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Synthesis and study of the SnO_2 nanowires growth

Ming-Ru Yang [a], Sheng-Yuan Chu [a,b,*], Ren-Chuan Chang [a]

[a] *Department of Electrical Engineering, National Cheng Kung University, Tainan 701, Taiwan*
[b] *Center for Micro/Nano Technology Research, National Cheng Kung University, Taiwan*

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Abstract

In this study, tin dioxide (SnO_2) nanowires were synthesized on a silicon substrate (1 1 1) using a direct gas reaction route on a large scale at 800 °C. These SnO_2 nanowires were characterized by X-ray powder diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Raman-scattering spectroscopy. XRD, SEM and TEM indicated that the products were tetragonal SnO_2 nanowires with lattice parameters of $a = 4.73$ Å and $c = 3.17$ Å. Three vibration modes were observed at 478, 634, and 776 cm^{-1} in the Raman spectra of the samples. Complex impedance analysis of SnO_2 nanowires well fitted with a simple RC electrical model. According to the current–voltage (I–V) measurements, it was found that the SnO_2 nanowires were a good sensing for detecting carbon monoxide. The response to 500 ppm CO of the SnO_2 nanowires reached 60%.

Keywords: SnO_2; Nanowires; Gas sensor; CO

1. Introduction

In the past decade, one-dimensional nanostructures, such as nanotubes, nanowires and nanobelts, had attracted considerable attentions from researchers because of their peculiar structure characteristics and size effects. Recently, a variety of one-dimensional nanostructures with different materials (ZnO, SnO_2, In_2O_3, CdO, MgO_2, PbO_2, etc.) were successfully synthesized [1–4]. Among these materials, SnO_2 is a very important n-type semiconductor with a wide bandgap ($E_g = 3.6$ eV at 300 K). As a transparent conducting oxide (TCO), it has been widely used as optoelectronic devices such as flat panel displays and thin film solar energy cells [5]. As an n-type semiconductor, tin dioxide has been actively explored as the functional component in detecting combustible gases such as CO, H_2 and CH_4 [6]. Most of these studies concentrated on devices, which were fabricated with polycrystalline films as the sensing units [7]. Recent investigating indicated that nanostructures of SnO_2 could also be employed to detect various gases [8–11]. Such single-crystalline nanowires as sensing elements have several advantages over conventional thin film oxide sensors: low operating temperature, no ill-defined coarse-grain boundaries, and a high surface-to-volume ratio.

Different synthesizing methods have been reported for producing SnO_2 nanostructures, such as thermal decomposition of $SnCl_4{\cdot}5H_2O$ in a melt salt (NaCl) [12], self-catalytic VLS (the vapor–liquid–solid process) growth [13,14], addition of tin oxalate to EG ($C_2H_6O_2$ ethylene glycol; when tin oxalate to EG and refluxed at 195 °C, white precipitate would start to appear in the reaction mixture after 2 h) [8], and the oxidation of tin vapor [16–20]. In our research, the vapor transport method was introduced to synthesize the SnO_2 nanowires. The tin vapor was supplied from tin powders heated in argon atmosphere and reacted with oxygen at 700–1000 °C. We have measured the temperature dependence of the resistances and the I–V curves of the SnO_2 nanowires. Based on the resistances data, we can also calculate the response magnitude of the SnO_2 nanowires to carbon monoxide (CO) of different concentration.

2. Experimental procedure

The synthesis process of the SnO_2 nanowires is briefly described by the following chemical reaction:

$$Sn + O_2 \rightarrow SnO_2 \quad (1)$$

* Corresponding author. Tel.: +886 6 2757575x62381; fax: +886 6 2345482.
E-mail address: chusy@mail.ncku.edu.tw (S.-Y. Chu).

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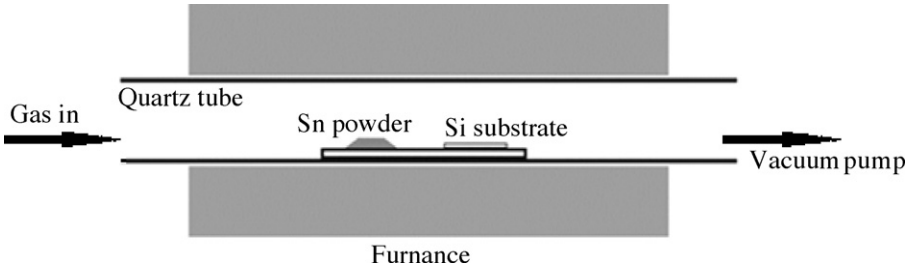

Fig. 1. Experimental setup. Tin powder and the silicon substrate were separated by 10 mm in the center of the quartz tube.

The SnO_2 nanowires were synthesized on a silicon substrate (1 1 1) by heating pure tin powder (325 mesh, 99.8%) at 800 °C in a quartz tube. An appropriate amount of tin powder (about 1 g) and the silicon substrate separated by 10 mm were put in the center of a quartz tube, as shown in Fig. 1. The substrate was located downstream of the Sn powder. The quartz tube was first evacuated at 10^{-2} Torr by a vacuum pump. Then, it was filled with argon. The quartz tube was heated to 800 °C rapidly (20 min) under a flowing argon (10 ml/min) atmosphere. Subsequently, it was kept at that temperature for 2 h, and a flow of oxygen about 50 ml/min was switched on. Finally, the quartz tube was cooled down to room temperature. After reaction, the SnO_2 nanowires were found on the substrate. In order to measure *I–V* characteristics of the SnO_2 nanowires, we used Ag as electrodes and the distance between two electrodes was 500 μm on a sapphire substrate. These nanowires were exposed to heat treatment in order to form ohmic junction between Ag electrodes and SnO_2 nanowires.

These products were then characterized by X-ray diffraction (XRD; Siemens D-5000 with Cu Kα radiation and a normal θ–2θ scan), scanning electron microscopy (SEM; Hitachi S-4100), transmission electron microscopy (TEM; Zeiss 10C), Raman spectroscopy (Triax 550 monochromator), and current–voltage measurement (*I–V*; Keithley 2400).

3. Results and discussion

Fig. 2 shows the SEM images of the products deposited at 800 °C and at a flow rate of O_2 of about 50 ml/min on a silicon substrates (1 1 1). It is seen that the products consisted of a large quantity of nanowires as well as particles underlying the nanowires. The diameters of SnO_2 nanowires range from several tens to several hundreds of nanometers with lengths of the order of millimeters, and the width-to-thickness aspect ratios of these nanowires are smaller than those of nanobelts. The mean width of SnO_2 nanowires notably increased with the temperature. This is because when the growth temperature increases, tin and oxygen atoms get more energy to grow into SnO_2 crystals, resulting in an increasing in diameter of SnO_2 nanowires. All these nanowires were smooth and uniform along the fiber axis.

The XRD pattern of SnO_2 nanowires synthesized at 800 °C is shown in Fig. 3. All of the diffraction peaks can be perfectly indexed to the tetragonal rutile structure of SnO_2 not only in peak position but also in relative intensity. The SnO_2 lattice constants of the nanowires calculated by the XRD data were $a = 0.473$ nm and $c = 0.317$ nm, which well agreed with the reported values ($a = 0.4732$ nm and $c = 0.3184$ nm) in JCPDS card No. 21-1250. A TEM image of a straight single SnO_2 nanowire with a diameter of about 20 nm is shown in Fig. 4. The selected-area electron diffraction pattern (SAED, inset in Fig. 4) taken from a section of the nanowire can be indexed on a tetragonal cell with lattice constants of $a = 0.474$ nm and $c = 0.318$ nm, agree with the XRD result. The SAED pattern also verifies that the nanowire is a single crystal of rutile SnO_2.

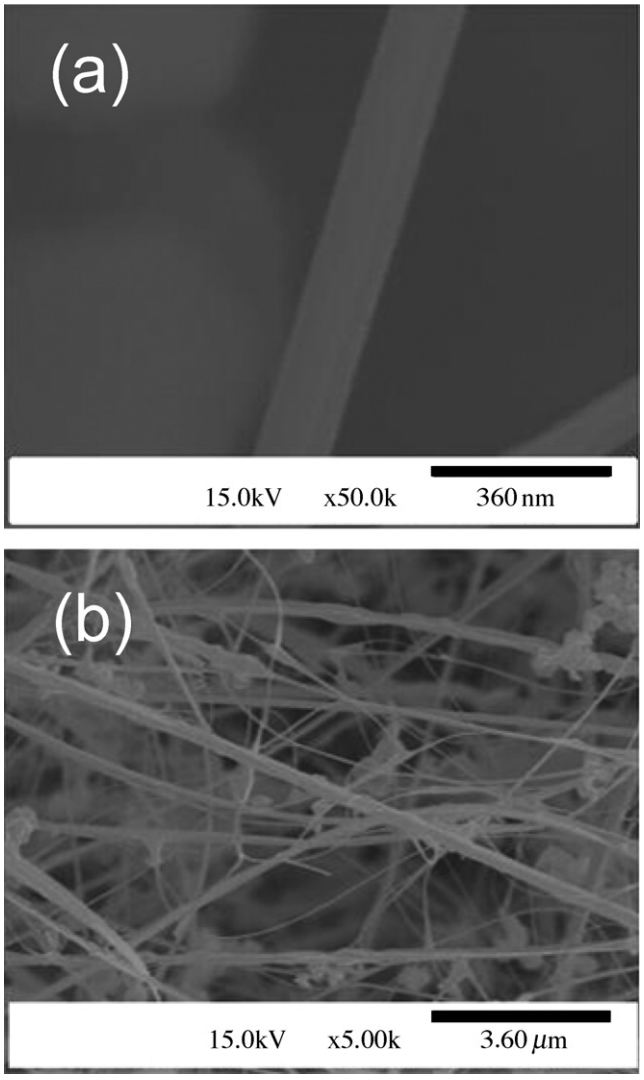

Fig. 2. The SEM images of SnO_2 nanowires synthesized at 800 °C on a Si (1 1 1) substrate.