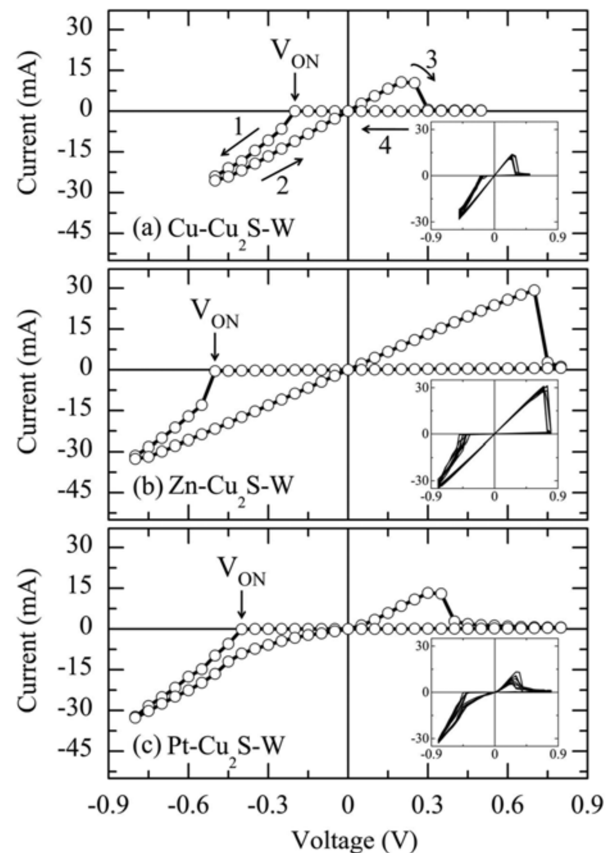

Fig. 2. I-V measurements of (a) Cu-Cu_2S-W, (b) Zn-Cu_2S-W, and (c) Pt-Cu_2S-W at 300 K. The arrows indicate the sweeping directions.

V_{ON} for the formation of filaments and a lower overall resistance than that of Zn-Cu_2S-W. The identical switching polarity for all the devices with the similar compositional gradients implies that the switching polarity is determined by the distribution of Cu ions in the solid electrolyte, not by the location of Cu electrode. Also, it should be noted that a rea-

sonably high V_{ON} of ~0.5 V and an operation voltage of ~0.9 V were achieved by employing Zn instead of conventional Cu. This higher V_{ON} is advantageous over the low V_{ON} (~ 0.15 V) of the Cu-Cu_2S-W structure, which may cause incorrect switching.[10,11] This can be qualitatively attributed to both the lack of an additional source of Cu ions and the low Cu concentration of the Cu_2S layer in the Zn-Cu_2S-W device.

In order to explain the switching behaviors, we employed a model in which the effective total area of the Cu bridges increases with the applied voltage.[4] Fig. 3(a) shows the simplified schematics of the modeled devices for various applied voltages along with the corresponding equivalent circuits. Total device resistance and the behavior of the dimensions of the Cu bridge can be described by the following equations,

$$\begin{aligned} R_{total} &= \frac{R_{high}R_{low}}{R_{high}+R_{low}},\ R_{high} = \rho_{Cu_2S}\frac{L}{A-A_{Cu}}, \\ &= \rho_{Cu}\frac{L_{Cu}}{A_{Cu}} + \rho_{Cu_2S}\frac{L-L_{Cu}}{A-A_{Cu}} \\ L_{Cu} &= L\left(\frac{V}{V_{ON}}\right)^{\alpha} for\ V<V_{ON}, \\ A_{Cu} &= A_{Cu_\max}\left(\frac{V}{V_{\max}}\right)^{\beta} for\ V \geq V_{ON} \end{aligned} \quad (1)$$

where, ρ_{Cu2S} (4.615×10^{-1} Ωm) and ρ_{Cu} (1.72×10^{-8} Ωm) are the resistivity of Cu_2S and Cu, respectively. L, A, L_{Cu}, and A_{Cu} are the thickness of the Cu_2S layer (50 nm), the top electrode area (5×5 mm^2), the length of the conducting Cu bridge, and the effective area of the conducting Cu bridge, respectively. $A_{Cu_\max}$ (= 8×8 nm^2) and V_{max} are the Cu bridge area for the maximum ON-state current and the maximum applied voltage, respectively. We determined the empirical parameters α (= 1.6) and β (= 1) by fitting the experimental values to the equations, which contain the information on the switching time dependence[4] and the migration rate of the metal ions. But those parameters were not considered in this work in order to focus mainly on the fundamental operation scheme. An abrupt increase in the current for V_{ON} can be attributed to the large difference in resistivity between Cu_2S and Cu. In general, the experimental values are in a good agreement with those simulated by the model as shown in Fig. 3(b) and (c).

Next, we discuss the switching characteristics of Pt-Cu_2S-W. In the case of (Cu, Zn)-Cu_2S-W, the resistive switching characteristics was reliably reproduced throughout the successive voltage sweeps. However, the Pt-Cu_2S-W structure has a critical problem with regard to non-volatility. As already shown in Fig. 2 (c), the ON-state is not Ohmic. Furthermore, after being turned ON, a degrading evolution of the ON-state current of the Pt-Cu_2S-W structure was observed in subsequently repeated measurements, in which the voltage sweeping direction was 0 V → −0.5 V → 0 V → −0.5 V. The ON-state was not maintained even without applying a reset bias (turn-OFF voltage). This suggests that the filament that was once connected was not completely disrupted but was partially_disconnected with a lower or no applied voltage. We suspect that it can be attributed to Pt's high affinity for Sulfur.[16]

To further clarify these observations, we assumed that the small portion of Cu filament in the vicinity of the Pt layer was narrowed. Fig. 4(a) provides the schematics to explain the different ON-state I-V behaviors of the Zn-Cu_2S-W and Pt-Cu_2S-W. The narrowed portion of the filament in the Pt-Cu_2S-W was assumed to have a thickness of L_{EDGE} and an area of A_{EDGE}. Employing this model, we calculated the ON-state current behavior of the (Zn,Pt)-Cu_2S-W by the parallel resistance model and the following equation with various $A_{Cu_\min}$ values and a fixed L_{EDGE} (see Fig. 4(a)).

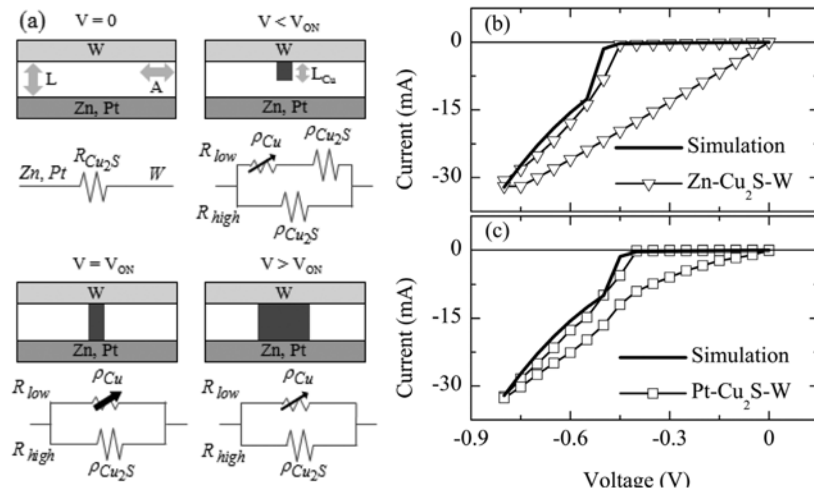

Fig. 3. (a) Schematics to show the formation of Cu conductive bridges at various input signals, and comparison of simulated *I-V* curves with the experimental for (b) Zn-Cu_2S-W and (c) Pt-Cu_2S-W at 300 K.

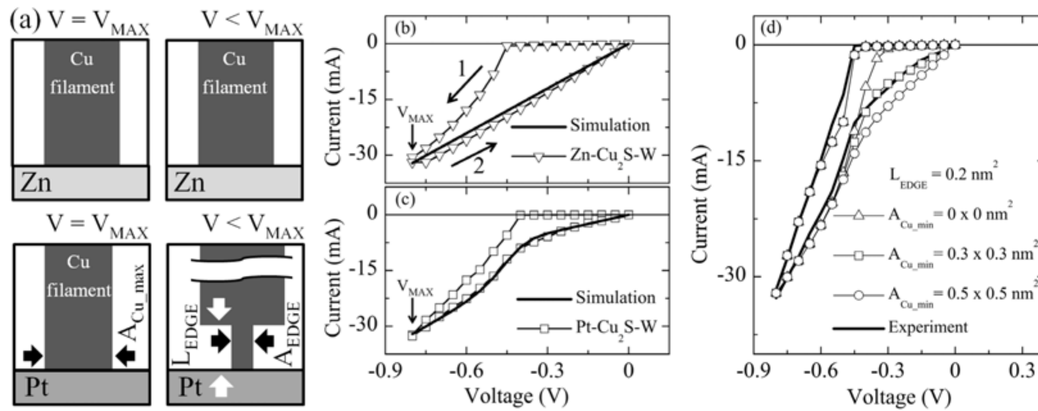

Fig. 4. (a) Schematics to show the different behaviors of ON-state I-V curves. Comparisons of the simulated and experimental curves for (b) Zn-Cu_2S and (c) Pt-Cu_2S-W. (d) Simulated *I-V* curves for various areas of the narrowed portion of the Cu filament.

$$A_{EDGE} = (A_{Cu_\max} - A_{Cu_\min})\left(\frac{V}{V_{\max}}\right)^{\chi} + A_{Cu_\min} \quad (2)$$

where, χ (= 10) is a fitting parameter that also contains the information on the switching time dependence[4] and migration rate of the metal ions as we mentioned previously. $A_{Cu_\min}$ and V_{max} are the areas of the locally narrowed Cu filament at the edge and the maximum operation voltage, respectively.

As shown in Fig. 4(d), the barely scarcely connected Cu filament at the Pt-Cu_2S interface ($L_{EDGE} = 0.2$ nm and $A_{Cu_\min} = 0.3 \times 0.3$ nm^2) faithfully reproduces an observed relaxing ON-state I-V characteristics. Therefore, Pt's strong tendency to bond with Sulfur is believed to compete with the Cu-Pt bondings[16] to reduce locally the effective area of the Cu filament at the Pt-Cu_2S interface. On the contrary, Zn-Cu_2S-W produced a stable and reliable ON/OFF switching behavior presumably because Zn has an excellent chemical adhesive property with Cu because Cu has high solubility in Zn. This implies that the various bottom electrodes can be applied to the fabrication of solid-electrolyte devices when a compositional gradient can be formed, which shows the possibility of improving the process compatibility with the concomitant operational advantages.

4. CONCLUSIONS

In conclusion, the effect of the BE material on resistive switching of (Cu,Zn,Pt)-Cu_2S-W device structures was investigated. Zn-Cu_2S-W and Pt-Cu_2S-W structures that do not even contain an oxidizable metal electrode exhibited the bistable switching characteristics owing to excessive Cu contents and the asymmetric distribution of those Cu elements in the solid electrolyte. These results indicates that the switching polarity is not determined by the asymmetric electrode but by the asymmetric distribution of the active (Cu or Ag) elements in the solid electrolyte. Moreover, a practically better switching behavior (appropriately larger V_{ON}) was achieved from Zn-Cu_2S-W compared to Cu-Cu_2S-W, which generated too low V_{ON}. However, the degrading evolution of the switching characteristics was observed in Pt-Cu_2S-W, which may be related to Pt's high affinity for Sulfur. The distinct *I-V* characteristics were explained by the suggested model and this model indicates that the non-volatile property is determined by the bonding property at the solid-electrolyte/metal interface.

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