The Microstructure Observation of Brownmillerite Thin Film as the Resistive Switching Memory with Ex-situ & In-situ TEM Research

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Physical and electrochemical properties of the transition metal oxides are controlled by the static and dynamic behavior of oxygen vacancies.[i] A spatial distribution of the oxygen vacancies is strongly related to the oxidation state of a transition metal, and can affect the metal oxide's structure and metal-insulator transitions. Many recent studies reported that resistive switching phenomena in the presence of an external bias are associated with the transition of oxygen vacancies. Resistive switching memory is currently receiving an attention as the next generation of memory to replace the traditional memory such as flash memories and DRAM. However, non-uniformity and low durability of the resistive switching memory are slowing down for the practical commercialization and are a challenge to overcome these issues.

Here, we employ a Photoemission-Electron-Microscope (PEEM) and an aberration corrected Transmission Electron Microscope (TEM) to understand the role of oxygen vacancies in resistive switching behavior of $Sr_2Fe_2O_5$ thin films. Pulsed laser deposition method was used for the epitaxial growth of $Sr_2Fe_2O_5$ brownmillerite structure on the $SrTiO_3$ [111] substrate, and $SrRuO_3$ was deposited as a bottom electrode for a resistive switching measurements. (Fig. 1, 2) Using the fast ion conductor on the brownmillerite structure, it is possible to block the random movement of oxygen ions.[ii]

It is difficult to locate conducting paths in the device with TEM sampling. To overcome this problem, we have investigated the conducting path by scanning the energy difference within the work function, Fe L edge and O K edge using PEEM on the surface of oxide layer as shown in Fig. 3. The conducting filaments and their chemical states were observed as the crystallographic SrFeO structure change through the electron energy loss spectroscopic analysis. To investigate the changes in atomic configurations as well as electronic structure caused by the transition of the oxygen vacancies, various electric fields were applied in real time with an in-situ TEM analysis (Fig. 4).

Electric fields were applied to the resistive switching memory device in the forming state created with the conducting path composed of the perovskite structure of $SrFeO_3$ in the metallic region and the brownmillerite structure of $Sr_2Fe_2O_5$ in the insulator. This formation of the conducting path reduces the electrical resistance of the device. Changes in the brownmillerite and perovskite structures occur as oxygen vacancies movement in an interface between the top electrode and SrFeO oxide layer by repeating the SET, RESET cycle. Also, the conducting filament was observed to be controllable, forming along the fast ion path of the brownmillerite structure, unlike conventional resistive switching memory, which was randomly formed. This provides a new direction to control the nanostructure of the memory devices to improve performance.

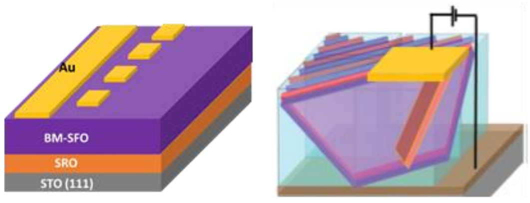

Figure 1 Resistive switching memory device with $Sr_2Fe_2O_5$

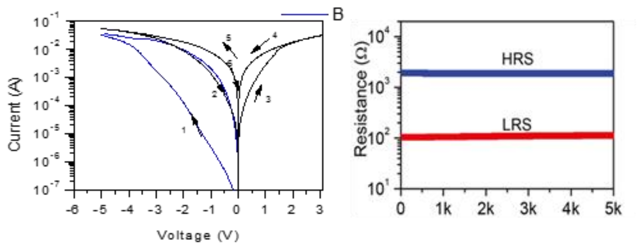

Figure 2 Measurements of I-V curve & resistance

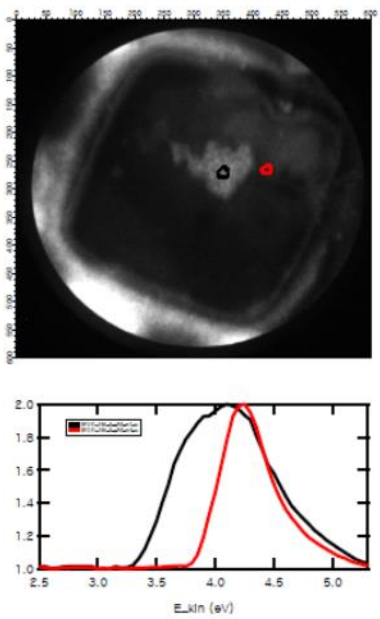

Figure 3 Work function scan by PEEM on the device

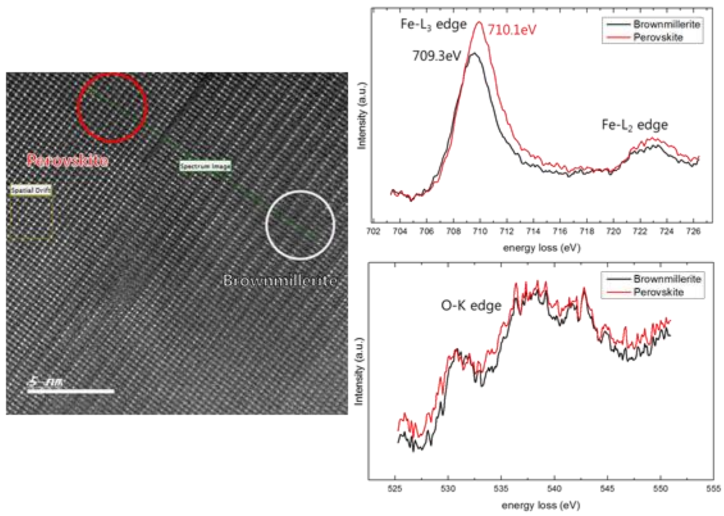

Figure 4 HAADF STEM image and EELS data between Perovskite and Brownmillerite structure.

[i] Jang, Jae Hyuck, et al. "In situ observation of oxygen vacancy dynamics and ordering in the epitaxial LaCoO3 system." *ACS nano* 11.7 (2017): 6942-6949.

[ii] Acharya, Susant Kumar, et al. "Brownmillerite thin films as fast ion conductors for ultimate-performance resistance switching memory." Nanoscale 9.29 (2017): 10502-10510.