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Synthesis and field-emission properties of the tungsten oxide nanowire arrays

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Abstract

High-density, uniformly distributed and quasi-aligned tungsten oxide nanowire arrays have been synthesized by a conventional thermal evaporation approach on indium tin oxide (ITO) coated glass substrates without any catalysts. The temperature of the substrate was 450−550 °C. The tungsten oxide nanowires are single crystalline with growth direction of [0 1 0]. For commercial applications, field emission properties of tungsten oxide nanowires were studied under a poor vacuum at room temperature. The electron field-emission turn-on field (E_{to}), defined as the macroscopic field required to produce a current density of 10 μA/cm^2, is about 3.6 V/μm. The performance reveals that the tungsten oxide nanowire arrays can be served as a good candidate for commercial application in field-emission displays.

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Keywords: Tungsten oxide; Nanowire arrays; Field emission

1. Introduction

One-dimensional (1D) nanomaterials have stimulated great attention due to their promising applications in nanodevices [1]. And field emission (FE) from various 1D nanostructures has been intensively investigated over the last several decades [2–8]. Especially, tungsten oxide 1D nanostructures have attracted more attention due to their high aspect ratio, low turn-on field, and highly stable emission [5,9,10]. Tungsten oxide is an n-type semiconductor with a work function in the range of 5.59–5.7 eV [11,12] which makes it attractive for the stated applications. Tungsten oxide has also been demonstrated to be suitable for various other applications such as electrochromic, optochromic and gasochromic coatings for smart windows, information display and various sensors [13,14].

Recently, various types of tungsten oxide nanostructures, including nanowires [15–19], nanotips [5], nanobelts [20], nanotubes [9], and 3D nanowire networks [10], have been synthesized. However, the tungsten oxide nanowires were grown at a relatively high temperature. For the practical application in devices, it is very necessary to synthesize tungsten oxide nanowire arrays at low temperature on alien substrate. Galléa et al. and Li et al. have synthesized tungsten oxide nanorods on Si substrate at low temperature by heating tungsten coil [21,22]. But, most of them use tungsten as the source reacting with H_2O or O_2 to synthesize tungsten oxide nanostructures. In this paper, we have successfully synthesized 1D tungsten oxide nanowire arrays on indium tin oxide (ITO) coated glass substrates without external catalysts by a conventional thermal evaporation approach, using tungsten oxide powders as the thermal evaporation source. The temperature of the substrate was 450−550 °C, and much lower than that having been reported by Zhou et al. [5,10]. For commercial applications, field-emission characteristics of these nanowire arrays have been measured under a poor vacuum condition.

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2. Experimental

The synthesis of tungsten oxide nanowire arrays in our experiment is based on thermal evaporation of tungsten trioxide powders (99.9%) under controlled conditions without any catalysts. The tungsten trioxide powders were placed at the center of an alumina tube that was inserted in a horizontal tube furnace. The ITO-coated glass (10 mm × 10 mm) as the substrates were placed at the end of the alumina tube. After evacuation to a pressure of about 2×10^{-3} Torr, the temperature in the center of the tube was elevated to 1100 °C at a rate of 20 °C min^{-1}, and the temperature of the substrate region was 450−550 °C. Under the gas flow of Ar and O_2 at rate of 100 sccm (standard cubic centimeters per minute) for 2 h, the total pressure of the chamber was kept at 200 Torr. After the furnace slowly cooled down to room temperature, the substrates covered with the resulting products were collected.

The as-deposited products were characterized and analyzed by X-ray diffraction (XRD) (Rigaku RINT2400 with Cu Kα radiation), scanning electron microscopy (SEM) (Hitachi S800), and high-resolution transmission electron microscopy (HRTEM) (JEM 2100, 200KV).

3. Results and discussion

Fig. 1 shows typical SEM images of tungsten oxide nanowire arrays grown on ITO-coated glass substrate. Fig. 1a is a top view image, and the tungsten oxide nanowires were high-density, large-scale and well separated from each other. Fig. 1b shows a cross section SEM image of the tungsten oxides nanowires, revealing that those nanowires with an average length of ~5 μm were grown perpendicular to the substrate, with a diameter of 100−150 nm. We suggest that the method in our experiment can be applied to manufacture large-scale, high-density and uniformly distributed tungsten oxide nanowire arrays.

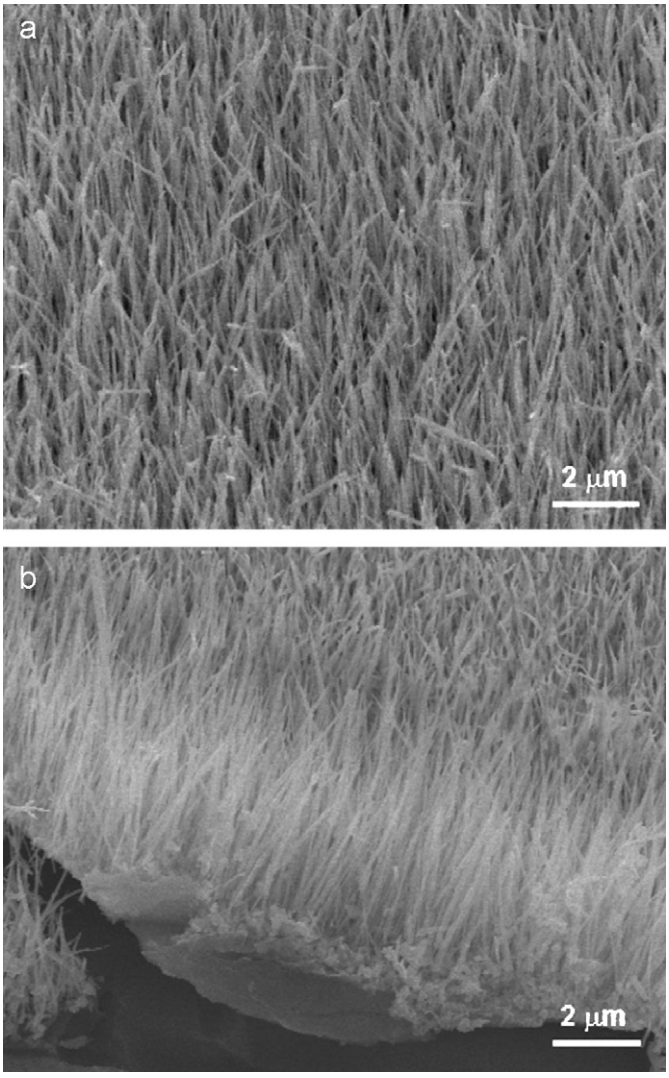

Fig. 1. SEM images of the quasi-aligned tungsten oxide nanowire arrays on ITO-coated glass substrate. (a) Top view image, (b) cross section image.

The XRD spectrums of the tungsten oxide nanowire arrays and ITO-coated glass substrate are shown in Fig. 2. The diffraction peaks (in Fig. 2a) can be well indexed to a monoclinic $W_{18}O_{49}$ phase (cell constants: $a = 18.28$ Å, $b = 3.775$ Å, $c = 13.98$ Å, $\beta = 115.20°$; JCPDS 05-0392), and the [0 1 0] direction is the major growth direction of the nanostructure. It is noted that no peaks associated with the ITO substrate (in Fig. 2b) can be observed in the tungsten oxide nanowire arrays, probably because of the high-density of the nanowires deposited.

To further illuminate the detailed microstructures of the tungsten oxide nanowires, HRTEM images of a nanowire are given in Fig. 3. The fast Fourier transform (FFT) pattern (inset of Fig. 3a) is calculated from the square-enclosed areas in Fig. 3a. These streaks in the FFT possible arise from the presence of planar defects parallel to the growth direction. Fig. 3b presents the enlarged HRTEM image of the nanowire. The lattice spacing is 0.378 nm correspond to (0 1 0) plane of monoclinic $W_{18}O_{49}$. FFT pattern and the spacing of the lattice plane measurement show that the monoclinic $W_{18}O_{49}$ (JCPDS 05-0392) nanowire is single crystalline with a growth direction of [0 1 0]. That is in good agreement with our XRD analysis.

No catalyst was used in our growth process, and the vapor–solid (VS) growth process may be suitable for our case [1]. The tungsten oxide vapor can be evaporated at a higher temperature zone directly deposits on ITO-coated glass substrates at a lower temperature region and grows into 1D nanostructure.

Field emission measurements were carried out in a chamber with a poor vacuum of $\sim 1.0 \times 10^{-5}$ Torr at room temperature. A rod-like aluminum probe with 3 mm^2 in cross section was used as an anode and the tungsten oxide nanowire arrays film served as a cathode. As with any emitter operated in commercial environments, the ability to withstand poor vacuum conditions can be crucial. Oxide