

Influence of growth time on the morphology of ZnO nanostructures prepared by low-temperature chemical bath deposition

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Abstract: Different zinc oxide (ZnO) nanostructured thin films were grown on glass substrates at low temperatures by combining successive ionic layer adsorption and reaction (SILAR) method and chemical bath deposition (CBD). Morphologies and structures of the samples were investigated by X-ray diffraction (XRD), energy-dispersive x-ray spectroscopy (EDX) and scanning electron microscopy (SEM). The reaction mechanism for the growth of ZnO microstructures is analyzed. The results show that the surface morphology of the ZnO nanostructures films changed from hexagonal nanorods into hexagonal nanodisc with increasing the growth time of ZnO. According to XRD, the growth of a preferred c-axis oriented ZnO nanostructured thin films in (002) orientation can be easily driven at such low growth temperature. The present approach demonstrates its potential for large-scale, low-temperature and controlled structural morphology of ZnO nanostructured films.

Keywords: CBD method; ZnO nanostructures; Morphology; XRD; SEM

I. Introduction

Nanostructures have been drawing special attention of scientists and technologists around the world due to its unique chemical, optical and electronic properties for a broad range of novel applications. Among various nanomaterials, zinc oxide (ZnO) nanostructures are widely used in many applications due to its wide band gap (3.1 - 3.4eV), large exciton binding energy (60 meV), and excellent thermal and chemical stability [1–4]. ZnO exhibits a dazzling variety of nanostructure configurations [5]. Also, ZnO is non-toxic, biosafety, and their large-scale production does not present environmental and health hazards [6]. Today, the applications of ZnO nanostructures including field emission [7], gas sensors [8], solar cells [9], field-effect transistors [10], antibacterial activities [11], self-cleaning [12] light emitting diodes [13], laser systems [14] and photocatalysts [15]. Controllable growth of ZnO nanostructures is an important topic in the field of practical applications. Various methods can fabricate different morphologies of ZnO nanostructures such as magnetron sputtering, atomic layer deposition [16], thermal evaporation [17], vapour phase epitaxy, solid-state reaction and hydrothermal method [18–25]. However, these methods are required to ultra-high vacuum, expensive equipment, high operation temperatures, catalysts or the use of noxious gas compounds. Compared with the methods mentioned above, preparing of ZnO nanostructures films by chemical bath deposition (CBD) is more attractive because of its excellent characteristics. This due to the CBD can accurate control the morphology and the orientation of ZnO by tuning the process parameters [26]. Also, it is a simple, rapid, inexpensive, working under low temperatures (< 100 °C), and applicable for large scale production using the variety of substrates [27]. Most of the previous researches with CBD mainly focused on the control of the ZnO nano structures morphology by changing the concentration and temperature of the solution [28–29]. In this paper, we present the effect of growth time on the ZnO nanostructures morphologies. The growth mechanism of the fabricated ZnO films was discussed.

II. Experimental details

2.1. Materials

Zinc acetate dihydrate ($\text{Zn}(\text{CH}_3\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, 99 %), Zinc sulphate ($\text{Zn}(\text{SO}_4)$, 99 %), ammonia (NH_4OH), sodium hydroxide (NaOH , 99.6 %), hexamethylene tetraamine ($\text{C}_6\text{H}_{12}\text{N}_4$ (HMT), 99.98 %), hydrochloric acid (HCl , 98 %) were purchased from Alfa Aesar, USA. Citric acid ($\geq 99.5\%$) was purchased from Sigma-Aldrich, USA. These chemicals were used as received from the suppliers.

2.2. Deposition of ZnO seed layer

The synthetic process of the nanostructured ZnO thin films at low temperature involves two-step chemical solution method. The first step is the deposition of the ZnO seed layer on a glass substrate by successive ionic layer adsorption and reaction (SILAR) method [30]. The second step is the deposition of a controlled ZnO nanostructured films onto different seed layer films by using simple chemical bath deposition (CBD) method [31].

The SILAR method is mainly based on the adsorption and reaction of the ions from the solution and rinsing between every immersion with deionized water to avoid homogeneous precipitation in the solution. Zn(SO₄) were dissolved in diluted NH₄OH to get a Zinc ammonium complex solution, which was then served as a cationic precursor. Double distilled (DD) water kept at 80° C was used as an anionic precursor. Microscope glass slides were used as substrates. Prior to use, the glass substrates were put in boiled dilute sulfuric acid (1:10 v/v) for 45 min and then thoroughly rinsed in ethanol, acetone, and de-ionized water subsequently. The cleaned glass substrate was immersed in Zinc ammonium complex ([Zn (NH₃)₄]²⁺) solution for 40 s, where [Zn (NH₃)₄]²⁺ adsorbed onto the glass substrate. Then, the glass substrate was immersed in DD water for 20 s, where the adsorbed zinc ammonia complex was converted into zinc hydroxide (Zn(OH)₂). After that, the Zn(OH)₂ coated substrate was subjected to ultrasonic agitation for 60 s to remove loosely bonded zinc hydroxide (Zn (OH)₂) molecules. Finally, the Zinc hydroxide coated substrate was immersed in the DD water bath that was maintained at 80° C for 20 s, where Zn (OH)₂ was converted into solid ZnO film. ZnO seed layer films were prepared at 20 cycles to allow a uniform coverage of the substrate. A drying period of 15 s was maintained before the start of another deposition cycle. The as-prepared ZnO seed layer films were subjected to annealing at 300°C for 1 h.

2.3. Growth of ZnO nanostructured thin films

The formation of controlled ZnO nanostructured films onto the seed layer films was carried out using simple chemical bath deposition (CBD) method. The chemical bath was prepared by mixing equimolar (0.05M) aqueous solution of Zn(CH₃COOH).2H₂O and HMT. The solutions were dissolved in 20 ml of de-ionized (DI) water. The pH of the reaction was controlled at 6.6 by adding a 0.1 M NaOH solution.

To fabricate different ZnO nanostructures morphology by a chemical bath, the ZnO seed layer/glass substrates were immersed vertically in the solution at h at 80° C for different deposition times ranging from 2 to 8 h. After successful completion of the deposition condition, the temperature of the water bath was allowed to cool down to ambient temperature. Finally, the samples were removed from the aqueous solution and cleaned carefully with DI water and acetone for several times to remove residual salts and then dried at room temperature.

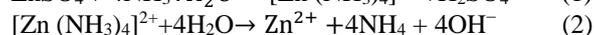
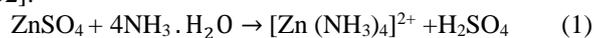
2.4. Characterization of ZnO nanostructures

Field emission-scanning electron microscope (FE-SEM, ZEISS SUPRA 55 VP and ZEISS LEO Gemini Column), X-ray diffraction (XRD, Philips X'Pert Pro MRD) using Cu K_α radiation (k = 1.5418 Å), and energy dispersive X-ray spectrometer (EDX; Oxford Link ISIS 300 EDX) were used to characterize the morphologies, chemical compositions, and structures of the ZnO nanostructures.

III. Results and discussion

3.1. Surface morphological analysis

The growth mechanism of ZnO seed by SILAR process are involved in the following chemical reactions, equations from (1) to (4), [32]:



The formation of ZnO seed-layer by SILAR method provides the nucleation sites for the growth of ZnO nanostructures by CBD method [33]. This due to the ZnO seed-layer decreases the nucleation barrier by decreasing the interface energy and makes the ZnO nanostructures easy to grow [34]. As the decomposition of zinc acetate dihydrate and hexamethylene tetra amine at elevated temperature in CBD process increased, the concentration of Zn²⁺ and OH⁻ increases correspondingly [35-36]. When the Zn²⁺, OH⁻ and Zn(OH)₄²⁻ concentration reaches a supersaturated degree, it leads to the rapid nucleation of ZnO. Subsequently, ZnO nanostructures begin to grow up along c-axis preferentially on seed surfaces in the reactive solution with an appropriate temperature. The morphology of ZnO nanostructures grown during CBD process can be influenced by many experimental parameters, such as pH of solution, time and temperature. Among these parameters, the time growth plays a significant role in tuning the morphology of ZnO nanostructures. Figure 1 shows SEM images of ZnO thin films grown on ZnO seed layer by chemical bath deposition methods with different reaction time: (a) 2, (b) 4, (c) 6 and (d) 8h. ZnO nanostructures undergo a gradual morphological evolution with reaction time as shown in this Figure.

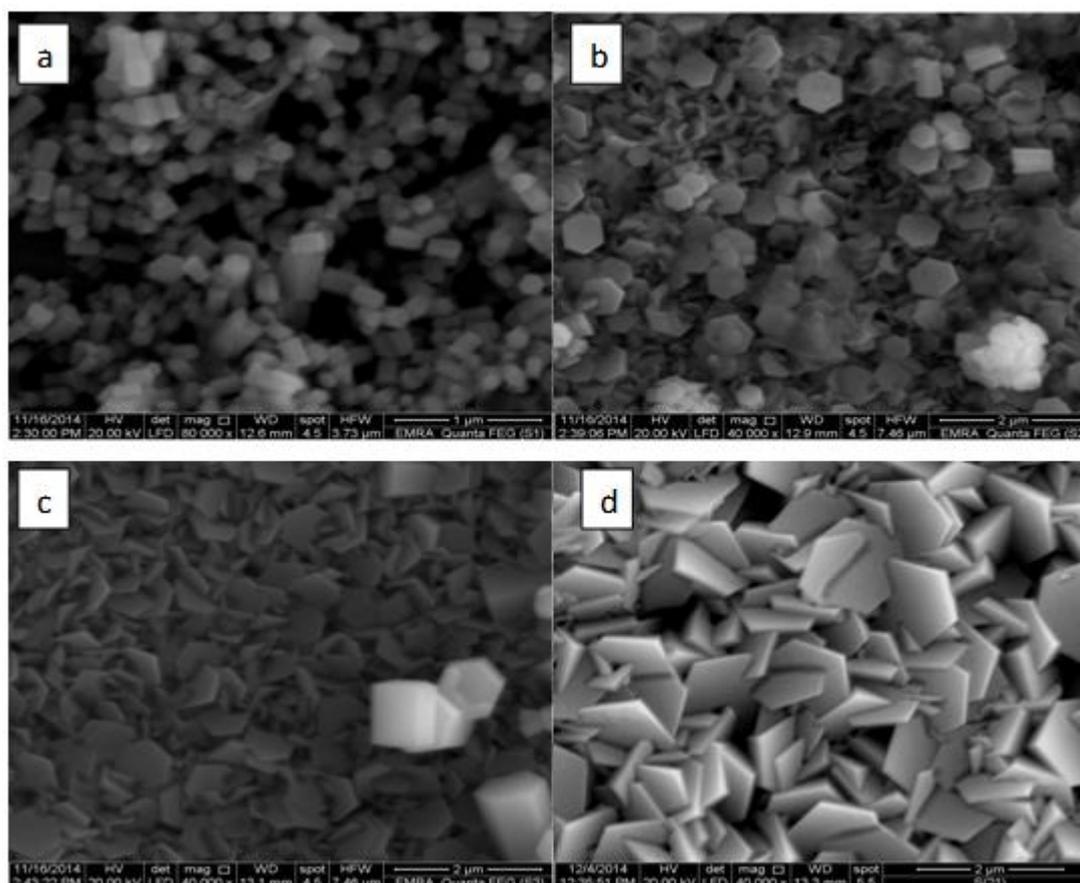


Figure 1. SEM images of nanostructured ZnO thin films with different growth periods of (a) 2, (b) 4, (c) 6, and (d) 8 h at 80°C.

When the deposition has been performed for 2 h, random distribution of nanorods was formed as illustrated in Figure 1(a). The disordered growth of ZnO nanorods is due to the polycrystalline glass influence. The top view SEM image indicates that all of ZnO nanorods have a perfect hexagonal shape throughout their lengths and grow preferentially along the c-axis direction overall sample area. These ZnO nanorods show the average diameter of 200 nm and length of ~600 nm.

Figure 1(b) displays the SEM image of ZnO nanostructured film grown for 4 h. Random distribution of hexagonal nanodisc was formed and accompanied with a few numbers of ZnO nanorods distributed in the ZnO film. The nanorods have average diameter and length of about 400 nm and 480 nm, respectively. The morphology of the grown ZnO film for 6 h, Figure 1(c), shows a high density of hexagonal nanodisc formed with a very small number ZnO nanorods distributed over the ZnO film. ZnO nanodisc takes different and random directions. As the deposition time is prolonged to 8 h, the number of nanodiscs increases and some cracks appear. Then, the simultaneous growth of an enormous number of nanodiscs limits their sizes to become thin and interfere with each other. At the same time, the nanorods are disappeared at the longer growth time as seen in Figure 1(d). The thickness of the samples was increased from 600 nm at 2 h to 1.4 μm at 8 h. Then, the vertical growth rate is 5 nm/min during the first two hours; then this rate decreased to ~ 3 nm as the growth time increased. The observations through the above SEM images 1(a-c) clearly reflect that the density of ZnO nanorods decreases and the surface morphology of the ZnO nanostructures films changed from hexagonal nanorods into hexagonal nanodisc as the growth time increases. I.e., nanorods numbers decrease and numbers of nanodiscs increase as the deposition time increased.

The same result was obtained in the previous study by increasing the concentration of OH⁻ in the precursor [37]. When the OH⁻ concentration is low, the crystal growth rate along the c axis is faster to any direction. Therefore, the ZnO sample shows the morphology of one-dimensional nanorods. At high OH⁻ concentration in the precursor, the (0001) surfaces of ZnO with tetrahedral zincs, usually, have terminal OH⁻ ligands in solution [38-39]. These ligands will prevent the newly produced ZnO clusters from incorporating into the ZnO crystallites effectively. Therefore, the crystal growth of the ZnO crystallites along the c axis is partially suppressed under this condition. However, they can still grow sideways and finally two-dimensional ZnO nanoplates are formed. In our experiment, ammonia reacts with water to produce ammonium hydroxide, which provides a continuous source of

OH⁻ for hydrolysis. Then, the concentration of OH⁻ in the solution is increased as the growth time increased. Hence, the hexagonal nanorods (Figure 1 (a)) are converted into hexagonal nanodisc (Figure 1 (c)). These results revealed that the growth duration plays an important role in the morphology of the ZnO nanostructures. The ZnO nanorod size increases and the nanorods densities decrease when increasing the deposition time due to the Ostwald ripening [40].

In order to check the chemical composition and phase structure of the fabricated ZnO nanostructures, the samples were analyzed by EDX and XRD. EDX, a complementary technique in SEM, which detects energies of X-rays generated by a sample upon excitation with an electron beam, can be used for elemental analysis and mapping of the ZnO nanostructures. Typical EDX pattern of the fabricated ZnO nanostructured thin film is presented in Figure 2. This EDX spectrum reveals the existence of Zn and O signals, which corresponds to the characteristic composition of ZnO. According to EDS analysis, the quantitative analysis is 84.7 % Zn, 10 % O. The peak marked with Si (5.3 %) in EDX pattern were corresponding to the glass substrate. In addition, Si (5.3 %) signal is detected from the glass substrate in the EDX pattern. This is because EDX has a larger interaction volume ($\geq 1 \mu\text{m}$ at the used accelerating voltage) than the thickness of the nanostructured ZnO film.

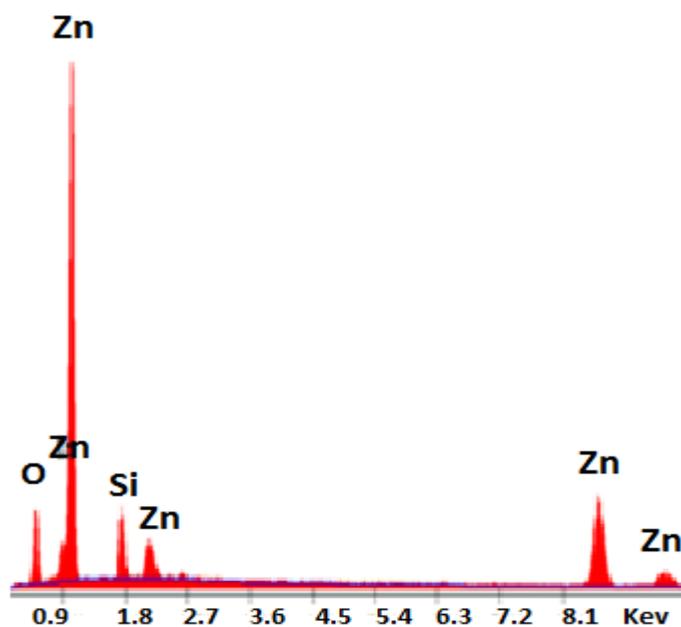


Figure 2. EDX spectrum of the fabricated ZnO nanostructured thin film.

XRD fingerprinting can provide information about the crystal structure and chemical composition of the ZnO sample. Figure 3 shows the X-ray diffraction (XRD) pattern of ZnO nanostructured film grown at 80°C. Obviously, a very sharp peak is observed at $2\text{-theta} = 34.40^\circ$ associated to the (002) crystalline orientation, which corresponds to wurtzite ZnO structure with highly orientated along c-axis (space group P63mc). The data is in matches with the JCPDS file # 36-1451.4. There are several reports on ZnO films showing a strong c-axis preferred orientation that is perpendicular to substrate surface [41]. Such orientation of ZnO is an acceptable point due to the (002) plane in ZnO structure has the highest atomic density and possesses the lowest surface free energy [42]. As a result, the growth of a preferred c-axis oriented ZnO nanorod thin films can be easily driven at such low growth temperature. Also, there are other minor peaks at 31.72° and 36.21° corresponds to (1 0 0) and (1 0 1) orientation plane of ZnO phase. These indicate the ZnO nanorods are preferred growth orientation along the C axis of hexagonal phase in accordance with SEM images, which is the nature of the ZnO crystal growth [43]. The average crystallite size, estimated by the Scherrer's equation using the diffraction intensity and The full width at half maximum (FWHM) of (0 0 2) peak, is about 75 nm. The strong and narrow diffraction peak (002) indicates that the material has a good crystallinity. At the same time, no diffraction peaks from other species could be detected, which indicates that all the precursors have been completely decomposed after the deposition process and the high purity of the fabricated ZnO nanostructures.

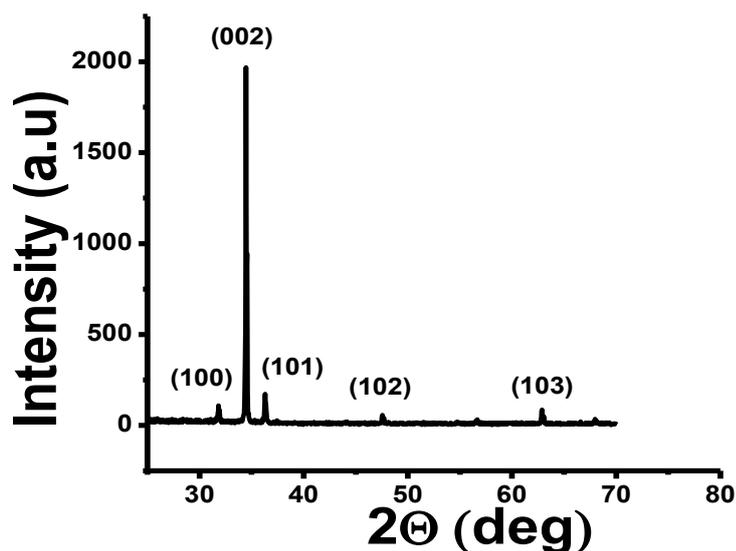


Figure 3. XRD spectrum of the fabricated ZnO nanostructured thin film.

IV. Conclusion

This work introduced a facile and low-cost method to fabricate and control the morphology of ZnO nanostructured thin films via two-step CBD method at low temperature. The surface morphology of the ZnO nanostructures films changed from hexagonal nanorods into hexagonal nanodiscs by controlling the growth time of ZnO thin film from 2h to 6 h. The density of the nanodiscs is increased as the time increased to 8h. However, the size of each disc decreased. EDX spectrum showed the high purity of the fabricated ZnO nanostructured thin films. XRD showed the growth of a preferred c-axis oriented wurtzite ZnO nanostructured thin films in (002) orientation plane. These nanostructures are suitable for many applications such as sensing, self-cleaning and photocatalytic.

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