

Direct Observation of Nanoscale Chemical Phase Change in Resistive Switching Memory Devices

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Introduction

The resistance switching (RS) effect between high- and low-resistance (high- R and low- R) states induced by an electrical stress in a metal/insulating oxide/metal structure has been attracting considerable attention because of its application in nonvolatile memories called resistance random access memories (ReRAMs) [1]. The RS effect has been observed in a wide variety of transition-metal oxides, but the microscopic mechanism of the RS effect has not yet been fully understood. In devices with binary transition-metal oxides, such as CuO and NiO, unipolar RS was observed where the switching between the high- R and low- R states occurs independently of the polarity of the applied electric field. In these devices, an initial voltage application, which is called the “forming process”, is commonly required before repeatable switching operations. It has been widely accepted that the formation of conductive filament(s) after the forming process, and the subsequent disconnection/reconnection of the filament give rise to the reversible RS. Indeed, in our recent study on a planar Pt/CuO/Pt device, the formation of a reduced conductive bridge structure (Cu + CuO_{1-x}) during the forming process was directly observed within the oxide channel by photoemission electron microscopy [2,3]. In such a filament scenario, the forming process may be viewed as a filament-like reduction of the insulating oxide to a metal. The switching then may be considered as the oxidation and reduction of a certain part of the filament. However, it still remains difficult to detect such local reduction and oxidation during the subsequent switchings because they occur in local regions of conductive bridge and such tiny chemical changes are easily masked by strong signals from the surrounding oxide matrix. In this study, we successfully captured evidence for the local chemical reactions by 3D nano-ESCA experiments using a newly developed nanowire-based switching device.

Experimental

To sensitively detect the local phase change in device, we fabricated Pt/Ni nanowire/Pt planar devices shown in the inset of Fig. 1. The Ni nanowire was designed to mimic the filamentary metallic path formed in conventional oxide-based RS devices, and, in air, functions as a unipolar RS device by reacting with ambient oxygen.

The Pt/Ni nanowire/Pt device was fabricated on a SiO₂/Si substrate. First, Pt electrodes and Au/Ti leads for electrical measurements were formed by sputtering and e-beam (EB) deposition, respectively. A Ni nanowire structure was then formed as bridging the Pt electrodes by EB lithography and EB deposition. The wire width, length, and thickness were 2.7 μ m, 340 nm, and 58 nm, respectively.

The pinpoint chemical state analysis was performed using a high spatial resolution 3D nano-ESCA installed at BL07LSU of SPring-8 [4]. Since the size and composition of the local phase change region may vary from sample to sample, we conducted on-site switching

measurements at the beamline, and evaluated the chemical state at each stage of the RS operation for the same device.

Results

Figure 1(a) shows the valence-band photoemission spectra taken at each stage of the switching operation: as-prepared state, high- R state, and low- R state. The measured signal was integrated over the Ni nanowire region. The resistance (R) of the as-prepared device was $R = 124$ ohm, and in the spectrum a clear Fermi edge was observed. After the switching from the initial state to the high- R state with $R = 13$ Mohm, a remarkable change was observed in the spectrum, gap formation at the Fermi level E_F . The observed spectrum, with a sharp peak centered at 2.0 eV, is consistent with that of NiO [5], indicating that the origin of current blocking in the high- R state is the oxidation of Ni to insulating NiO. According to the filament model, this insulating state can be transformed to the low- R state by creating a new metallic path within the oxide. This was clearly observed as the recovery of the density of states at E_F [blue curve in Fig. 1(a)]. As displayed in Fig. 1(b), the spectrum of the electroformed low- R state ($R = 263$ ohm) can be excellently reproduced by a linear combination of spectra of the initial and high- R states. This demonstrates that a certain part of NiO is reduced to Ni metal upon the switching to the low- R state. These results provide conclusive evidence for the proposed switching mechanism.

References

- [1] For example, A. Sawa, *Mater. Today* **11**, 28 (2008).
- [2] K. Fujiwara *et al.*, *Jpn. J. Appl. Phys.* **47**, 6266 (2008).
- [3] R. Yasuhara *et al.*, *Appl. Phys. Lett.* **95**, 012110 (2009).
- [4] K. Horiba *et al.*, *Rev. Sci. Instrum.* **82**, 113701 (2011).
- [5] M. Taguchi *et al.*, *Phys. Rev. Lett.* **100**, 206401 (2008).

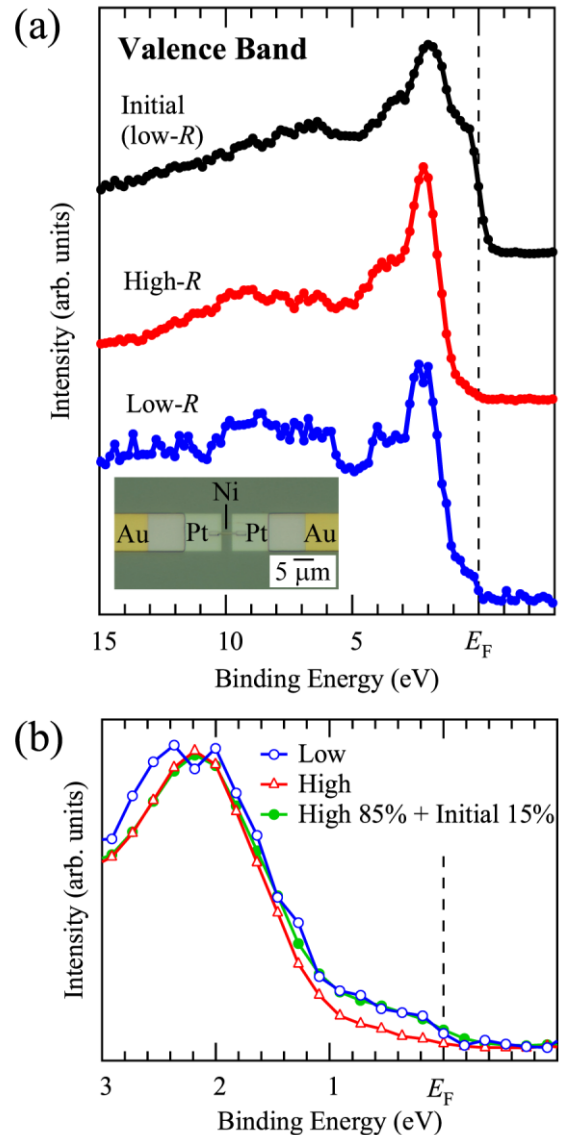


Fig. 1. (a) Valence-band spectra measured for three different resistive states: initial metallic state, high- R state, and low- R state. Inset shows an optical microscopic image of Pt/Ni nanowire/Pt device. (b) Expanded view near E_F .