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STUDY OF ZnO, SnO_2 AND ZnO/SnO_2 NANOSTRUCTURES SYNTHESIZED BY THE GAS-TRANSPORT

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Abstract. Zinc oxide (ZnO), tin dioxide (SnO_2) and compounds ZnO/SnO_2 (ZTO) nanostructures have been synthesized successfully from the vapor phase. XRD analyses showed that ZnO hexagonal wurtzite crystal structure, SnO_2 with a rutile crystal structure and zinc stannate ($ZnSnO_3$) and/or dizinc stannate (Zn_2SnO_4) were condensed from the vapor phase when Zn and/or Sn metal or their oxides individually or mixed were used as the starting materials. The formation of either zinc or dizinc stannate was controlled by the Zn/Sn ratio and growth technique. SEM investigations showed that ZnO grew mainly in the form of nanostructures. These are believed to be originated from the common tetrapod structure of ZnO. While SnO_2 grows in the form of tetragonal nanowires with rectangle-like cross section and nanoparticles, ZTO grows in the form of nanostructures.

Keywords: ZnO, SnO_2. ZnO/SnO_2, tetrapods, nanorods, nanowires, nanobelts, vapor phase growth.

INTRODUCTION

Research in the area of nanoscale materials is motivated by the possibility of processing and designing nanostructured materials with unique properties and important applications. Due to their finite small size and the high surface-to volume ratio, nanostructred materials often exhibit novel, and sometimes unusual properties [1—6]. The optical, electrical, magnetic, thermal, and chemical properties

depend to a large extent on the particle size and shape of these materials [4—6]. Meanwhile the large number of surface and edge atoms provides active sites for catalyzing surface reactions. In the areas of optoelectronic devices such as transparent semiconductor electrodes in liquid crystal displays, light emitting transport conductors and solar-electrical energy converters and chemical and gas sensitive semiconductor devices and nanoelectronics, ZnO, SnO_2 and their composites are finding great interest and attention in recent years [4—10].

Zinc oxide (ZnO) is an *n*-type wide band gap (3.20—3.43 eV at 298 K) semiconductor with a large exciton energy of 60 meV and a wurtzite structure [10, 11]. Tin dioxide (SnO_2) is an *n*-type semiconductor of rutile crystal structure with a wide band gap (3.6—3.97 eV) and high power gas detecting/sensing capabilities at low operating temperatures [12, 13]. Zinc and tin oxides have recently attracted considerable attention because they exhibit interesting technological properties. Transparent conducting oxides such as zinc stannate (ZTO) in the phase space SnO_2—ZnO, such as *n*-Zn_2SnO_4 or $ZnSnO_3$ are promising candidates as new *n*-TCOs. Zn_2SnO_4 is a ternary spinel-type oxide material having a cubic spinel structure, whereas $ZnSnO_3$ is a perovskite-type oxide material. The reported band gap energy of this compound oxide is 3.4—3.6 eV. The band gap values depend on the type of material, single crystal or bulk, method of preparation, size and shape. They are interesting semiconductors and have promising applications in photovoltaic devices and functional coatings in addition to the above-mentioned applications. Zn_2SnO_4 has high electron mobility, high electrical conductivity, sufficient thermodynamic stability, high temperature durability and low visible absorption and might show better properties than ZnO and SnO_2 alone [13]. While the data on the synthesis of $ZnSnO_3$ are ambiguous and contradictory [14], Zn_2SnO_4 is still less studied. Furthermore, among the large studies of materials with belt-like structures, the details on ternary oxide systems with spinel or perovskite structure have been rarely published [13, 14]. On the basis of the promising features of these materials (ZnO, SnO_2 and ZTO) it is expected that their nanostructure forms may represent building blocks for special nanodevices and may offer exciting opportunities for fundamental research and technological applications. It has been shown that some ternary oxides have even better properties than the binary oxides in applications for gas sensing and nanoelectronic devices [5, 6, 14].

The ability to systematically manipulate the shapes of inorganic nanocrystals remains an important goal of modern materials chemistry. The shape and size of inorganic nanocrystals control their widely varying electrical, electronic, magnetic and optical properties. One means of achieving shape control is by the use of a static template to enhance the growth rate of one crystallographic face over another [15]. Organizing nanoscale materials building blocks into complex nanostructures especially periodic ones is always a target for researchers. Self-organized growth provides an effective approach for fabrication of these structures [9, 15—17]. Various morphological nanostructures, including wires, belts, rods, tubes, cables, ribbons, nails, sheets, diskettes, tetrapodes, cones, flowers, dendrites, cages and others have been fabricated using various methods and techniques [9, 10, 15, 18—22].

In this paper we report on the growth and characterization of single ZnO and SnO_2 systems and also on multi oxide systems (ZTO) from the vapor phase using the vapor-liquid-solid mechanism. In addition we also show how and to what extent we could control the size and/or the shape of these nanostructures by these different approaches.

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. First, the 1D nanostructures of SnO_2 were prepared by using Sn metal. Sn metal was placed in an alumina boat positioned at the centre of the quartz tube. The temperature in the furnace was rapidly ramped up to 1050—1100° C and kept for 90 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. Subsequently, the nanostructures of ZnO were prepared by the same way of SnO_2 with the replacement of Sn by Zn metal. Finally, the nanostructures of ZnO/SnO_2 were prepared by same way with the mixture of Sn and Zn metals together in the alumina boat. The alumina boat was put in the middle of quartz tube inserted in a horizontal tube furnace. Our synthesis follows the well-known vapor-liquid-solid (VLS). The morphology and crystal structure of the synthesized nanostructures were characterized by X-ray diffraction (XRD) using a DRON 4 utilizing Cu K_α radiation, scanning electron microscopy (SEM) employing a JSM-6380LV.

RESULTS AND DISCUSSIONS

Tin dioxide (SnO_2). The XRD) pattern (Fig. 1) of SnO_2 nanowires revealed that there were eight peaks with 2θ values of 26.48°, 33.87°, 37.91°, 38.98°, 51.72°, 54.85°, and 57.97°, corresponding to SnO_2 crystal planes of (110), (101), (200), (111), (211), (220), and (002), respectively. All the diffraction peaks can be indexed to the tetragonal rutile structure of SnO_2 with lattice constants $a = b = 4.734$ Å and $c = 3.185$ Å, which are consistent with the standard values of bulk SnO_2 (JCPDS 88-0287). Fig. 2 shows typical scanning electron microscopy images of the synthesized product. They indicated that the SnO_2 nanowires are long and straight, and the surface is pure enough. The cross-section size crystallite is ~100

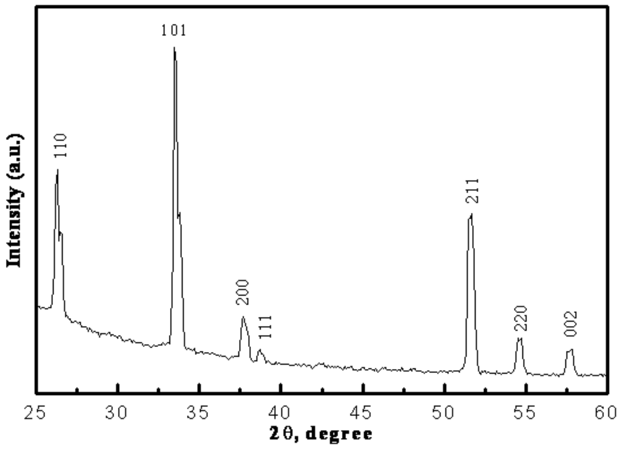

Fig. 1. A typical XRD pattern of the SnO_2 nanowires obtained from Cu K_α radiation

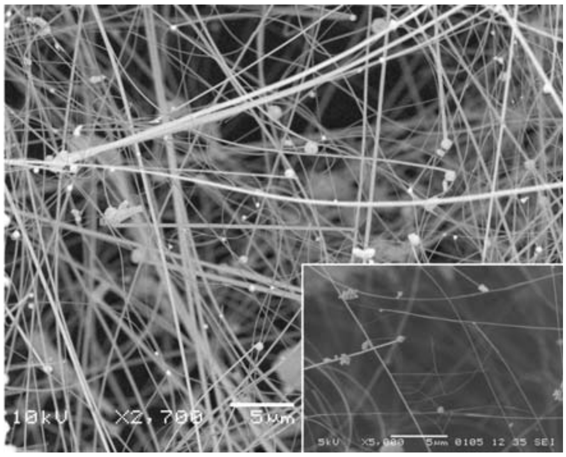

Fig. 2. SEM images of the SnO_2 nanowires prepared by the gas-transpor

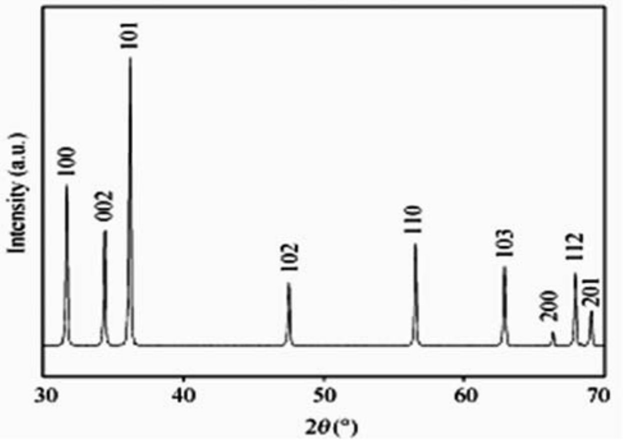

Fig. 3. XRD patterns of the as-synthesized ZnO nanorods with a wurtzite (hexagonal) structure prepared by the gas-transport

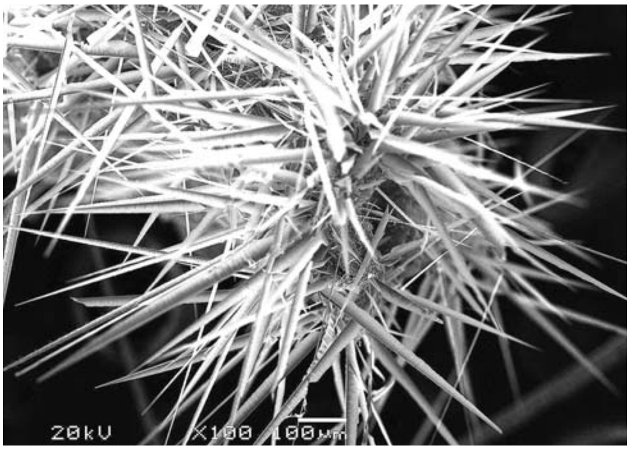

Fig. 5. SEM micrograph of whiskers of ZnO, prepared by the gas-transport

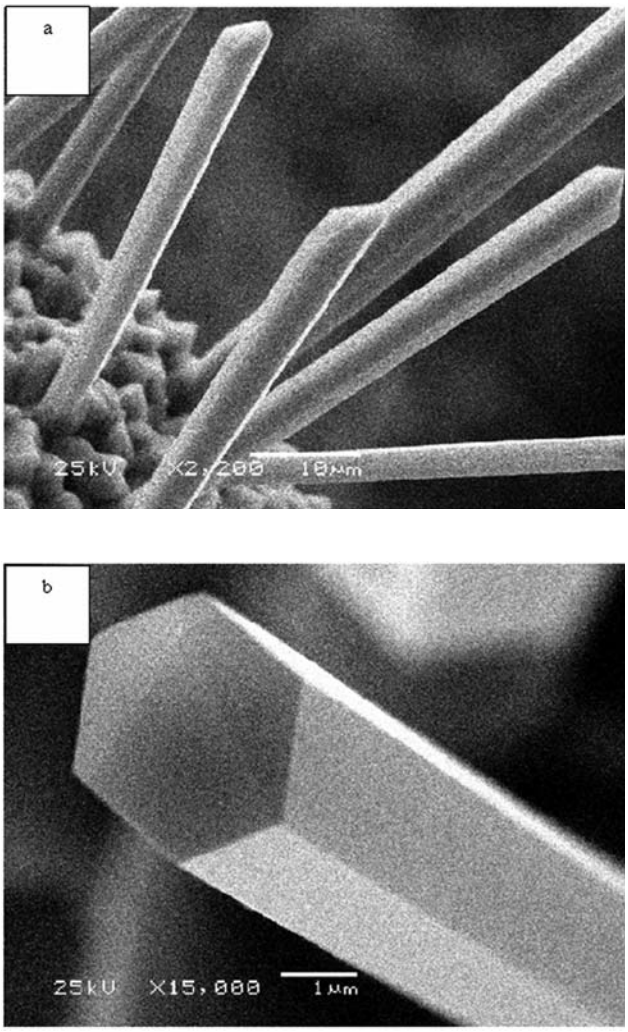

Fig. 4. ZnO nanorods having regular hexagonal surfaces with hexagonal faceted prepared by the gas-transport: *a* — low-magnification images, *b* — high-magnification images

nm, and the attitude cross-section to the longitudinal size is ~1000 nm. Micro drops of tin on the ends crystallite testify to the mechanism of their growth of vapor-liquid-solid.

Zinc oxide (ZnO). The XRD pattern of the as-synthesized product is shown in Fig. 3, where all Miller indices of peaks are presented. The whole diffractogram can be indexed in peak positions to a crystalline ZnO phase and a typical hexagonal (hexagonal wurtzite with lattice parameters of a = 3.2 Å and c = 5.2 Å) is indicated, which is consistent with that of a bulk ZnO crystal (JCPDS Card File, No. 89-511). Moreover, no diffraction peaks from other impurities have been found. Fig. 4*a*—*b* shows the SEM image of ZnO nanostructures grown on ZnO buffer layer coated on Si substrate by gas-transport. It is noticeable that, ZnO nanostructures grew in [0001] direction with hexagonal cross-section. Fig. 5 shows SEM micrograph of whiskers of ZnO nanostructures, obtained by the method of synthesis gas-transport.

Zinc oxide — Tin dioxide (ZTO). SEM images of zinc stannate (ZTO) are shown in Fig. 6*a* and *b* by mixing Zn metal with Sn in a weight ratio of 12 : 1. The general view gives cotton-like structures with stick-like deposits, Fig. 6*a* Focusing on these sticks shows that they are mainly a group of nanowires. Its diameter is less than 1 µ whereas its length in the range of tens of microns. The flexibility of these nanowires can be clearly seen from the bending structures shown in Fig. 6*b*.

A belt-like structure of the ZTO was observed when the tin dioxide weight ratio increased to 2 as can be seen in Fig. 6*c*. The inset in Fig. 6c shows two crossing belts, the scale bar is 1 µm.

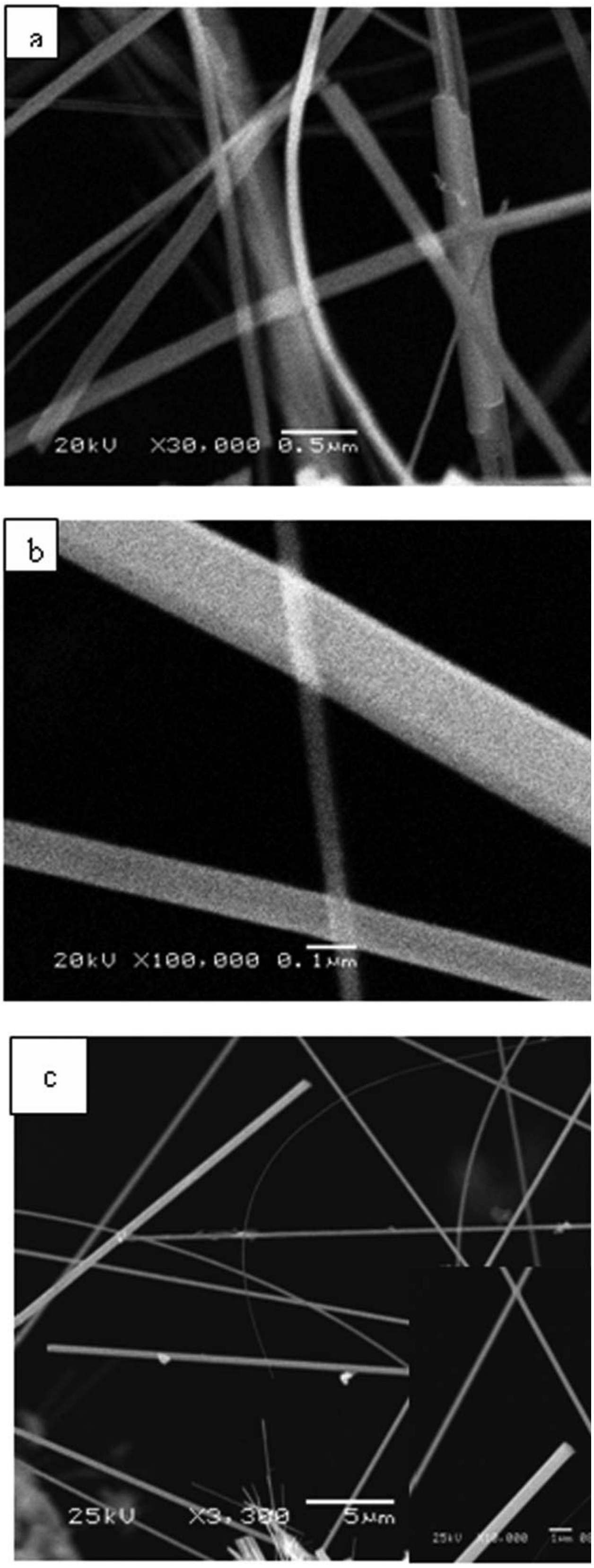

Fig. 6. SEM images of the ZTO nanowires prepared by the gas-transport: *a, b* — high-magnification images, *c* — low-agnification images

SUMMARY

Nanometer-sized functional semiconductor oxides of ZnO, SnO_2 and mixed ZnO/SnO_2 have been grown successfully from the vapor phase using three different approaches. The structure, composition and morphology could be controlled by controlling the reaction parameters. The formation of different nanostructures is believed to be a self-catalyzed process since no foreign metallic catalysts have been detected within the entire structures. The formation of different nanostructures is believed to be a self-catalyzed process since no foreign metallic catalysts have been detected within the entire structures. The driving forces for the growth of nanowires, nanorods, nanobelts, and nanoparticles were found to be vapor density or supersaturation, temperature, pressure and place of deposition from the source materials.

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