

FORMATION OF ZINC MICROSPHERES BY CHEMICAL VAPOR DEPOSITIONS (CVD)

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ABSTRACT

Zn microspheres have been prepared by heating a mixture of ZnO/graphite powders using the chemical vapor deposition (CVD) and vapor transport on Si (1 0 0) substrates. The synthesis process of the Zn microspheres was accomplished within a fast reaction time without catalyst. Since the oxidation process required for the synthesis of zinc nanomaterials not required, reducing the number of experimental processes than conventional synthetic methods. Good crystalline Zn microspheres was analyzed using a variety of surface analysis apparatus. We also proposed the synthesis mechanism of Zn microspheres.

Keywords: Zn microspheres, Chemical Vapor Deposition (CVD), Structural and optical properties, Surface analysis.

INTRODUCTION

In nanotechnology, it is important to synthesize specifically shaped nanostructures, which could serve as building blocks in the assembly process [1]. Among all the nanomaterials, Zn attracted a lot of attention with its various architectures as an excellent candidate for self-assembly [2-3]. Zn is also promising for device applications due to its unique material properties such as wide and direct band gap and a large free exciton binding energy [4], high optical gain [5-6] and high mechanical and thermal stabilities [7-8]. Zn microspheres have been studied due to their potential applications in nanocomposite materials. For example, Sulieman et al. [9] have reported a vapor transport synthesis of hollow-opened ZnO/Zn or Zn/ZnO microspheres on Si substrate using high purity Zn and ZnO powder as sources. Duan et al. [10] employed an integrated autoclave and pyrolysis process to synthesize partially opened ZnO hollow microspheres. In both cases, high temperatures (600 °C or higher) were used to react the Zn powder with oxygen and the ZnO shells are consisted of multi-crystalline domains or particulates [1]. In this study, we report a very simple atmospheric pressure thermal evaporation route to grow novel Zn microspheres without use of catalyst. The process is based on CVD with metallic zinc-oxide powder in a tube furnace at 1400K. In addition, we propose a possible growth mechanism and discuss factors that influence the formation mechanism of the Zn microspheres. The crystal structure morphologies, transformation and photoluminescence evolution of the Zn microspheres were studied and investigated with X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy dispersive spectroscopy (EDS), and photoluminescence (PL) spectra. The specific structure of the highly oriented two-dimensional microspheres may find applications in nanoelectronics, nanophotonics, and nanomedicine.

EXPERIMENTAL DETAILS

Our fabrication of Zn microspheres was based on CVD process of ZnO powder without the

presence of a catalyst. The synthesis process was carried out in a quartz tube (diameter 25mm, length 100 mm). The source material was pure ZnO powder mixed with graphite (weight ratio 1:1), which was placed at the center of thermal furnace. Metallic zinc-oxide powders (100mesh, 99.998%) acquired from Sigma-Aldrich were used as source materials. The quartz tube was inserted into a horizontal tube first furnace heated to 1400K. The temperature gradient at the location between the source material and the open end of the quartz tube was placed another furnace at the approximately 700K. The end of the quartz tube was open to the atmosphere. High-purity argon (Ar) gas (99.9%) flow of 150 Standard Cubic Centimetres per Minute (sccm) was used for the vapor transport inside the tube during thermal evaporation. The mixture was heated at 1400K while the substrates were kept at different temperature zones that were fixed 700K inside the tube for the growth of nanostructures. After 60 min evaporation, the quartz tube was drawn out from the furnace and cooled down to room temperature. The sample material was studied with a scanning electron microscope (SEM, JOEL JSM 5300), an energy dispersive spectrometer (EDS), and an X-ray diffractometer (XRD, Rigaku Geigerflex, 2000W) with Cu-K α (1.54Å) as the incident radiation. Photoluminescence spectra (PL) were measured at 300K with a xenon arc lamp-based fluorescence spectrometer with an excitation wavelength of 320 nm.

RESULTS

After thermal evaporation and condensation, it was found that the silicon substrate was deposited with white product. The morphology of the product obtained after thermal evaporation for 60 min is well aligned Zn microspheres. Figure 1 is a low-magnification SEM image which clearly shows that the whole substrate is covered with Zn microspheres with diameters ranging from several to several tens of micrometers.

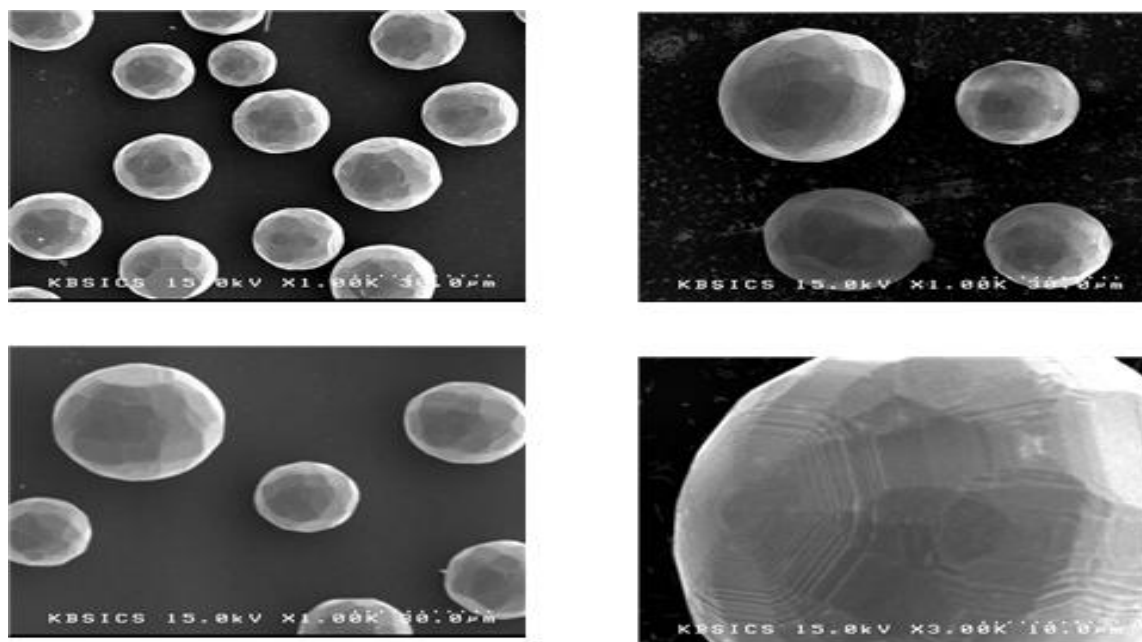


Figure 1. A typical low-magnification SEM image of the as-synthesized Zn microspheres on the substrate surface

A representative energy dispersive X-ray spectrum (EDS) spectrum of the nanostructures is shown in Fig. 2. Only peaks associated with Zn and O atoms are seen in this EDS (the Si-related peak in the spectrum comes from the Si substrate), leading to the fact that the nanomaterials are indeed Zn material. The peak comparison also shows that there is a fair

amount of nanomaterials deposited over the substrate.

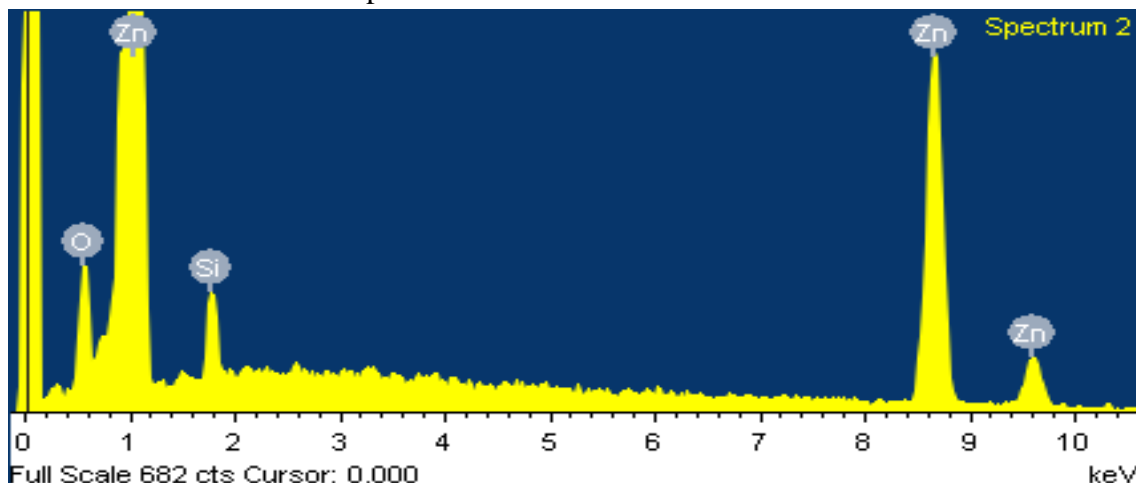


Figure 2. EDS spectra of as-made Zn microspheres.

XRD studies were performed of the products after thermal evaporation of zinc oxide powder for reaction times to obtain information about the evolution of the phase transformation from ZnO powder to Zn microspheres. Figure 3 shows the series of XRD patterns of the products obtained at 60 min. All peaks are sharp and strong, suggesting that the products are highly crystallized, and all the visible diffraction intensities agree well with the peaks of Zn wurtzite structure with the lattice constants of $a = b = 0.32489\text{nm}$ and $c = 0.52062\text{ nm}$ [11].

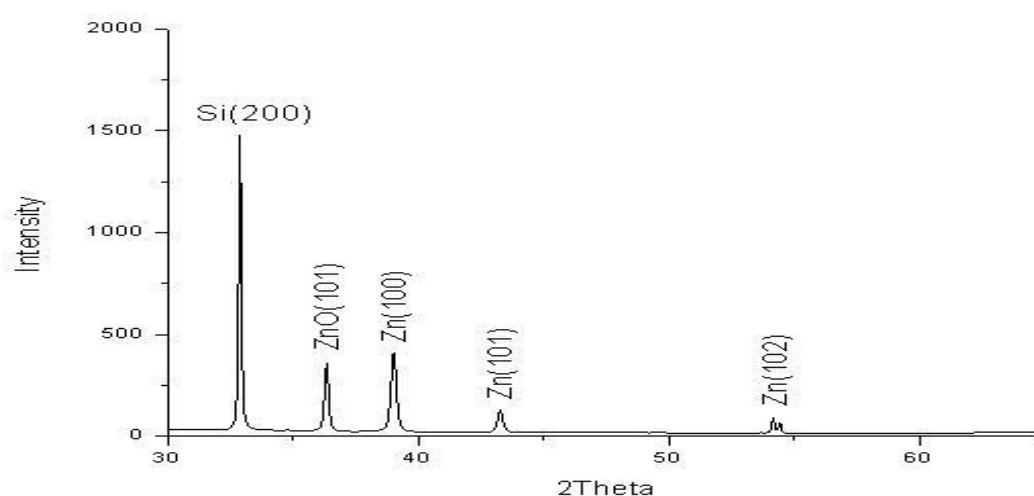


Figure 3. XRD pattern of as-prepared Zn microspheres grown on Si (100) showing wurtzite structure and high crystallinity

No intensities of zinc oxide or other impurities are found in the spectrum, which also shows that the Zn microspheres are rather pure ZnO wurtzite. The XRD pattern of the product obtained after 60 min indicates that ZnO has been completely transformed into Zn, which is in good agreement with the EDS results.

Also a good candidate in the application of the photoluminescence, the optical properties of the Zn have attracted much attention. In this paper, the PL spectrum of the Zn microspheres at room temperature is measured for sample and shown in Figure 4. The PL spectrum of the Zn consists of two distinct emissions: a weak ultraviolet (UV) emission band centered at 383

nm and a strong green emission band centered at 493 nm. It is well known that the UV emission which is originated by the band-edge transition or the exciton transition is the characteristic emission of the Zn. In addition, the UV emission centered at 383nm appears a red shift in the near band-edge emission, which differs from the band gap of bulk Zn (around 380 nm). Fu et al. [12] reported that the red shift of the UV emission is attributed to the quantum confinement effect and this phenomenon is probably due to the large size of the Zn microspheres, which is consistent with the result of the SEM images in Figure 1. The green emission is most likely related to the structural defects such as the singly ionized oxygen vacancies and the interstitials of the zinc [13-14]. Therefore, the green emission may indicate the existence of the oxygen vacancies with in the Zn microspheres. In our experiment, no directional air current flows through the furnace, the products were grown in the atmosphere with the insufficient oxygen. Therefore, oxygen vacancies for Sample are formed easily during the growth process. In addition to the emission in UV region, broad visible emission can be observed where two main peaks can be identified (~383 and ~493 nm), which is similar to the results reported by Fu et al. [12].

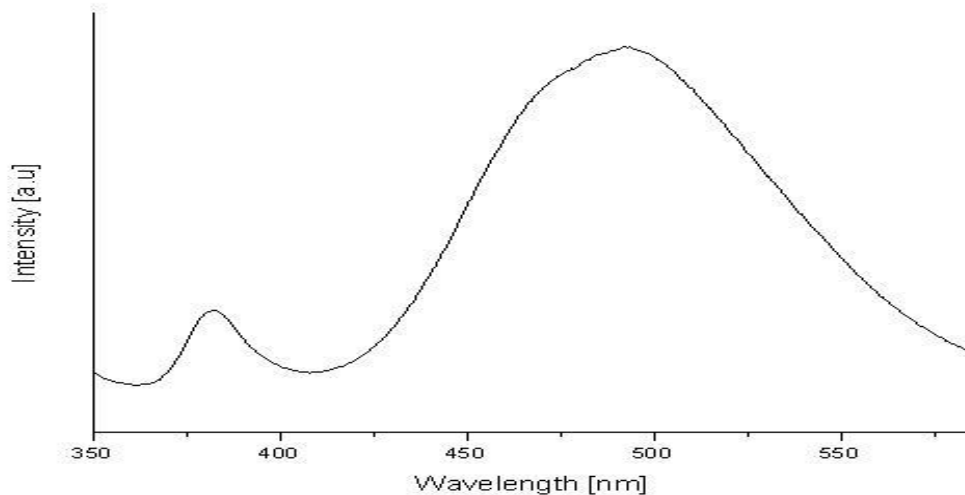


Figure 4. The room-temperature photoluminescence (PL) of Zn microspheres prepared under conditions

DISCUSSION

According to our experimental results of the morphological and structural characterizations of Zn microspheres can be understood on the basis of the growth mechanism proposed below. We propose a growth mechanism for the formation of Zn microspheres elaborated in three steps and illustrated in Figure 5.

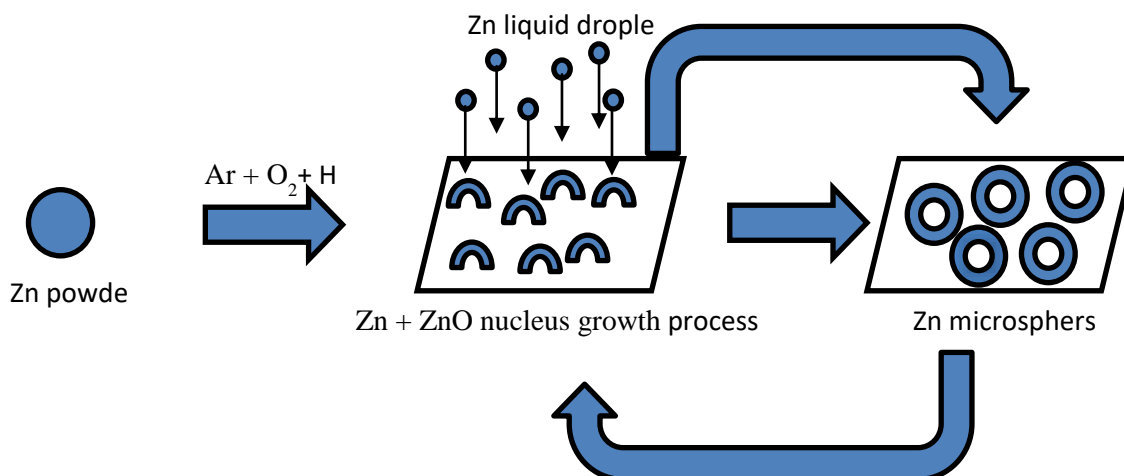
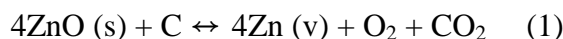


Figure 5. Schematic illustration of the growth mechanism of Zn microspheres.

Firstly, when zinc-oxide powder is heated in Ar gas environment inside horizontal tube furnace, increased temperature conditions at the center of the furnace, due to argon gas flow and concentration diffusion, these Zn vapors are transported downstream towards the comparatively low-temperature region and condense on the surface of Si substrate.



They aggregate together and form the Zn liquid droplets. These droplets are oxygenated easily. So there are a lot of mixed liquid droplets of the Zn and the ZnO on the surface of the substrate. These mixed droplets can absorb the blended steam of the Zn and the ZnO effectively during the nucleus growth process which is from vaporizing the zinc oxide powder. In such enhanced temperature environment, the residual and/or leaky oxygen plays its role to react with the zinc on the surface of Zn microspheres to form Zn nuclei and further heating converts it into vapors due to vapor–liquid equilibrium.



Secondly, the condensing Zn vapors convert into droplets and nucleate into the micro-sized zinc spheres repeatedly. Lastly, with prolonged reaction, small Zn spheres sprout out epitaxially from the surface via a self-catalytic mechanism and finally large Zn microspheres are formed.

The growth of Zn microspheres was comprised of vaporization of ZnO powder, solidification of liquid droplets, surface oxidation and self-catalytic growth of two-dimensional nanomaterials.

DISCUSSION

In summary, novel Zn microspheres were synthesized by using a very simple atmospheric pressure chemical vapor deposition (CVD) process on silicon substrate with zinc oxide powder as the source material. The crystal structure morphologies, transformation and photoluminescence evolution of the Zn microspheres were studied and investigated scanning

electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and photoluminescence (PL) spectra. The room-temperature photoluminescence spectrum (PL) of the as-synthesized Zn microspheres exhibits a weak ultraviolet (UV) emission band centered at 383 nm and a strong green emission band centered at 493 nm which are assigned to the near band-edge emission and the deep-level emission, respectively. Structural characterizations of the as-grown products revealed that these structures have a good crystalline with wurtzite crystal phase. These novel nanostructures may find uses in a variety of areas such as the fabrication of advanced electronic and optoelectronic nano devices.

ACKNOWLEDGEMENTS

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