UDC 538.915:621.315.592

SYNTHESIS AND CHARACTERIZATION OF In₂O₃/SnO₂ HETERO-JUNCTION BEADED NANOWIRES

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Received to editors: 09.11.2009

Abstract. Hetero-junction beaded nanowires were synthesized from the mixture of Sn and In metals by the gas-transport. These nanowires were characterized with XRD, SEM, TEM. Many single-crystal In_2O_3 beads epitaxially grown along the axis of the single-crystal core SnO_2 nanowires form the beaded nanowires. The In_2O_3 beads have definite orientations along the [200] direction of the core SnO_2 nanowires and show regular rhombohedral morphology. A possible growth mechanism for the beaded nanowires is proposed.

Keywords: In₂O₃/SnO₂ nanostructures, nanofabrications, transmission electron microscopy.

INTRODUCTION

One-dimensional (1D) nanoscale semiconducting materials have attracted significant research interest due to their importance in understanding the fundamental roles of dimensionality and their potential applications in electronic/optical nanodevices. During the past few years, considerable efforts have been made to fabricate some important semiconducting materials with 1D nanostructures, e.g., ZnO, SnO₂, In₂O₂, ZnS and GaN [1-4]. Many nanostructures with different morphologies such as nanotubes, nanobelts, nanocombs and beaded nanowires have been synthesized successfully using different methods [5-8]. Among these structures, beaded nanowires have attracted much attention due to their technological potential as unique types of nanoscale building blocks for future optical and electronic devices.

Recently, synthesis of nanowire building blocks composed of different functional materials has become a target of researchers because it is crucial to the realization of nanodevices. Although the approaches for fabricating simple binary semiconducting nanostructures have progressed greatly in recent years, the fabrication of hetero-structures in nanoscale is still a challenge [6, 8—12]. Only a few investigations of complex structures such as superlattice nanowires and hetero-nanostructures have been reported [13, 14]. Two key wide-band semiconducting oxides, SnO₂ and In₂O₃, have distinctive properties and are now widely used as electronic devices and gas sensors. Nanostructures of SnO_2 and In_2O_3 are studied widely in recent years [8, 15].

In the present study, we report a simple method to synthesize composite beaded nanowires, in which the bead and the core are made of single-crystal In_2O_3 and SnO_2 , respectively. The beads and the core nanowires have a definite crystallographic orientation and thus form a series of hetero-junctions along the axis of the nanowires. These beaded nanowires may have important applications for nanowire-based devices including diodes, gas sensors and optical devices.

EXPERIMENTAL TECHNIQUES

In our materials synthesis, a 100 cm long horizontal quartz tube with an inner diameter of 50 mm open on one side was mounted inside a high-temperature quartz tube furnace. The nanostructures of In₂O₂/SnO₂ were prepared from the mixture of In and Sn metals together in the alumina boat. The alumina boat was put in the middle of quartz tube inserted in a horizontal tube furnace. The temperature in the furnace was rapidly ramped up to 1050-1100°C and kept for 60 min. During the process, the tube was then purged with 0.01 % oxygen diluted in argon. After that the furnace was cooled down, the sample was removed from the furnace. The morphology and crystal structure of the synthesized nanostructures were characterized by X-ray diffraction (XRD) using a DRON 4 utilizing Cu K_a radiation, scanning electron microscopy (SEM) employing and transmission electron microscopy.

RESULTS AND DISCUSSION

The SEM image shown in Fig. 1 gives an overview of the morphology of the synthesized products. In Fig. 1, many straight beaded nanowires are observed in the products. The diameters of the core nanowires are estimated to be about 50—100 nm, and the sizes of the beads vary from 60 to 200 nm. The beads aredistributed irregularly on the core nanowires with a distance of about several nanometers to several hundred nanometers.

The crystal structure and phase purity of the asprepared nanowires were examined by XRD. A typical XRD pattern of the as-grown beaded nanowires is shown in Fig. 2. The sharp diffraction peaks can be



Fig. 1. SEM image of the beaded nanowires

indexed to rutile-structured SnO₂ (JSPCD, No. 88-0287) and cubic In₂O₃ (JSPCD, No. 76-0152), respectively. The diffraction peaks of In₂O₃ were indicated by the empty circle and diffraction peaks of SnO₂ were indicated by the shaded circle. No other intermediated phase was detected in the XRD pattern, which indicates that the beaded nanowires consist only of SnO₂ and In₂O₃.

TEM is used to further characterize the beaded nanowires. Fig. 3 displays a bright-field TEM image of a typical beaded nanowire. The faceted In_2O_3 beads grown along the axis of straight SnO_2 nanowires with consistent orientation can be observed clearly in the image.

In our experiment, it is possible that the core SnO_{2} nanowires form first in the substrate. At the reaction temperature, Sn vapors are transported to the substrate by the carried gas because the Sn metal in the reactants is metastable and it can decompose to the Sn and SnO₂ at the reaction temperature. These SnO₂ nanoparticles will be the nuclei of the SnO₂ nanowires. Subsequently, the growths continue and the SnO₂ nanowires form in the substrate. This process is similar to the oxideassisted growth of semiconducting nanowires [16]. The reaction of In metal will take place when the temperature rises to about 1000° C and tiny Indium droplets will form. Then, these tiny Indium droplets are transported to the substrate by the carrier gas, and attach on the surface of the existing SnO₂ nanowires. Since the Indium droplet is in a liquid state at the



Fig. 2. XRD pattern of the beaded nanowires. The rutile-structured SnO₂ and cubic-structured In₂O₃ can be indexed



Fig. 3. TEM image of beaded nanowires

growth temperature, it tends to adsorb the newly arriving Indium and O species and then grows into larger In_2O_3 beads. Here, we present a schematic diagram to illustrate the formation process and structural models of the beaded nanowires (Figs. 4(a)—(c)).

SUMMARY

In summary, composite In_2O_3 —SnO₂ beaded nanowires were successfully synthesized by the gastransport method. The faceted single-crystal In_2O_3 beads and the single-crystal SnO₂ nanowire form hetero-junctions along a consistent orientation. Successful growth of composite beaded nanowires is important both for understanding of the novel nanostructures and fabrication of novel functional nanodevices. Moreover, the synthesis method is simple and cost effective. By alteration of the different oxide reactants, the present method may be used to grow different oxide hetero-structures in nanoscale.

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Fig. 4. The formation process and structural models of the beaded nanowires. (*a*) First, SnO_2 nanowires form. (*b*) In droplets attach on SnO_2 nanowires. (*c*) Beaded nanowires form. (*d*) Schematic diagram of the structural relationships of the faceted beaded nanowires [17]

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