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Metal Oxide Nanowires: Synthesis and Memristive Properties

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1. Introduction

Electrically induced nonvolatile resistive switching (RS) in metal/oxide/metal junctions, so-called ReRAM and/or Memristor, has attracted much attention as an alternative to conventional flash memory, synaptic computing device, reconfigurable logic circuit and other circuit family. However the RS mechanism is still not fully understood due to the inherent difficulties in extracting such nanoscale RS events in the capacitor structure. Use of self-assembled oxide nanowire offers a powerful approach not only to explore the intrinsic characteristics of RS by extracting the RS into nanowire but also to realize the extremely small RS devices. In this paper, we demonstrate the nonvolatile RS using self-assembled oxide nanowire (NiO_x, CoO_x, TiO_{2-x}) with excellent performance and the crucial nanoscale RS mechanism.

2. Results and Discussion

Figure 1(a) shows FESEM image of CoO_x nanowires. Figure 1(b) shows the HRTEM image of the nanowire. The uniform shell layer growth with ~5 nm of thickness can be seen along the nanowire. Figure 2(a) shows a typical current-voltage (I-V) characteristic of CoO_x nanowire device. After the forming process, which is the initial process to create the conducting paths into insulative nanowire with high electric field (~1.6×10^6 V/cm), the device showed the polarity dependent RS, called bipolar RS.[1-3] When the positive electric field was applied, the current increased and the device changed into the low resistance ON state (LRS: SET process), whereas applying the negative electric field changed the device into high resistance OFF state (HRS: RESET process). The polarity of SET was always consistent with the polarity of forming process, and such polarity can be arbitrary defined by selecting the polarity of forming process since our metal/nanowire/metal junctions has a symmetric geometry. Note that the switching endurance of ~10^8 times and the power consumption of ~10^{-6} W/switch in our nanowire device are much superior to conventional thin film device (Figure 2(b)). [4]

Here we performed the atmosphere controlled retention experiments using both CoO_x and TiO_{2-x} nanowires. Since a redox affects a carrier of oxides, the experiments allow us to identify the conducting properties of RS. In RS, the LRS is a sort of excited state and the HRS is a ground state, therefore LRS retention data in various ambient should show the intrinsic characteristics of RS conduction. Figure 3(a) and (b) show the LRS retention data in CoO_x and TiO_{2-x} nanowires with varying the ambient atmosphere. In TiO_{2-x}, the LRS current tended to decrease with chemically oxidized ambient. This trend is well-corresponding to typical *n*-type nature where the oxygen vacancies play crucial role on the conduction with electron carriers since the oxygen vacancies should be compensated by the oxidization atmosphere. However, on the other hand, in CoO_x, the LRS current tended to increase with chemically oxidized ambient. Although the trend was consistent with typical *p*-type nature where the cation vacancies or the extra oxygen create the conduction with hole carriers, it was inconsistent with the prevailing 'anodic oxidization' model where the oxygen vacancies play an important role on RS events. Conventionally, the mechanism of RS has been frequently discussed with the presence of oxygen vacancies or the precipitation of metal. Therefore, the results from TiO_{2-x} nanowire are understandable since the trend is consistent with the anodic oxidization model. In CoO_x, if the presence of oxygen vacancies or Co metals is responsible for the RS conduction, the LRS current must decrease with an oxidation, which is completely opposite to the present experimental trend. Even considering the possibility of the co-existence of Co metal and *p*-type conduction paths, the decrease of LRS current when reducing the atmosphere cannot be explained because the LRS current must be maintained in the presence of Co metal conduction paths. Thus, these experimental results highlight that redox events with *p*-type conduction paths play a crucial role on a bipolar nanoscale RS of cobalt oxides. [5]

The carrier type of LRS conduction can be directly identified by utilizing the nanowire FET structure. Figure 4(a) shows the FESEM image of the planer FET structure composed of source (S), drain (D) and gate (G) electrodes. We utilized the CoO_x nanowire here to reveal the conduction nature of cobalt oxide in RS. In the FET experiments, a negative voltage was applied to the drain and the source was grounded. After the SET process, the electric field was applied between the gate and the source electrodes. Figure 4(b) shows I_{SD}-V_{SD} curves of the cobalt oxide nanowires when varying the gate voltages (V_G), where I_{SD} and V_{SD} are the current and voltage between drain and source, respectively. Note that the range of all I_{GS} with varying V_G was at least 2 orders of magnitude smaller than that of I_{SD}, indicating negligible effects of current leakage in these measurements. I_{SD} decreased when applying the positive +8 V of

V_G, whereas I_{SD} increased for the negative -8 V of V_G. The inset of Figure 4(b) shows V_G dependence of I_{SD} measured at -15 V. I_{SD} systematically decreased with increasing V_G. These results clearly confirmed that the major carriers of the LRS conduction in cobalt oxides are holes (i.e. *p*-type). [5-8] Overall, all obtained implications as to *p*-type cobalt oxide are inconsistent with the prevailing 'anodic oxidization' model. Here we propose the physical RS model for *p*-type cobalt oxides. When the high electric field is applied, the negatively charged oxygen ions move to positively biased anode and create the oxygen rich region. Since the extra oxygen creates hole carriers and the electronic state near the valence band, the anode side must change to be conductive. The continuous movement of oxygen ions creates the conducting paths from the anode toward the cathode. When the paths reach to the cathode, the device changes into LRS. This is the inverse analogue to the *n*-type oxygen vacancy model.

3. Conclusion

We demonstrate the nonvolatile RS in a single oxide nanowire (CoO_x, NiO_x, TiO_{2-x}) with tens nanometer scale. The nanowire device exhibited the excellent memory characteristics with 10^8 times of the endurance and ~10^{-6}W/switch of the power consumption. Furthermore, we have revealed the nature of bipolar RS by using the planar-type RS devices, which had been buried in a capacitor-type device.

Acknowledgements

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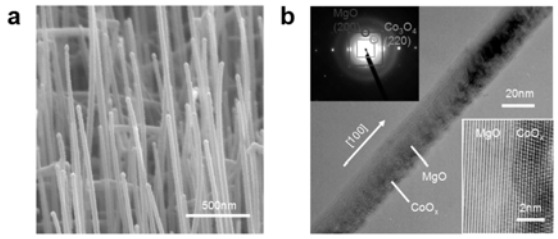

Fig. 1 (a) FESEM and (b) HRTEM images of CoO_x nanowire. Upper left inset: selected area electron diffraction (SAED) pattern. Lower right inset: magnified image of interface.

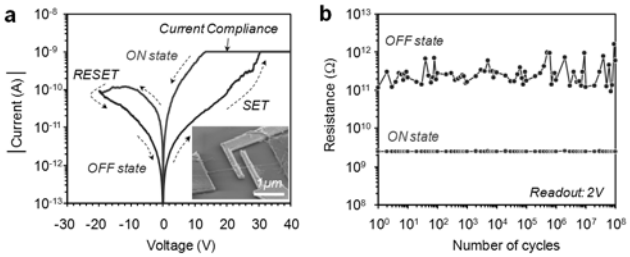

Fig. 2 (a) I-V curve of single CoO_x nanowire device. Inset shows the FESEM image of the device. Nanogap spacing is ~250 nm. (b) Switching endurance data. The applied SET voltage, RESET voltage, and compliance current were 15 V (500 μs), -3 V (200 μs), and 10^{-7} A, respectively.

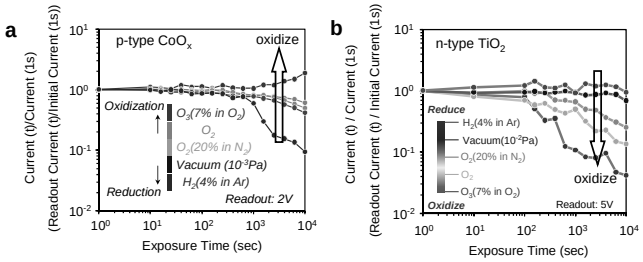

Fig. 3 LRS retention data in (a) CoO_x and (b) TiO_{2-x} nanowire device with various atmospheres. Prior to the measurement, the device was changed into LRS, and then the gases were fed into the chamber by controlling the ambient pressure with 1 Pa.

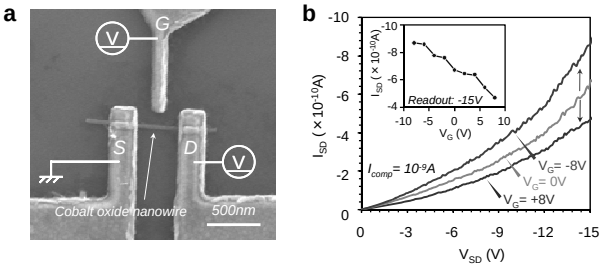

Fig. 4 FESEM image of the nanowire FET device. The nanogap spacing in this device was ~400 nm. (b) I_{SD} and V_{SD} characteristics with applying the gate voltage (V_G = -8~+8 V). Inset shows I_{SD}-V_G data.