Observation of Local Electrochemical Phase Change in Resistive Switching Devices

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Introduction

Resistive switching (RS) effect between high- and low-resistance states observed in binary transition metal oxides such as NiO, Fe_2O_3, and CuO has attracted considerable interest because of its potential application to a nonvolatile memory called resistance random access memory.[1–4] The device structure exhibiting the RS consists of a simple capacitor-like sandwich of metal/oxide/metal. Although the physical origin of the change in conductance is not yet fully understood, some key factors required for the RS have been identified during the past few years of intensive research. An initial soft breakdown process called "forming" is commonly required to exhibit the RS. After the forming, so-called unipolar (nonpolar) RS, where the switching does not depend on the polarity of the applied voltage, is observed. It is widely accepted that the formation of conductive (metallic) filaments by the forming, rupture (oxidation) and reformation (reduction) of the filaments give rise to the reversible RS operation. This scenario is called the conductive filament model.

By fabricating a planar Pt/CuO/Pt RS device, we have recently succeeded in directly imaging the formation of such a conductive bridge structure by scanning electron microscopy.[5] A series of experiments, including energy-dispersive X-ray analysis, photoemission electron microscopy,[6] and secondary ion mass spectrometry,[7] have revealed that the bridge structure is made of a mixture of a metallic Cu network (filaments) and reduced CuO_{1-x}. However, the observation of the opposite oxidation process, switching from a low-resistance state (LRS) to a high-resistance state (HRS) called "reset", has remained elusive. In this study, to capture direct evidence for the conjectured local oxidation, we fabricated a device based on a transition metal nanochannel, which mimics the filamentary metallic path formed in conventional oxide RS devices. Using the structure, we successfully observed the local oxidation of a nanochannel associated with RS by atomic force microscopy (AFM).

Experimental

We previously succeeded in directly observing the formation of a conductive bridge by fabricating a planar RS device. The device structure used in this study also has a planar configuration, consisting of two Au electrodes and a Nb nanochannel constricted by insulating NbO_x regions. The steps in the fabrication process are summarized in Fig. 1. First, a Nb film with a thickness of 4.5 nm was grown on a SiO_2/Si substrate through a stencil mask by e-beam deposition [Fig. 1(a)]. A Au film with a thickness of 40 nm was evaporated onto the Nb film to serve as electrodes [Fig. 1(b)]. Part of the Nb film was then removed by focused ion beam (FIB) processing [Figs. 1(c) and (d)]. Finally, insulating NbO_x regions were formed by anodizing Nb using an AFM conductive tip (known as AFM probe oxidation[8,9]). Thus, a Nb nanochannel structure was obtained [Fig. 1(e)].

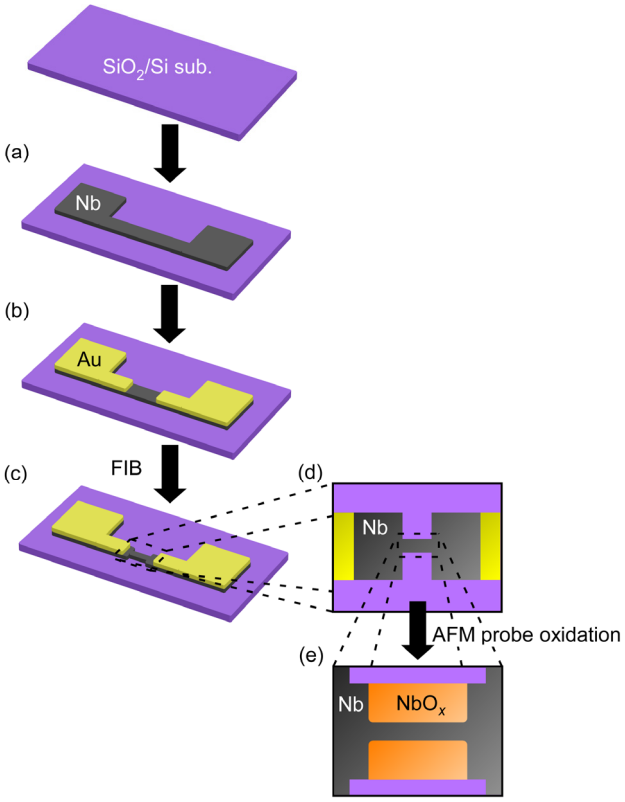

Fig. 1. Device fabrication process.

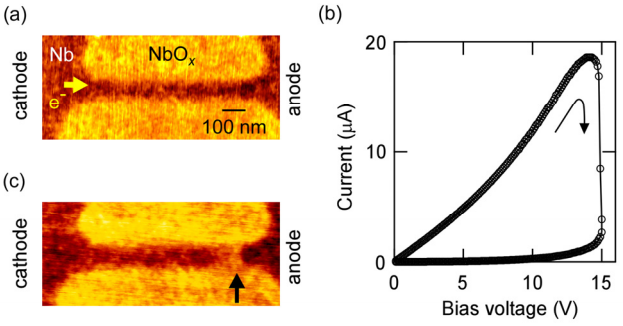

Fig. 2. Nb nanochannel device. (a) AFM image taken in the pristine state. (b) Resistive switching. (c) AFM image taken in the HRS after RS. A barrier structure can be recognized in the nanochannel region.

The current–voltage characteristics of the device were measured at room temperature in air using a source-measure unit (Keithley 237). The surface observation of the nanochannel region was conducted by AFM (SII-NT SPA-400).

Results and Discussion

Figure 2(a) shows an AFM image of the Nb nanochannel region of the device. The pristine device was in the LRS with a resistance of 1.1 MΩ. With increasing bias voltage, a threshold-type switching was observed at 14.7 V, and the system switched to the HRS with a resistance of 243 MΩ, as shown in Fig. 2(b). There was a noticeable change in the AFM image after the switching; a barrier-like structure was created in part of the nanochannel as indicated by the arrow in Fig. 2(c). The slight difference in contrast between the barrier and the anodized NbO_x means that their heights are similar, indicating that a volume expansion from the pristine state occurred in the barrier region. The temperature dependence of resistance exhibited insulating (or semiconducting) behavior with an activation energy of 160 meV, which agrees reasonably well with values for insulating NbO_x films. From these observations, it is naturally concluded that the Nb nanochannel is partly oxidized during the RS and that the conduction of the nanochannel is completely blocked by the insulating Nb oxide barrier. This result clearly supports the prevailing mechanism that the local reduction and oxidation of a filamentary metallic path give rise to the nonvolatile RS effect.

Another point that should be noted from Fig. 2(c) is that the Nb oxide barrier was created next to the anode. This was reproducibly observed. Although the mechanism responsible for the reset has so far been discussed mainly in terms of Joule heating because of the unipolar switching characteristics, the present results suggest that the ionic behaviors of constituent elements, such as oxygen migration, play a certain role in the local oxidation process. Therefore, engineering the ionic transport processes at the interface between the transition metal nanostructure and the oxygen supply layer (oxygen gas or oxide dielectric) will be the key to improving device performance as in Li ion batteries and fuel cells.

Having confirmed the RS operation in the metal nanochannel structure, one may envision a simpler RS device, with only the minimum ingredients, a single transition metal nanowire and oxygen gas (or an oxide cover layer). To test this idea, we fabricated such a nanowire device by e-beam lithography. In this device, the formation of an oxide barrier associated with RS as in the present study was again clearly observed, demonstrating the essential role of local redox reactions in this class of RS device. This simple nanowire RS device may eventually have an advantage over oxide devices in that the process should be compatible with current CMOS technologies.

Conclusion

We successfully observed the local oxidation process in RS by fabricating a transition metal nanochannel structure. In addition, the role of ionic transport processes during the oxidation was proposed. These results are expected to increase understanding of the microscopic mechanism of RS, and may offer a new approach for high-performance memory design.

References

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