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Metal–insulator transition in Au–NiO–Ni dual Schottky nanojunctions

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Abstract

Ni nanowire arrays were fabricated through electrochemical deposition on a template. After a nanoscale NiO layer was formed on the top of the nanowires, a layer of Au paint was coated on the top of the nanowire arrays to construct Au–NiO–Ni dual Schottky nanojunctions, and the structure was characterized at different scales. Within a small range of voltages, extraordinary current jumps were observed at room temperature and at 77 K. The resistance switch effect can be repeated at room temperature, while switching is irreversible at low temperature. The significant change in resistance of the samples does not require doping and may find future applications.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Materials with excellent resistive switching characteristics have been under the spotlight recently. With a nonlinear current–voltage relationship, materials can exhibit notable current change with the variation of voltage or other external factors, which may be useful for applications such as in electrical switching devices and acute sensors. Many nanostructures have been explored within this arena, such as magnetic tunnel junctions, resistance random access memory (RRAM), and nanoscale gap junctions [1–3]. Among them, one class of resistive switching phenomena is based on the electrically stimulated change of the resistance of a metal–insulator–metal (MIM) structure, in which 'M' represents any good electron conductor and 'I' denotes a poor conductive matter, often ion-conducting [4]. Various 'I' candidates have been studied in this kind of MIM architecture, such as VO_2 [5, 6], CeO_2 [7], GaAs [8], $SrTiO_3$ [9], and $CaCu_3Ti_4O_{12}$ [10], and switching between a conductive ON state and a less conductive OFF state has been reported. Nevertheless, some of these materials entail sophisticated fabrication processes, such as plasma-enhanced atomic layer deposition and sputtering, which make them difficult to produce on a large scale. Furthermore, the threshold voltage that switches between the ON state and OFF state is quite high, ranging from several to dozens of volts. One possible reason for this is that the insulator or semiconductor layer is quite thick, usually more than a hundred nanometers. Thus, a large electric field is required to excite the carriers. If the insulator layer thickness can be controlled, a lower threshold voltage may be achieved. Therefore, structures that process small threshold voltages and can be produced by easily scalable techniques are essential to further advances in nanodevices.

Because of their convenient preparation, integration ability, and high density, nanowire arrays have been seen as one of the most competitive candidates for the nanoelectronics industry of the future [11–13]. We have demonstrated that an Ni–NiO Schottky nanojunction shows strong nonlinear current–voltage characteristics before it finally reaches linearity [14]. To enhance the resistance ratio between the high resistance state and the low resistance state, the Ni–NiO forward Schottky current should be restrained before the metal–insulator transition (MIT). A face-to-face dual Schottky configuration can suppress the forward current and ensure reverse bias characteristics [15]; similar Schottky barrier double diodes have been fabricated by many semiconductor companies such as Phillips and Fairchild. Therefore, another kind of metal can be introduced into the Ni–NiO nanojunction to form two face-to-face Schottky contacts. In this paper, we prepare an Au–NiO–Ni nano-heterojunction composed of two face-to-face Schottky contacts, namely Au–NiO and NiO–Ni. A large change in resistance was observed with quite a small

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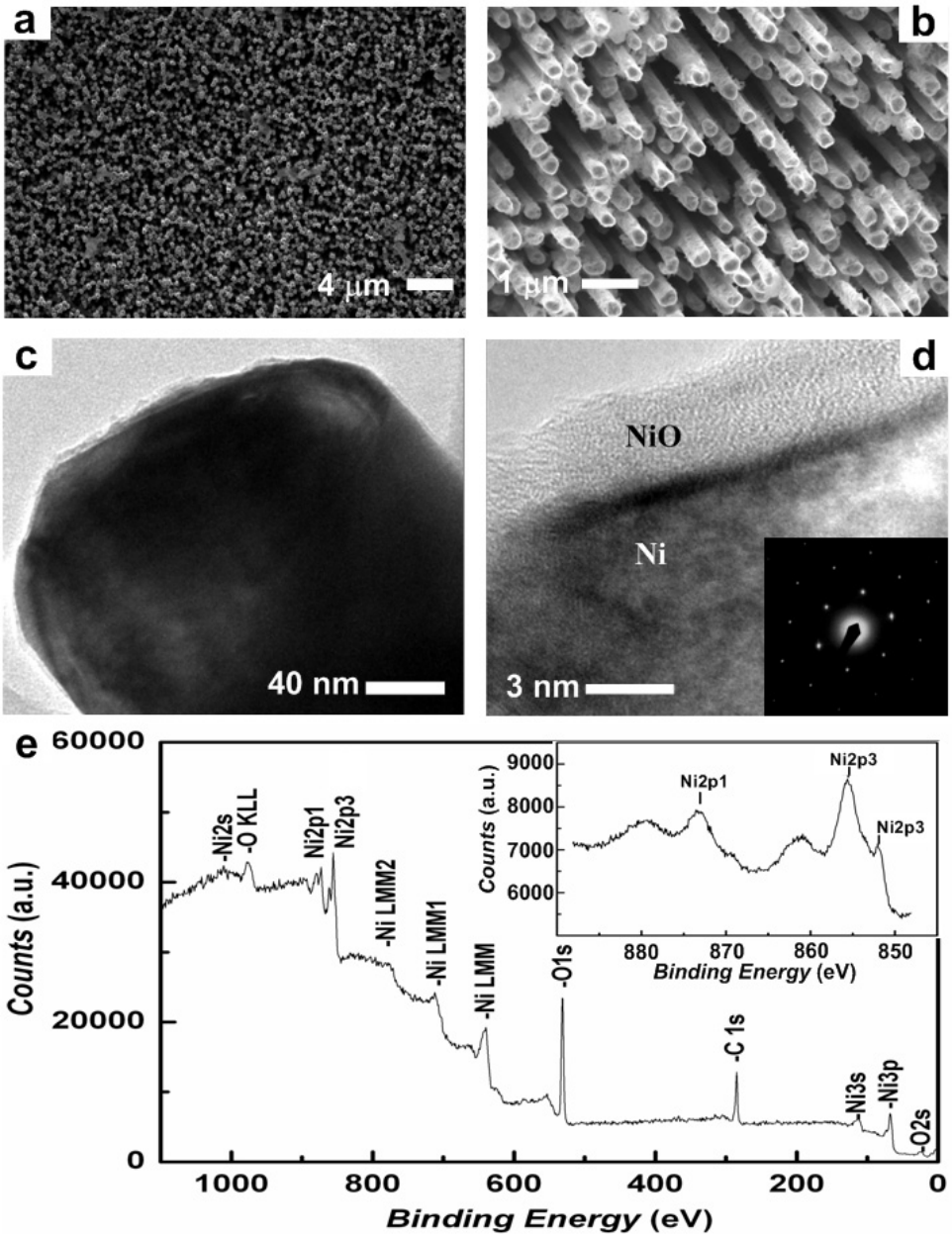

Figure 1. (a) Top view SEM image of the Ni nanowires on the template after removal of the AAO surface. (b) The Ni nanowires at a higher resolution. (c) TEM image of a Ni nanowire tip after oxidation in air for 12 h. (d) HRTEM image of the interface between the Ni core and NiO layer. Inset: SAED pattern of a single Ni nanowire. (e) A survey of XPS of the Ni nanowires. Inset: narrow spectrum of the Ni 2p core level.

switch voltage. The switching behavior is irreversible at low temperature, and theoretical fitting of the I–V behavior based on the double Schottky barrier model is close before the MIT. In contrast, at room temperature, repetitive MIT can be realized by undergoing a treatment of applying the reverse voltage.

2. Experimental details

Ni nanowire arrays were synthesized using the electrochemical deposition method with an anodic aluminum oxide (AAO) template at room temperature. The Ni electrolyte contained a mixture of 300 g l^{-1} $NiSO_4 \cdot 6H_2O$, 50 g l^{-1} $NiCl_2 \cdot 6H_2O$, and 40 g l^{-1} H_3BO_3 solution and was adjusted to a pH of 2.5. A constant voltage of 1.35 V was applied during the process. The mean diameter and length of the nanowires are 200 nm and 60 μm, respectively. The scanning electron microscopy (SEM) images in figures 1(a) and (b) show the fabricated Ni nanowire arrays after etching the surface of the aluminum oxide template. After being rinsed with deionized water several times, the sample was oxidized in air for about 12 h at room temperature to allow the exposed part of the Ni nanowire to form an Ni core/NiO shell architecture, as shown in the transmission electron microscopy (TEM) picture in figure 1(c) and the high resolution transmission electron microscopy (HRTEM) image in figure 1(d). The mean thickness of the NiO layer was about 3 nm. The single

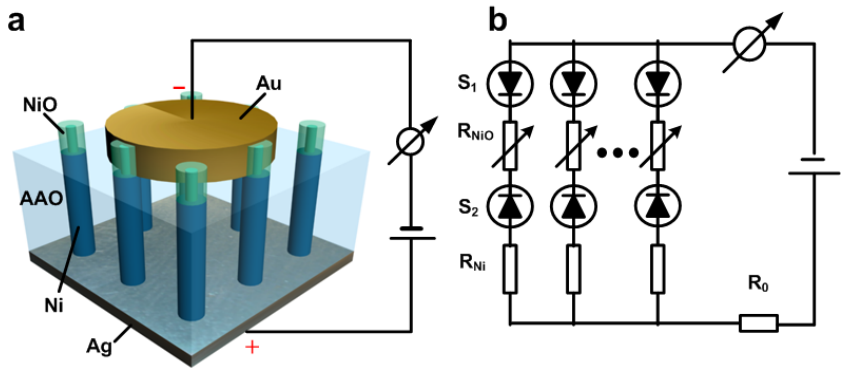

Figure 2. (a) Schematic diagram showing the structure of the Ni nanowire arrays with a NiO nanolayer on top. (b) The equivalent electric circuit of the nanowire arrays.

crystal structure of an individual Ni nanowire was confirmed by selected area electron diffraction (SAED) experiments, shown in the inset of figure 1(d). The NiO–Ni nanojunction arrays were characterized by x-ray photoelectron spectroscopy (XPS). Figure 1(e) shows a survey of the arrays and the inset specifies the narrow spectrum of the Ni 2p core level. The peaks obtained at binding energies of 855.6 eV (Ni $2p_3$) and 873.5 eV (Ni $2p_1$) indicate the formation of NiO [16, 17].

3. Results and discussion

Figure 2(a) is a schematic of the experimental setup with a positive applied voltage. The conductive silver paint layer on the back of the template forms the bottom electrode and a gold paint layer covering the top of the NiO–Ni nanojunction arrays serves as the top electrode. The typical dimensions of the gold electrode are 300 μm × 300 μm. Considering the hole density of the AAO template is about 13–15 μm^{-2}, the overall number of nanowires in the sample can be estimated at about 10^6. A SourceMeter (Keithley 2400, scanning step of the bias voltage = 1 mV, scanning speed of the bias voltage = 12.5 mV s^{-1}) was used in the measurements. In this experiment, the positive direction of the applied electric field is defined as being from Ni to Au. Here, the Schottky barrier height can be viewed as homogeneous since no chemical pretreatment except natural oxidation is introduced in this process. Besides, the nickel nanowire arrays are made under identical circumstances. Therefore, no extraneous negative ion that will change the barrier height [18] can be found in our fabrication.

We first placed the sample in a vacuum cryostat at the temperature of liquid nitrogen. Figure 3(a) shows the I–V behavior of one Au–NiO–Ni Schottky contact array sample at 77 K. Line 1 shows that when the voltage was swept to a positive value of about 0.59 V, an abrupt jump of current occurred and the ON state of NiO was achieved. The switch ratio of the current of the ON and OFF states is about 300. The sample exhibits linear I–V characteristics in the ON state with a resistance of 2.78 Ω. Line 2, the subsequent measurement performed after line 1, demonstrates that the sample remains in the low resistance state. In this experiment, the sample stayed in the low resistance state after the initial MIT. We have previously demonstrated that under the positive voltage that was used in this experiment, the Ni–NiO nanojunction is forward-biased [14]. Thus, the Au–NiO junction is under reverse bias in this scenario and the I–V relationship in the dual Schottky junction ought to be determined mainly by the reverse bias.

Figure 3(b) shows the fit of line 1 to the Schottky model of the reverse bias. According to the thermionic-emission, the reverse bias I–V characteristics of the Schottky contact can be described as [19–21]:

$$I_R = I_{S0} \exp(q\Delta\phi/kT) \tag{1}$$

$$\Delta\phi = C(V_D + V - kT/q)^{0.25}. \tag{2}$$

So, from equations (1) and (2):

$$\ln I_R = \ln I_{S0} + (qC/kT) \times (V_D + V - kT/q)^{0.25} \tag{3}$$

where I_R is the reverse current, I_{S0} is the hypothetical saturation current, q is the electronic charge, k is Boltzmann's constant, T is the absolute temperature (77 K here), $\Delta\phi$ is the lowering of the Schottky barrier due to the image force, V_D is the built-in voltage in the contact, V is the applied reverse voltage, and C is a parameter described by Arizumi and Hirose [21]. Here, $\ln I_{S0}$ is −13.7, C is 0.046 and V_D remains constant at 0.006 68 V. As we can see, the result closely fits the experimental data, providing that the I–V relationship of the sample is dominated by the reverse-biased Au–NiO Schottky diode before the MIT.

Figure 3(c) denotes the I–V behavior of one Au–NiO–Ni Schottky contact array sample at room temperature. Line 1 shows that when the voltage was swept to a positive value of about 0.82 V, a significant current jump occurred and the ON state of NiO was achieved. The ratio of the current before and after the jump is about 6600, which means the sample experiences an extraordinary resistance switch. The sample presents virtually linear I–V characteristics in the ON state with a resistance of 5 Ω. Line 2 displays the subsequent measurement performed after line 1, and demonstrates that the array sample stays in the low resistance state after the initial MIT, as was the case at 77 K. In some other reports [5–10], the abrupt current jump effect, described as the Mott transition,

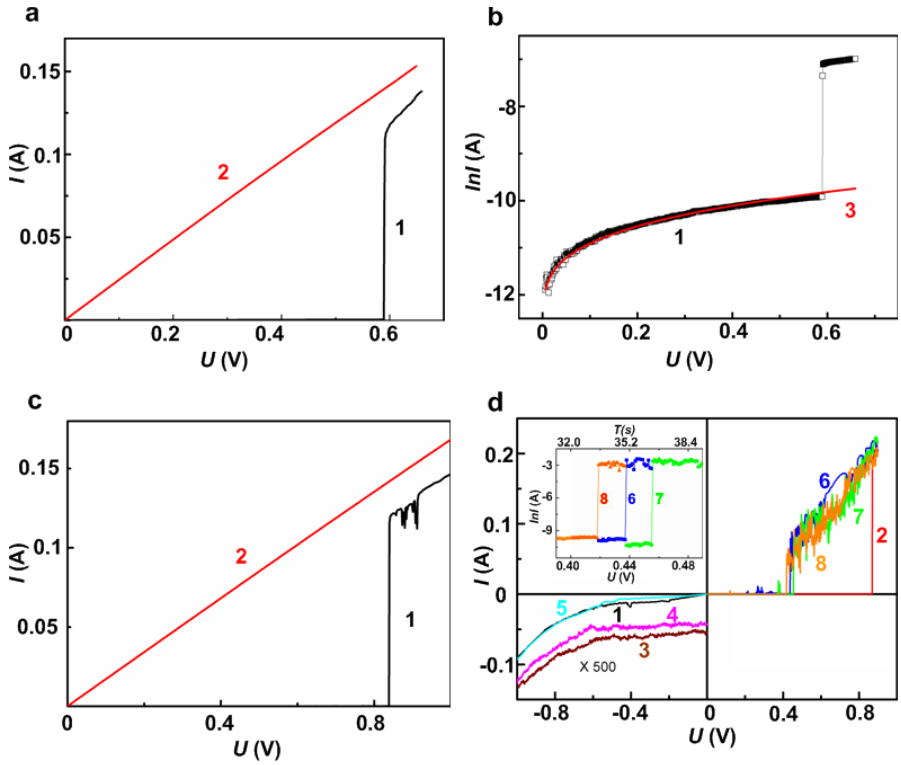

Figure 3. (a) I–V behavior of a Au–NiO–Ni Schottky nanojunction at 77 K. (b) Fitting of experimental data (square line) to the reverse bias Schottky mode (line 3). (c) I–V behavior of a Ni–NiO–Au Schottky nanojunction at room temperature. (d) The repeated MIT after negative electric field treatment at room temperature. Inset: the magnification of the switch parts of lines 6, 7, and 8. The timescale is labeled as well.

can be reproduced by decreasing the applied voltage. In this experiment, it is believed that the transition is caused by electron excitation mediated by the nickel defects [22]. During the transition, two Ni^{2+} will be transformed into Ni^{3+} caused by the nickel vacancies to fulfil charge neutrality and the local lattice is distorted as a result. The small-polaron hole Ni^{3+} hops about the nickel vacancies and thus the abrupt current jump is composed of both the electron current and the polaron hopping current. When the voltage reached the threshold point, electrons were excited into the conduction band and became carriers while nickel ions were also removed from their original positions, which meant that the number of carriers in the sample increased dramatically. After the threshold voltage has reached 0.82 V for the first time, the excited electrons cannot be recaptured by the ions because of the dramatic lattice deformation and thus the sample remains in the ON state. However, if the ions do not deviate greatly from their former locations in the lattice and can return to their original places, they might be able to recapture the electrons and the whole sample could revert to the OFF state as a result.

In this experiment, the threshold voltage is the predominant indicator of the extent of lattice deformation because the greater it is, the stronger electric field the NiO nanolayer has to assume and the more drastic the lattice deformation would be. Therefore, if the threshold voltage can be reduced, the nickel ions may be able to return to their original positions and the sample could return to the high resistance state after removal of the applied electric field. To demonstrate this proposal, we used another Au–Ni–NiO Schottky contact nanowire array sample using the same fabrication process. As illustrated in figure 3(d), firstly, the I–V behavior of the sample under a small negative voltage was recorded (line 1). Then the sample underwent a MIT (line 2) with a threshold voltage of about 0.85 V. After that, the applied voltage was switched to exert the opposite electric field on the sample so the NiO–Ni Schottky nanojunction was reverse-biased accordingly. We found that the carrier concentration was the highest after the MIT (line 3) and then began to decline (line 4). In the end, the sample returned to the OFF state (shown by line 5 coinciding with line 1). The scanning process of the negative voltage part lasted 80 s each time and was repeated three times (line 3, 4, and 5) without intermission. Note that the scale of the reverse current has been magnified by 500 times in the figure so that the sample did not undergo a MIT under the reverse current. After the sample returned to the OFF state, we applied the positive voltage once more and found that the threshold voltage had decreased to about 0.41 V (line 6), which was much smaller than the previous 0.85 V. By repeatedly sweeping the positive voltage, the sample presented similar MIT, as evidenced by lines 7 and 8. Thus, the opposite electric field treatment is able to reduce the threshold voltage and realize repetitive MIT. One possible reason for this is that there are many defects on the Au–NiO interface during the formation of the NiO nanolayer, and these defects would carry a large portion of the applied voltage so the loaded voltage on NiO is discounted. When a positive voltage is employed, the Au–NiO nanojunction is reverse-biased and the barrier of Au–NiO would become quite high in this circumstance. According

to the tunnel effect, electrons from the Au part have to own higher energy to pass the barrier, which makes them unable to fall into the energy states of defects. Therefore, the excited electrons will remain in the conduction band after the MIT and the subsequent I–V behavior would be linear because of the increased number of carriers. In contrast, if the voltage direction is reversed after the MIT, the Au–NiO nanojunction will be positive-biased so the defect states will be able to capture the electrons more easily and become saturated. This conjecture is demonstrated by lines 3, 4, and 5 as the current decreases gradually. As a result, the NiO nanolayer can accept a larger portion of the voltage when the positive voltage is employed, thus facilitating the occurrence of the MIT. The fluctuations of the curves may relate to the crystal quality of the NiO nanolayer at high temperature. The inset of figure 3(d) is the magnification of the switch processes of lines 6, 7, and 8. It reflects the switching characteristics of the Au–NiO–Ni dual Schottky nanojunctions. The timescale is indicated on the upper axis. The inter-record gap of the equipment is about 80 ms with an interval of 1 mV, so the switch process is completed in 80 ms since no measurement record is shown in this period.

4. Conclusions

In conclusion, Au–NiO–Ni heterojunctions composed of two face-to-face Schottky contacts were fabricated using Ni nanowire arrays and were characterized in detail. An abrupt current jump was observed in the nanostructures at 77 K. The sample remained consistently in the low resistance state after the MIT, which may be caused by the increased number of carriers in the sample. A reverse bias model was used to analyze this result and the fit is consistent with the data of the OFF state. At room temperature, an appreciable current switch was observed with a gain ratio of about 6600. Furthermore, after being treated with a small reverse electric field, the sample can return to the high resistance state and a repetitive MIT effect is realized. This enormous resistance switching with fast response could be used in future applications.

Acknowledgments

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