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Resistive switching behavior of hexagonal sodium tungsten bronze nanowire

Le Lei[1], Yanling Yin[1], Chang Liu, Yong Zhou, Yuehua Peng, Fang Zhou, Jing Ling, Weichang Zhou, Dongsheng Tang*

Synergetic Innovation Center for Quantum Effects and Application, Key Laboratory of Low-dimensional Quantum Structures and Quantum Control of Ministry of Education, College of Physics and Information Science, Hunan Normal University, Changsha 410081, PR China

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ABSTRACT

Highly purified hexagonal sodium tungsten bronze nanowires, with diameters of 100–400 nm and lengths of 7–10 μm, have been synthesized via a hydrothermal method. Energy-dispersive X-ray Spectrometer quantitative analysis demonstrated directly that sodium ions can be drived to transport along the nanowire by the applied bias voltage. The current-voltage measurement results show that the Au/Na_xWO_3 nanowire/Au device exhibit different resistive switching behaviors under small and large bias voltage. The drift of sodium ions under a relatively large bias voltage might induce distinct changes in its concentrations near the junctions between Na_xWO_3 nanowire and Au electrodes, which will change the heights of these two Schottky barriers and switch this device to high or low resistance state accordingly. The existence of sodium ions also might induce strong disorder in WO_3 lattice, which will lead to the localization of states in the conduction band tail. The localized states can be filled or drained under a relatively small bias voltage, which will also switch the device to high or low resistance state. These two resistive switching mechanisms compete with each other, which endows the Au/Na_xWO_3 nanowire/Au system with more abundant resistive switching properties.

1. Introduction

The resistive switching behaviors of tungsten oxide (WO_3), as well as its electro-(photo-, gas-, thermo-)chromism, photocatalysis and gas sensor behaviors, have been investigated intensively [1–10]. In metal oxides, the resistive switching behaviors can be attributed to the formation and rupture of conductive filament or the increase and decrease of the contact barrier height, which might result from the drift of the positive-charged oxygen vacancies or metal cations from the active electrode under the electric field induced by bias voltage [11–17]. As for WO_3, the tunnel structures constructed from WO_6 octahedra leave more empty interstices in the oxygen sublattice, and then WO_3 can behave as a solid solvent towards the accommodation of external species into its solid framework to form stable intercalation compounds [18–19]. Particularly in hexagonal WO_3 (h-WO_3), there are one-dimensional hexagonal and trigonal tunnels along the *c* direction, which makes it easier for ions to transport reversibly and repeatedly. Therefore single crystalline h-WO_3 nanowires might be an ideal platform for studying the effect of electron-ion-coupled transport, and might be the best candidate for fabricating nanoscale resistive switching devices with stable and reliable performance.

In our previous researches, the two-terminal Au/h-WO_3nanowire/Au devices do exhibit memristive effect or resistive switching phenomenon, which can be modeled as two Schottky barriers with adjustable height connected back to back. By unidirectional bias voltage sweeping, the two-terminal resistive switching device can even be reconfigured gradually and reversibly from non-rectifying state to either a forward or reverse rectifying state [20–22]. The resistive switching performance of the Au/h-WO_3 nanowire/Au device can be enhanced remarkably when there is a water film on the surface, which might be attributed to the drift, accumulation and release of water-oxidized hydrogen ions in the water film [23]. The resistive switching performance of h-WO_3 nanowire can even be converted into digital type when the water-oxidized hydrogen ions are implanted into WO_3 lattice [24]. The inserted ions in the channel of h-WO_3 do offer a new technique for modulating the resistive switching performance. However, the hydrogen ions on the surface or in the lattice of WO_3 nanowire can easily be reduced to hydrogen gas by oxygens adsorbed on the surface or hot electrons injected from the electrode, and then its potential applications in field of resistive random access memory will be hindered seriously by the ubiquitous oxygen and even bias voltage.

In this work, sodium tungsten bronze (Na_xWO_3) nanowires have been successfully synthesized by hydrothermal method, and the effects of the transport of the sodium (Na^+) ions in the tunnels of h-WO_3 on its

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* Corresponding author.
E-mail address: dstang@hunnu.edu.cn (D. Tang).

[1] Le Lei and Yanling Yin contributed equally to this work.

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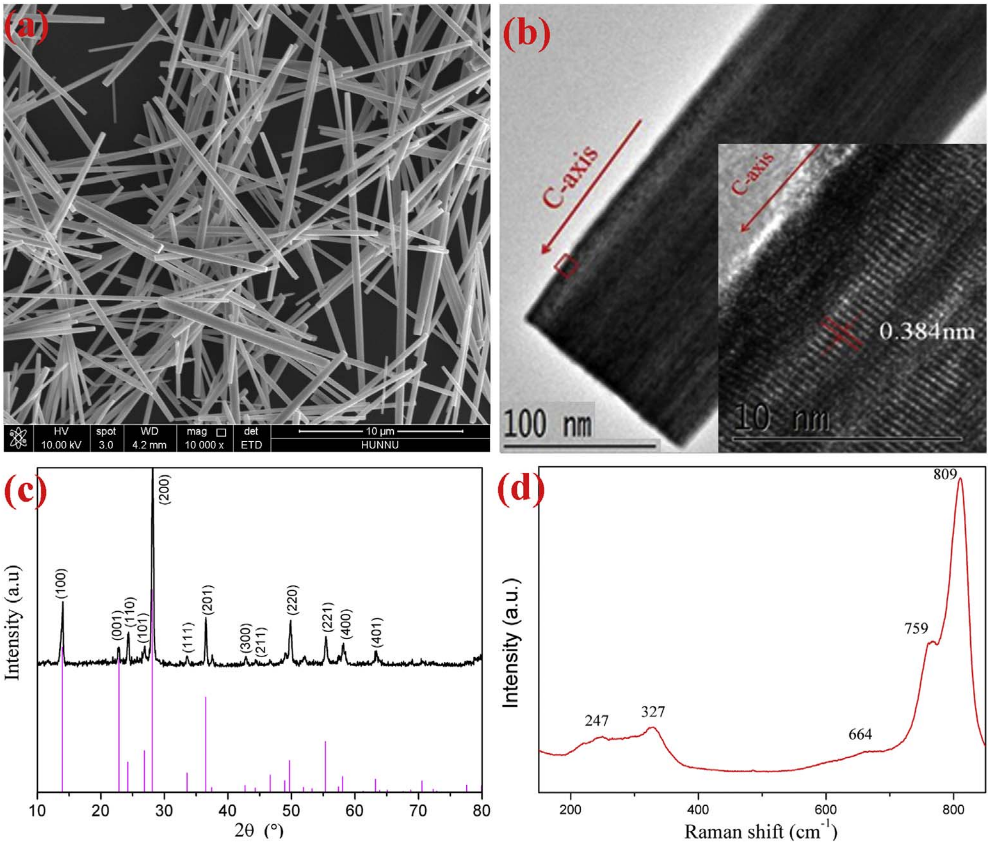

Fig. 1. SEM image (a), TEM image (b), XRD pattern (c) and Raman spectrum (d) of the as-synthesized products. The standard XRD pattern of hexagonal WO_3 (JCPDS card:75-2187) also shown in the bottom side of (c).

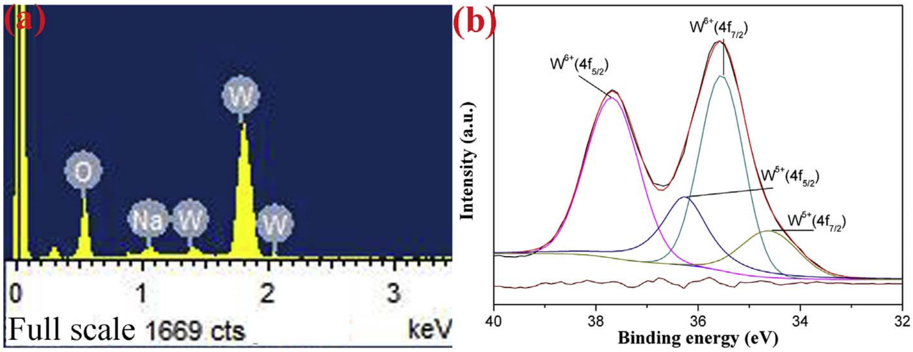

Fig. 2. EDS profile (a) and W_{4f} core-level XPS spectra (b) of the as-synthesized Na_xWO_3 nanowires.

resistive switching performance have been investigated based on the Au/h-Na_xWO_3 nanowire/Au sandwich structure with asymmetric contact barriers. Experimental results show that Na^+ ions can be drived to transport by applied bias voltage, and the Au/Na_xWO_3 nanowire/Au device exhibit different resistive switching behaviors under small and large bias voltage. These two resistive switching mechanisms endow the Au/Na_xWO_3 nanowire/Au system with more abundant resistive switching properties.

2. Experimental details

The Na_xWO_3 nanowires were synthesized by a simple hydrothermal method as previously reported [18]. All the reagents are of analytical grade and were used without further purification. In a typical synthesis process, sodium tungstate ($Na_2WO_4 \cdot 2H_2O$, 8.25 g) and oxalic acid ($H_2C_2O_2$, 6.3 g) were firstly dissolved in 240 mL deionized water. Secondly, a 60 mL volume of the mixed solution was transferred into a 100 mL teflon-lined stain less-steel autoclave, and then sodium sulphate (Na_2SO_4, 1.0 g) and hydrochloric acid (HCl, 14 drops) were added to the solution. The autoclave was sealed, heated at 240 °C for 24 h and then cooled down to room temperature naturally. The precipitates in the solution were filtered, washed sequentially with deionized water and ethanol to remove possible remnant ions, and then dried at 60 °C.

The sizes and morphologies of the as-synthesized products were characterized on scanning electron microscope (SEM, FEI, NovaSEM-450) and transmission electron microscope (TEM, FEI Tecnai G2 F20). The phase compositions and crystal structures of the samples were determined by X-ray diffraction analysis (XRD, Bruker D8 Advance, CuKα1, $\lambda = 0.15406$ nm) and Raman spectrometer (Bruker, E55 + FRA106, 514.5 nm, 5 mW). Energy-dispersive X-ray spectrometer (EDS, Oxford X-max20) was employed for approximate elemental analyses. The valence states of the element in samples were determined by X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific-Escalab 250Xi).

The individual Na_xWO_3 nanowires based electronic devices were fabricated on heavily n-doped Si substrate covered with a 100 nm thick thermally grown SiO_2 layer. As-synthesized Na_xWO_3 nanowires were first dispersed in ethanol by ultrasonic vibration and purified by centrifugation. Then, they were deposited on the substrate by dropping one droplet of the suspension on the surface. Then the Au contacts were