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Journal of Solid State Chemistry 178 (2005) 819–824
JOURNAL OF SOLID STATE CHEMISTRY
www.elsevier.com/locate/jssc

Controllable growth of zinc oxide micro- and nanocrystals by oxidization of Zn–Cu alloy

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Received 26 November 2004; received in revised form 4 January 2005; accepted 8 January 2005

Abstract

A simple and fast, controllable gas vaporization of alloy method for producing various micro- and nanostructures of ZnO in air atmosphere with a large yield was presented in this paper. The presence of Cu was proved to strongly affect the growth morphology of the synthesized ZnO through the control of the partial pressure of zinc, which could be fulfilled by changing the composition of Zn and Cu for the used reactants. Given the simplicity of the procedure, and the economic advantages, the method described here is likely to be of interest in industrial-scale applications.

PACS: 73.61.Tm

Keywords: Nanostructures; Nanowire; Vapor–liquid–solid growth; Zinc oxide; Semiconducting materials

1. Introduction

Zinc oxide (ZnO) has received great attention in recent years for its potential applications in photonic material. It possesses a direct bandgap of 3.37 eV at room temperature with a large exciton binding energy of 60 meV. The strong exciton binding energy, which is much larger than that of GaN (25 meV) and the thermal energy at room temperature (26 meV) can ensure an efficient exciton emission at room temperature under low excitation energy [1]. As a consequence, ZnO is recognized as a promising photonic material in blue-UV region. For example, as a UV laser it can allow reading compact disks with much more information, greatly increasing the amount of data stored. Room-temperature UV emission properties have recently been demonstrated from ZnO epitaxial films, microcrystalline thin films, and nanoclusters [2]. In addition, low cost, high chemical flexibility and low threshold intensity make ZnO nanostructures an ideal candidate for commercial miniaturized laser light sources [3].

Owing to these promising applications, one-dimensional ZnO nanostructures such as nanowires [3], nanobelts [4,6], nanotubes [5], and nanodendrites [6] have been synthesized by a variety of methods. However, most methods are relatively complicate and have low yield, not suitable for commercial production. The traditional approaches to synthesize one-dimensional ZnO nanostructures are usually by means of a vapor-phase transport process with the assistance of metal catalysts or a template-assisted growth [3–6]. Furthermore, considering that electrical and optical properties of nanomaterials depend sensitively on both shape and size, it is important to obtain the expected shape and size in a controllable way. In this work, we describe a method to synthesize high-purity ZnO micro- and nanocrystals and nanowires in air by a controllable gas vaporizing by alloy (CGVA) method, which only includes a simple, fast process, and may be applied for commercial production.

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doi:10.1016/j.jssc.2005.01.006

2. Experimental

ZnO micro- and nanocrystals were synthesized using a chemical vapor transport and condensation system developed in our lab. In a typical synthesis processes, 5 g of pure metal Zn (99.99%) or Cu–Zn (99.99%) mixed powders at certain weight ratio (Cu/Zn = 2/8, 4/6, 5/5, 6/4, 7/3, and 9/1, respectively) were put in a small alumina boat to serve as the source material. The alumina boat was then pushed to the central of the alumina tube in air atmosphere at 1250 °C and held for several minutes. After the reaction, a large amount of white powder could also be collected at the alumina boat and the downstream area of this alumina tube. A representative yield for the reactions of Cu/Zn = 6/4 was ~7.0%.

ZnO nanowires were synthesized in the same manner by oxidizing a block of brass (41.51 wt% of Zn) with the weight of 46 g. The furnace was first heated to 1250 °C and held for 30 minutes under the protection of an argon flow of 80 standard cubic centimeters per minute. Followed let the melted brass exposed to the air atmosphere and reacted for several minutes. After the reaction, the alumina tube was clogged up with a cotton-like ZnO product. The collected product in the tube weighted ~4.0 g and the yield was ~8.7%. Small brass bean remained in the alumina boat.

Morphology, structure and chemical composition of the samples were examined using an X-ray diffraction (XRD, D/max-rB, Cu$K\alpha$ radiation), a scanning electron microscopy (SEM, Hitachi X-650) equipped with an EDS, and transmission electron microscopy (TEM, JEM-100C).

3. Results and discussion

Fig. 1 shows a typical XRD pattern of the as-synthesized white powder sample (Cu/Zn = 4/6, weight ratio). The diffraction peaks can be indexed to a hexagonal structure of ZnO with cell constants of $a = 3.24$ and $c = 5.19$ Å. No diffraction peaks produced from Cu and CuO could be found from the pattern, though there are some weak peaks from small amount of A: zinc that has not been oxidized and B: zinc nitride from the reaction of zinc and nitrogen in the air.

Further structural characterization of the products was performed using TEM and SEM. Fig. 2 shows typical SEM images of the ZnO micro- and nanocrystals. When pure Zn was used as reactant, uniform sprout-like ZnO tetrapod microstructures were obtained (Fig. 2a). When Cu was added to the Zn with the weight ratio 2/8, bullet-like product with hexagonal cylinder microstructures was achieved (Fig. 2b). However, when more proportion of Cu was added, the ZnO with tetrapod micro- and nanostructure appeared (Fig. 2c Cu/Zn = 4/6, Fig. 2d Cu/Zn = 5/5, and Fig. 2e Cu/Zn = 6/4). The diameter of the arms in the tetrapod structure decreases with increasing Cu content. The thin tetrapods generally have the needle-shaped arms (Fig. 2d), while the thick ones have two kinds of uniform structures: special edge-like arms (Fig. 2c) and hexagonal cylinder arms (Fig. 2e and the inset), which are unique morphologies of ZnO nanocrystals compared to that reported previously [6]. Furthermore, while a further higher Cu proportion was used, microwires with a radiation flower (Fig. 2f, Cu/Zn = 7/3) and chrysanthemum petal-like microcrystals (Fig. 2g, Cu/Zn = 9/1) were obtained.

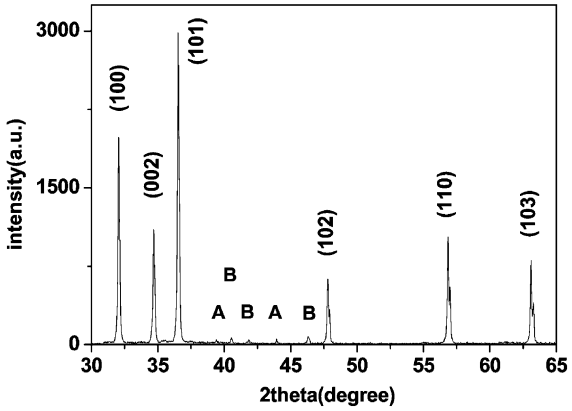

Fig. 1. XRD pattern of the as-synthesized dendrite ZnO nanocrystals (Cu/Zn = 4/6 weight ratio). Indices of the peaks are specified above the peaks ((A) peaks of purity of zinc, (B) peaks of purity of zinc nitride).

High yield of ZnO nanowires can be produced by oxidation of melted brass with a commercial purity (41.51 wt% of Zn) using the same CGVA method. Fig. 3 shows the typical SEM and TEM images of these ZnO nanowires. Determined from TEM images (Fig. 3b), the diameter of the ZnO nanowires varied from 10 to 150 nm. The observed variation in diameter may be related to the inhomogeneous sizes of the nuclei of the oxide nanowires [7]. The lengths of these nanowires distributed from 3 to 10 um. The nanosheets and nanoscale tripods, as by-products, often appear in the products (Fig. 3a). XRD pattern confirms a hexagonal structure of ZnO (Fig. 3c). Some weak peaks from small amount of zinc and zinc nitride are also detected, same as those in Fig. 1.

Understanding the growth mechanism will be important in order to control and design nanostructures. All experiments in this study were carried out in air atmosphere. It is apparent that the synthesis of ZnO nanostructures discussed here is based on the oxidation of thermal evaporation of Zn powder under the controlled conditions. The crystal growth may be dominated mainly by the following two growth