In-situ TEM Observation of Resistive Switching of Oxide Thin Film Devices

Oh, S.H.[1]

[1] Department of Energy Science, Sungkyunkwan University (SKKU), Suwon, Republic of Korea, Republic of Korea

Many metal - insulator - metal (MIM) systems show electrically resistive switching effects and have therefore been considered as the basis for future non-volatile memories. It becomes evident that classical insulating oxides behave as solid electrolytes when their thickness is reduced to a few to some tens of nanometers, allowing transport of either host ions and/or dissolved foreign metal ions at substantial rates under a voltage bias. The ion migration processes are coupled to either local redox reactions or homogeneous interfacial electrochemical reactions which cause the change in the resistance of the whole MIM system. The latter types of resistive switching are often observed for semiconducting or conducting oxides in the pristine state where oxygen vacancies (or oxygen ions) that migrate are distributed along an interface with a metal electrode that controls the conductivity of the MIM structure. The interface-type resistive switching devices exhibiting bipolar and multi-level resistive switching have been considered as the key component for neuromorphic device applications.

To directly observe the microscopic details of underlying electrochemical redox reactions occurring at a metal/oxide interface, we implemented in-situ resistive switching of TiN/$Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO)/Pt junction devices in a transmission electron microscope (TEM) (**Fig.1**) [1]. The-in situ TEM observations directly show that an intermediate reaction layer (TiO_xN_y), growing and shrinking in the thickness range of a few nanometers at the TiN/PCMO interface in response to the applied voltage (**Fig.2**), mainly determines the device resistance by limiting the transport of charge carriers via the Poole - Frenkel conduction mechanism. A detailed analysis of in situ TEM observations demonstrates that electrochemical redox reactions at the TiN/PCMO interface are facilitated by the electric field driven drift of oxygen as well as Ti ions with a much stronger influence of the oxygen ions. As such, the reaction kinetics are governed by the electric field acting across the TiO_xN_y reaction layer. This layer defines the critical field for the onset of switching, which is measured to be of the order of 10^6 Vcm^{-1}, a typical value at which the ionic drift velocity starts increasing exponentially with the field according to the nonlinear ionic drift model. The present results indicate that understanding the nature of the electric field driven drift of ions in a nanoscale solid electrolyte is a key to the precise control of the resistive switching of metal/insulator/metal junction devices via voltage stimulations.

References

[1] K. Baek et al., *Nanoscale* **9**, 582 (2017).

Acknowledgement
This research was supported by the SK Hynix Inc., MOTIE (Ministry of Trade, Industry & Energy (10080654) and KSRC (Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

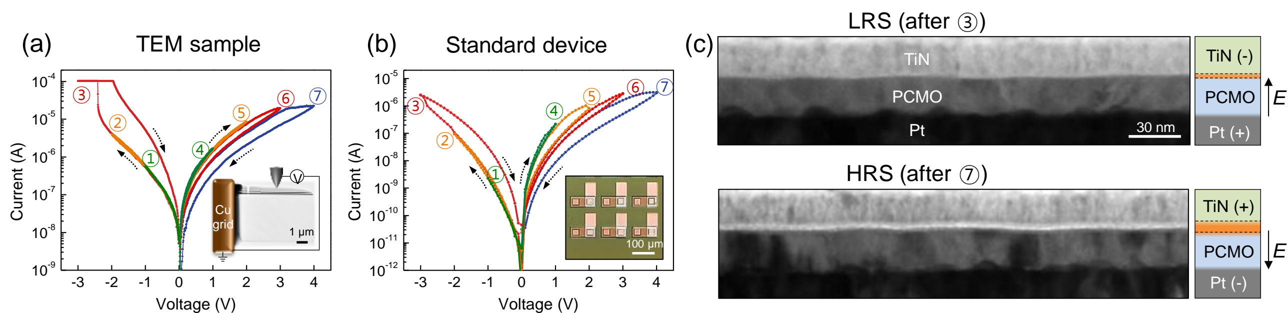

Fig. 1. *In situ* and *ex situ* resistive switching of a TiN/PCMO/Pt junction device. (a) *I-V* characteristics of the cross-sectional TEM sample of a TiN/PCMO/Pt junction device measured *in situ* in the TEM. The switching sequence and direction are numbered and arrowed. (b) Typical *I-V* characteristics of a standard TiN/PCMO/Pt junction device with 30 × 30 μm^2 of the active device area. (c) TEM images showing the intermediate reaction layer at the TiN/PCMO interface after switching to the LRS by applying -3 V (top) and the HRS by applying 4 V (bottom).

Fig. 2. *In situ* TEM resistive switching of a TiN/PCMO/Pt junction device to the HRS. (a) A series of TEM snapshots captured at V_{RESET} during sequential positive bias sweeps (0 +V_{RESET} 0) by applying V_{RESET} from 1 V to 5 V in 1 V increments. Changes in the thickness of the *a*-TiO_xN_y reaction layer are indicated by red arrows. (b) Movement of the two reaction fronts of the *a*-TiO_xN_y layer, i.e., the *a*-TiO_xN_y/TiN and the PCMO/*a*-TiO_xN_y interfaces, traced with the increase in V_{RESET}. The *a*-TiO_xN_y/TiN interface (upper) moves faster than the PCMO/*a*-TiO_xN_y interface (lower) indicating that the drift of not only oxygen but also Ti ions contribute to the growth process with stronger influence of the oxygen ions. (c) Plot of the change in thickness (*d*) of the *a*-TiO_xN_y layer with V_{RESET}. (d) Simultaneously measured *I-V* curves during *in situ* TEM resistive switching. (e) ln (*I*/*V*) versus $V^{1/2}$ plot of the measured *I-V* curves. The linear fit to each curve is indicated by black lines. (f) Plot of the change in normalized slope (s_n/s_2) with the change in thickness of *a*-TiO_xN_y $(d_2/d_n)^{1/2}$ versus V_{RESET}.