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Growth of ultra-long sodium tungsten oxide and tungsten oxide nanowires: Effects of impurity and residue deposition

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ABSTRACT

Ultra-long nanowires of sodium tungsten oxide and tungsten oxide were synthesized by simply heating tungsten source under a low oxygen pressure environment. The nanowires have diameters of ~40 to 500 nm and lengths from tens to several hundred microns. The majority of the nanowires were found to be triclinic $Na_5W_{14}O_{44}$ with small amount of monoclinic WO_3. Triclinic $Na_2W_4O_{13}$ microplates with a rectangular shape grown together with the nanowires were also identified. The formation of ultra-long nanowires is explained by the vapor–solid (VS) growth mechanism. Effects of impurity and residue deposition have been thoroughly investigated. With a low concentration even smaller than 10 ppm (parts per million), the sodium impurity in the tungsten source could result in the formation of sodium tungsten phases. The growth of nanowires could be enhanced with the presence of residue deposition and the enhancement was attributed to the production of local vapor pressure from the residue deposition.

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1. Introduction

Tungsten trioxide (WO_3) is a versatile semiconductor material with a wide range of applications [1], such as smart devices (e.g., electrochromic [2], photochromic [3], and gasochromic devices [4]), solar water splitting [5], gas sensors [6], memory devices [7], filed emission [8], and photodetectors [9], etc. At room temperature, the most stable phase is the monoclinic γ-WO_3 which has a tilted ReO_3-type crystal structure with corner-sharing WO_6 octahedra [10,11]. Light ions, such as H^+, Li^+, and Na^+ can be easily intercalated into the WO_3-framework forming a family of different metal tungsten oxides (i.e. tungstates or tungsten bronzes) with a general formula of $M_x^{(z)}WO_{3-y+zx/2}$, where M is the bronze-forming metal, z the valency of M, and y characterizes oxygen deficiency with $y \neq zx/2$ [12]. Among them, sodium tungsten oxides ($Na_xWO_{3-y+x/2}$) are one group of tungsten bronzes which have been extensively studied due to their unique character of tuning material structures and properties by composition control. For example, the Na_xWO_3 bronzes ($0<x<1$), formed by doping the insulating WO_3 host with Na ions, can change from n-type semiconductor ($x<0.3$) to metallic conductor ($x>0.3$) by increasing the x value [12,13]. Attractive two-dimensional high-temperature superconductivity of Na-doped WO_3 has also been observed with a surface composition of Na_xWO_3 ($x=0.05$–0.07) [13–15]. With the increase of x, the Na_xWO_3 can have a continuous color change from blue to violet, red, and golden, as well as a crystal structure change from monoclinic through orthorhombic, tetragonal, to cubic [16]. Sodium tungsten oxides have wide applications in photocatalysis [17], chemical analysis [18], fuel cells [19], smart windows [20], and near-infrared shielding [21].

Recent years, with the advancement of nanoscale research, nanostructured WO_3 especially the one-dimensional (1D) nanostructures (e.g., nanowires, nanobelts, and nanorods, etc.) have attracted intensive research efforts on material synthesis, property measurement, and device testing [22]. However, the study of 1D sodium tungsten oxide nanostructures is limited so far with only a few papers published on cubic Na_xWO_3 nanorods and nanobelts [23], hexagonal $Na_{0.17}WO_{3.085} \cdot 0.17H_2O$ and $Na_{0.3}WO_3$ nanorods [21], $Na_2W_4O_{13}$ nanofibers [24], cubic and tetragonal Na_xWO_3 nanobundles [25], and triclinic $Na_{0.5}WO_{3.25}$ nanoplates [26].

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In this work, we report the growth of ultra-long nanowires of sodium tungsten oxide and tungsten oxide with diameters of ~40 to 500 nm and lengths from tens to several hundred microns by simply heating tungsten source under low pressure oxygen environment. The majority of the nanowires were found to be triclinic $Na_5W_{14}O_{44}$ with small amount of monoclinic WO_3. Rectangular microplates of triclinic $Na_2W_4O_{13}$ grown together with the nanowires were also identified. It was observed that the formation of nanowires could be enhanced with the presence of residue deposition on the wall of reaction chamber. The growth mechanism of the ultra-long nanowires will be discussed. The impurity effect on the formation of sodium tungsten phases and the effect of residue deposition on the enhanced nanowire growth have been thoroughly investigated.

2. Experimental details

Samples were synthesized using a chemical vapor deposition (CVD) method. A home-built hot-wall low pressure CVD system with a reaction chamber of 1" diameter quartz tube heated by two semi-cylindrical ceramic fiber heaters was employed for the growth. Similar CVD systems have been used for the growth of nanostructures of boron [27], borides [28], titanium oxide [29], and tungsten oxide [30]. Silicon (100) substrates with a 1-μm-thick thermally grown oxide layer (SiO_2–Si, University Wafer) were used in this study. Substrates were first cut into rectangular pieces with a size of 10 mm × 35 mm, and then were ultrasonically cleaned with acetone and alcohol for about 10 min each followed by blow-drying with nitrogen gas. Tungsten powders with a purity of 99.9% (Alfa Aesar 39749, Lot #: H17Q06, −325 mesh) were mainly used as the source materials for the growth. Other tungsten sources with different purities and sizes were also used for control experiments. In a typical experiment, about 2 g tungsten powders were loaded into a quartz boat at its upstream end with a substrate located about 63 mm apart at the downstream end. The boat was then loaded inside the reaction chamber with the tungsten source located at the center of the furnace. The reaction chamber was first pumped down to an ultimate vacuum pressure of ~7 mTorr, and then brought up to 110 mTorr with 1 sccm (standard cubic centimeter per minute) O_2 and 10 sccm Ar. The system was then ramped to a heating temperature of 1000 °C at the center in 30 min and held for 4 h, followed by cooling down to room temperature in about 5 h. Variations of nanostructure morphologies were observed if multiple growths were employed repeatedly in the same reaction chamber of quartz tube. Hence, a series of experiments were performed in the same reaction chamber with the increase of the growth number (defined as the order of the growths employed in the same reaction chamber).

The morphology and composition of the as-synthesized samples were analyzed by scanning electron microscopy (SEM, JEOL JSM-6480) and energy dispersive X-ray spectroscopy (EDS, Oxford Instrument INCA). Crystal structures were characterized using X-ray diffraction (XRD, PANXpert X'pert Pro MRD with Cu K_α radiation at $\lambda = 1.5418$ Å) and transmission electron microscopy (TEM, JEOL JEM-2100 LaB_6 operated at an accelerating voltage of 200 kV). Micro-Raman spectroscopy (Horiba Scientific, Jobin Yvon Labram HR800 with 532 nm excitation laser) was performed to confirm the phases of different nanostructures.

3. Results and discussion

3.1. Morphology and structure characterization

Fig. 1(a) shows SEM images of typical morphologies of the as-synthesized nanostructures grown on a SiO_2–Si substrate. The nanostructures are ultra-long nanowires with lengths from tens of microns up to several hundred microns and diameters about 40–500 nm. The deposition of nanowires was generally located on the substrates with a growth temperature range from 660 to 420 °C. Close-up observations at high magnification revealed that some nanowires were cylinder-shaped and some were belt-shaped (shown in the inset of Fig. 1(a)). At some locations, microplate structures with a regular rectangular shape were grown among the nanowires as demonstrated in Fig. 1(b) and its inset. The chemical compositions of these structures were identified by EDS. A representative EDS spectrum in Fig. 1(c) shows the existence of W, Na, O, and Si signals in the specimen, where

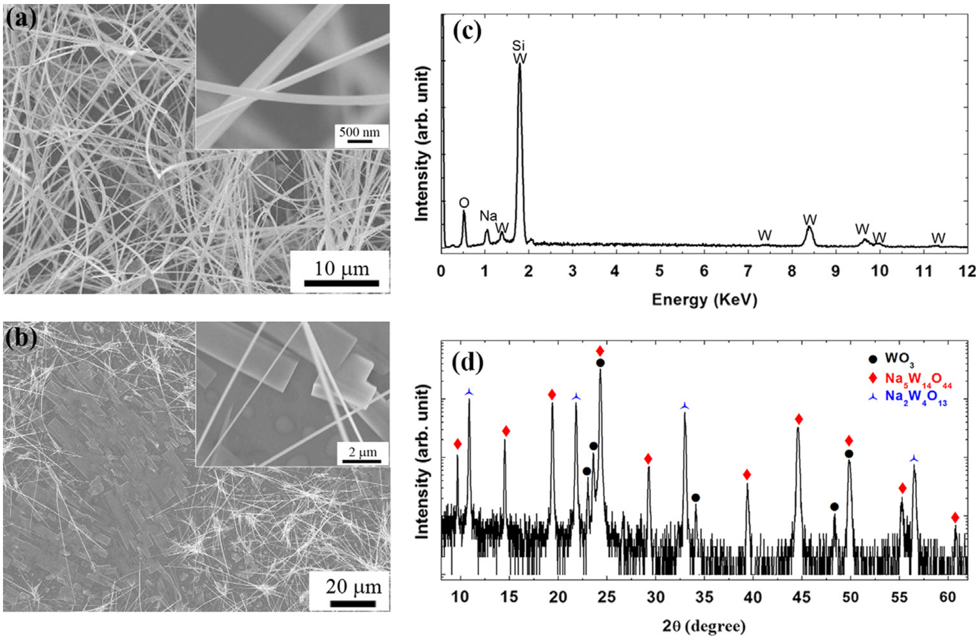

Fig. 1. SEM images of (a) dense array of the as-synthesized ultra-long nanowires on SiO_2–Si substrate and (b) the rectangular microplates grown among the nanowires. The insets show corresponding close-up views. (c) EDS and (d) XRD spectra showing the chemical compositions and phases of the deposition.

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