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*Research Article*

# Room-Temperature Voltage Stressing Effects on Resistive Switching of Conductive-Bridging RAM Cells with Cu-Doped $SiO_2$ Films

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$SiO_2$ or Cu-doped $SiO_2$ (Cu:$SiO_2$) insulating films combined with Cu or W upper electrodes were constructed on the W/Si substrates to form the conductive-bridging RAM (CB-RAM) cells. The CB-RAMs were then subjected to a constant-voltage stressing (CVS) at room temperature. The experimental results show that the room-temperature CVS treatment can effectively affect the current conduction behavior and stabilize the resistive switching of the memory cells. After the CVS, the current conduction mechanisms in the high resistance state during the set process of the Cu/Cu:$SiO_2$/W cell can be changed from Ohm's law and the space charge limited conduction to Ohm's law, the Schottky emission, and the space charge limited conduction. Presumably, it is due to the breakage of the conduction filaments during the CVS treatment that the conduction electrons cannot go back to the back electrode smoothly.

## 1. Introduction

As the charge storage memory is approaching its scaling limit [1], the next generation nonvolatile memory (NVM) technologies have been widely investigated in recent years. New types of NVMs include the resistive random access memory (RRAM), magnetic random access memory (MRAM), and the phase-change random access memory (PRAM). The conductive-bridging RAM (CB-RAM) is one of the RRAMs within which metal cations, such as copper or silver, can form conductive bridges or break the conduction filaments between the top and the bottom electrodes via ion migration. The CB-RAMs can be switched between the high resistance state (HRS) and the low resistance state (LRS) under different bias polarities [2, 3]. The insulating materials between the active electrode (e.g., Cu or Ag) and the inert electrode (e.g., W or Pt) play important roles in the resistive switching (RS) operation and are called the solid electrolytes. Several kinds of the insulating materials, such as chalcogenide [4, 5], oxide-based [6–9], carbide [10], and amorphous silicon [11], have been used for the CB-RAMs. Among these materials, $SiO_2$-based films have advantages such as simple composition, no toxicity, compatibility with the COMS technology, and low cost. In addition, most of the resistive switching improvement works of the RRAMs were done at elevated temperatures [12–14]. There is no room-temperature process of Cu doping in oxide found in the literature. This work has tried to develop the room-temperature process of Cu doping into oxide following the constant-voltage stressing (CVS) treatment for the RRAM application. In this work, improvement on the switching characteristics of the $SiO_2$-based CB-RAM cells has been investigated with room-temperature constant-voltage stressing (CVS). The conduction mechanisms and the role of ion migrations in the resistive switching behavior of the conductive $SiO_2$-based films are also discussed.

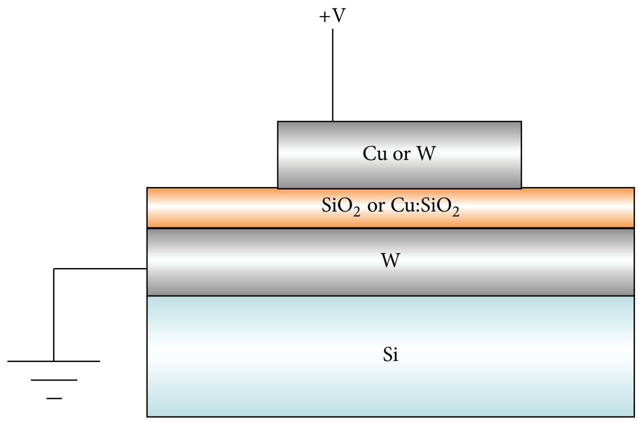


Figure 1: Schematic diagram of the CB-RAM cell.

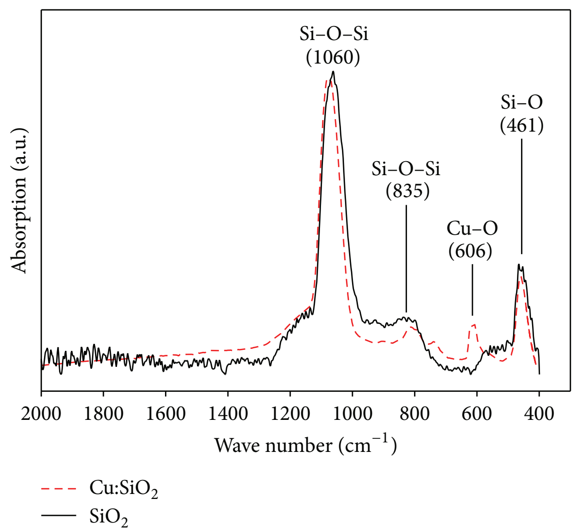


Figure 2: FTIR analysis of the deposited $SiO_2$ and $Cu{:}SiO_2$ films.

## 2. Experiment

In this work, $SiO_2$ or Cu-doped $SiO_2$ ($Cu{:}SiO_2$) insulating films combined with Cu or W top electrodes were constructed on the W/Si substrate to form the CB-RAM cell as shown in Figure 1. First, the tungsten (W) bottom electrode of 100 nm thickness was deposited onto the Si substrate by DC sputtering. Secondly, $SiO_2$ or $Cu{:}SiO_2$ films of 10 nm in thickness were deposited onto the W/Si substrates by RF sputtering. Then, the Cu or W top electrodes of 100 nm in thickness and 100 $\mu$m in diameter were deposited by DC sputtering with metal mask. The elemental compositions of the as-deposited oxide films have been measured with the X-ray photoelectron spectroscopy (XPS). Analysis of the atomic percentage of the solid-electrolyte films will help the explanation of the resistive switching behavior. The molecular bonding of the oxide films was examined with the middle infrared Fourier transform infrared (FTIR) spectroscopy. The resistive switching characteristics of the $SiO_2$-based films before and after the electrical stress treatment were measured by the semiconductor parameter analyzer Agilent 4156C. The top electrode was applied with the bias voltage while the bottom electrode was grounded during the electrical measurement. In this work, the electrical CVS of the Cu/$Cu{:}SiO_2$/W cell was carried out at −1 V with stress time of 300 sec at room temperature.

## 3. Results and Discussion

The FTIR results of the as-deposited $SiO_2$ and $Cu{:}SiO_2$ films are shown in Figure 2. The Si–O–Si bonding and the Si–O bonding were observed at 1060 $cm^{-1}$, 835 $cm^{-1}$, and 461 $cm^{-1}$, respectively, in the $SiO_2$ film. For the $Cu{:}SiO_2$ film, there was additional Cu–O bonding appearing at 606 $cm^{-1}$. Besides, the intensity of the Si–O bonding of the $Cu{:}SiO_2$ film is lower than that of the $SiO_2$ film. It indicates that some of the Cu atoms have bonded with the oxygen atoms in the $Cu{:}SiO_2$ film. The bonding energy of the Si–O–Si becomes weaker after the Cu doping in the oxide. Therefore, the Si–O–Si signal of the $SiO_2{:}Cu$ has shifted to higher wave numbers as compared to pure $SiO_2$ sample.

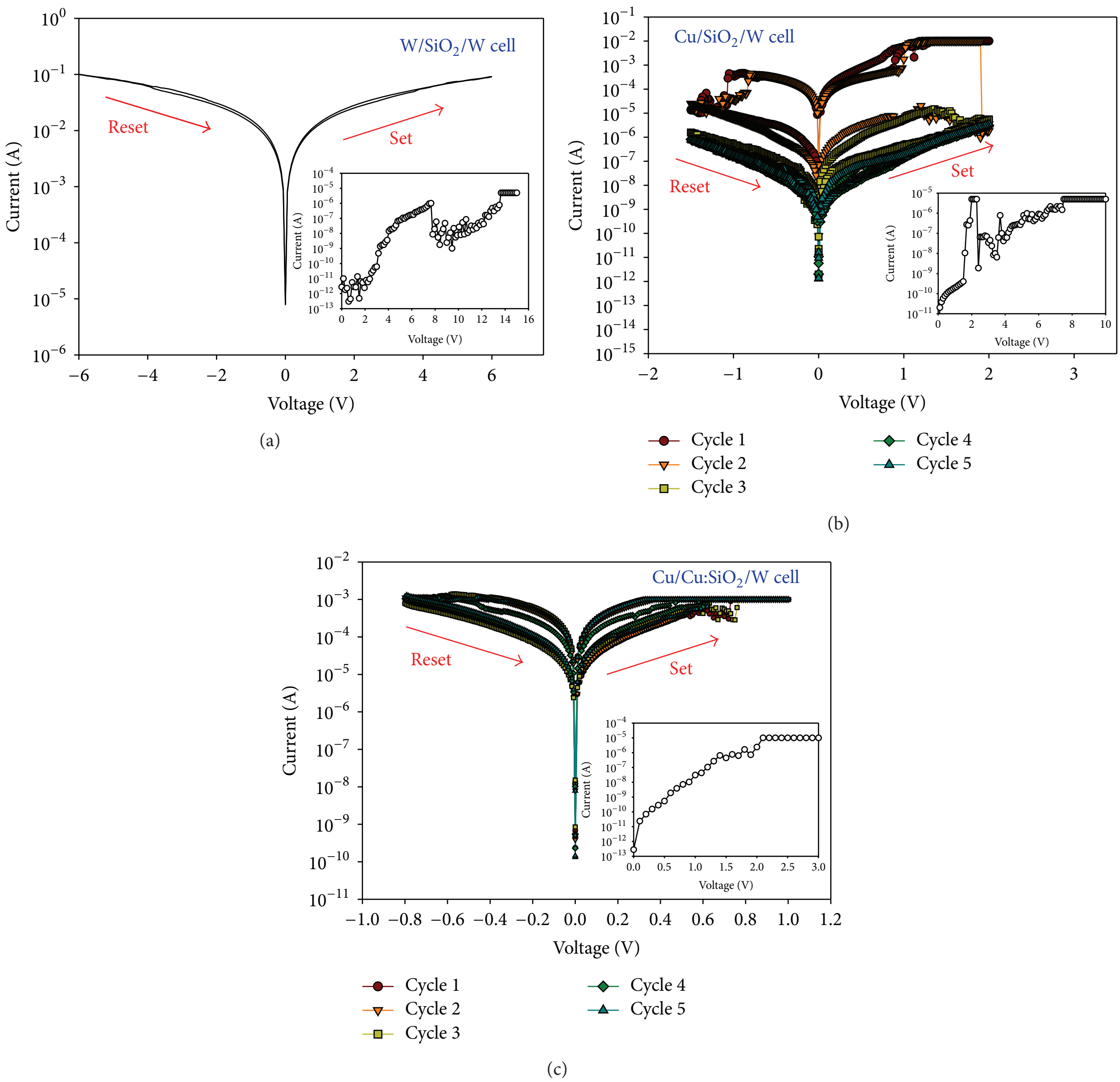


FIGURE 3: *I-V* characteristics of (a) W/$SiO_2$/W, (b) Cu/$SiO_2$/W, and (c) Cu/Cu:$SiO_2$/W cells.

Figure 3 shows the *I-V* characteristics of the W/$SiO_2$/W, the Cu/$SiO_2$/W, and the Cu/Cu:$SiO_2$/W cells, respectively, after the electrical forming process. In Figure 3(a), the W/$SiO_2$/W cell shows no resistive switching behavior after all. For the W/$SiO_2$/W device, the W atoms cannot be ionized by the applied electric field to form the conduction paths during the first forming process. After the soft breakdown, the oxide layer is completely damaged and cannot be recovered. That is why the W/$SiO_2$/W device shows high conductivity.

If the W top electrode is replaced by copper (Cu), the Cu/$SiO_2$/W cell exhibits the bipolar resistive switching between the HRS and the LRS, as shown in Figure 3(b). For the Cu/$SiO_2$/W device, the Cu atoms from the top electrode can be ionized by the applied electric field to form the conduction paths in the oxide layer during the forming process. After the soft breakdown, the oxide layer is not damaged completely. As the Cu/$SiO_2$/W device is biased reversely, the Cu ions will go back to the Cu electrode forced by the applied electric field and the Cu conduction paths are broken. Therefore, the Cu/$SiO_2$/W device shows high resistance state. Consequently, replacing the W top electrode with Cu can improve the RRAM behavior. However, the Cu/$SiO_2$/W cell is not stable after continuous operation with DC sweeping cycles and the resistive switching will eventually go off.

Furthermore, Figure 3(c) shows that the bipolar resistive switching *I-V* characteristics of the Cu/Cu:$SiO_2$/W cell are more stable than those of the Cu/$SiO_2$/W cell. For the Cu/Cu:$SiO_2$/W RRAM device, the set voltage is 0.78 V with a set current of 0.9 mA, and the reset voltage is

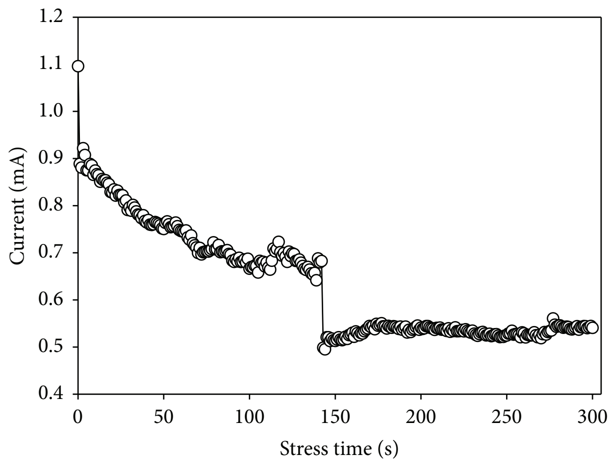


Figure 4: Constant-voltage stressing treatment of the Cu/Cu:$SiO_2$/W cell.

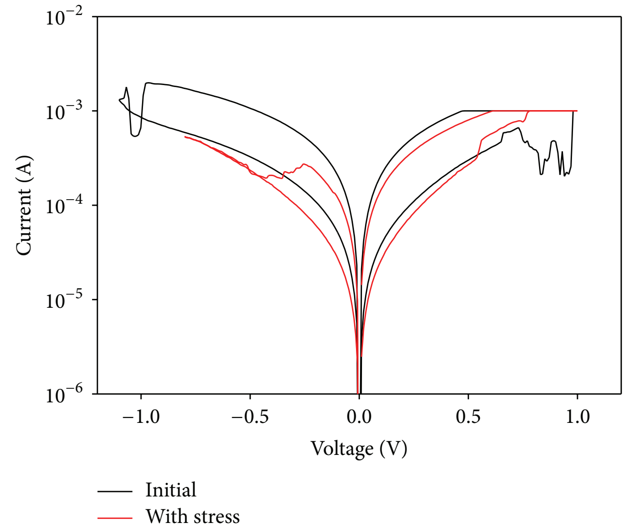


Figure 5: *I-V* characteristics of the Cu/Cu:$SiO_2$/W cells without and with CVS treatment.

−0.75 V with a reset current of 1.0 mA. According to the XPS analysis results, the $SiO_2$ film has a Si : O ratio of 30.8 at.% : 69.1 at.%, while the Cu:$SiO_2$ film has a Cu : Si : O ratio of 6.22 at.% : 29.6 at.% : 64.18 at.%. These results indicate that the oxygen content is richer in $SiO_2$ film than in the Cu:$SiO_2$ film. When a positive bias is applied to the Cu electrode, the Cu ion ($Cu^+$) will be generated and migrate towards the W electrode along the electric field in the $SiO_2$ film. The redox reaction will result in thin Cu connecting filaments in the $SiO_2$ film that exhibits the resistive switching behavior. At the same time, lots of oxygen ions ($O^-$) will also be generated and migrate towards the Cu electrode and then recombine with the Cu ions. This will eventually cause the resistive switching behavior to go off. With the Cu:$SiO_2$ film, the Cu/Cu:$SiO_2$/W cell shows better stability in resistive switching because extra Cu atoms are doped in the $SiO_2$ film to effectively trap the extra oxygen ions avoiding the breakage of the Cu connecting filaments.

Figure 4 shows the condition of the CVS treatment to the Cu/Cu:$SiO_2$/W cell. The current value was slowly decreased with increased CVS time. During the electrical stressing, the current value decreases drastically at a CVS time of 140 sec. It can be attributed to the major breakage of the Cu conduction filaments. In this work, the Cu/$SiO_2$/W device is biased reversely during the DC stress treatment. The Cu ions will go back to the Cu top electrode forced by the applied electric field and the Cu filaments will be broken eventually.

Figure 5 shows the *I-V* characteristics of the Cu/Cu:$SiO_2$/W cells without and with the CVS treatment. It shows that the operation power of the cell can be reduced after the CVS treatment. Besides, the $R_{HRS}/R_{LRS}$ ratio is more stable after the CVS treatment that the resistive switching behavior of the cell can be enhanced by the CVS treatment. In the HRS during the set process of the Cu/Cu:$SiO_2$/W cell without the CVS treatment, two different conduction mechanisms, Ohm's law ($I \propto V$) and the trap-fill limited ($I \propto V^n$), are dominant, as shown in Figure 6(a). In the low bias regime, the injected carrier density is lower than the thermally generated carrier density that the Ohm's law conduction mechanism dominates the conduction behavior. However, in the high bias regime, the space charge limited conduction (SCLC) with trap model is dominant [15–20]. The SCLC characteristics include the Ohm's law, the trap-filled limit behavior, and the Child's law ($I \propto V^2$) [15, 16]. Figure 6(b) shows that the Cu/Cu:$SiO_2$/W cell after the CVS treatment has three different conduction mechanisms. In the low bias regime, the Ohm's law conduction mechanism is dominant. As the bias increases, the conduction mechanism changes to the Schottky emission mechanism ($\ln(I) \propto \ln(V^{1/2})$) in the middle bias regime (0.13–0.55 V). The transition of the conduction mechanism might be due to the breakage of the conduction filaments during the CVS treatment that the conduction electrons cannot go back to the back electrode smoothly. As the positive bias increases further to 0.56 V, the conduction current increases drastically. This might be attributed to the reconnection of several conduction filaments and the SCLC mechanism of Child's law is dominant in this regime [21].

In addition, the endurance characteristics of the Cu/Cu:$SiO_2$/W cell after the CVS treatment have been measured that, after 100 continuous switching cycles, the HRS/LRS ratio remains almost the same, as shown in Figure 7. For the Cu/Cu:$SiO_2$/W device, there are more Cu conduction filaments and the size of the Cu conduction filaments is larger before the CVS treatment. Some of the Cu filaments cannot be broken completely during the RESET process. Therefore, the RRAM behavior of the device is not stable enough. After the CVS treatment, both the number and the size of the Cu conduction filaments are reduced. The Cu/Cu:$SiO_2$/W device becomes easier to be operated between the SET and RESET processes so that the RRAM behavior of the device is improved. Therefore, the CVS treatment can effectively affect the current conduction behavior and stabilize the resistive switching of the CB-RAM cell.

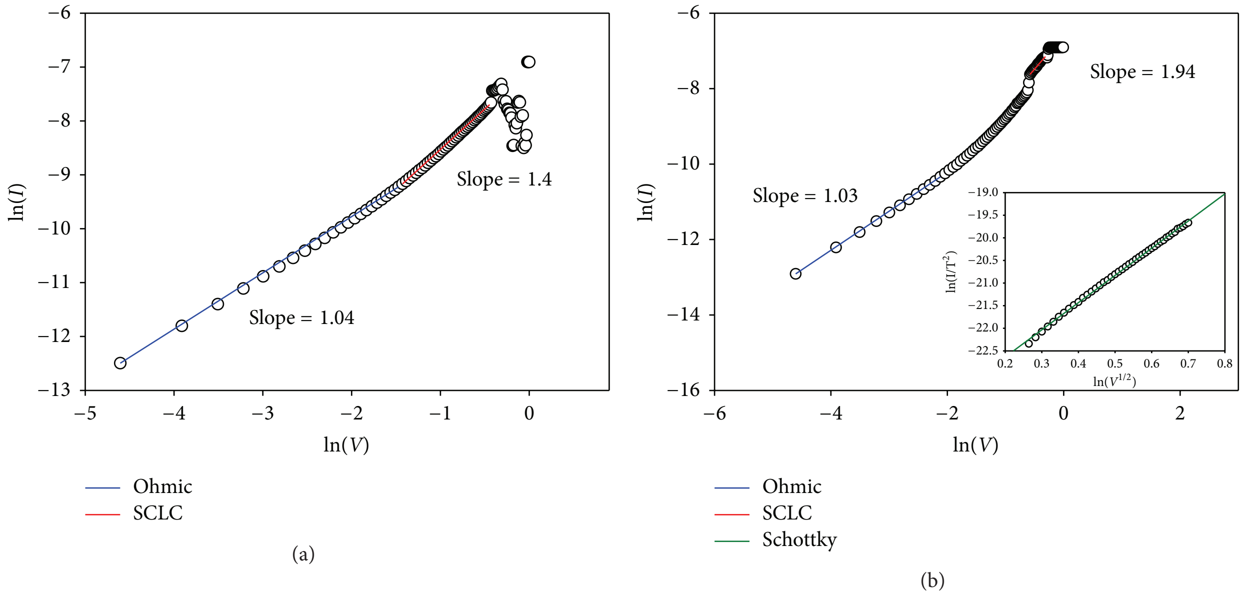


FIGURE 6: Current conduction mechanisms of the $Cu/Cu:SiO_2/W$ cell: (a) without CVS treatment and (b) after CVS treatment.

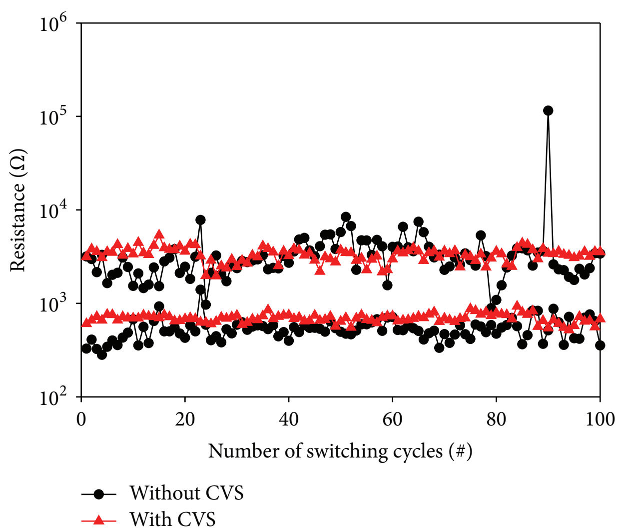


FIGURE 7: Endurance characteristics of the $Cu/Cu:SiO_2/W$ cells without and with CVS treatment.

## 4. Conclusions

In this work, room-temperature CVS has been used to improve the bipolar resistive switching characteristics of the CB-RAMs with $Cu:SiO_2$ insulating film. After the CVS treatment, the current conduction mechanisms in the HRS during the set process of the $Cu/Cu:SiO_2/W$ cell can be changed from Ohm's law and SCLC to Ohm's law, Schottky emission, and SCLC. Besides, the switching characteristics of the $Cu/Cu:SiO_2/W$ memory cell exhibit a more stable $R_{HRS}/R_{LRS}$ ratio due to the reduction of the conduction filaments. The room-temperature CVS treatment developed in this work shows high potential to improve the operation performance of the CB-RAM cells.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgment

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