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Studies on the optoelectronic properties of the thermally evaporated tin-doped indium oxide nanostructures

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ABSTRACT

Indium oxide (In_2O_3) nanorods, nanotowers and tin-doped (Sn:In = 1:100) indium oxide (ITO) nanorods have been fabricated by thermal evaporation. The morphology, microstructure and chemical composition of these three nanoproducts are characterized by FE-SEM, HRTEM and XPS. To further investigate the optoelectronic properties, the *I–V* curves and cathodoluminescence (CL) spectra are measured. The electrical resistivity of In_2O_3 nanorods, nanotowers and ITO nanorods are 1.32 kΩ, 0.65 kΩ and 0.063 kΩ, respectively. CL spectra of these three nanoproducts clearly indicate that tin-doped (Sn:In = 1:100) indium oxide (ITO) nanorods cause a blue shift. No doubt ITO nanorods obtain the highest performance among these three nanoproducts, and this also means that Sn-doped In_2O_3 nanostructures would be the best way to enhance the optoelectronic properties. Additionally, the growing mechanism and the optoelectronic properties of these three nanostructures are discussed. This study is beneficial to the applications of In_2O_3 nanorods, nanotowers and ITO nanorods in optoelectronic nanodevices.

1. Introduction

During the last few years, many researchers have been obsessed with investigating low-dimensional nanostructures due to their exceptional characteristics and applications. Thanks to large surface-area-to-volume ratios and super-dense oxygen vacancies, plenty of semiconductor nanostructures, such as SnO_2, ZnO, Ga_2O_3, In_2O_3 and so on [1–5], have been widely applied in many fields. For instance, the SnO_2 and ZnO nanowires can be used for detecting toxic gas and harmful light sensors. Similarly, the Ga_2O_3 nanowires are able to be used as optical devices. In terms of optoelectronic properties, the In_2O_3 nanostructures are second to none in all nanomaterials. Indium oxide (In_2O_3) is a world-renown n-type wide direct bandgap (3.65 eV at room temperature) transparent semiconductor [6–8]. To improve In_2O_3 properties, researchers have successfully synthesized various nanostructures, e.g., nanorods, nanotowers, nanowires and nanotubes. According to these literatures [7–10], it is clear that different morphologies and phase structures of In_2O_3 nanostructures lead to diverse properties. On the other hand, doping tin into In_2O_3 nanostructures would be another effective method to enhance In_2O_3 properties [8,11–14]. Tin-doped indium oxide (ITO), an n-type wide band gap (over 3 eV) degenerated semiconductor, owns high optical transmission (over 80%) and low electrical resistivity (less than 10^{-3} Ω cm) and has been intensively investigated recently [6–8].

Several theoretical studies have demonstrated that In_2O_3 nanostructures can be obtained by several ways including laser ablation, sol-gel process, hydrothermal method, electrochemical deposition and thermal evaporation [15–21]. Most of all, thermal evaporation is a quite efficient technique to produce high-performance semiconductor nanostructures. By modifying the process parameters, such as adjusting atmosphere, reaction time, temperature and holders' shapes, various morphologies and phase structures are under control easily [20,21].

In this task, the authors have successfully fabricated In_2O_3 one-dimension nanorods, nanotowers and ITO nanorods via thermal evaporation. In order to discuss the optoelectronic properties of different morphologies and chemical ingredients in In_2O_3 nanostructures, the cathodoluminescence spectrum (CL) and *I–V* curve are measured, accordingly.

2. Experimental

In advance, for the preparation of In_2O_3 and ITO nanostructures, an Au film (about 30 Å) as the catalyst was coated on silicon substrates by DC sputtering at room temperature. In_2O_3 and ITO nanorods were synthesized using a boat-like holder of diameter 55 mm in a horizontal quartz tube furnace. To prepare In_2O_3 nanorods, high quality 0.3 g indium powder (purity 99%) was placed as the In evaporated source in an aluminum boat, and

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Table 1
Synthesis conditions and morphology characteristics of In_2O_3 and ITO nanostructures.

Nanostructure	Source materials	Evaporation temperature [°C]	Pressure [torr]
In_2O_3 nanorods	Indium powders	900	2
In_2O_3 nanotowers	Indium powders	900	900 m
ITO nanorods	In + Sn powders (In:Sn = 100:1)	900	2

several silicon substrates were put on another side of an Al boat. In terms of ITO nanorods, 0.003 g tin powder (purity 99%) was added into 0.3 g indium powder, as the ITO vapor source. In_2O_3 nanotowers were grown using a one-end tube holder of diameter 55 mm instead of a boat-like one, and other conditions were the same as the synthesis of In_2O_3 and ITO nanorods. During the growing process, the source was heated from room temperature to 900 °C at 10 °C/min. When the reaction temperature reached 900 °C, the system was held for 1 h at 900 °C. After the reaction being done, the chamber was cooled to room temperature. The chamber was filled with a mixed atmosphere including Ar + 10% H_2 with 120 sccm and O_2 with 2 sccm, and the operating pressure was 2 Torr.

The surface morphology and crystalline structure of the samples were characterized by field emission scanning electron microscopy (FESEM, JEOL JSM-6335F) and high resolution transmission electron microscopy (HRTEM, JEOL, JEOL-3000F). The structure of the sample was confirmed using an X-ray diffraction (XRD, Shimadzu LabX XRD-6000). The chemical compositions and bonding of the nanostructures were identified by energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS, PerkinElmer model PHI 1600). In order to test the optoelectron properties of the indium oxide and ITO nanostructures, the measurement of *I–V* curves via a constant voltage (±5 V) and the cathodoluminescence (CL) were handled. The CL of the indium oxide and ITO nanostructure was verified using a field emission scanning electron microscopy (FESEM, JEOL JSM-7001F) with an accelerating voltage 15 kV. With the use of a parabolic mirror and lens, luminescence created by an electron beam was focused on the entrance slit of a monochrometer with the grid of 1200 lines/mm and blazed at 300 nm.

3. Results and discussion

Three kinds of In_2O_3 and ITO (Sn:In = 1:100) nanostructures are successfully synthesized in this experiment and the typical parameters are given in Table 1. The morphologies of In_2O_3 nanorods, nanotowers and ITO nanorods are shown in Fig. 1, respectively. The SEM image (Fig. 1(a)) shows that the abundant In_2O_3 nanorods with the diameters mostly ranging from 245 to 375 nm and the lengths from 5 to 10 μm are on the silicon substrate. The SEM image (Fig. 1(b)) displays that the product comprises of a large amount of In_2O_3 nanotowers with the diameters chiefly ranging 210–250 nm at the top, 1.2–1.4 μm at the bottom and the lengths from 8 to 15 μm. The SEM image (Fig. 1(c)) reveals plenty of ITO nanorods with the diameters mainly ranging 250 to 300 nm and the lengths from 5 to 20 μm.

The XRD patterns of In_2O_3 and ITO nanostructures are shown in Fig. 2, respectively. The main planes in In_2O_3 nanorods and nanotowers are corresponding with JCPDS: 88-2160. All diffraction peaks demonstrate body-centered cubic In_2O_3 structure with lattice constants a_0 = 10.11 Å. From the XRD pattern of ITO nanorods, three main peaks appear at 2θ = 30.54, 35.41, and 50.95, which correspond to (2 2 2), (4 0 0) and (4 4 0) planes of the BCC ITO structure (JCPDS: 06-0416). The red numbers are the three main planes in

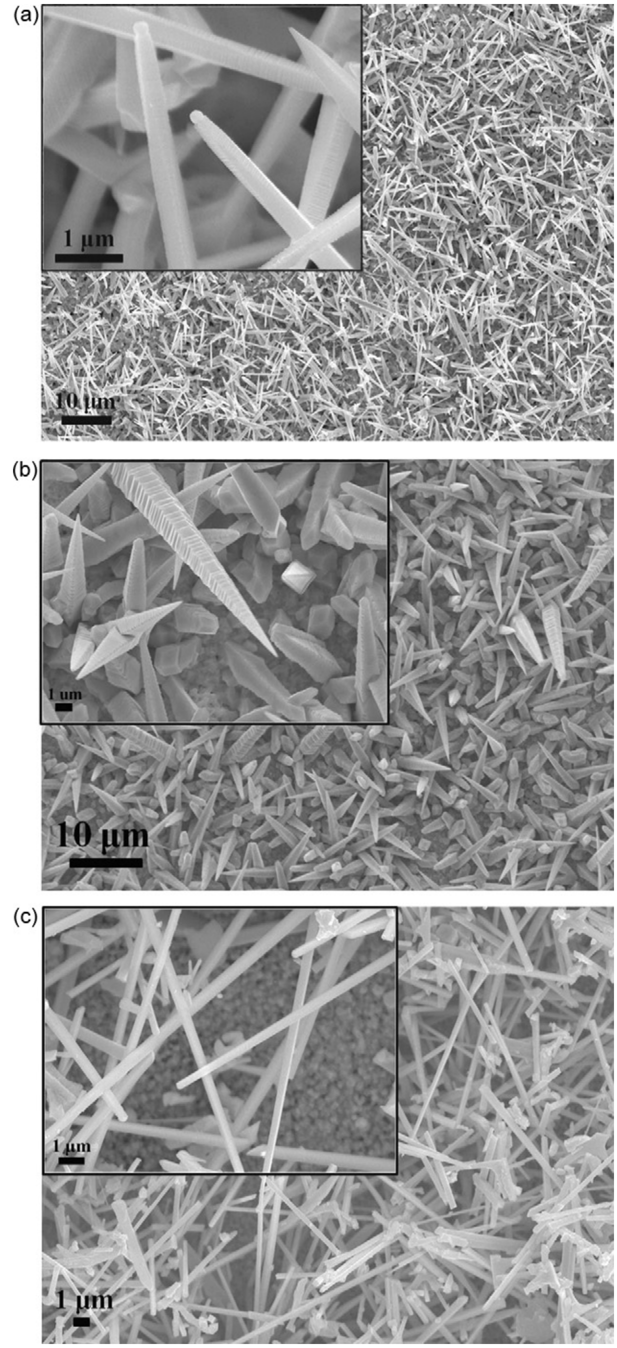

Fig. 1. (a) SEM images of In_2O_3 nanorods. Inset: Enlarged image. (b) SEM images of In_2O_3 nanotowers. Inset: Enlarged image. (c) SEM images of ITO nanorods. Inset: Enlarged image.

SnO_2 with the correspondence of JCPDS: 78-1063, and it is also confirmed that rare tin is successfully doped into In_2O_3 nanorods.

To further investigate the detailed characterization of In_2O_3 and ITO nanostructures, taking images by TEM examination was handled as well. The low-magnification TEM image of a single In_2O_3 nanorod with diameter around 210 nm is shown in Fig. 3(a). Fig. 3(b) shows the high-resolution TEM image and selected area diffraction (SAD) pattern of a single In_2O_3 nanorod, respectively. From HRTEM images, the growth direction of In_2O_3 nanorod is [1 0 0] and the lattice spacing of (1 0 0) is 0.48 nm. The In_2O_3 nanorods belong to body-centered cubic (BCC) structure confirmed by SAD analysis. TEM-EDS analysis of a single In_2O_3 nanorod (in Fig. 3(c)) indicates that the nanoparticle on the tip is totally