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Resistive-Switching Memory Effects of NiO Nanowire/Metal Junctions

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Resistive switching (RS) memory effects of metal/oxide/metal junctions, frequently called "ReRAMs"[1] and/or "Memristors",[2] have attracted much attention because of their potential applications in next-generation nonvolatile memories as alternatives to current flash memory technology. Among various oxide materials, NiO has been particularly considered as a promising material for RS.[3] Although the importance of the effects of nanoscale chemical and physical events on RS has been highlighted in previous studies using NiO thin-film devices,[4] investigating the occurrence of RS on the nanoscale and the exact RS mechanisms has been difficult. Self-assembled oxide nanowire-based ReRAMs offer an alternative solution not only for reducing the size of the NiO cells beyond the limitation of current lithographic length scales but also for extracting the underlying nanoscale RS mechanisms. Previously we have demonstrated the occurrence of bipolar RS within NiO nanowires by utilizing conductive atomic force microscopy (C-AFM).[5] Although a symmetric metal/nanowire/metal junction is ideal, a methodology for constructing well-defined junctions has not been well-established. Here we demonstrate the construction of highly stable RS junctions by utilizing NiO nanowires and well-defined nanogap electrodes and use them to elucidate the crucial role of redox events in the nanoscale RS.

An in situ technique for creating heterostructured nanowires was used to fabricate NiO nanowires, as reported elsewhere.[5,6] NiO shell layers were formed on MgO nanowires[7] without atmospheric exposure to realize the well-defined heterointerface[5,6] [see the Supporting Information (SI)]. We utilized the following procedure to construct NiO nanowire/metal junctions. NiO nanowires grown on the substrate were sonicated and dispersed in 2-propanol, and then the dispersed NiO nanowires were transferred onto a degenerately doped n-type silicon substrate capped with a 300 nm SiO_2 layer. We performed photolithography and electron-beam lithography processes to define electrode patterns on the SiO_2/Si substrate, and this was followed by metal depositions of Pt (20 nm) and Au (100 nm). The gap spacing of the fabricated electrodes was typically 300 nm. It should be noted that the use of a Pt electrode is crucial to avoid an interfacial oxidized layer and obtain reliable junctions.[8] The transport properties were measured using a semiconductor analyzer (Keithley 4200) at room temperature under various gases.

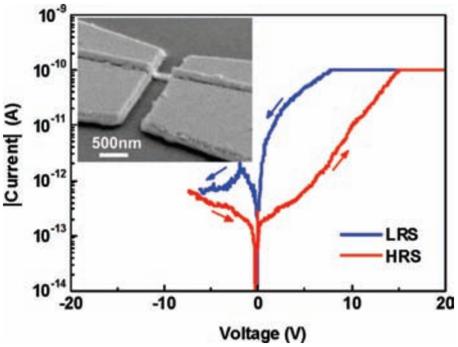

Figure 1. Typical $I-V$ curve for a NiO nanowire/metal junction. The inset shows a field-effect scanning electron microscopy image of a fabricated junction.

Figure 1 shows a typical $I-V$ curve for a fabricated Pt/NiO nanowire/Pt junction with a compliance current of 10^{-10} A. When a positive electric field was applied, the junction resistance tended to decrease, whereas applying a negative electric field resulted in an increase in junction resistance at ~2 V. After each RS process, the junction resistance was kept constant as long as the electric field was applied with the same polarity. Notably, the electric field intensities (~10^7 V/m) for RS processes were comparable with those in a NiO thin-film sandwich structure that exhibits the same bipolar RS (see the SI), indicating that the observed bipolar RS in nanowire junctions is comparable with the RS in thin-film structures. We further confirmed the occurrence of the RS within the NiO shell by performing the measurements on only the MgO nanowire core. Thus, the fabricated junction exhibits bipolar RS with bistable states including a high-resistance state (HRS) and a low-resistance state (LRS). In fact, the presence of bipolar RS in NiO nanowires is consistent with results obtained using C-AFM.[5] Notably, the fabricated junction exhibited highly stable RS properties with an endurance of up to 10^6 (see the SI). This is in contrast with the case when C-AFM was used, where the endurance was confirmed only for several times because of the instability of the conductive tips.[5] Thus, the present NiO nanowire/Pt metal junctions are much superior to C-AFM in terms of the stability. In addition, the present junction exhibits multistate RS upon variation of the compliance current (CC) value (see the SI). These results highlight the fact that the present nanowire junctions are highly stable and offer an important system and platform for investigating nanoscale RS mechanisms of NiO down to the 10 nm scale.

Next we examined the nanoscale RS mechanisms utilizing the present junctions. Since previous investigations of RS mechanisms of NiO had been conducted on film sandwich structures,[3] extracting the internal RS events had been difficult. Our strategy to tackle this issue was to utilize intentionally a chemical reaction with the surroundings by introducing various atmospheres. In RS, the LRS is a sort of electric-field-induced excited state and the HRS is the ground state. Therefore, the time evolution data for the LRS current during reaction with the surroundings should represent the nature of LRS conductions. Figure 2 shows retention data for the LRS current when the atmosphere gas was varied. The LRS current tended to decrease as the atmosphere gas tended to be chemically

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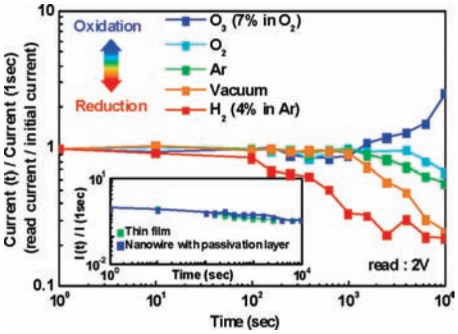

Figure 2. Retention data for the LRS current upon variation of the atmosphere gas. The inset shows retention data for a junction with a passivation layer in comparison with a thin-film device.

reduced, while an oxidizing atmosphere such as O_3-containing gas resulted in an increase in the LRS current. It should be noted that the above atmosphere dependence of the RS was not observable for NiO thin-film structures. This trend has two important implications regarding the nanoscale RS mechanisms of NiO. First, redox events should dominate the occurrence of bipolar RS within nanoscale NiO, because the LRS conductivity was sensitive to the degree of redox events. Second, the conducting path within an insulative NiO matrix seems to be similar to that of p-type semiconductor, since the LRS conductivity decreased as the atmosphere gas was chemically reduced.[9] In fact, this extracted implication is inconsistent with some previous reports, where precipitation of Ni metal within the insulative NiO matrix to serve as a conducting path has frequently been discussed.[3,4] In the presence of Ni metal, the LRS conductivity must decrease upon oxidation, which is completely opposite to the present experimental trend. Even if the coexistence of a Ni metal conduction path and a p-type conduction path is assumed, the decrease in the LRS current when the atmosphere gas was reduced cannot be explained, as the LRS current must be maintained in the presence of a Ni metal conduction path within nanowires. These experimental results highlight the fact that redox events with a p-type conducting path play a crucial role in bipolar nanoscale RS of NiO. Since the conductivity of bulk NiO is well-known to originate in a cation vacancy as $Ni_{1-\delta}O$,[9] the nanoscale p-type conducting path might contain such a cation vacancy. There is further indirect experimental evidence that supports the above mechanism. First, the transition from the LRS to the HRS occurred at an electric field lower than that for the transition from the HRS to the LRS. This trend is consistent with the redox-based scenario, since in the RS measurement atmosphere (air), the ground state is the HRS, so the transition from the LRS to the HRS (corresponding to a reduction) should be more favorable than the one from the HRS to the LRS. Second, redox events via ambient oxygen should be significant on the basis of the redox-based mechanism. There was a discrepancy between nanowire junctions and thin-film sandwich structures in the retention data, although both structures exhibited the same bipolar RS. This implies that the nanowire junctions react with ambient oxygen more actively than the thin-film structures, where the redox events occur via surrounding oxygen in the solid. To validate this speculation, we performed the RS experiments on NiO nanowire junctions with a SiO_2 passivation layer (see the SI). The inset of Figure 2 shows the retention data for nanowire junctions with the passivation layer. The retention time of the junction with the passivation layer was longer than those of the junctions without the passivation layer. This demonstrates the importance of a reaction with surrounding oxygen for RS. The mechanism based on redox events with cation vacancies for bipolar RS of NiO implies that the electrochemical reactions occur via the migration of cation vacancies induced by an electric field, although further real-time observations during RS would be required to give direct experimental evidence of this. Since NiO has been well-known to act as a redox catalyst,[10] the occurrence of redox events within NiO is not surprising. The important implication of this study is that bipolar RS in nanoscale NiO (down to the 10 nm scale), which is induced by an electric field, is governed by redox events with a p-type conduction path.

In summary, we have demonstrated the construction of highly stable RS junctions with a Pt/NiO nanowire/Pt structure and the crucial role of redox events with a p-type conduction path in the nanoscale bipolar RS. The presented approaches offer an important system and platform for investigating nanoscale RS mechanisms of various oxide materials.

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Supporting Information Available: Complete ref 3 and detailed explanations of the formation, measurements, and RS properties of nanowire junctions and RS properties of NiO film-based devices. This material is available free of charge via the Internet at http://pubs.acs.org.

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