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Switching Properties of Titanium Dioxide Nanowire Memristor

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We present the memristive switching properties in a single nanowire device made of titanium dioxide. We constructed the single oxide nanowire device made of titanium dioxide on a Si substrate. First, we confirmed the existence of memristive switching in a 10 nm scale nanowire device. We successfully extracted the carrier-types for memristive switching by utilizing atmosphere control measurements. Although cobalt oxide and nickel oxide showed the p-type behavior reported previously, the present titanium dioxide nanowire memristor exhibited n-type behavior. Our results highlight the fact that carrier-type of memristive switching seems to be consistent with that of a bulk material, but this is in fact somehow contradictive to a model based on precipitation of metals within an oxide matrix. Since, in conventional capacitor-type memristors, it has been impossible to measure the carrier-type in memristive switching because memristive events are buried within a solid, the open-top planar-type "nanowire memristor" is clearly a powerful device for extracting the intrinsic features of memristive switching phenomena.

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1. Introduction

Self-assembled nanowires promise a novel alternative fabrication methodology for nanoscale electric devices to current lithographic technology because they can be designed at the atomic scale.[1–3] Many interesting nanoscale devices have been proposed utilizing the unique geometrical and physical features of nanowires. Group-IV- and III–V-based nanowires have revealed various interesting nanoscale properties and have also given rise to completely new nano-devices.[2–4] Since transition-metal oxides exhibit a wide variety of interesting physical properties, including ferroelectricity, ferromagnetism, superconductivity, and memristive switching,[5–44] the incorporation of such transition-metal oxide materials and their interesting physical properties will markedly expand the applicability of nanowire-based devices, but the feasibility of such transition-metal oxide nanowires has not yet been demonstrated owing to the absence of a fabrication methodology. We have demonstrated the fabrication of transition-metal oxide nanowires and the single nanowire device.[45–66] We combined two techniques: conventional vapor–liquid–solid (VLS) one-dimensional (1D) nanowire growth via metal catalysts[45–59] and a heterostructured formation technique.[60–66] By adopting this combined technique, we can design transition-metal oxide nanowires and a single nanowire device.[52] Previously, we demonstrated the usefulness of such a single nanowire device as a memristive device.[64–66] In those investigations, the cobalt oxide and nickel oxide were utilized to reveal their memristive features at the nanoscale. In particular, a hole carrier has been identified for these materials by utilizing the single nanowire device.[66] On the other hand, the feasibility of such a nanowire memristor for titanium dioxide, which is one of the most well-investigated memristive materials, has not yet been clarified. Here, we report memristive switching in a single oxide nanowire device made of titanium dioxide.

2. Experimental Procedure

To fabricate transition-metal oxide nanowires, we fabricated the core-shell nanowires by the *in situ* nanowire template method with pulsed laser deposition (PLD; Lambda Physik ArF excimer, $\lambda = 193$ nm). MgO nanowires were fabricated on MgO(100) substrates via Au-catalyzed VLS growth.[45–59] We utilized PLD. The details of MgO nanowire growth conditions can be found elsewhere.[45–50] TiO_2 shell layers with a thickness of 5 nm were deposited without exposure to atmosphere. The nanowire morphology was characterized by field effect scanning electron microscopy (FESEM; Hitachi S-4300) at an accelerating voltage of 30 kV. High-resolution transmission electron microscopy (HRTEM; JEOL JEM-3000F) coupled with energy dispersive spectroscopy (EDS) was used to evaluate the microscopic device structure, the crystal structure, and the composition of TiO_2. TEM measurements were performed at an acceleration voltage of 300 kV. After the above-described fabrications of transition-metal oxide nanowires, the fabricated nanowires were transferred onto a SiO_2 (300 nm)/Si(100) substrate.[64–66] Typical electron beam (EB) lithography was carried out to define the electrode pattern for bridging a single nanowire. Pt electrodes with a 100 nm thickness were then formed by RF sputtering (50 W, 1 Pa in Ar atmosphere), and finally, the planar-type nanowire device was fabricated. The electrical characterization of the devices was carried out by a two-probe method using the Keithley 4200SCS semiconductor parameter analyzer. Prior to resistive switching, a forming process, which is the initialization process to induce electrical conduction into the insulative switching matrix, was performed. Transport measurements were performed at room temperature, 25 °C.

3. Results and Discussion

Figure 1 shows SEM and TEM images of the fabricated heterostructured transition-metal oxide nanowires made of MgO/TiO_{2-x}. The use of the *in situ* heterostructured formation technique allows us to avoid detrimental degradations of the interface within nanowires. Figure 2 shows a SEM image of the fabricated single oxide nanowire device on the Si substrate. Figure 3 shows the current–voltage (I–V) curves for the fabricated single nanowire device measured at 0.5 Pa. It is clear that the bipolar-type memristive switching behavior occurs in the TiO_{2-x} single nanowire device. This bipolar-type memristive switching behavior is consistent with our previous results for CoO_x and NiO_x nanowires.[41–43] It is noted that the occurrence of memristive switching at the 10 nm scale is promising for high-density nonvolatile memory applications.

Here, we extract the carrier-type of the present TiO_{2-x} single nanowire device by utilizing atmosphere control

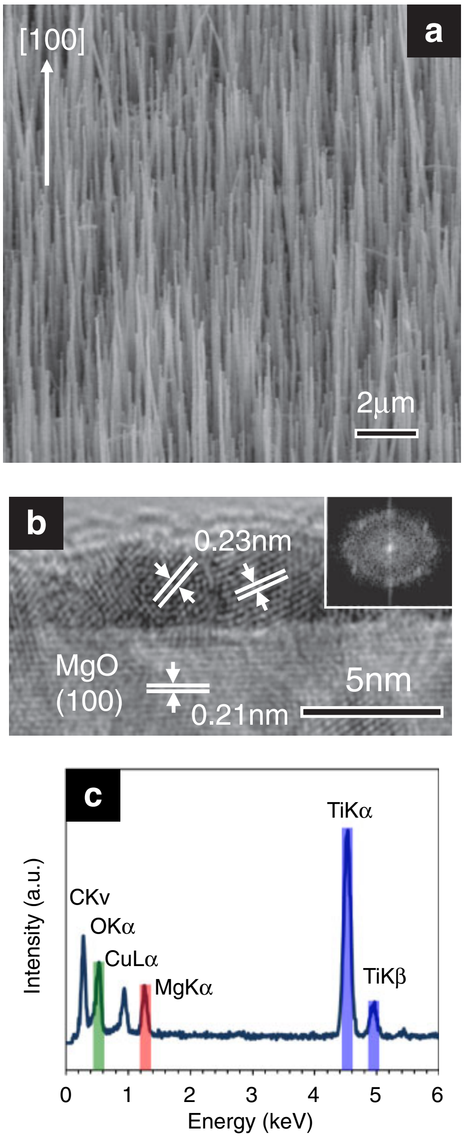

Fig. 1. (Color online) (a) SEM image of MgO/TiO_{2-x} heterostructured nanowire grown on MgO(100) substrate. (b) TEM image of MgO/TiO_{2-x} heterostructured nanowire. Inset shows FFT pattern. (c) EDS data of MgO/TiO_{2-x} heterostructured nanowire.

experiments. It should be noted that in the case of conventional capacitor devices, it is difficult to identify the carrier-type of memristive switching because the memristive switching events are buried within a solid. Figure 4 shows the effect of ambient atmosphere on the ON-state-current time-series data. As can be seen, the ON-state-current decreases when introducing oxidized reactive gas such as ozone-containing gas. This result indicates that redox events must be closely related to the occurrence of bipolar memristive switching in the TiO_{2-x} single nanowire device, since the ON-state conduction is strongly dependent on the occurrence of redox in atmosphere. In addition, the trend of chemical reactions with the surroundings in ON-state conduction seems to be consistent with that of n-type oxide semiconductors, because, in the case of n-type oxides, electron carriers must be compensated by oxidization. Thus, the trend of the decreasing ON-state-current when introducing oxidized atmosphere can be interpreted in terms of a compensation effect of electron carriers via oxidization

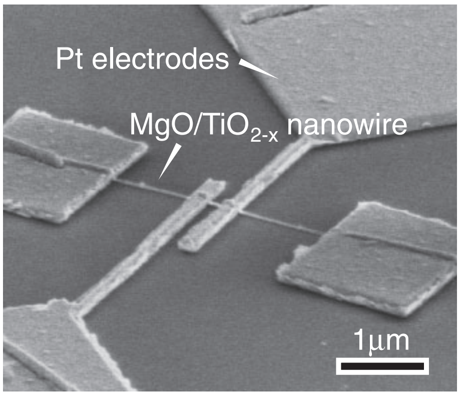

Fig. 2. SEM image of typical single TiO_{2-x} nanowire device constructed on SiO_2 (300 nm)/Si(100) substrate.

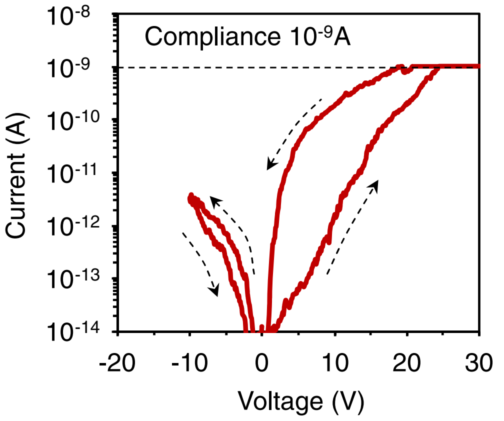

Fig. 3. (Color online) *I–V* characteristics of single MgO/TiO_{2-x} nanowire device measured at room temperature.

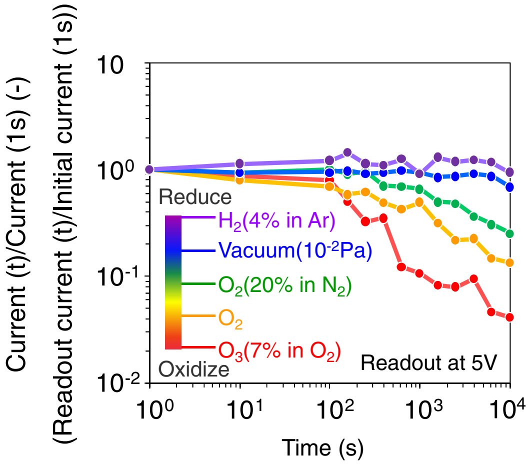

Fig. 4. (Color online) Effect of ambient atmosphere on the ON-state-current time-series data for single MgO/TiO_{2-x} nanowire device.

through reaction with the surroundings. These experimental results highlight that redox events with an n-type conducting path play a crucial role in the bipolar nanoscale memristive switching of the TiO_{2-x} single nanowire device. Interestingly, this trend is in sharp contrast with our previous results for cobalt oxide and nickel oxide, where the ON-state-current decreased upon introducing reduced reactive gas

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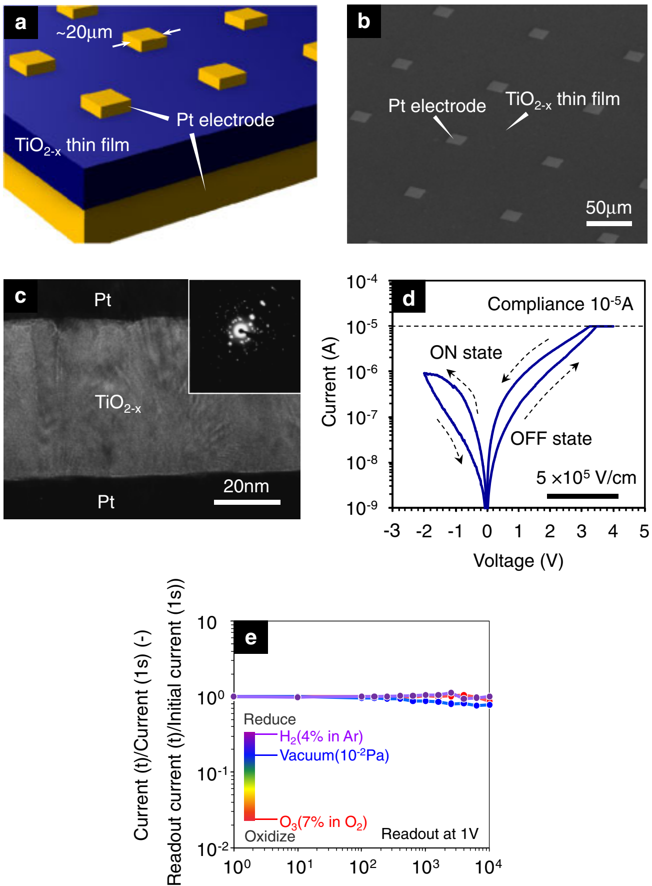

Fig. 5. (Color online) (a) Schematic of Pt/TiO_{2-x}/Pt capacitor-type device. (b) SEM image of Pt/TiO_{2-x}/Pt capacitor-type device. (c) Cross-sectional TEM image of Pt/TiO_{2-x}/Pt capacitor-type device. The inset shows ED pattern. (d) Typical I–V data of Pt/TiO_{2-x}/Pt capacitor-type device. (e) Effect of ambient atmosphere on the ON-state-current time-series data for Pt/TiO_{2-x}/Pt capacitor-type device.

such as hydrogen-containing gas, highlighting their p-type nature.[65,66] The comparison of the present data and the previous results highlights that the carrier-type for memristive switching at the nanoscale seems to be consistent with the carrier-type of bulk material, which is somehow contradictive to some models based on the precipitation of metals within oxide matrix, because the ON-state-current must decrease when introducing oxidized atmosphere as long as such metal precipitation area exists and responsible for the electrical conduction.

Next, we compare the above TiO_{2-x} single nanowire devices with capacitor-type devices. Figures 5(a)–5(c) respectively show the schematic, FESEM, and TEM-ED images of the fabricated Pt/TiO_{2-x}/Pt capacitor devices. A capacitor-type TiO_{2-x} device was fabricated by PLD at 300 °C and 1 Pa of oxygen. The thickness of TiO_{2-x} thin films was 45 nm. Bottom 100 nm Pt electrodes were deposited onto the SiO_2 (300 nm)/Si(100) substrate prior to PLD. Top 100 nm Pt electrodes of $20 \times 20\,\mu m^2$ area were deposited after TiO_{2-x} deposition. Figure 5(d) shows the I–V curve for this device, and indicates the bipolar memristive switching behavior. Figure 5(e) shows the effect of ambient atmosphere on the ON-state-current time-series data for Pt/TiO_{2-x}/Pt capacitor devices. As can be seen in Fig. 5(e), the capacitor-type device is clearly insensitive to the surroundings, which is in sharp contrast with the TiO_{2-x} single nanowire device. This is because the specific surface area of devices critically determines the effect of the surroundings on the memristive switching. In TiO_{2-x} single nanowire devices, the channel, which is responsible for memristive switching, is spatially open and easily interacts with the surroundings. While in the capacitor-type device the electrical conduction area is surrounded by solid materials including TiO_{2-x} itself and Pt electrodes. Thus the interaction with the surroundings significantly differs from that between the two types of devices. From the viewpoint of memristive mechanisms, the use of a planar-type single nanowire device with surrounding effects is useful in extracting underlying features, which has been intrinsically difficult to measure for a solid of capacitor-type devices.

4. Conclusions

In summary, we presented the memristive switching properties of a single nanowire device made of titanium dioxide. We constructed the single oxide nanowire device of titanium dioxide on a Si substrate. First, we confirmed the existence of memristive switching in a 10 nm scale nanowire device. We successfully identified the carrier-types for memristive switching through atmosphere control measurements. Although cobalt oxide and nickel oxide showed the p-type behavior reported previously, the present titanium dioxide nanowire memristor exhibited n-type behavior. Our results highlight the fact that the carrier-type of memristive switching seems to be consistent with that of a bulk material, but this is in fact somehow contradictive to the model based on the precipitation of metals within a oxide matrix. Since, in conventional capacitor-type memristors, it has been impossible to measure the carrier-type in memristive switching because the memristive events are buried within a solid, the open-top planar-type “nanowire memristor” is clearly a powerful device for extracting the intrinsic features of memristive switching phenomena.

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