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Synthesis and self-assembly of dumbbell shaped ZnO sub-micron structures using low temperature chemical bath deposition technique

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HIGHLIGHTS

- Controlled growth of Dumbbell shaped ZnO using Chemical Bath Deposition (CBD).
- Growth mechanism of dumbbell shaped ZnO by self-assembling was discussed.
- Quick Transformation of ZnO dumbbell structures in to tubular structures by dissolution.
- Sharp UV Emission at 370 nm from both dumbbell and tubular structures.

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ABSTRACT

We report well dispersed horizontal growth of ZnO sub-micron structures using simplest technique ever known i.e. chemical bath deposition (CBD). A set of samples were prepared under two different cases A) dumbbell shaped ZnO grown in CBD bath and B) tubular ZnO structures evolved from dumbbell shaped structures by dissolution mechanism. Single phase wurtzite ZnO formation is confirmed using X-ray diffraction (XRD) technique in both cases. From the morphological investigations performed using scanning electron microscopy (SEM), sample prepared under case A indicate formation of hex bit tool (HBT) shaped ZnO crystals, which observed to self-organize to form dumbbell structures. Further these microstructures are then converted into tubular structures as a fragment of post CBD process. The possible mechanism responsible for the self-assembly of HBT units to form dumbbell structures is discussed. Observed free excitonic peak located at 370 nm in photoluminescence (PL) spectra recorded at 18 K indicate that the micro/nanostructures synthesized using CBD are of high optical quality.

1. Introduction

In nanofabrication techniques, self-assembly of various nanostructures offers the possibility of individual components to self-organize themselves to form higher order structures. Self-assembly technique involves van der Waals forces, electrostatic forces or hydrophobic interactions as fundamental forces involved in the formation of various novel nanoarchitectures. These structures are of particular interest due to their lower densities and higher surface areas which make them fascinating for understanding the mesoscopic physics along with possible fabrication of nano and micro scale devices [1,2].

Among number of advanced functional materials, Zinc oxide (ZnO) has received specific attention due to its unique properties such as wide band gap (3.37 eV), large exciton binding energy (60 meV), bio-compatibility, low friction factor, piezoelectricity, etc [3–6]. Researchers are exploring various nanostructures of ZnO in order to enhance these properties further. Till today variety of ZnO nanostructures (for e.g. nanowires, nanorods, nanobelts, nanotubes, hexagonal nano columns, nanostars, nanoflowers, etc. [7,8]) are synthesized by employing various synthesis methods (such as sol–gel, spray pyrolysis, gas-phase reaction method, laser ablation thermal evaporation, etc. [9]). Most of these techniques require either high temperature or high vacuum. Keeping in mind the

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challenge of cheaper and more user-friendly technique to grow ZnO nanostructures, wet chemical bath deposition (CBD) method is used. The method is inexpensive, low temperature, reproducible and environmental friendly [10,11]. Among various ZnO nanostructures, hexagonal rods are centre of attraction not only to explore the fundamental studies but also to use them in micro and nano device fabrications [12]. Recently CBD grown ZnO ultrathin nanowires showed IQE of more than 20% useful for photonic devices [13].

In this article we report well dispersed horizontal growth of ZnO sub-micron structures on SiO_2/Si substrate. The growth is demonstrated using zinc acetate along with NaOH in de-ionized (DI) water considering the green chemistry. Possible mechanism responsible for the self-assembly of ZnO dumbbell structure is discussed herewith. We have also reported the transformation of these microstructures to produce tubular structures as a fragment of post CBD process. The photoluminescence (PL) characterization of these structures at low temperature shows a strong UV emission.

2. Experiment

Sub-micron sized ZnO dumbbells were synthesized on 200 nm of thermally grown SiO_2/Si substrate by CBD route at low temperature (80 °C) using zinc acetate dihydrate and sodium hydroxide. Substrates were cleaned using trichloroethylene, acetone, isopropyl alcohol and DI water in ultrasonic bath to remove the surface contamination. Simple precipitation method described by Lee et al. [14] was followed. For this 20 ml of 2 M NaOH and 200 ml of 0.1 M zinc acetate (S. D. Fine Chemicals, 99%) aqueous solutions were prepared in DI water. Under steady stirring conditions, NaOH solution was dropwise added into zinc acetate solution to adjust the pH of solution to 7. Substrates were dipped into the solution by adjusting their heights in the chemical bath for 2 h. In case of sample A, the substrate was completely immersed in the solution throughout the experiment which results in growth of dumbbell shaped ZnO. Further these microstructures are converted into hexagonal tubes when exposed only to evaporate from the same solution for 40 min, refered as sample-B. Sample A and B were rinsed several times by ethanol, DI water and finally dehydrated at 100 °C for 2 h in ambient conditions. The structural and morphological evolutions of deposits were investigated by X-ray diffraction (XRD), scanning electron microscope (SEM) techniques (FEI-INSPECT). Elementary excitations of ZnO at microscopic level were studied using micro Raman spectroscopy (Renishaw Invia, UK) in back scattered geometry with excitation source of Ar^+ laser ($\lambda = 514$ nm, output power = 25 mW). The photoluminescence (PL) was measured (at temperature 300 and 18 K) using Acton Spectrapro2750 (Princeton measurements) ultraviolet-visible spectrophotometer with He–Cd laser as an excitation source.

3. Results and discussion

Fig. 1 (a and b) presents the X-ray diffraction patterns of sample A and B, respectively. In both cases, the XRD patterns showed sharp peaks positioned at $2\theta = 31°, 34°, 36°, 47°, 56°, 62°, 67°$, and 69°. Observed peak positions are in accordance with the standard peaks listed for wurtzite ZnO crystal [15]. The diffraction planes corresponding to observe 2θ in both cases are (100), (002), (101), (102), (110), (103), (112), and (201) respectively and they further confirms single phase formation of a typical wurtzite ZnO.

The morphology of the deposits in both samples was investigated by FESEM technique. Fig. 2 presents microscopy images recorded for ZnO structures developed in the case A. The image indicates growth of well dispersed ZnO dumbbells. Many of these structures are observed to grow horizontally onto the substrate and

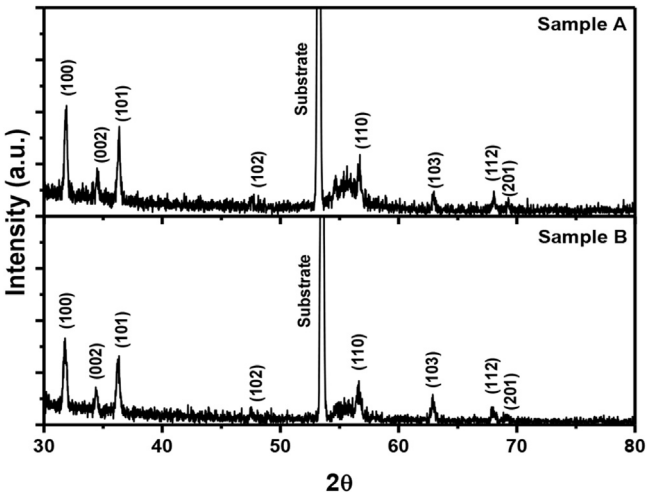

Fig. 1. X-ray diffractgram for sample A (dumbbell structures) and B (tube structures).

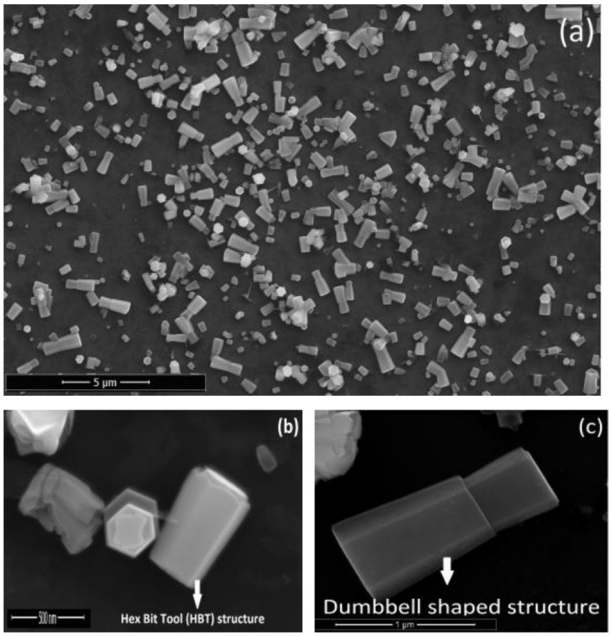

Fig. 2. (a) FESEM image recorded for case A (b) High resolution FESEM image indicating Hex Tool Bit (HBT) structure and (c) High resolution FESEM image indicating dumbbell shaped structure.

are self-organized in the form of dumbbell shaped structures (indicated as Fig. 2 (c)). The sizes of dumbbell structures are about 1–2 μm, while the widths of these structures at one end are in the range of 200–300 nm and at the other end are 250–400 nm. It is believed that the growth of the crystallite in twin (i.e. dumbbell structures) takes place along the c-axis by means of the incorporation of the growth units on the growth interfaces such as (0001) or (000$\underline{1}$). Various twining mechanisms based on the linkage/incorporation of the growth units explaining formation of bipyramidal and dumbbells like twinned crystals are already proposed by many researchers [16–19].

In one such mechanism formation of a dumbbell like twinned crystal structure is proposed by B. G. Wang et al. assuming the Na^+ ions to act as a bond bridge in between the growth units, leading towards the formation of dumbbell like twinned crystallites under hydrothermal conditions [20]. However, after careful observations