

Behind the Switching Mechanism in Resistive Memory

This report features the work of Deok-Yong Cho and his co-workers published in *Adv. Mater.* **24**, 2552 (2012).

Non-volatile memory in a data storage device can preserve information even when a computer is switched off. An ideal non-volatile memory should exhibit a large density and a small cost, rapid writing and reading, small power consumption, and rewrite endurance. Flash memory is currently the most eminent device with non-volatile memory, but its drawbacks such as slow response, large power consumption and poor endurance remain. To prevail against the current flaws, several alternative approaches have been proposed. Most notably, resistive-based random access memories (ReRAM) have drawn much attention because their performance fulfills the criteria mentioned above.¹ Moreover, they can be scaled down to an atomic level, which is beneficial to an increased density of data storage. Electrochemical metallization memory (ECM) is a promising resistive-based memory under development for a next-generation non-volatile memory.

The basic ECM cell has a metal-insulator-metal (MIM) configuration comprising an active electrode, an inert electrode, and a solid electrolyte of an ion conducting layer, sandwiched between. A SET process occurs when a sufficiently positive bias voltage is applied to the active electrode. An anodic dissolution of the active electrode occurs, and the cations are driven from the active electrode. Under an electric field, the cations migrate across the solid electrolyte layer toward the inert electrode. A cathodic deposition then occurs: the cations are reduced and electro-crystallized at the surface of the inert electrode, forming a metallic filament growing in the direction of the active electrode, resulting in a state of small resistance (ON-state).

When a sufficient reversed bias is applied, it undergoes a RESET process. The filament is dissolved electrochemically, switching back to a highly resistive state (OFF-state). The resistive switching phenomena caused by formation and rupture of the conductive path make ECM a prospective device for information storage.

GeS_x is known as a promising solid electrolyte for an ECM cell. When a little Ag dissolves in the GeS_x electrolyte, the resistivity becomes considerably decreased. The chemical states of Ag, Ge and S are, so far, poorly known as the change of their electronic structure is insignificant and requires a proper analytical approach. As a result, the origin of the conducting path is still under debate. Cho and his co-workers from RWTH Aachen University unraveled the secret behind the switching mechanism in electrochemical metallization memory.² In their recent article “Direct Observation of Charge Transfer in a Solid Electrolyte for Electrochemical Metallization Memory” published in *Advanced Materials*,¹ they reported X-ray absorption spectra (XAS) at beamlines **BL11A1** and **BL16A1** at NSRRC and presented detailed spectral analyses of the electronic structure of Ge, S and Ag. The researchers reported an inherent chemical instability of Ag at the Ag- GeS_x interface, and suggested that Ag is ionized in the interface with a preferable transfer of the electron from Ag to a Ge 4s orbital. As a result, the dissolution of Ag into GeS_x would produce an Ag filament and significantly affect the ON/OFF state. It is thus of crucial importance to understand the microscopic mechanism of this process to be able to control the stability of the ECM cells. XAS is a tool that can probe an unoccupied electronic structure projected on specific atomic sites. The charge state of the specific element is diagnosed according to the energy of the absorption edge.

According to their results,² the XAS spectral profiles of the two films of GeS_x with $x = 1.6$ and 2.2 after Ag deposition are identical but differ much from those of Ag foil and Ag/ SiO_2 , as shown in Fig. 2(a). The differences are more obvious in Fig. 2(b) that shows the corresponding deriva-

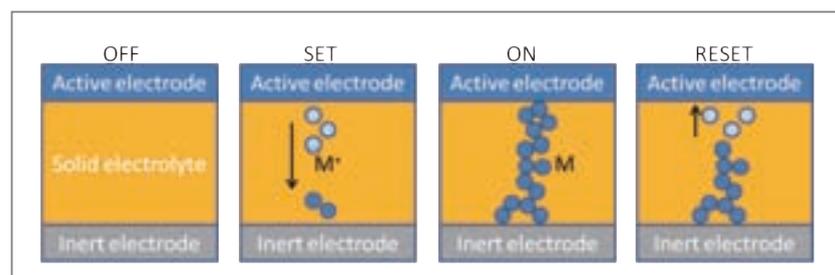


Fig. 1: Simple sketch of the switching process in an electrochemical memory cell with an active electrode, inert electrode, and solid electrolyte between: (From left to right) (a) Off state; (b) SET state; (c) ON state; and (d) RESET state.

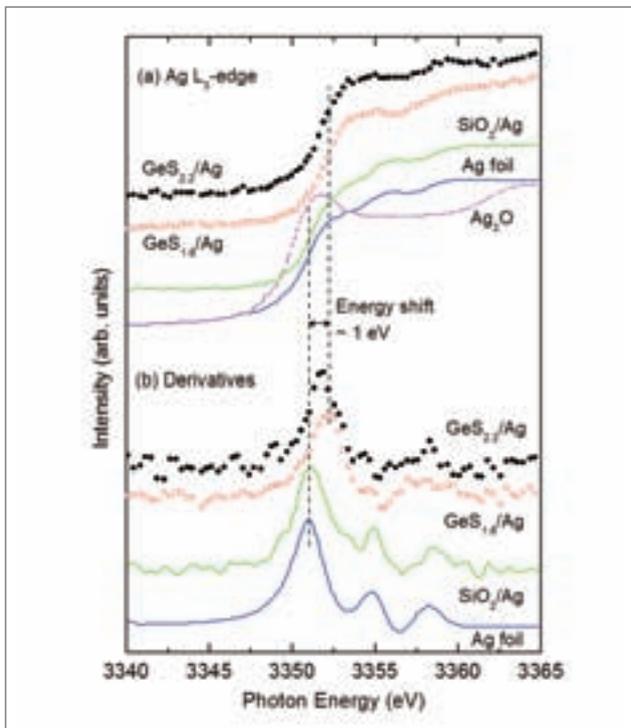


Fig. 2: XAS spectra of GeS_x films ($x = 1.6$ and 2.2) at (a) Ag L_3 -edge and (b) their derivative spectra, after Ag deposition. The references of Ag foil, Ag_2O and SiO_2/Ag are included for identification of the charge state. The differences of the absorption edge energies and the position of maximal signal in the spectra of the GeS_x films relative to others imply that the Ag ions are ionized in GeS_x . (reproduced from Ref. 2)

tive spectra and indicates the similarity in the spectra of GeS_x/Ag films and of SiO_2/Ag and Ag foil. The energy shift in GeS_x/Ag relative to SiO_2/Ag or Ag metal indicates that the Ag atoms in GeS_x exhibit a state of greater charge, implying they might lose some charge at the Ag site; hence Ag atoms are ionized in the GeS_x films. The authors suggested that the excess electron transfers to the electrolyte layer GeS_x . The electron is expected most likely to transfer to an S site that has a greater electron affinity, but, intriguingly, the electrons are accepted mostly on the Ge ions, instead of the S ions, which is evident from the work on the Ge L-edge and S K-edge XAS.

Figure 3 shows Ge L_3 - and L_1 -edge XAS of GeS_x samples and the spectra upon Ag deposition. The feature at 1,220 eV arises from an electronic transition to an unoccupied Ge 4s/4d orbital. The intensity clearly decreases with Ag deposition. The authors ascribed this condition to the fact that the Ge 4s orbital gains charge from the Ag ionization. Ge L_1 -edge XAS further confirm the Ag-Ge charge transfer by the position of the absorption edge as well as the maximal absorption intensity:

they both shift toward to smaller energy after deposition of Ag. Unlike the case of the Ge L-edge that shows this remarkable variation, the changes of S K-edge spectra of GeS_x films before and after Ag deposition are insignificant. This condition indicates that the electronic structure of S ions is unaffected by the presence of Ag. The authors concluded that the excess electrons from Ag ionization preferentially transfer to the Ge 4s states and that the S ions do not benefit from the Ag deposition.

Their findings provide clear experimental evidence of the effect from the ionization of an active metal

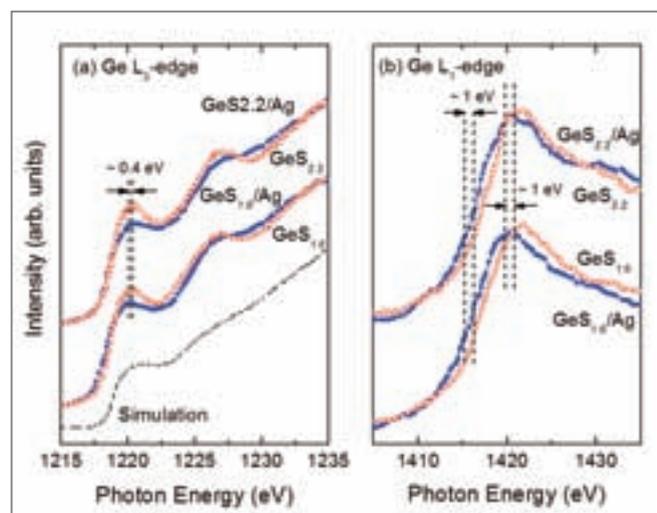


Fig. 3: XAS of (a) Ge L_3 - and (b) Ge L_1 -edge of GeS_x films before and after Ag deposition. After Ag deposition, the absorption peaks shift to smaller energies implying that Ge might gain some charge donated by Ag ions, verified by the decline of the Ge 4s feature. A simulation displayed as a dashed line, performed by FEFF8, is appended at the lower part of (a). (reproduced from Ref. 2)

electrode and a consequent instability arising from an electron transfer between the active electrode and the solid electrolyte. The authors hence concluded that the origin of the conduction explained by the conductive path not only depends on the metallic filament but also originates from a Ag-Ge-S glassy phase. This work of Cho and co-workers might provide increased insight to understand the resistive switching mechanism in ReRAM materials, allowing scientists to advance this technology for the next-generation non-volatile memory.

References

1. R. Waser, R. Dittmann, G. Staikov, and K. Szot, *Adv. Mater.* **21**, 2632 (2009).
2. D.-Y. Cho, I. Valov, J. van den Hurk, S. Tappertzhofen, and Rainer Waser, *Adv. Mater.* **24**, 2552 (2012).