Resistance Switching Properties in $Cu/Cu\text{-}SiO_2/TaN$ Device

Shyankay Jou, Bohr-Ran Hwang, and Chia-Jen Li

Abstract—**A metal-insulator-metal (MIM) cell comprising copper-doped silica as the insulator, copper as the top electrode, and tantalum nitride as the bottom electrode was fabricated by sputter deposition for the study of resistive random access memory (RRAM). The MIM cell demonstrated bipolar switching of resistance upon dc voltage sweeps. The MIM cell was switched to a low resistive state (LRS) at a forward bias voltage of about +0.5 V, and then switched back to a high resistive state (HRS) at a reversed bias voltage of about –0.2 V. Electrical conduction of the MIM cell followed Ohmic behavior in LRS, whereas conduction mechanisms varied in HRS in different voltage sweep cycles. In the first few sweep cycles, conduction in HRS featured Schottky emission. After the MIM cell has been switched for more than 20 cycles, electrical conduction in HRS changed to the space-charge-limit-current mechanism. The changes of conduction mechanisms in HRS were possibly attributed to the variation of interfaces between tantalum nitride electrode and copper-doped silica.**

Index Terms—**Copper-doped silica, resistive memory, Schottky emission, space-charge-limit conduction**

I. Introduction

RESISTIVE random access memory (RRAM) has been considered as a promising candidate for advanced nonvolatile memory applications [1], [2]. RRAM has a simple metal/insulator/metal (MIM) structure in which resistance can be reversibly switched between a high resistive state (HRS) and a low resistive state (LRS). The mechanisms for resistive switching in RRAM have been categorized by their conducting paths such as conducting filaments inside insulator and interface–typed conduction across electrode and insulator. Furthermore, complex conductive behaviors have been observed when an interfacial layer was present between the insulator and the electrode in RRAM [3]–[5].

Electrochemical migration of metal ions to form and to rupture conductive filaments has been regarded as the driving mechanism for RRAM with the presence of an active electrode made of Ag, Au, or Cu [1], [2]. In this regard, metal ions would migrate from an active metal anode and condense as metallic form on the surface of an insert cathode, and eventually produce continuous filaments across the insulator while a forward bias voltage was applied to an electrochemical metallization MIM cell. Subsequent reverse bias induced dissolution of metal filaments locally. Platinum has often been utilized as an inert electrode and copper as an active electrode in the study of $Cu–SiO_2$–, $Cu–ZrO_2$–, and $Cu–MO_3$–based electrochemical metallization MIM cells [5]–[9]. Tungsten has also been used as an inert electrode for $Cu–SiO_2$–based MIM cells [10], [11]. Replacing expensive Pt electrode with other electrode materials is needed for feasible production of RRAM. In our previous study, we demonstrated bipolar resistive switching both in $Cu/Cu–SiO_2/Pt$ and $Cu/Cu–SiO_2/Al$ cells [5]. The MIM cell using an Al electrode had higher resistance ratio between HRS and LRS than that using a Pt electrode. But the $Cu/Cu–SiO_2/Al$ cell had a high switch–on voltage above 3 V, which might limit its application in advanced nonvolatile memory. In this study, we report on the switching properties of $Cu–SiO_2$–based RRAM using tantalum nitride (TaN) as the bottom electrode. The switching voltages for RRAM were reduced. The mechanisms for electrical conduction were discussed.

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II. Experimental Procedure

A. $Cu/Cu\text{-}SiO_2/TaN$ Fabrication

$Cu–SiO_2$–based RRAM cell was composed of a thin layer of copper-doped silica film, a copper top electrode (TE), and a TaN bottom electrode (BE). The $Cu–SiO_2$ film of 50 nm thick was prepared by co-sputter technique using a Cu target and a SiO_2 target as described previously [12]. The as-deposited $Cu–SiO_2$ film was composed of dispersed Cu_2O nanoparticles inside an amorphous SiO_2 matrix [5], [12]. $Cu/Cu–SiO_2/TaN$ cell was prepared by sequential deposition of TaN, $Cu–SiO_2$, and Cu. A TaN stripe of 90 nm thick and 50 μm wide was first deposited on an oxide-covered Si(100) substrate by reactive sputtering of a Ta target in a flowing N_2–Ar gas mixture, through a shadow mask. The base pressure and working pressure were 1.6×10^{-3} Pa and 1.2 Pa, and the N_2 to Ar ratio was 1:9 for the sputter deposition of TaN. After depositing the $Cu–SiO_2$ film on top of the TaN stripe, a Cu stripe of 200 nm thick and 50 μm wide was deposited by sputtering of a Cu target in pure Ar, through a shadow mask. The Cu stripe was perpendicular to the TaN stripe, and $Cu(TE)/Cu–SiO_2/TaN(BE)$ formed a crossbar MIM cell with an area of 50 × 50 μm^2, as shown in Fig. 1.

B. Electrical Characterization

Current–voltage (I–V) measurements were performed on the cross–bar MIM cell using a Keithley 237, through two tungsten probes of 5 μm in diameter in contact with electrode pads extended from the electrode stripes, as shown in Fig. 1. The TaN(BE) was grounded, and the Cu(TE) was biased with sweeping dc voltages for the I–V measurements. The bias sweeps were conducted in the direction 0 V → 0.8 V → 0 V → −0.5 V → 0 V. The MIM cell was continuously measured with several cycles of voltage sweeps.

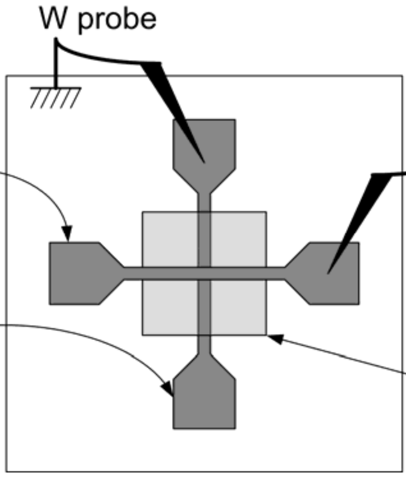

Fig. 1. Schematic of crossbar MIM cell with extended electrode pads. Bottom electrode (BE) was grounded and top electrode (TE) was biased in I-V measurement.

III. Results and Discussion

A. Switching Performance

The Cu(TE)/Cu–SiO_2/TaN(BE) cell exhibited bipolar switching at the beginning cycle of I-V measurement, without a prior high-voltage forming procedure. Hysteresis I-V curves were obtained in the first few cycles of voltage sweeps across positive and negative voltage polarities. Fig. 2 shows a typical switching characteristic for the 5th cycle of voltage sweep. The current increases with bias voltage and jumps to a compliant current at a positive SET voltage around +0.45 V, in which the cell switches from HRS to LRS. LRS remains while the bias is swept back from positive voltages to 0 V and to negative voltages. Then the cell is switched from LRS to HRS while the voltage is further swept to a RESET voltage around –0.2 V. Afterward, switching proceeds repeatedly following counterclockwise cycles of voltage sweep.

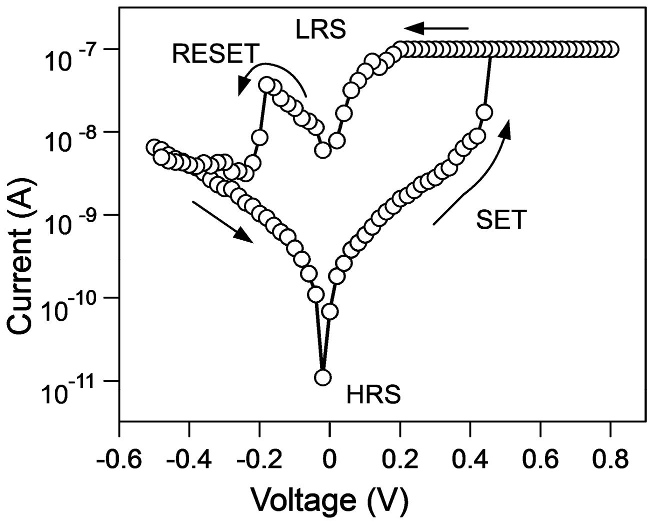

Fig. 2. Current-voltage characteristics of the Cu/Cu-SiO_2/TaN cell in the 5th cycle of voltage sweep.

Bipolar switching behaviors remained when the MIM cell was swept for 100 cycles. A typical I-V curve for the 26th cycle is shown in Fig. 3. The SET and RESET voltages are around +0.5 V and –0.15 V, respectively. The currents for LRS are about the same for the 5th and 26th cycles of voltage sweeps. On the other hand, the currents for HRS in the 26th sweep cycle are about one order higher than those in the 5th sweep cycle. In comparison to the abrupt jump of current at SET voltage in the 5th sweep cycle, the current gradually increases to the compliant current when the MIM cell is SET

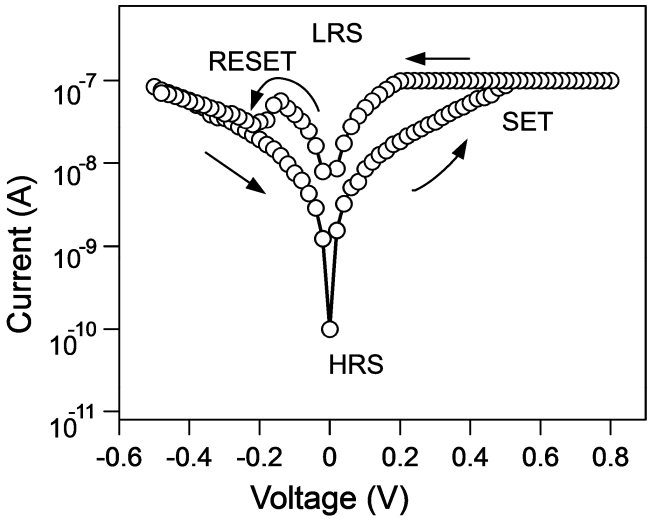

Fig. 3. Current-voltage characteristics of the Cu/Cu-SiO_2/TaN cell in the 26th cycle of voltage sweep.

to LRS in the 26th sweep cycle.

Resistance ratios of R_{HRS}/R_{LRS} measured at +0.1 V are 90 in the 5th sweep cycle and 5 in the 26th sweep cycle. As a result, the MIM cell had a high resistance ratio in first few sweep cycles. The resistance ratio reduced and achieved a stable value for a number of sweep cycles. The changes in I-V characteristics possibly correlated to the structures in the MIM cell and corresponding conduction mechanisms.

B. Conduction Mechanisms

Fig. 4(a) displays a logarithmic plot for the I-V curve for the MIM cell in the 5th sweep cycle in the positive branches of the forward and reverse sweeps. The upper curve for LRS is linear (slope = 1.08), featuring Ohmic conduction ($I \propto V$). Therefore, conductive filaments [13] possibly formed inside the bulk Cu-SiO_2 film after the MIM cell is SET to LRS. Linear relation is not observed in the lower curve for HRS. Thus other mechanisms govern the conduction in HRS in this cell. Fig. 4(b) shows a curve of ln I against $V^{1/2}$ for the HRS of the MIM cell in the 5th sweep cycle at voltages below +0.4 V. The plot is linear, and therefore the conduction in HRS follows Schottky emission [14], [15]. Schottky emission is an electrode-barrier-limited conduction mechanism, rather than a bulk conduction mechanism. In our previous study of Cu/Cu-SiO_2/Al cell, Schottky emission was correlated to the

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presence of an Al-O layer spontaneously formed between Al (BE) and Cu-SiO_2 film [5]. Also a shift of voltage for minimum current accompanied the presence of Al-O interface layer [5]. The shift of voltage for minimum current has been correlated with nonuniform distribution of space charges in [14]. In present study, the voltage for minimum current in the I-V curve of the 5th sweep cycle shifts for about –0.02 V in the forward sweep in HRS, as shown in Fig. 2. A spontaneously generated Ta-O-N interface between TaN and Cu_xO has been reported to influence conduction behavior in a TaN/Cu_xO/Cu cell [4]. Herein, a thin Ta-O-N interface may also form between Cu-SiO_2 and TaN (BE) during preparation of our Cu/Cu-SiO_2/TaN cell. The Schottky emission and the shift of voltage for minimum current in the first few sweep cycles were possibly attributed to the charge trap on the Ta-O-N interface.

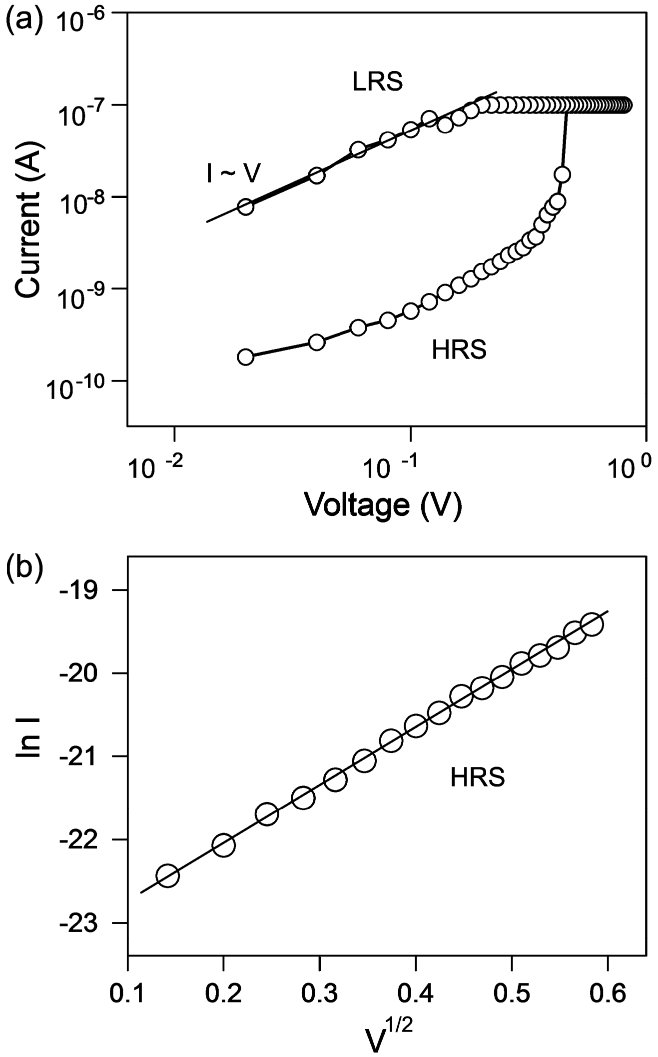

Fig. 4. (a) Logarithmic I-V plots and (b) ln I-$V^{1/2}$ plot of the Cu/Cu-SiO_2/TaN cell in the 5th cycle of voltage sweep.

Fig. 5 shows a logarithmic plot of the I-V curve for the MIM cell in the 26th sweep cycle in the positive branches of the forward and reverse sweeps. Similar to the plot for the 5th sweep cycle in Fig. 4(a), the upper curve shows linear I-V relation (slope = 1.06), featuring Ohmic conduction in LRS. The lower curve for HRS, however, shows altered I-V relations with two linear regions. The low-voltage region exhibits Ohmic conduction, having a slope of 1.07. The high-voltage region has a slope of 1.9, featuring Child's square law ($I \propto V^2$) [16], [17]. As a result, the electrical conduction in HRS of Cu/Cu-SiO_2/TaN cell in the 26th sweep cycle follows the space-charge-limited current (SCLC) mechanism [14], [16], [17]. SCLC is a bulk limited conduction process involving charge injection and trap in insulating material [14]. The resultant conduction mechanism for Cu/Cu-SiO_2/TaN cell in the 26th sweep cycle is the same as that of Cu/Cu-SiO_2/Pt cell in our previous study [5].

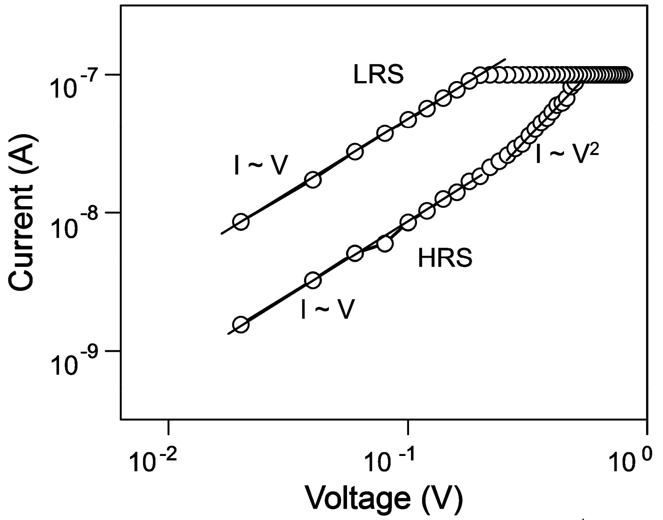

Fig. 5. Logarithmic I-V plots the Cu/Cu-SiO_2/TaN cell in the 26th cycle of voltage sweep.

C. *Interfacial Ta-O-N Layers*

According to the altered mechanisms for electrical conduction in HRS, the structure of Cu/Cu-SiO_2/TaN cell differs in the 5th and 26th sweep cycles. An interfacial Ta-O-N layer was present in the first few sweep cycles, and electrical conduction obeyed Schottky emission in HRS. The interfacial layer possibly disappeared after the cell was cyclically swept for many times, and electrical conduction for the cell changed to SCLC, a bulk limited conduction mechanism.

Stability of interfacial oxide layer in Cu/Cu-SiO_2/TaN cell in this study is different from that in Cu/Cu-SiO_2/Al cell in our previous study [5]. The Al-O layer permanently existed between Cu-SiO_2 and Al, whereas the Ta-O-N layer was present at the beginning but disappeared after few sweep cycles. The unlike stability of these two interfacial oxides may originate from differences in oxygen affinity between their metallic counterparts and SiO_2. Surface of Ta(BE) and Al(BE) would become oxidized by exposure to air or oxygen during sample preparation. After a Cu-SiO_2 film was deposited on the surface of the Ta(BE) or Al(BE), solid-state redox reaction would take place at interfaces. Al has higher oxygen affinity than Si [18], thus Al-O is stable. Ta has lower oxygen affinity than Si [18], [19], thus Ta-O-N is not stable at the Cu-SiO_2/TaN interface. The as-deposited Cu-SiO_2 film was deficient in oxygen [12]. Therefore, the originally formed Ta-O-N layer would be reduced back to TaN by releasing oxygen to Si after few cycles of voltage sweeps.

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IV. CONCLUSIONS

In this study, we evaluate TaN as the bottom electrode to replace Pt for Cu-SiO_2-based resistive memory. The Cu/Cu-SiO_2/TaN cell exhibited bipolar switching characteristics, similar to the cells using Pt or Al as the bottom electrode. The cell with a layer of spontaneously formed interfacial Ta-O-N has higher R_{HRS}/R_{LRS} ratio than that without an interfacial layer. However, the thin Ta-O-N layer could disappear after few cycles of voltage sweeps in this study. Future work on increasing stability of Ta-O-N layer may improve performance of Cu/Cu-SiO_2/TaN memory cell.

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