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Large-quantity synthesis of ZnO hollow objects by thermal evaporation: Growth mechanism, structural and optical properties

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Abstract

Synthesis of large-quantity uniformly distributed ZnO hollow objects, i.e. cages and spheres have been performed on Si(1 0 0) and steel alloy substrates by the direct heating of metallic zinc powder in the presence of oxygen. Extensive structural observations revealed that the formed products are crystalline ZnO with the wurtzite hexagonal phases. The Raman-active optical phonon E_2 modes, attributed to wurtzite hexagonal phase of ZnO, were observed at 437 cm^{-1} for the products grown on both the substrates. The room-temperature photoluminescence spectra showed a broad band in the visible region with a suppressed UV emission, indicating the presence of oxygen vacancies and structural defects in the as-grown structures. Additionally, post growth annealing was also carried out to further investigate the photoluminescence properties of the as-grown products. It was observed that the formation of hollow objects consists of several stages which include the formation of Zn clusters, oxidation on the sheath and sublimation/evaporation of the Zn from the interiors, resulted in the formation of hollow objects.

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1. Introduction

The controlled synthesis of semiconductor nanostructures in terms of size and shape has been strongly motivated because it is believed that the properties of the nanostructures are strongly dependent on their sizes and shapes and hence they are presenting wide ranges of practical applications in optics, sensors, catalysts, solar cells, data storage, drug delivery and so on [1–4]. In this endeavor, recently scientists are inclined to pay much attention on the fabrication of materials with specific morphologies because of the expectation of novel properties. For the use of specific applications, so far a variety of ZnO nano- and microstructures are already fabricated and reported in the literature which include ZnO rods and wires [5–14], tubes [15,16], belts [17], propeller [18], stars [19], helixes, springs and rings [20], nanosheet networks and hexagonal disks [21], nanobridges and nails [22], columns [23], hierarchical structures [24], flower-shaped structures [25], nano and micro hollow shells, cages and spheres [26–30], and so on. Among these diverse morphologies of ZnO, the nano- and microspheres with hollow interiors/cages, because of their lower densities and higher surface areas, are presenting an appealing structural design as compared to their bulk materials. Due to their extensive and special architecture these cages and spheres are widely applicable in various fields such as fillers, photonic crystals, pigments, drug delivery, chemical storage, catalysis, coatings, gas separators, protection of biologically active agents, etc. [31,32]. For such multifarious applications, the cages, shells and spheres of other materials like carbons, polymers, metals, and inorganic materials were also synthesized and reported in the literature [33–35]. Thus far, only few reports have been available in the literature related to the fabrication of nano- and micro-sized ZnO cages, shells and spheres [26–30]. Previously reported micro-sized ZnO hollow cages/shells by Gao and Wang, were synthesized by the mixture of ZnO, SnO_2, and graphite powders

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at a high temperature (1150 °C) on alumina substrate by thermal evaporation method [26]. Fan et al. also fabricated the ZnO microcages by the thermal evaporation method using metallic Zn powder at 800 °C on Si(1 0 0) substrates [27]. In addition to this, single-crystalline polyhedral sub micrometer-sized hollow beads of ZnO were synthesized using the ethanol droplets as soft templates at 600–700 °C [28]. In all the cases, the source materials were placed either in an alumina boat or directly in the quartz tube and during the high-temperature evaporation process the Zn vapors, for the deposition of ZnO hollow structures, were transferred from the boat to the substrate.

In this paper, a very easy, cost effective and simple method was proposed for the large scale direct-synthesis of ZnO hollow objects, i.e. cages and spheres on the substrates. For this synthesis, we performed a different approach compared to the previously reported results, hence, the high purity metallic Zn powders was coated directly onto the substrates instead of keeping in the alumina boat. Moreover, the synthesis was performed at low temperature (500–600 °C) compared to previously reported results. This method produced uniformly distributed and high-density ZnO hollow objects, i.e. cages and spheres as compared to the case of putting the Zn source in the alumina boat. Furthermore, to check the effect of the substrate, different substrates were employed in this synthesis, i.e. Si(1 0 0) and steel alloy substrates. Moreover, the possible growth mechanism and detailed structural and optical properties of the as-grown ZnO hollow objects were explored in this research.

2. Experimental details

Commercially available Si(1 0 0) and steel alloy (Fe: 72.8%, Cr: 22%, Al: 5%, Y: 0.1% and Zr: 0.1%) have been used as substrates for the synthesis of ZnO hollow objects. The synthesis was performed in a horizontal thermal reactor which consists of a horizontal quartz tube. High purity metallic Zn powders (99.999%) and oxygen gas (99.999%) have been used as precursors of Zn and oxygen, respectively. Before using the substrates, they were scratched by the fine sand paper and washed with the alcohol and acetone sequentially. Prior to the reactions, the metallic zinc powders were ultrasonicated for 30 min in ethanol. After ultrasonication, the obtained solution containing zinc powders was dropped onto the cleaned substrates and baked on hot plate at 85 °C for 10–20 min to get bonded with the substrate. Finally, a thin layer of zinc powder was deposited onto the substrates which were loaded into the reaction chamber. After loading the zinc-coated substrates, the chamber pressure was down to 3 Torr using rotary vacuum pump, which was slightly increased after the introduction of gases into the chamber. Initially, the substrates were pretreated by H_2 and N_2 gas mixture (20 sccm of each) at 450 °C for 20 min. After the pretreatment, high purity O_2 and N_2 were introduced with the flow rates of 15–30 and 10–20 sccm, respectively at the temperature range of 500–600 °C. Gray colored products were deposited on both the substrates which were characterized in terms of their structural and optical properties. Furthermore, to investigate the annealing effect on

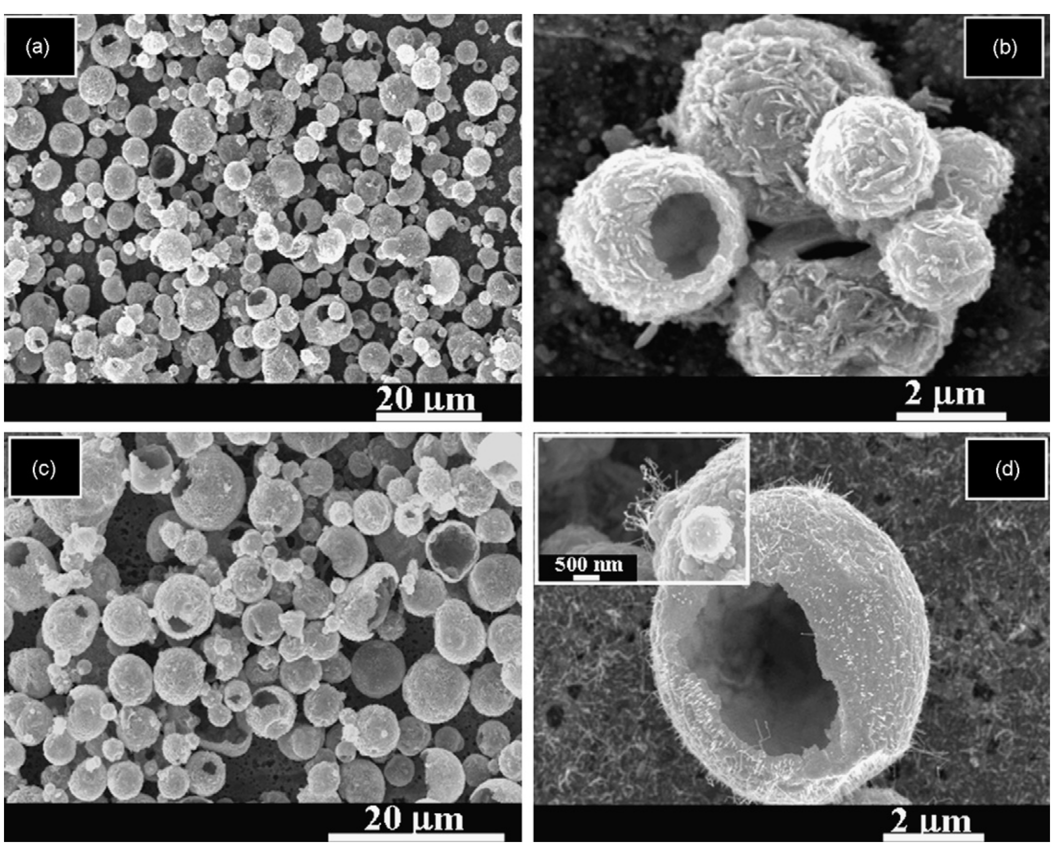

Fig. 1. Typical SEM images of ZnO hollow objects grown on Si(1 0 0) (a and b) and steel alloy (c) and (d) substrates.