2012 12th IEEE International Conference on Nanotechnology (IEEE-NANO)
The International Conference Centre Birmingham
20-23 August 20112, Birmingham, United Kingdom

Resistive Switching in Copper Oxide Nanowire-based Memristor

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Abstract- A copper oxide nanowire (CuO NW) based memristor is designed for the non-volatile random access memories (NVRAM) and the resistive memory effect based transducers. The devices are prototyped using a copper oxide and cuprous oxide (CuO-Cu_2O) hetero-junction formed from as-grown CuO NWs. We report an experimental investigation of using electron beam irradiation in fabricating such devices. Experiments have been performed using nanorobotic manipulation inside a transmission electron microscope. Because the memristor is conducted as a dynamical resistor, the bipolar resistive switching (BRS) behaviors of the as-fabricated device demonstrated typical ones of memristors. Furthermore, the as-fabricated nanowire memristor is sensitive to the electron bombardment. The irradiation ratio of NWs and the memristor effect are co-related, which is promising for the application in a transducer. The CuO NW based memristor will enrich the binary transition oxide family and holds a simpler design than the traditional thin-film version. Owing to these advantages, the CuO nanowire based memristors will facilitate their applications in nanoelectronic and potentially in micro-/nano-electromechanical systems (MEMS/NEMS).

Index Terms— resistive switching, nanowire, hetero-junction, memristor.

I. INTRODUCTION

The investigation in the binary transition oxides, such as TiO_2, Nb_2O_5 and NiO, has stimulated fast expanding interests due to their applications in resistive random access memory (RRAM) and crossbar architectures for logic devices [1-2]. However, most existing works were based on 2-dimensional (2D) thin-film metal-oxide-metal (MOM) structures. The resistive switching (RS) behaviors of 1D nanowires (Figure 1(a)) have proceeded much slower although their advantages in achieving compact sizes and faster access speeds have been recognized.

Here we report an *in situ* experimental investigation of the bipolar resistive switching (BRS) and memristive behavior in individual CuO-Cu_2O hetero-junctions fabricated using as-grown copper oxide nanowires (CuO NWs). The nanowire based RS nanoelectronic devices have unique properties such as high R_{off}/R_{on} ratios and lower electroforming currents/voltages. Likewise, a nanowire memristor will also open new grounds in micro-/nanoelectromechanical system (MEMS/NEMS); providing an additional transduction mechanism to piezoresistivity /piezoelectricity, magnetoresistivity, and capacitance. For instance, the resistive switching behavior can be modulated during the e-beam based forming step as well as applying an

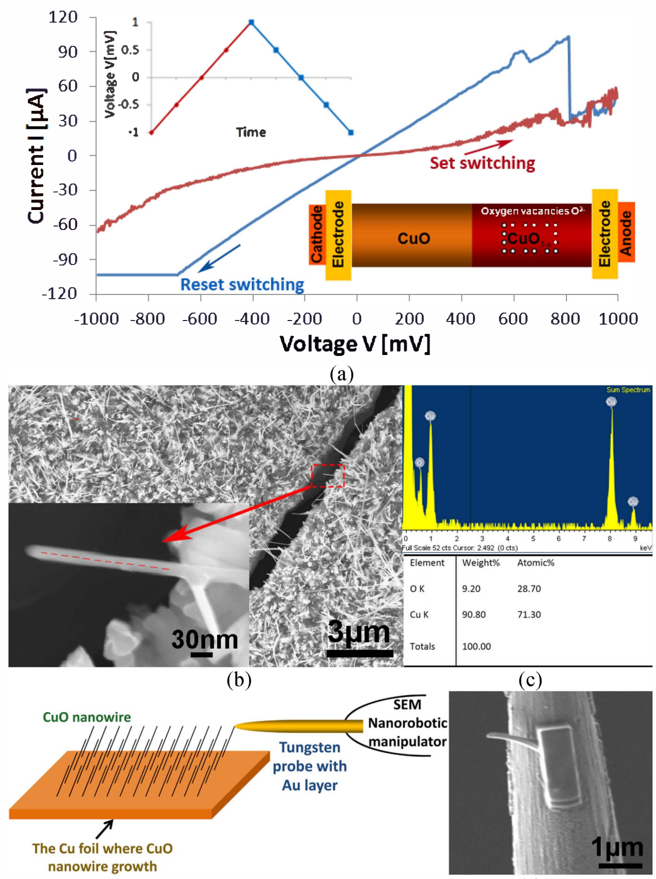
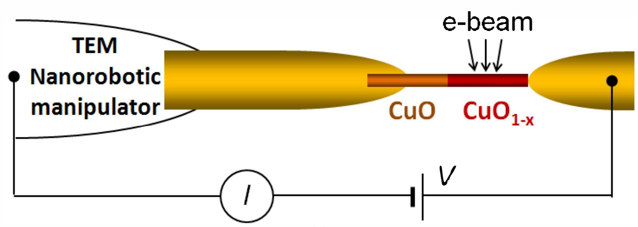


Fig. 1 (a) The resistive switching behavior in a CuO NWs based memristor. (b) SEM image of CuO NWs. The non-flaking nanowire arrays were synthesized on a copper foil in air by heating up into 500 ℃ for 2 hours. (c) EDX spectroscope of the as-grown nanowire. The atomic percentage of the copper and the oxygen were 70% and 30% accordingly. (d)(e) Single nanowire picking up process. By using a nanorobotic manipulator, a single CuO nanowire was picked up onto a probe and fixed there using a FIB deposit.

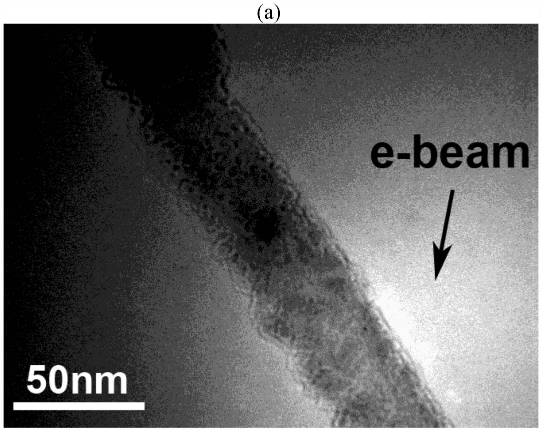
external pressure on the two ends of the nanowire. The electron irradiation energy and the applied force/deformation information can be recorded and read out; enabling a memristor sensor, or a memsensor. We will first describe the fabrication of such devices from nanowires, and then address the understanding of its memristive mechanism as well as the applications as a memsensor.

II. E-BEAM BASED FORMING

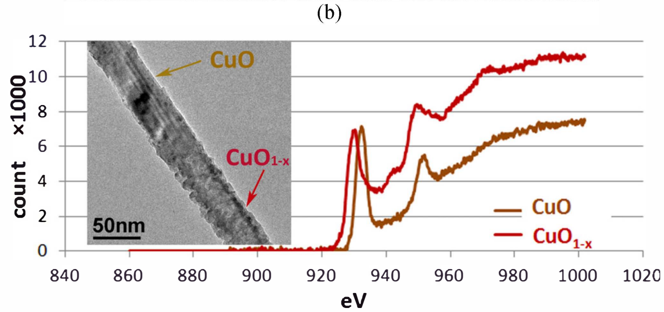
We synthesized the CuO NWs starting from a copper foil [3]. After 2-hour incubation in a box oven at 500 ℃, non-flaking nanowire arrays were growth on the surface of the foil (Figure 1(b)). The diameters of the nanowires range from 30 to 50 nm. The inset of Figure 1(b) shows the



(a)



(b)



(c)

Fig. 2 (a) The setup for E-beam forming. The electron beam of the TEM bombards part of nanowire and deoxidizes it; forming a $CuO\text{-}CuO_{1-x}$ heterojunction. (b) E-beam forming process. (c) EELS analysis of the $CuO\text{-}CuO_{1-x}$ hetero-junction. The oxygen vacancy transition between the $CuO\text{-}CuO_{1-x}$ segments is confirmed with the distinctive changes of the Cu L-edge in EELS.

detailed image of a single nanowire. The energy-dispersive X-ray (EDX) spectroscopy of it (Figure 1(c)) illustrates that the nanowire was composed by copper and oxygen. The atomic percentages of the elements are 70% copper and 30%

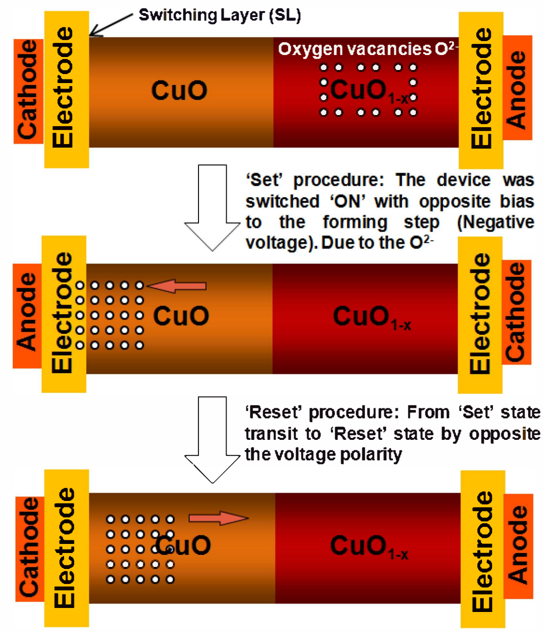


Fig. 3 BRS process in CuO nanowire based memristor. Initially, after the forming step, the oxygen vacancies are sufficient in the segment of CuO_{1-x}. However, the dynamic resistance property after forming is still not appear, because the other half part of the nanowire is still CuO, which has a high resistance in the gigaohm range. In 'set' procedure, the anode is placed on the end of CuO_{1-x} and the cathode is in the CuO side. As sweeping the bias from -1000 to 1000 mV, the vacancies in CuO_{1-x} part are transport all through the nanowire that driven by the electric force. Meanwhile, the conductive paths were formed follow the direction of the applied electric field. Therefore, the conductivity of it was decreased. In 'reset' procedure, the electric force direction was switched according to the alternate of external polar, which in turn broke the conductive path along the nanowire and makes the resistance back to the original high status.

oxygen, respectively, which demonstrate that this nanowire is a high purity CuO nanowire.

As-synthesized CuO NWs (Figure 1(b), inset) are used as raw materials for the memristors [2, 4]. A single nanowire was picked up onto a probe (Figure 1(d)) using a nanorobotic manipulator installed inside a scanning electron microscope (SEM) and fixed there using focused-ion-beam (FIB) induced deposition (Figure 1(e)). A "forming" step [5] is then applied to enable the nanowires with resistive switching characteristics to make it as a memristor.

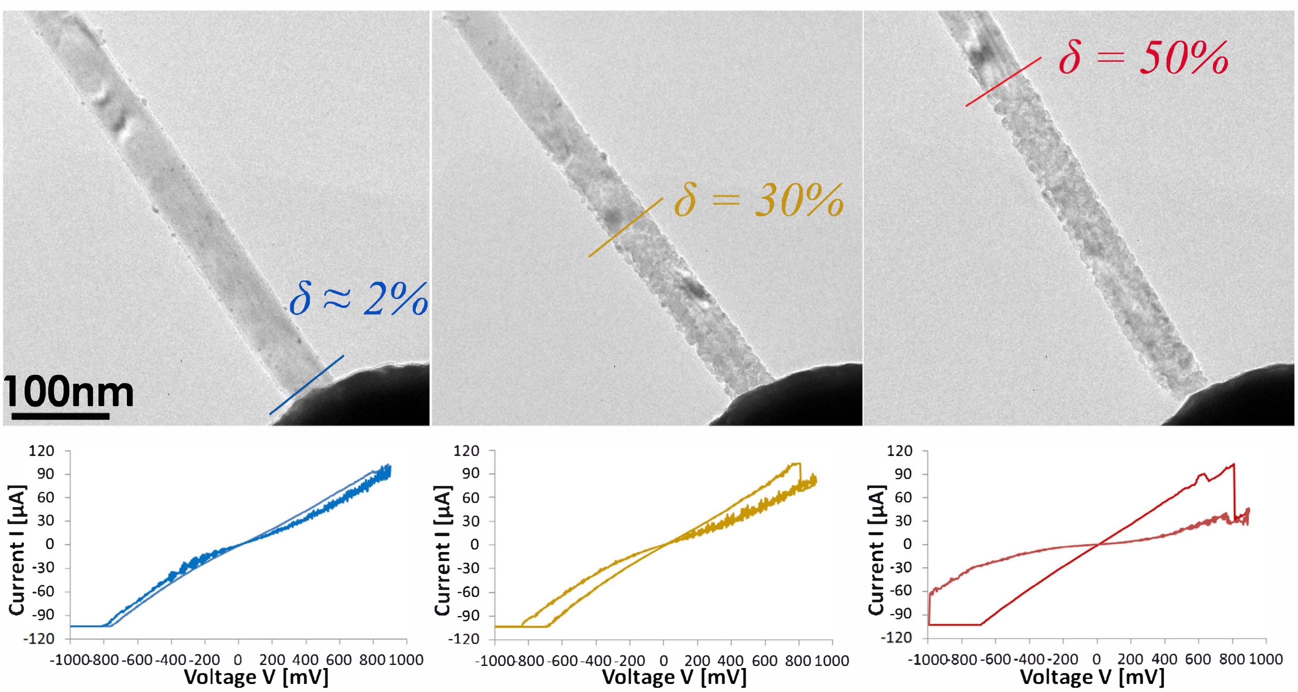
A number of "forming" processes to induce the dynamic resistance from oxides have been explored. Among them, the electroforming process [5-6] and the physical forming process [7-8] are most used. However, due to the cylindrical structure of the nanowires, the joule heating energy will be injected into the nanowire and cause the hard breakdown in the center of the wire if we apply the traditional electroforming. The physical forming is designed specifically to the thin-film memristor device, which in turn makes it unsuitable for our nanowire version. We developed a forming process using the electron beam of a transmission electron microscopy (TEM) to activate the CuO NWs into an memristor. Initially, in order to prevent the vibration of a suspended nanowire, the wire was contacted and fixed on the other end. Meanwhile, an electrical circuit is established to measure the change of electrical transport properties (Figure

2(a)). Secondly, by focusing the beam on a part of the nanowire (Figure 2(b)), a segment of the CuO was deoxidized into a metal phase as CuO_{1-x} with oxygen vacancies [5]. It acts as a reservoir of vacancies, providing the doping source for the rest of CuO. The transition of oxygen vacancies between the CuO and CuO_{1-x} segments is confirmed by the distinctive change of the Cu L-edge in the spectrum obtained from EELS (Figure 2(c)). Potentially, by measuring the energy shift between the Cu edges, it is possible to quantify the relative oxygen vacancy distribution along the nanowire. Based on the creation and electromigration of the oxygen vacancies, the insulating oxide is in turn transforming into an electrically conductive doped semiconductor [7]. From the experimental results and the former research, we conclude the possible mechanism for the nanowire based memristor and discuss the applications of it.

III. BRS IN CUO NANOWIRE BASED MEMRISTOR

The concept of the memristor was first defined in 1971 [4]. It was predicted that a fourth fundamental circuit element must exist to match with the resistor, capacitor and inductor. This circuit element is termed as “memristor” (as the short for the “memory resistor”), which conducts as a dynamical resistor with the state change according to the external applied bias voltage or current. There are two kinds of resistive switching behaviors [6, 8-9] existing in memristor device, the unipolar resistive switching (URS) and bipolar resistive switching (BRS). We have realized the bipolar switching in CuO nanowire based memristors, where the decrease in resistance takes place only under the polarities alternative of the external bias voltage and the resistance returns to the original status when the polarities change again [10]. There are several hypotheses to the mechanism of BRS existing, among them, we choose the vacancies-drifting mechanism to explain the BRS in CuO nanowire. As creating the oxygen vacancies by the forming step, these cations will migrate under the external bias. To the thin-film memristor configuration, these vacancies generate on a two-dimensional planar space. Once these planar defects extend all through the device, they form an interconnecting network of conduction pathways. The transport of charges, as well as oxygen, occurs through the network of these defect networks. Thus, the change in the electrical conductivity from cathode to anode is taking place during the transport process.

In our experiments, the e-beam based forming step creates the vacancies on a three-dimensional segment. Moreover, the *I-V* curve we have got is typically a BRS curve (Figure 1(a)), with the characteristic of the asymmetric trace. The asymmetric distribution of cations might lead to the asymmetric behavior, and the conducting and insulating states are switched with opposite bias polarities [6]. The switching processes are as follows: Initially, after the forming step, the oxygen vacancies are sufficient in the segment of CuO_{1-x}. However, the dynamic resistance phenomenon did not appear even after the forming process, because the other half part of the nanowire is still CuO, which has a high resistance in the gigaohm range. In ‘set’



(a) (b) (c)

Fig. 4 Electron irradiation sensing with CuO nanowire based memristor. (a) The device demonstrates the hysteresis alike *I-V* traces as the proportion of the irradiation area δ reaches 2 ~ 5%. (b) The dual *I-V* traces as δ reaches 30%. The ratio of the R_{off}/R_{on} increased when it compares to the original status. (c) The ratio of the R_{off}/R_{on} linearly increased as δ reaches 50%.

procedure, the anode is placed on the end of CuO_{1-x} and the cathode is in the CuO side. As sweeping the bias from -1000 to 1000 mV, the vacancies in CuO_{1-x} part transport all through the nanowire driven by the electric force. Meanwhile, the conductive paths were formed following the direction of the applied electric field. Therefore, the conductivity of it was decreased. In 'reset' procedure, the electric force direction was switched according to the alternate of external polar, which in turn broke the conductive path along the nanowire and makes the resistance back to the original high status.

The nanowire based memristor we developed here not only shows the unique circuit properties such as voltage-current hysteresis and time-dependant resistance as traditional type, but also enables with a functional cylinder structure, which potential the applications in many areas.

IV. Memsensor

We investigate the use of a CuO nanowire as a memristor device by developing an e-beam forming method. The formed CuO_{1-x} segment serves as a reservoir of vacancies for the resistive switching process; providing cations to construct conductive path network along the nanowire. If we define the resistance in lower status as R_{off} and the higher status as R_{on}, it is noted that the ratio of the R_{off}/R_{on} is largely related to the proportion of the e-beam covered segment to the whole nanowire during the experiment of deoxidization of CuO into CuO_{1-x}. This is of particular interest for the application as electron irradiation sensors. Moreover, because an RS device can memorize the current that passed through it, a combination with a piezoresistive sensor can have the historical force/deformation information recorded; enabling a memristor based sensor.

It is found that the needed threshold proportion for the switching behavior is very low. About 2 ~ 5% of the partial nanowire e-beam irradiation will activate the memristor and induce the hysteresis alike *I-V* trace (Figure 4(a)). By further increasing the e-beam covered proportion δ, the ratio of the R_{off}/R_{on} increases further accordingly (Figure 4(a-c)).

Moreover, it has also been noted from these dual traces that the 'set' threshold voltage (right side) remains the same for the different irradiation situation (about 800 mV). However, the 'reset' threshold voltage (left side) varies. The difference of them is largely attributed to the nature of BRS; according to the form/rapture of the conductivity network path. The data collection for the reset transition procedure is insufficient, where the data are restricted by the sweeping range and the compliance current. Despite the fragmentary data for the reset, the switching behavior difference is remarkable. While further investigation is ongoing to develop the nanowire memristor into an accuracy transducer, the advantages are clear: the R_{off}/R_{on} ratio is obviously different on the 'set' end and the transition behavior is evident on the 'reset' side.

V. Conclusions

In summary, we have developed a BRS memristor based on CuO NWs with $CuO\text{-}Cu_2O$ hetero-junctions fabricated by e-beam-induced local de-oxidation. The BRS behavior is characterized *in situ* and the non-ohmic *I-V* characteristics have provided a solid evidence of the BRS switching. The EELS investigation has not only confirmed the transition between the copper oxides, but also possesses the potential to quantify the oxygen vacancy distribution. The mechanism of the switching has also been discussed. The CuO NW BRS memristor has enriched the binary transition oxide family and holds potential application as a memsensor. Owing to these advantages, the CuO NW based memristor will facilitate their applications in nanoelectronic and potentially in MEMS/NEMS.

Acknowledgment

This work is partially supported by the NSF (IIS-1054585).

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