

Atomic switch: Development of resistive switching memories based on nanoscale migration of cations in oxide thin films

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Abstract

Resistive switching memories based on the formation and dissolution of a metal filament in simple metal/insulator/metal (MIM) structures are attractive because of their potential high scalability, low-power consumption, and ease of operation. From the standpoint of the operation mechanism, this type of memory devices can be referred to as a gapless-type atomic switch. Here, we present our recent results of MIM structured atomic switches consisting of thin layers of inorganic and organic oxides, focusing on their switching characteristics and mechanisms.

As the downscaling of flash and dynamic random access memories approaches the physical limits, new solutions for volatile/nonvolatile storage are being investigated at the research level. Among several emerging technologies, cation-migration-based resistive memory is one of the most attractive alternatives to the current memory technologies. Several years ago, a conceptually novel switching device, called an ‘atomic switch’, was proposed, whose resistance across a nanometer gap is controlled by migration of metal ions and solid-state electrochemical reactions under electrical bias.^[1] Similar resistive switching has been observed for simple metal/insulator/metal (MIM) cells, in which a thin layer of metal-ion conductor is sandwiched between an electrochemically active electrode (usually Cu and Ag) and an inert metal electrode (for example, Pt). Because migration of metal ions plays a crucial role on the switching behavior, we call this MIM structured cell a ‘gapless-type atomic switch’. In the beginning, mixed electronic and ionic conductors such as Ag₂S and Cu₂S were employed,^[2] but then oxide materials were used as the metal-ion conductor in order to increase the threshold voltages of resistive switching above the operating voltage of complementary metal-oxide-semiconductor devices.^[3] However, their resistive switching mechanism is not yet fully understood. A complete understanding of the mechanism is very important for the development of this type of cells for commercial electronic devices.

To address this issue, we have investigated current-voltage (*I-V*) and current-time characteristics of cross-point structured Cu/Ta₂O₅/Pt cells.^[4] The cells were initially SET from the OFF state to the ON state when a relatively higher positive bias was applied to the Cu electrode, as shown by the blue curve in Fig. 1a. This first SET operation corresponds to the first formation of a metal filament between the electrodes by inhomogeneous nucleation and subsequent growth of Cu on the

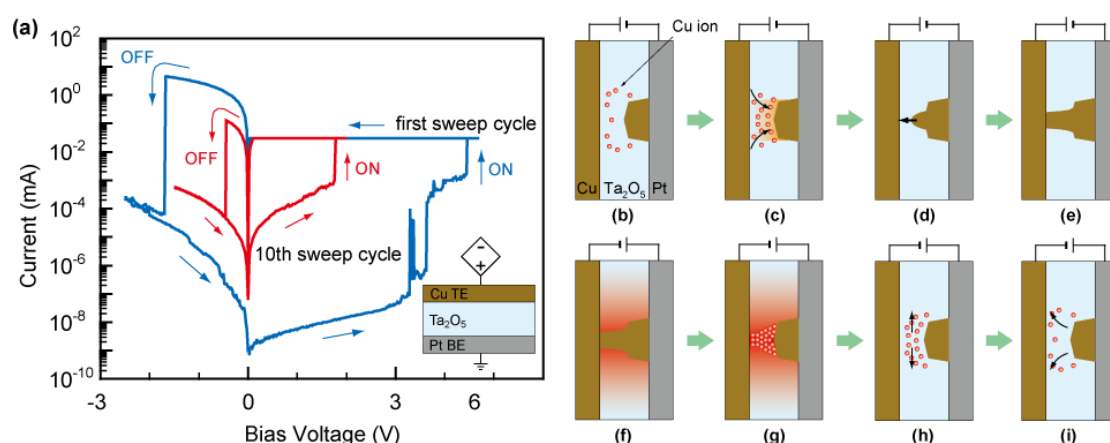


Figure 1 Typical I-V characteristics of a Cu/Ta₂O₅/Pt cell (a) and switching mechanism (b) - (i)

Pt electrode, based on the migration of Cu ions into Ta₂O₅ layer from the Cu electrode. After the formation of the metal filament, the cells exhibited bipolar switching behavior with the repetition of SET and RESET (from the ON state to the OFF state) operations, as shown by the red curves. The SET process corresponds to the reformation of the metal filament on a remaining Cu by nucleation (or, electrodeposition) as shown in Figs. 1b to 1e, while the RESET process is attributed to the thermal dissolution of the metal filament due to the Joule-heating-assisted oxidation followed by the diffusion of Cu ions under the concentration gradient and the applied electric field as illustrated in Figs. 1f to 1i.

Since the SET and RESET processes are based on thermochemical reactions, the switching behavior should depend on ambient temperature. We performed *I-V* measurements as a function of temperature to determine the validity of our switching model.^[5] The SET and RESET voltages decreased in magnitude with increasing temperature, as shown in Fig. 2a. From calculations of the nucleation rate of Cu nuclei based on the classical nucleation theory, it was found that the observed temperature variation of the SET voltage is determined by supersaturation in the vicinity of the Pt

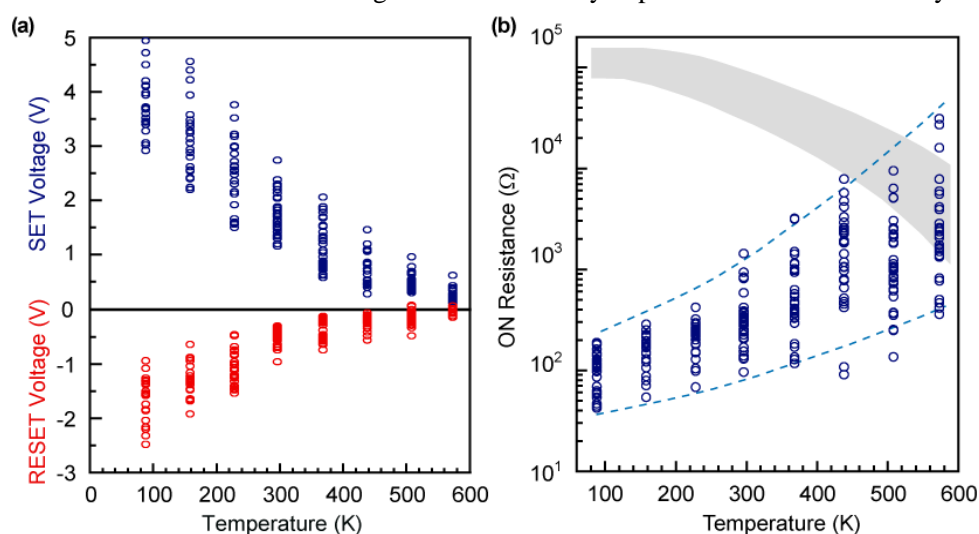


Figure 2 Temperature variations of SET/RESET voltages (a) and ON resistances (b)

electrode and migration speed of Cu ions in the Ta₂O₅ layer, which are controlled by the application of positive bias. The ON resistance increased with increasing temperature (Fig. 2b), which was the opposite behavior expected given the SET and the current compliance (represented by the gray-shaded area). This discrepancy is probably due to varied growth speed of a Cu nucleus after nucleation at different temperatures or in different supersaturation conditions. The RESET voltage is determined by the size of the metal filament formed at a given temperature and its thermal stability against the surrounding temperature. These results are consistent with the proposed switching model.

The effects of moisture on the operational characteristics were also examined.^[6] Figures 3a and 3b plot the SET and RESET voltages of Cu/Ta₂O₅/Pt and Cu/SiO₂/Pt cells as a function of ambient pressure. Both the SET and RESET voltages of the Cu/Ta₂O₅/Pt cell were nearly constant, but the Cu/SiO₂/Pt cell exhibited a two-fold increase in magnitude of those voltages with a reduction in the ambient pressure. FT-IR measurements indicated the presence of a certain amount of residual water in both the Ta₂O₅ and SiO₂ layer, which is absorbed from the ambient air. From the results obtained, we concluded that the ionization of Cu at the anode interface is attributed to chemical oxidation via residual water. The moisture absorption also results in the formation of a hydrogen-bond network at grain boundaries in the oxide layers, and Cu ions are likely to migrate along the grain boundaries, as illustrated in Fig. 3c. Due to strong hydrogen bonds in the Ta₂O₅ layer, the operational voltages of the Cu/Ta₂O₅/Pt cell are independent of the ambient H₂O pressure. However, the switching behavior of the Cu/SiO₂/Pt cell is significantly influenced by ambient conditions because of weak hydrogen bonds in the SiO₂ layer.

We also demonstrated that the atomic switch can be realized using solid polymer electrolytes (SPE).^[7] MIM cells were fabricated with a mixture of polyethylene oxide (PEO) and AgClO₄.

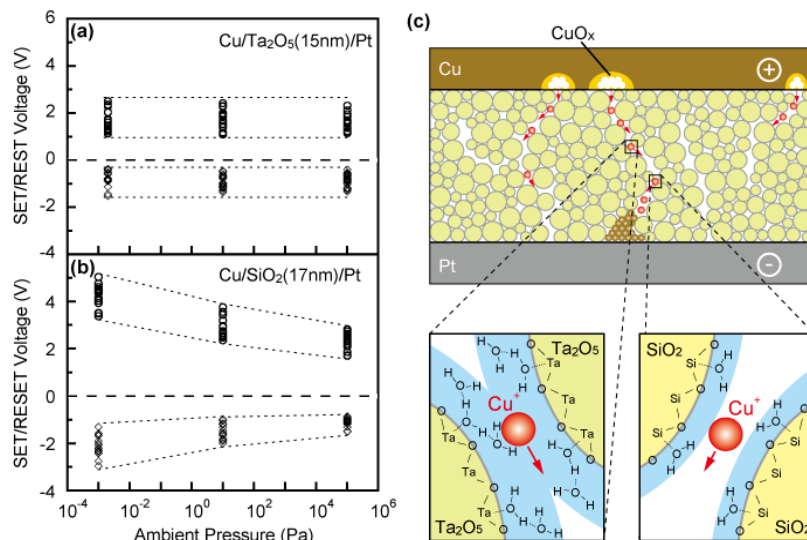


Figure 3 Variation in SET and RESET voltages of Cu/Ta₂O₅/Pt (a) and Cu/SiO₂/Pt (b) cells for different ambient water pressures and potential mechanism for the moisture effects (c)

Figure 4a shows a typical resistance-voltage (R - V) curve of an Ag/PEO+AgClO₄/Pt cell with an AgClO₄ concentration of 3 wt%. The cell exhibited bipolar switching behavior with a high ON/OFF resistance ratio of about 10^5 . From the results of thermal, transport, and electrochemical measurements, it was concluded that the observed switching originates from the formation and dissolution of a metal filament inside the SPE film caused by electrochemical reactions, similar to inorganic electrolyte-based atomic switches, as illustrated in the schematics of Fig. 4a. Moreover, the cell showed high programming speed ($< 1\mu\text{s}$) and long retention time (> 1 week) at this early stage, as seen in Fig. 4b. Now we are trying to fabricate the cell on a flexible substrate using an inkjet technique.

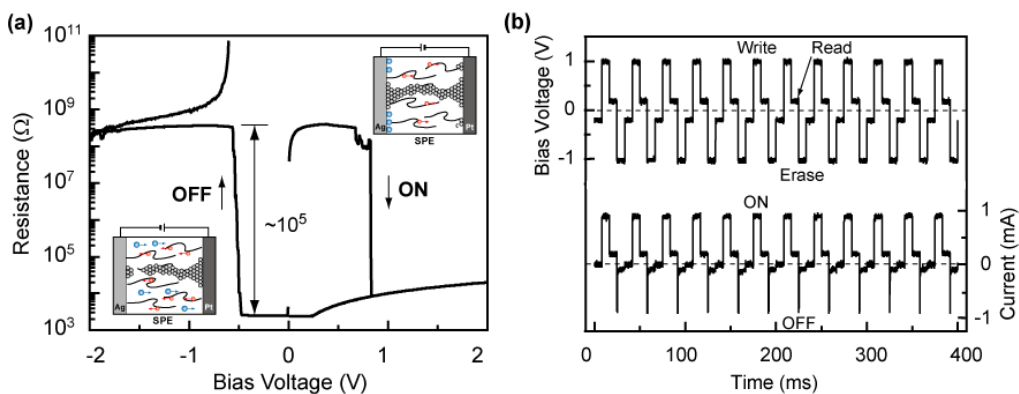


Figure 4 Typical R-V characteristic (a) and write-read-erase-read cycle test (b) of Ag/PEO+AgClO₄/Pt

Atomic switches are a new type of nanoionics devices that are operated by transport of metal ions and solid-state electrochemical reactions on a nanometer scale. Because of the unique operation mechanism, they show novel characteristics such as nonvolatility, low-power consumption, low ON resistance, and high ON/OFF resistance ratio. Much research effort is still needed to explore the potential of resistive switching effect and develop for practical device applications.

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