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Nonvolatile Bipolar Resistive Memory Switching in Single Crystalline NiO Heterostructured Nanowires

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Nickel oxide (NiO) has recently attracted much attention due to the resistive memory switching phenomena based on the electrically stimulated change of the resistance of a metal−insulator−metal (MIM) memory cell, frequently called resistive switching RAM (ReRAM).[1,2] The NiO ReRAM devices are expected to be future nonvolatile memory devices used as alternatives to the current flash memory technology.[1] The nonvolatile memory characteristics of NiO have been intensively investigated using the thin film forms, and excellent memory characteristics have been demonstrated.[3−15] However, to achieve high-density memory and improve the performance of the devices, it is crucial to reduce the size of the NiO cells beyond the limitation of current lithographic length scales. In addition, details of NiO resistive memory switching mechanisms, including the switching types (bipolar and/or unipolar), have not been well understood. Thus the scaling down of the NiO structures is strongly desired not only for understanding the underlying memory mechanisms within a confined nanoscale but also for improving the device characteristics of ReRAM.[14] The bottom-up approach using self-assembled nanowires is a promising solution for scaling down the size of memory devices. Thus, single crystalline NiO nanowires formed via a self-assembling fashion would be a candidate for overcoming the above issues. However difficulties in both fabricating well-defined single crystalline NiO nanowires and evaluating electrically the insulative NiO nanowires (band gap, nearly 4 eV) have impeded investigation of the resistive memory switching events in single crystalline NiO nanowires. Here we demonstrate for the first time the nonvolatile bipolar resistive memory switching in single crystalline NiO heterostructured nanowires.

Single crystalline NiO heterostructured nanowires were synthesized by an in situ heterostructured nanowire formation technique using laser MBE.[18] The NiO shell layers were deposited onto single crystalline MgO nanowires by ablating the NiO pellet target (99.99%, Kojundo Chemical). The MgO nanowires were fabricated by the metal catalyst-mediated vapor−liquid−solid (VLS) mechanism, and details of MgO nanowire formations can be seen elsewhere.[16] Note that the NiO shell layer formations onto the MgO nanowires were performed without atmospheric exposures. Figure 1 shows the field emission scanning electron microscopy (FESEM) and the high-resolution transmission electron microscopy (HRTEM) images of fabricated NiO heterostructured nanowires. The NiO shell layer was formed under 800 °C and 10 Pa of oxygen pressure. The FESEM image (Figure 1a) reveals the macroscopic uniformity of NiO heterostructured nanowires without any agglomerations of NiO shell layers. The microscopic uniformity of NiO heterostructured nanowires can be seen in the HRTEM images (Figure 1b). The well-defined heterointerface was maintained for samples prepared above 300 °C. The single crystalline nature of NiO heterostructured nanowires was further confirmed by a magnified image (inset of Figure 1b). The XRD measurements for NiO heterostructured nanowires also confirmed the epitaxy growth of single crystalline NiO shell layers (Supporting Information). In addition, the inverse FFT analysis for the HRTEM image clarified the absence of any observable crystal dislocations at the heterointerface, revealing the well-defined heterointerface of the single crystalline NiO heterostructured nanowires. The size of NiO heterostructured nanowires can be easily controlled by varying the MgO core-nanowire diameter[16] and changing the NiO shell thickness in the unit cell. It should be emphasized that the ideal crystal combination between NiO and MgO, including the same crystal structures (rock-salt) and the small lattice mismatch (0.7%), and the use of the in situ heterointerface formation technique are essential to fabricate the well-defined single crystalline NiO heterostructured nanowires.

The resistive memory switching behavior of single crystalline NiO heterostructured nanowires was investigated by electrical measurements using a conductive-atomic force microscopy (C-AFM) method.[17] The electrical properties were investigated by measuring the current (I)−voltage (V) curve of a single crystalline NiO heterostructured single nanowire at room temperature. The measurement structures were fabricated by transferring synthesized NiO heterostructured nanowires onto an oxidized Si substrate, and then a Pt electrode with a sharp edge was deposited onto the substrate.[17] After confirming the exact location of the nanowires on the substrate using a nondestructive tapping mode, the C-AFM measurements were performed at the nanowire position ∼1000 nm away from the Pt electrode using a conductive Ir/Pt coated Si cantilever (details in Supporting Information). Figure 2 shows the typical $I-V$ curve of a NiO heterostructured nanowire with a 30 nm diameter (10 nm, MgO core-nanowire diameter; 10 nm, NiO shell thickness). The cross-sectional area of NiO shell layers for resistive switching is $\sim 10^{-3}$ μm^2, which is in fact at least 5 orders of magnitude smaller than the values of previously reported NiO thin film devices, typically 10^2 μm^2.[3−15] In the $I-V$ measurement, initially the NiO nanowires were very insulative and the resistivity was over 10^{11} Ω. When applying the negative electric field, the current through the NiO nanowire increased drastically up to 10^{-8} A from the 10^{-11} A range, indicating the occurrence of a “SET” process. After the SET process, the low resistance of a NiO nanowire was kept constant as long as the electric field was negative. On the other hand, when a positive electric field was applied, the current through the NiO nanowire decreased drastically down to 10^{-11} A, indicating the occurrence of a “RESET” process. Thus, we demonstrate for the first time that the single crystalline NiO heterostructured nanowires exhibit a bipolar resistive memory switching. Note that the electric fields for SET and RESET were comparable with previous data using NiO thin film devices with bipolar switching.[15] The repeatability of the SET and RESET processes was confirmed over several cycles (Supporting Information). We further confirmed the occurrence of the resistive memory switching within the nanowires by performing the measurements

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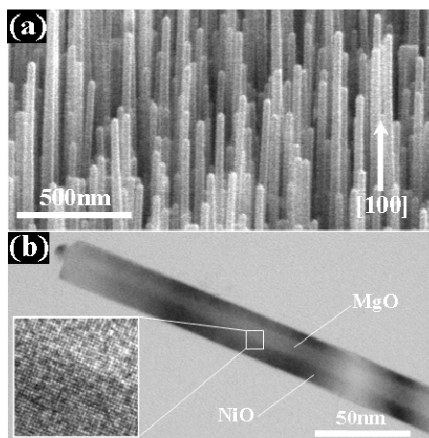

Figure 1. (a) FESEM image of NiO heterostructured nanowires grown on single crystal MgO substrate; (b) HRTEM image of single crystalline NiO heterostructured nanowires. Inset figure shows the magnified image.

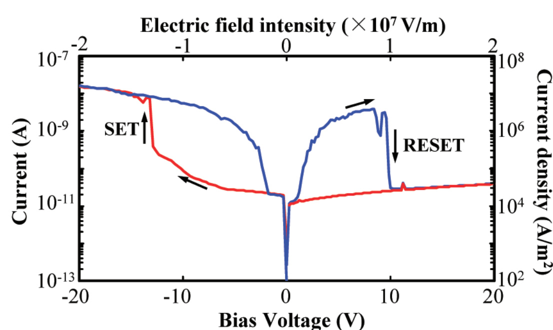

Figure 2. *I*−*V* characteristics of single crystalline NiO heterostructured nanowires using C-AFM method.

on more conductive NiO heterostructured nanowires obtained by varying the shell layer formation.[18] As the conductivity of NiO nanowires increased, *I* by C-AFM increased. There are several interesting implications from these experimental results when compared with previous works as to NiO ReRAM thin film devices.[15] Single crystalline NiO heterostructured nanowires down to several tens of nanometers exhibit bipolar resistive memory switching, not unipolar memory switching. In the bipolar switching, the polarity is closely related to the switching mechanism including a charged crystal vacancy and others, while the unipolar switching can occur without the polarity change. Thus the bipolar switching behavior of single crystalline NiO nanowires essentially differs from the unipolar switching behavior of polycrystalline NiO thin films. Although only a few reports exist of NiO epitaxial thin film devices showing the bipolar switching,[15] which is similar to our results using single crystalline NiO nanowires, the switching type for the single crystalline NiO nanostructures had not been evident.[19] Thus our experimental results infer that the bipolar switching mechanism governs the NiO ReRAM effect on the nanoscale. Although the complex switching mechanisms in NiO need to be further investigated, these experimental findings would be invaluable not only for understanding the detailed switching mechanisms of NiO on a confined nanoscale but also for developing nanoscale memory devices.

In conclusion, we have demonstrated nonvolatile bipolar resistive memory switching in single crystalline NiO heterostructured nanowires for the first time. The self-assembled NiO nanowires are expected to open up opportunities to explore not only the detailed nanoscale mechanisms in NiO resistive memory switching but also next-generation nanoscale nonvolatile memory devices with the potential for high-density device integration and improved memory characteristics.

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Supporting Information Available: Detailed explanations as to the evaluations of NiO heterostructured nanowires and the conductive AFM measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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