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Microstructural Change in Cu/WO_x/TiN during Resistive Switching

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Abstract

***In-situ* TEM was applied to a Cu/WO_x/TiN film during ReRAM switching for the first time. In *forming*, a Cu filament appeared from both Cu and the TiN electrodes. In succeeding switching, microstructural change was only occasionally seen. This indicates that ReRAM switching occurred very locally. Increasing current, Cu came into the WO_x layer in wide area.**

1. Introduction

Resistive RAM (ReRAM) has a high potential as a next-generation nonvolatile memory [1-4]. The system of Cu and the solid electrolyte yields the ReRAM switching, where conductive filaments (CFs) are believed to contribute to the operation. While CFs were recently observed by *in-situ* transmission electron microscopy (TEM), there were few reports on dynamical change of CFs in plural switching cycles. In this work, we dynamically investigated structural change in Cu/WO_x/TiN during *I-V* switching cycles.

2. Experimental

The Pt/Cu_{30nm}/WO_{x20nm} ReRAM film was deposited on the TiN/Si bottom electrode (BE) by sputtering at RT. The reference device made by photo-lithography and the TEM sample [5] are shown in Figs. 1(a) and 1(b), respectively. Fig. 1(c) is the experimental system. A probe was contacted to the Pt/Cu top electrode (TE), and measurements were done through the Si substrate by applying voltage to TE.

3. Result and Discussion

Typical bipolar switching of the reference device is shown in Fig. 2. Clear *I-V* switching cycles were seen with a good endurance property. In Fig. 3, *I-V* curves during *in-situ* TEM observations are shown. Ten switching cycles were investigated with increasing the compliance current (I_{comp}). The black curves denote the *Set* cycle converting the high resistance state (HRS) to the low resistance state (LRS). In the first *Set* from the pristine state (*forming*, Fig. 3(a)), the voltage giving LRS was 2.4 V, and it was lower after the second *Set*. In many cases, the *Set* switching was sharp. The red curves were *Reset* giving HRS from LRS, which were measured with intervals after *Set*. Black and red curves were smoothly bound, and LRS was kept in the interval. The maximum current in the *Reset* cycle ($|-I_{max}|$) increased with I_{comp} (Fig. 4(a)). The resistance change is summarized in Fig. 4(b). The difference of double figures was seen. The results obtained during TEM observations satisfactory fitted to those from the reference device.

In-situ TEM images of the first *Set* (*forming*) are shown in Fig. 5. Just before *forming* (state 2), no change was seen from state 1. At *forming* (state 3), the dark contrast appeared within one video frame (30 ms), which can be assumed to be Cu as in [6, 7]. The contrast of both electrodes swelled into WO_x. This cannot be explained only by electrochemical reaction, where the CF grows from BE to TE. Because of this abrupt forming with overshoot current, another factor should also contribute to CF formation. After this switching, no clear change in TEM contrast was seen (states 4-6) because the current was limited to be low (20 μA). The *Reset* operation is shown in Fig. 6, where microstructural change was seen only at the arrowed CF. Thus, the other CF-like contrast is thought not to be the current path. At *Reset* (state 2), no clear contrast change was identified. When the negative voltage was increased, the CF started to shrink (states 3-5), and the HRS was obtained. In this series, clear change on the filament was only occasionally identified even with ReRAM switching. This may indicate that switching occurred only at a local region. TEM images after *Set* are compared in Fig. 7. With increasing I_{comp}, a thick filament appeared. At the same time, the WO_x layer became thin. This indicates that current flew not only around the filament region under the condition with high I_{comp}, and Cu moved in a wide area and deposited at the interface. This may lead to the switching instability.

4. Summary and Conclusion

The ReRAM microstructure of Cu/WO_x/TiN was investigated during *I-V* switching cycles by *in-situ* TEM. The Cu CF bound between BE and TE in the *Set* cycle. The CF appeared from both BE and TE. Not only the semi-static electrochemical reaction but also other factors are thought to influence switching. In the *Reset* cycle, the CF shrunk. However, clear change in the image was only occasionally identified. Local area of the CF may contribute to switching.

Acknowledgements

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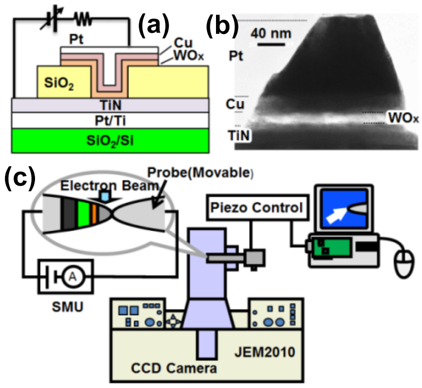


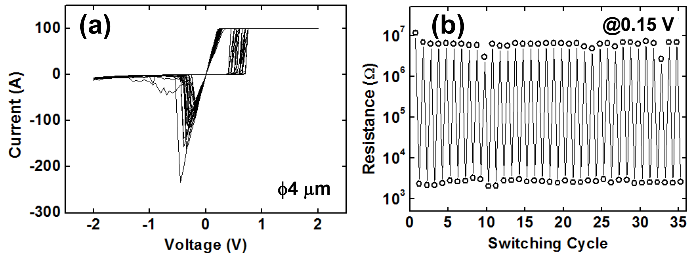
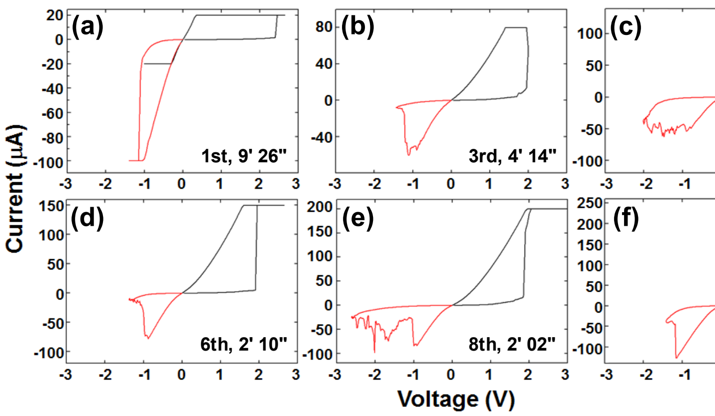


Fig. 2 Switching property of a conventional WO_x device shown in Fig. 1(a). (a) The *I-V* switching cycles of a device (ϕ4 μm). (b) Endurance evaluated at +0.15 V from (a). Note that the resistance larger than ~ 100 MΩ and less than ~ 1 kΩ cannot be measured due to sensitivity of the instrument and the load resistor.

Fig. 1 Cu/WO_x/TiN ReRAM samples and TEM observation system. (a) Schematic drawing of the device for conventional measurements. To prevent permanent breakdown, a resistor of 1 kΩ was serially connected with the ReRAM device. (b) Cross-sectional TEM image of the sample for *in-situ* TEM observations. A clear stack of Cu (30 nm) and WO_x (20 nm) is seen. (c) The observation system .



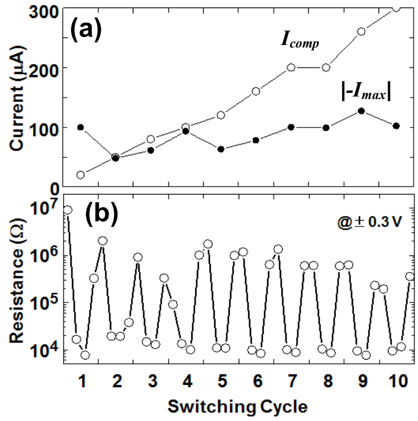
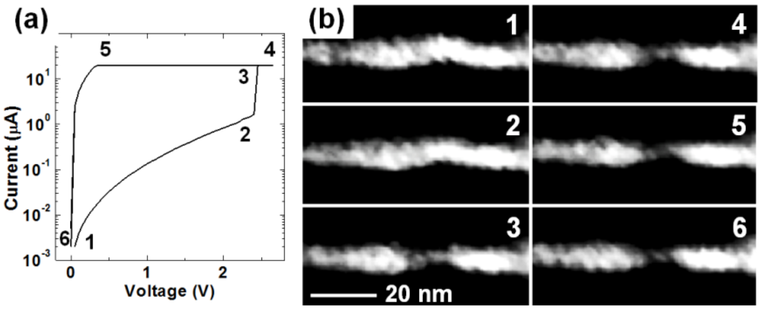


Fig. 3 *I-V* curves during *in-situ* TEM where I_{comp} increased gradually. The device size was about ϕ210 nm. (a) Switching from the pristine state and (b)-(f) in succeeding cycles. Continuously bound black and red curves correspond to *Set* and *Reset* operations, between which the intervals are shown in graphs. The low resistance state was kept at least in this time.

Fig. 4 ReRAM properties during *in-situ* TEM which were evaluated from *I-V* curves in Fig. 3. (a) I_{comp} and -I_{max}. I_{max} increased with I_{comp}. (b) Endurance property of *Set* and *Reset* (@ ±0.3 V). The minimum resistance was limited by the resistance of the substrate (~ 10 kΩ).



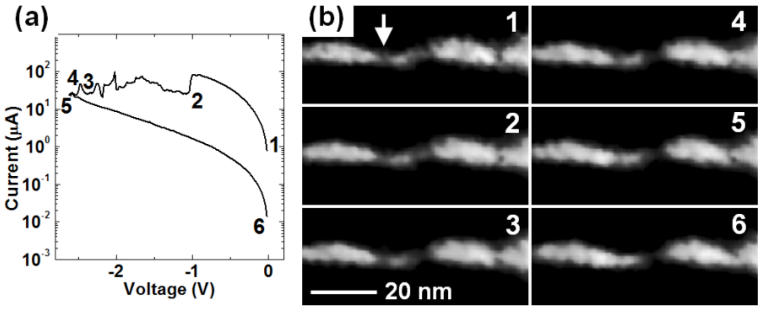


Fig. 5 (Left above) Microstructural change in the 1st (*forming*) cycle. (a) *I-V* curve corresponding to Fig. 3(a). (b) *In-situ* TEM images showing the filament evolution from the Cu and the TiN electrodes.

Fig. 6 (Left below) Filament shrinkage in the 8th *Reset*. (a) *I-V* curve corresponding to Fig. 3(e). (b) Corresponding *in-situ* TEM images. The filament indicated by an arrow is thought to mainly contribute to electric conduction.

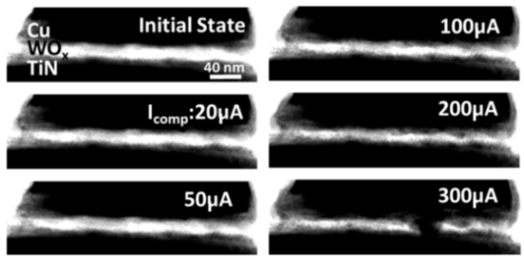


Fig. 7 TEM images after *Set* with increasing I_{comp}. The filament thickened and its position changed. The bright region corresponding to WO_x narrowed.