

Structure and field-emission properties of W/WO_{2.72} heterostructures fabricated by vapor deposition



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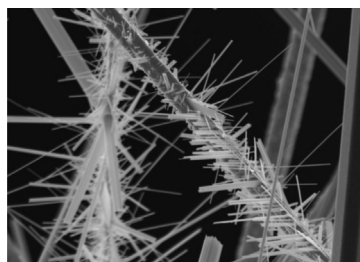
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HIGHLIGHTS

- W/WO_{2.72} heterostructures were synthesized by the chemical vapor deposition process.
- The long and straight central axial W whiskers grow along [1 1 0] direction.
- WO_{2.72} grows on side surface of the W whiskers, with [0 1 0] as the growth direction.
- The heterostructures have enhanced field emission property over the W whiskers.

GRAPHICAL ABSTRACT

A SEM image shows that a large number of the nanowires grow on the side surface of the W whisker stems.



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ABSTRACT

One dimensional W/WO_{2.72} heterostructures were successfully synthesized using WO₃ as the raw material by a simple two-step chemical vapor deposition process. The morphology and microstructure of the W/WO_{2.72} heterostructures were characterized using scanning electron microscopy and transmission electron microscopy. The results indicate that the long and straight central axial W whiskers grow along [1 1 0] direction, while the branched WO_{2.72} nanowires grow on the side surface of the W whiskers along the radial direction, with [0 1 0] as the growth direction. The as-synthesized heterostructures exhibit enhanced field emission property over the single W whiskers, and could be used as a candidate for field-emission devices and ultrahigh sensitivity sensors due to their unique composition and structure.

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1. Introduction

One-dimensional (1-D) nanostructures attract extensive attentions and show potential applications as functional materials due to their fascinating properties [1]. Among 1-D nanostructures, 1-D heterostructures with modulated compositions and interfaces show unique characteristics and potential applications as nanoscaled building blocks for future optoelectronic devices and systems [2].

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The well-designed and controlled heterostructures usually have special properties because the cores and branches are composed of various materials with different characteristics. For example, core/shell structured CdS/ZnS heterojunctions have enhanced photoluminescence efficiencies and electrical response, compared to those of the single CdS nanorods [3]. Core/shell structured TiO₂/CdS nanorods show potential applications for the reversible conversion between solar energy and electrical energy, due to their long-lived charge-separated state and large photo current density [4]. As one of the best electrode materials for high-performance super capacitors, core/shell structured Co₃O₄/NiO nanowire arrays exhibit excellent super capacitor performance with high specific capacitance and good cycling stability. The dual phase ZnS with tetrapod tree-like

heterostructures and branched architectures have excellent field-emission properties due to their specific crystallographic feature and cone shape patterned branch with nanometer-sized tips [5,6]. The hierarchical core-shell structures consisting of primary ZnS nanotubes, indium (In) core nanowires, and ZnS nanowire secondary branches present multifold enhanced field-emission property [7]. Till now, many methods have been developed to fabricate 1-D nanostructures, such as vapor phase methods, solution phase methods, lithography processes, electro spinning and template methods [2]. Various types of the 1-D heterostructures have been reported, including core/shell and core/multi-shell nanocable structures, coaxial nanowire heterojunctions, epitaxial nanorod heterostructures, and hierarchical heterostructures [8]. For example, Shen et al. successfully synthesized co-axial and C-coated ZnS core/shell nanocables by thermal evaporation of a mixture of ZnS and SnS powders in a graphite crucible [9]. Ren et al. reported the fabrication of a hierarchical ZnO/In₂O₃ nanostructure using a simple evaporation method [10]. It should be noted that most of the 1-D heterostructures are the combination of various semiconductors, and the reports on metal/metal oxide 1-D heterostructures are very rare. Till now, most reported metal/metal oxide heterostructures are limited to Zn/ZnO [10].

Tungsten (W) is a refractory metal with a series of outstanding physical and chemical properties, such as the highest melting point of about 3420 °C and the lowest vapor pressure among all metals, the decent strength and rigidity at room and elevated temperatures, the excellent corrosion resistance against metal and oxide vapors and a near-ideal midgap work function [8,11]. W can be used in metal gates in the applications of complementary metal oxide semiconductor (CMOS) technology in nanodevices smaller than 100 nm [8], and can also be used as field emission (FE) gun [11]. Previous studies have revealed that individual tungsten nanowires possess an ultra-high field enhancement factor and a high stability of the FE current density [11,12].

Tungsten oxides are particularly applicable in flat panel displays, photoelectrochromic smart windows, optical modulation devices, writing–reading–erasing optical devices, lithium-ion batteries, dye-sensitized solar cells, catalysts and gas sensors [13–19]. When the size decreases to the nano-scale, tungsten oxide nanostructures exhibit some fascinating properties and applications superior to their bulk counterparts, such as ultra sensitive and highly selective gas sensors [20], and excellent field-emission properties [21,22]. Although 1-D nanostructures of W and WO_x have been studied extensively, with a variety of nanometer-scaled structures of W and WO_x being synthesized and their structures and properties being also investigated thoroughly, few studies on W/WO_x heterostructures have been reported. Baek et al. reported the fabrication of a novel W/WO₃ hierarchical heterostructures, with single-crystalline W nanothorns grown on WO₃ nanowhiskers using Ni as the catalyst by a two-step evaporation process [8]. However, the growth process and morphology cannot be controlled effectively [8]. Our previous work showed that W whiskers can grow on Si, SiO₂ or Al₂O₃ substrate, and WO_{2.72} nanowires can grow on W substrate using the vapor deposition method [11,23]. It is therefore reasonable to propose that WO_{2.72} nanowires can grow on W whiskers. In this paper, a novel hierarchical heterostructure with single-crystalline WO_{2.72} nanothorns growing on W whiskers (referred to W/WO_{2.72}) was fabricated successfully. The morphology, microstructure, growth mechanism and field emission property of the heteronanostructure were investigated.

2. Experimental

The heterostructures were fabricated using chemical vapor deposition in a system similar to that reported previously [23].

The synthesis process took place in a conventional tube furnace without vacuum pump. Tungsten trioxide powders (99.9% in purity) were used as the raw material and Si wafers (6 mm × 4 mm × 1 mm) were used as the substrate. WO₃ powder and Si substrates were placed on both sides of the small exit (3 mm × 3 mm) of a quartz tube (20 mm in diameter), and the quartz tube was placed in the horizontal tube furnace (60 mm in diameter and 600 mm in length). High-purity Ar with a constant flow of 200 standard cubic centimeters per minute (sccm) was introduced into the quartz tube and H₂ with a constant flow of 100 sccm was introduced into the furnace tube. The pressure in the reactor was 1 bar during the whole reaction process. Then the temperature of the furnace was increased from room temperature to 950 °C with a rate of 10 °C/min. When the furnace was heated to 600 °C, Ar gas contained water vapor was introduced into the system (the content was controlled by water bath's temperature). After maintained at 950 °C for 4 h, the furnace was naturally cooled down to 700 °C and the H₂ flow was shut off. Then the furnace was holding at 700 °C for 30 min, 2 h and 4 h. After the furnace was naturally cooled down to room temperature, the samples were taken out for characterization. The final products were investigated using X-ray diffraction (XRD, D/max 2550VB with Cu K α -radiation), scanning electron microscopy (SEM, Nova Nano SEM 230) and transmission electron microscopy (TEM, JEOL-2100F) operating at 200 kV.

Field-emission property of the W/WO_{2.72} heterostructures was tested at room temperature, using a two-parallel-plate configuration in a lab-built high vacuum system with a pressure of 10^{−7} Pa. The Si substrate was fixed on a Mo holder that acts as cathode. A rod-shaped copper probe with an equivalent cross-sectional area of 0.8 mm² was used as anode. The distance between the anode and cathode was kept at 320 μ m. A high voltage source measurement system was used to sweep the applied voltage from 0 to 4000 V with an increment of 100 V per step. At the same time, the emission current was measured.

3. Results and discussion

3.1. Morphology and structure characterizations

Fig. 1a is a typical SEM image of the 1-D heterostructures holding at 700 °C for 4 h, showing that a large number of nanowires grow on the side surface of the W whisker stem. The whisker stem is of a diameter of 200–500 nm and a length of 5–15 μ m. The branched nanowires are straight and smooth with a typical length of several hundred nanometers and a diameter ranging from 20 to 50 nm. Fig. 1b is the SEM image of the heterostructures holding at 700 °C for 2 h, clearly showing that much less nanowires grow on the W whisker stem, with the length and diameter being much smaller than those of the heterostructures synthesized for 4 h. Fig. 1c is the SEM image of the 1-D heterostructures holding at 700 °C for only 30 min, from which a small number of nanowires with quite short lengths were observed, indicating that the growth of the nanowires on W whiskers has just started. Further observation on the heterostructure in Fig. 1c indicates that the nucleation and growth of nanowires on W whiskers are not homogenous, leading to the inhomogeneous length and diameter of nanowires (Fig. 1a) during the following growing process. One should be noted that the diameter of the W stems in Fig. 1a differs from that in Figs. 1b and c. In general, the diameter of the W whiskers are controlled by growth temperature and the distance between Si substrate and the exit of the quartz tube substrate, as shown by Liu et al. and Wang et al. [11,24]. In this study, the difference in diameter of the W stems is due to the distance between the Si substrate and the exit of the quartz tube substrate, since the growth temperature

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