

Formation of ZnO nanostructures by chemical bath deposition route: Observation of growth and optical properties

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Abstract

ZnO films have been synthesized on a zinc foil by chemical bath deposition route from an electrolyte of $\text{ZnCl}_2 + \text{H}_2\text{O}_2$ at ambient conditions. The structures, morphologies and chemical compositions of the films were characterized by X-ray diffractometer (XRD), scanning electron microscope (SEM) and energy-dispersive X-ray spectrometer (EDS). The XRD pattern shows well peaks, which can be indexed to the wurtzite hexagonal phase of ZnO. The SEM observations reveal that with an increase in deposition time, the rod structures converted to cauliflower structures. The EDS result indicates the presence of Zn and O atoms only. Photoluminescence (PL) studies evaluated different visible emissions originated from different defect mechanism. According to the obtained results, the possible growth mechanism for the variation in the morphology is discussed. This method may have a potential use in fabricating other metal oxide at low cost for technological applications.

PACs: 78.67.Bf; 61.46.Df; 81.16.Pr; 78.67.Rb

Keywords: Chemical bath deposition; ZnO; Rod; Cauliflower; SEM; XRD; EDS.

1. Introduction

Over the past few years, various kinds of nanostructures have been synthesized using large number of techniques. Among them, zinc oxide (ZnO) nanostructures have received considerable attention due to their properties such as, wide direct band gap energy (3.37 eV) and large excitation binding energy (60 meV), suggest a great deal of possible practical applications. In addition, ZnO seems to have the richest family of nanostructures among all materials such as, particles, rods, tubes, wires, nail, belts, marigolds/multipods, flowers, rings, helixes/springs, etc [1-8].

Up to now, different methods have been employed to prepare ZnO nanostructures including chemical deposition [1-2], thermal evaporation [3-8], pulsed laser deposition [9], chemical vapor deposition [10] and catalysis driven molecular beam epitaxy [11]. Among them, chemical bath deposition (CSD) is a simple, low equipment cost, large scale and room temperature process. In addition, many efforts have been made to synthesize ZnO nanoforms by adjusting effective parameter in the CSD method such as concentration and type of precursor, temperature of growth and substrate. However, the precise control of ZnO crystal evolution in the CSD process is a formidable task and therefore it is necessary to study the relationship between deposition condition and morphology of ZnO nanostructures for practical applications.

As the property of nanostructures is the size and morphology dependence, thus the main aim of the present work is to study the influence of deposition time on the growth process and optical properties of ZnO nanostructures by the chemical bath deposition. From the results, it is found that by increasing deposition time the rod-like converted to cauliflower-like morphology.

2. Experimental procedure

2.1. Synthesis

The growth of the ZnO nanostructure films on Zn substrate was performed by chemical bath deposition technique, using a mixture of ZnCl_2 and H_2O_2 (analytical grade) with concentration of ~ 0.016 M and ~ 0.04 M, respectively. The electrolyte (mixed solution) was stirred for 5 min and placed in a glass beaker with suitable cap. The substrates immersed in the electrolyte and fixed perpendicular to the solution surface. Prior to each experiment, the polycrystalline Zn foil (size: 1 cm x 2 cm and purity: $\sim 99.99\%$, Alfa Aesar) was ultrasonically cleaned in acetone and methanol, for 10 minutes in each solvent, respectively. In order to study the effect of deposition time on the formation of ZnO nanostructure, the deposition was performed on zinc foil for 2, 4, 7 and 10 days, respectively. The glass beaker was conducted in dark area at room temperature. After the induction period, the specimens were thoroughly washed in gentle flow of distilled water and dried in air at 50°C for 5 min. At least three specimens were synthesized under identical experimental conditions and characterized by analytical

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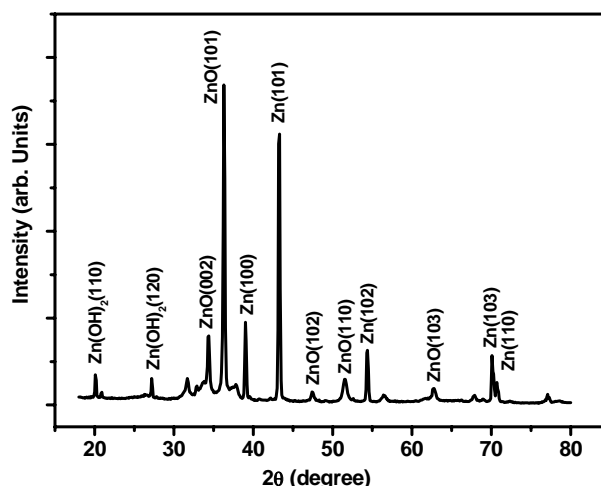


Fig. 1. XRD pattern of the ZnO nanostructures film grown on the zinc foil for deposition time of 10 days.

technique in order to check the reproducibility and repeatability of the results.

2.2. Characterization

The structure and morphology of the films were characterized using X-ray diffractometer (XRD, Model-D8, Advance, Bruker AXS) and scanning electron microscope (SEM, JOEL, JSM-6360A). The elemental composition was obtained using energy-dispersive X-ray spectrometer (EDS) attached to the SEM. The XRD was used in 2θ mode, i.e. ($20^\circ - 80^\circ$) with operating voltage of ~ 20 kV and the Cu K α (λ : 1.5406 Å) as the radiation source. The SEM images were recorded with an accelerating voltage ~ 20 kV and filament

current ~ 60 μ A. The EDS spectra were obtained from at least 4 to 5 different spots (total area ~ 25 μm^2) and the collection duration was ~ 80 seconds, for each spot. The EDS spectrometer was calibrated using a standard specimen of gold. The optical properties were investigated from the UV-visible (UV-vis) and the photoluminescence (PL) spectra recorded at room temperature. The UV-vis diffuse reflectance spectra were recorded using a UV-visible JASCO, UV-670 spectrophotometer over the wavelength range 200-800 nm. The PL was measured with a Perkin Elmer-LS-55, photoluminescence spectrometer using a Xenon lamp as the source with the excitation wavelength of ~ 305 nm.

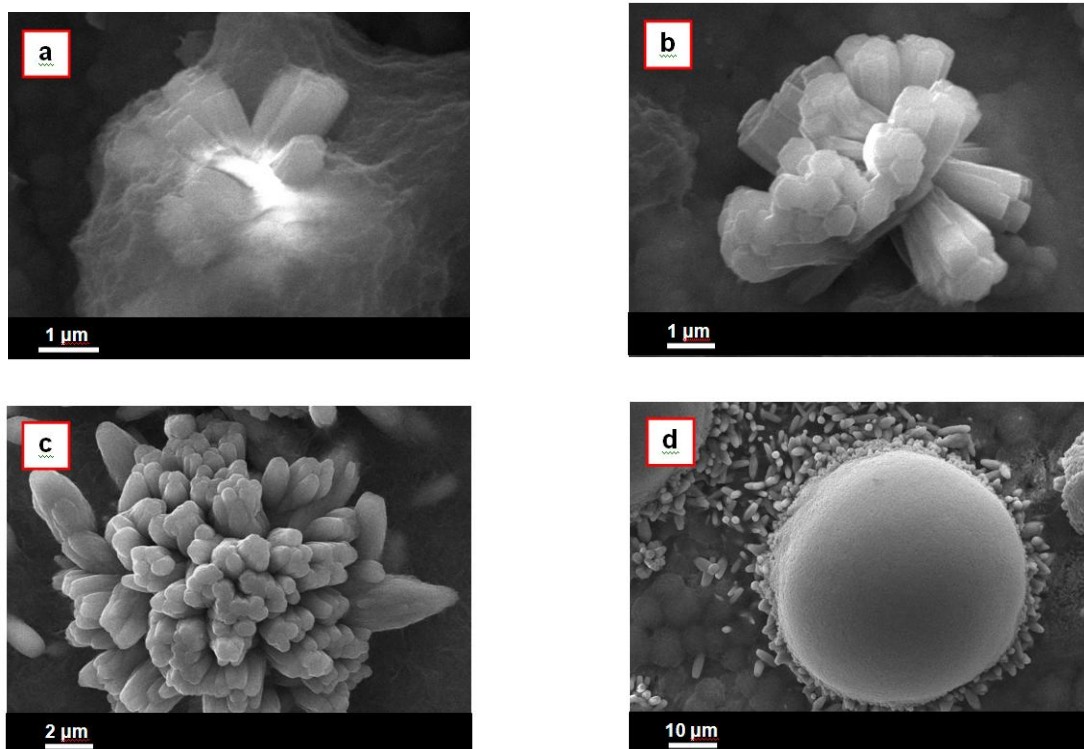


Fig. 2. SEM images of the ZnO nanostructure films grown on the zinc foil for deposition time of (a) 2, (b) 4, (c) 7 and (d) 10 days.

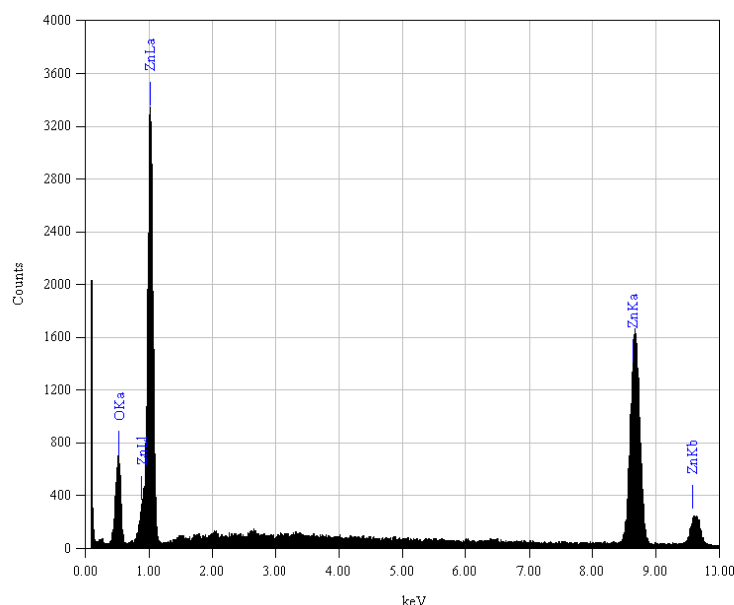
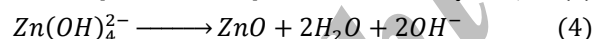
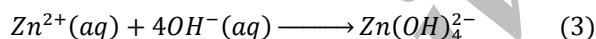
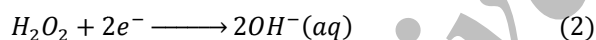
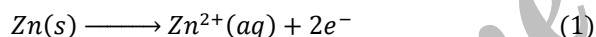


Fig. 3. EDS spectrum of the ZnO nanostructure film grown on the zinc foil for deposition time of 10 days.

3. Results and discussion

The growth of ZnO films is based on the formation of solid-phase from the aqueous solution, which includes two steps, (i) nucleation and (ii) growth.

The nucleation can occur by reduction and oxidation of H_2O_2 and Zn foil on the surface of substrates. This can be explained as:



During the deposition, surface of zinc foil is dissolved by oxidation (reaction 1) and also H_2O_2 is reduced to OH^- ions (reaction 2). The OH^- ions react with Zn^{2+} ions in the electrolyte to form $Zn(OH)_4^{2-}$ as growth unit for ZnO films (reaction 3). The formed $Zn(OH)_4^{2-}$ is more stable than that of Zn^{2+} ions [12]. Subsequently, growth unit $Zn(OH)_4^{2-}$ ions bonded together to form ZnO nuclei via dehydration reaction (reaction 4). Developing the growth unit ($Zn(OH)_4^{2-}$) can act as the building blocks incorporated into the crystal lattice.

The wurtzite structure of ZnO exhibits polar and non polar surfaces. The polar surfaces have positively Zn^{2+} -terminated (0001) and negatively O^{2-} -terminated (000 $\bar{1}$) planes. The non polar planes such as {01 $\bar{1}$ 0} and {2 $\bar{1}$ $\bar{1}$ 0} are thermodynamically more stable polar planes [13]. The polar planes often undergo atomic rearrangement to minimize their surface energy. Thus, ZnO rods will form hexagonal shape. This process makes ZnO rods in the initial steps and flowers morphology in the final steps.

The XRD pattern of the ZnO film is shown in Fig. 1. The XRD pattern exhibits a set of well defined diffraction peaks which are indexed to the wurtzite hexagonal phase of ZnO and $Zn(OH)_2$. The deposition carried out in room temperature and due to low thermal energy available, the $Zn(OH)_2$ was not completely decomposed to ZnO phase. The appearance of the diffraction peaks corresponding to Zn is due to the fact that Zn foil is used as a substrate.

The SEM images of ZnO nanostructures are demonstrated in Fig. 2. Fig. 2(a) shows the SEM image of nanostructures deposited after 2 days. It can be seen that the formed ZnO consists of agglomerated particles with poor crystallization (i.e. less sharp edges) and few rods can be observed. However, as the deposition time increased from 2 to 4 days, the ZnO rods with well-defined crystallization and average diameter of 500 nm were formed on the zinc foil as shown in Fig. 2(b). It is suggested that the dehydration reaction rate of $Zn(OH)_2$ to ZnO increases. These rods are connected to each other at one end to form flower-like morphology. When, the deposition time increased to 7 days, bigger ZnO flower formed (Fig. 2(c)). This is due to more available zinc precursor for deposition. Finally, the cauliflower morphology with uniform deposition on the top of the rods can be seen in Fig. 2(d) for deposition time of 10 days. All the SEM images show that the density of rod on the zinc substrate strongly depends on the deposition time.

The chemical purity of the ZnO nanostructures as well as their stoichiometry was investigated by the EDS analysis attached to the SEM. A typical EDS spectrum of the specimen for deposition time of 10 days (Fig. 3) shows the presence of Zn and O with atomic percentage of 52% and 48%, respectively.

Fig. 4 shows the UV-visible diffused reflectance spectroscopy (DRS) plot of the specimen for deposi-

tion time of 10 days. The DRS spectrum reveals that the band gap absorption edge is ~ 347 nm. To estimate the optical band gap (E_g) using the equation of $E_g = 1240/\lambda$ [14], the E_g can be calculated as 3.57 eV. The value is higher than the value for bulk ZnO (3.37 eV).

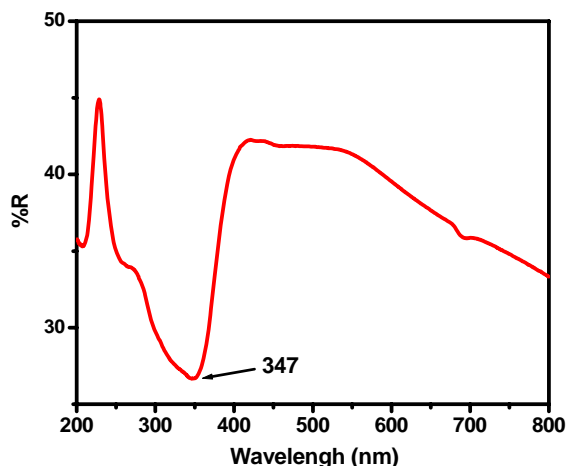


Fig. 4. UV-vis diffuse reflectance spectrum of the ZnO nanostructure film grown on the zinc foil for deposition time of 10 days

The room temperature PL spectrum of the ZnO nanostructure film grown on the zinc foil for deposition time of 10 days is depicted in Fig. 5. It can be seen that the specimen shows peaks at 377, 395, 424, 485 and 520 nm. The ultraviolet emission band located at 377 nm is attributed to the near-band edge (NBE) free exciton transition from the localized level below the conduction band to valance band [15]. The violet, blue

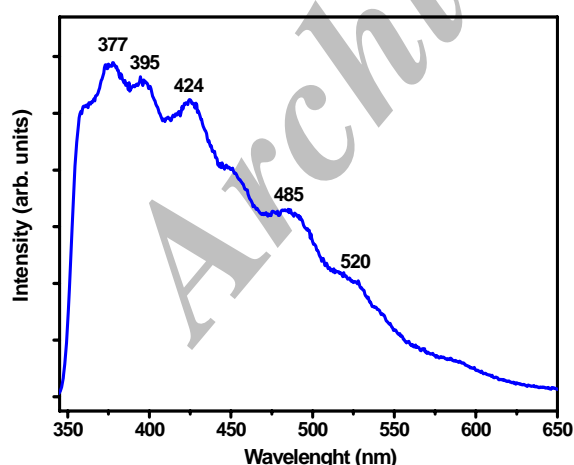


Fig. 5. PL spectrum of the ZnO nanostructure film grown on the zinc foil for deposition time of 10 days.

and green emission band is observed at 395, 424, 485 and 520 nm, respectively. It is originated from different deep-level emission (DLE). The DLE is mainly related to the point defect such as oxygen vacancies

and zinc interstitials. Cheng *et al.* [16] have attributed the appearance of blue emission bands originating from the oxygen vacancy. Vanheusden *et al.* [17] have attributed that the green transition corresponds to the singly ionized oxygen vacancy in the ZnO and the emission results from the recombination of the photo-generated hole with the singly ionized charge state of this defect. The blue-green emission can originate from oxygen vacancies and Zn interstitials [18,19].

Conclusion

ZnO with different morphologies, such as the rod and cauliflower have been successfully fabricated by chemical bath deposition. The structural characterization reveals well defined peaks, which could be indexed to the wurtzite hexagonal phases of ZnO and $Zn(OH)_2$. The morphology of ZnO nanostructures depends on deposition time. Growth at longer time showed that the formed ZnO becomes bigger, thicker, and exhibits higher density. The chemical studies showed presence of Zn and O atoms in the films. The optical studies revealed that the different visible emission originated from different defect mechanism. This method could be employed to synthesis some other metal oxides nano/micro structures.

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