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Simple Hydrothermal synthesis of the ZnO hexagonal nanotubes

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ABSTRACT

Zinc oxide (ZnO) hexagonal nanotubes were successfully synthesized on glass substrate by using a simple hydrothermal method. Glass bottles with rubber caps were used as reactor vessels (100 ml). Hexahedral zinc nitrate Zn $(NO_3)_2$.$6H_2O$, Hexamethylenetetramine (HMT) $C_6H_{12}N_4$ and deionized water were the starting materials for the chemical reaction in the presence of heat. The influence of the synthesis process on the morphology and the optical properties crystallinity and structural properties are studied by X-ray diffraction and field emission scanning electron microscope (FE-SEM). The diffractogram of the films show that XRD reflection peaks can be assigned to the wurtzite hexagonal-ZnO in accordance with the FE-SEM images. The optical property of ZnO tubes was studied in UV-Visible range and photoluminescence PL shows good UV to blue-green intensities ratio.

INTRODUCTION

Quasi-one-dimensional nano- materials such as nanorod, nanobelts, and nanotube have become the focus of intensive research owing to their exceptional applications in fabrication of nanoscale devices (Lupan, O., *et al*., 2010), ZnO nanostructures have attracted a considerable attention due to their unique properties and various applications such as photo catalysts (Lupan, O., *et al*., 2010), photoconductivity, gas sensory, chemical sensors, detecting ultraviolet (UV) radiation and optoelectronic devices (Lupan, O., *et al*., 2009; Chai, G.Y., *et al*., 2011).

Because of its large exaction-binding energy 60 meV as well as a wide optical band gap of ZnO is 3.37 eV at room temperature. In addition ZnO has the same crystal structure and optical properties as those of GaN based compounds (Chow, L., O. Lupan and G. Chai, 2010; Lupan, O., *et al*., 2007). Synthesis of ZnO nanostructures is subject to intense research lately due to very rich nano shapes such as wires, tubes, rods, flowers, sheets/flakes, particles, stars, belts and hexagonal prismatic using various methods such as the evaporation, chemical vapor deposition and wet chemical process like template-based, surfactant-assisted precipitation, hydrothermal and solvothermal methods (Lupan, O., *et al*., 2010; Byrappa, K., T. Adschiri, 2007).

Compared with other techniques to achieve ZnO nanotubes, low-temperature solution growth process has been generally applied due to its simplicity, low coast and ease of fabrication; however, the mechanisms that rule the tube-shaped morphology have received little attention. (Lupan, O., *et al*., 2010; Bin Liu and Hua Chun Zeng, 2009).

As a specific one-dimensional (1D) morphology, ZnO nanotubes attract extensive attention due to their high aspect ratio, low density and good surface permeability as well as hollow textures, turning into a promising candidate for lots of potential applications (Vayssieres, L., *et al*., 2001).

Three different approaches have been reported for the fabrication of ZnO tubular structures:

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(i) Solution synthesis (Bin Liu and Hua Chun Zeng, 2009; Vayssieres, L., *et al*., 2001; Shi-Yong Yu, *et al*., 2007l; Yanhong Tong, *et al*., 2006), This approach normally includes a two-step process in which nanorods ZnO are first formed, In the second step, the core of ZnO nanorods is selectively etched in proper etching solutions (Vayssieres, L., *et al*., 2001; Quanchang Li, *et al*., 2005; Jiyuan Yang, *et al*., 2012; Kebbab, Z., *et al*., 2008). The dissolved axial part materials can be either ZnO itself or other templating materials (Quanchang Li, *et al*., 2005). (ii) The second approach requires a template, i.e. synthesis of coaxial-layered nanostructures, namely, nanocables, in which the component phases are separated in the radial direction. in which ZnO is first formed on the external surfaces of metallic zinc nanowires and nanorods, and the removal of metallic cores into the vapor phase at elevated temperatures subsequently gives rise to tubular structures of ZnO (Jih-Jen Wu, *et al*., 2002; Hu, J.Q., *et al*., 2003). (iii) The third approach involves reactions that can be carried out with pulsed laser deposition (PLD), chemical vapor deposition (CVD) and metalorganic chemical vapor deposition (MOCVD) (Bin Liu and Hua Chun Zeng, 2009; Hu, J.Q. and Y. Bando, 2003; Jong Seok Jeong, *et al*., 2005).

Among these methods, hydrothermal is one of the most common and promising methods for the synthesis of isometric nanotube ZnO crystals[19], this method enjoys advantages such as a one-step synthesis without any additional processes like etching or milling etc…. (Qi, T. *et al*., 2008), low level of aggression, high purity nonpolluting, inexpensive and narrow particle size distribution. Moreover the hydrothermal method due to the low temperature reaction in water under a sealed environment is consider as the green chemistry study.

The structure of the film plays important role affect the electrical and optical properties of the films. Many parameters determined the structure properties of the materials such as grain size, the shape of the grain, micro strain and dislocation density.

The grain size can be defined as the cubic root of the volume of a single crystallite (Kobrinskya, V., *et al*., 2010). The micro strain depends on the deposition conditions (Chougule, M.A., *et al*., 2012), while the dislocation is a kind of defect in the crystal associated with the misregistry of the lattice in one part of the crystal with that in another part (Kathirvel, P., *et al*., 2009). In this paper, we report the fabrication of ZnO hexagonal nanotubes by one step simple hydrothermal method using glass autoclave then study the structural and optical properties of the product ZnO hexagonal nanotubes, It is expected that these ZnO hexagonal nanotube might be convenient for the fabrication of electrical and optoelectrical devices such as dye-sensitized solar cells, sensors, and electroluminescent devices.

Experiment:

ZnO films were prepared using aqueous solutions of $Zn(NO_3)_2.6H_2O$(>99% sharlu, Spain), hexamethylenetetramine $C_6H_{12}N_4$ (HMT)(>99% Aldrich Germany). 0.04M of the aqueous solution [weighed amounts of both materials 0.95 g of zinc nitrate and 0.448 g of HMT] was dissolved in 80 ml of de-ionized water in a glass beaker under stirring without heating for 5 min until the solution became transparent. When it became transparent, the solution transferred in to glass autoclave of volume 120 ml and pre cleaned glass substrate was putted inside the autoclave. in addition, the autoclave was closed firmly and putted in oven and kept at 90 ˚C for 4 hours. Finally the autoclave cooled down naturally and gradually about 12h (cooling time). As a result a white thick film was deposited on the glass substrate. In order to remove any contamination from the substrate, the glass substrate was dipped carefully in de-ionized water to wash the film and dried in air. The preparation process repeated several time to obtain extra films in order to study the physical properties.

The prepared thick films were examined by X-ray diffraction (miniflex II Rigaku, Japan) (Cu, kα), atomic force microscope (AFM) to study the surface morphology of the film and field emission scanning electron microscope (Hitachi S-4160) (FESEM) to study the structural properties of the films.

Also the optical behavior of the film was studied using Shimatzu UV-Visible spectrophotometer.

RESULTS AND DISCUSSION

Structural properties:

X-ray diffraction of the thermal treated thick film shows polycrystalline structure with major peaks in the direction (100), (002) and (101) see figure (1).

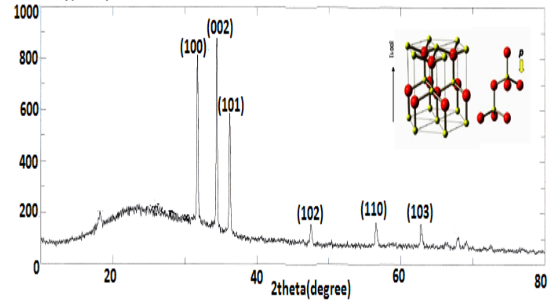

Fig. 1: X-ray diffractogram of the ZnO deposition.

Table 1: Estimated structure parameters with dislocation density and micro strain of ZnO thick film peaks

Plane N0.	D(grain size)nm	Latice parameter a(A˚), c(A˚)	Dislocation Density $\delta x10^{15}$ ($line^2/m^2$)	Micro strain ε x 10^{-3}
100	26.9	3.252 5.311	1.38	1.28
002	29.5		1.14	1.37
101	27.3		1.34	1.26

From the diffraction pattern it's obvious that all these diffraction peaks can be indexed as hexagonal wurtzite structures of ZnO, and no peaks for other impurities were detected in the spectra. The sharp and intense peaks (0 0 2) indicate that ZnO nanotubes are in general oriented with their c-axis. The lattice parameters (a and c) are calculated by the relation (Lngford, J.I. and A.J.C. Wilson, 1978):

$$d_{hkl} = \frac{a}{\sqrt{\frac{4}{3}\left(h^2+k^2+hk+\frac{l^2a^2}{c^2}\right)}} \quad (1)$$

The grain size is calculated using Scherer's equation (Kebbab, Z., *et al*., 2008):

$$D = 0.9\lambda/(\beta cos\theta) \quad (2)$$

Where D: the grain size

λ= 1.5406 A˚

β: Full Width Half Maximum(FWHM)

θ: diffraction angle

The thick film undergoes a micro strain and dislocations in its structure, due to the heat treatment process (Riad, A.S., *et al*., 2001).

Therefore, the dislocation density is calculated by the equation (Ali Mohammad, M., 2011):

$$\delta = 1/D^2 \quad (3)$$

Where δ is the dislocation density.

In addition, the micro strain of the film is estimated using this equation

$$\varepsilon = \beta cos\theta/4 \quad (4)$$

The estimated structure parameters as shown in table 1 were found closed to typical results. Also the micro strain and dislocation density were estimated. Both of them depend on the deposition condition such as the temperature. Our results were found closed to other researchers (Kebbab, Z., *et al*., 2008; Ali Mohammad, M., 2011).

The atomic force microscope gives us good information about the surface morphology of the film as shown in Fig. 2. The granularity normal distribution report of scanning probe microscope (SPM) shows a high percentage grain size less than 100 nanometer. Beside, the average on the surface was found 90 nm with the roughness of the surface was 1.38 nm.

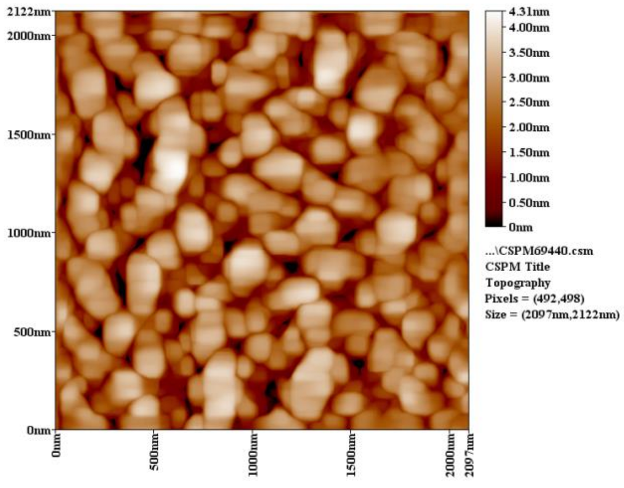

Fig. 2: Two-dimensionalimage AFM of the prepared film.

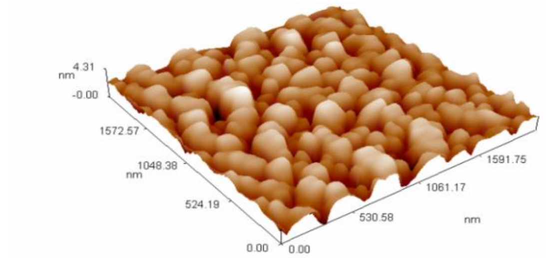

Fig. 3: Three-dimensional morphology AFM image of the surface of the thick film.

Figure 4. A, B, and C displays the typical FE-SEM micrographs of ZnO hexagonal nanotubes with different magnification powers,it is observed that the length of ZnO hexagonal nanotubes is in the range of 3-9.8 µm and the wall thickness is about 20 nm.

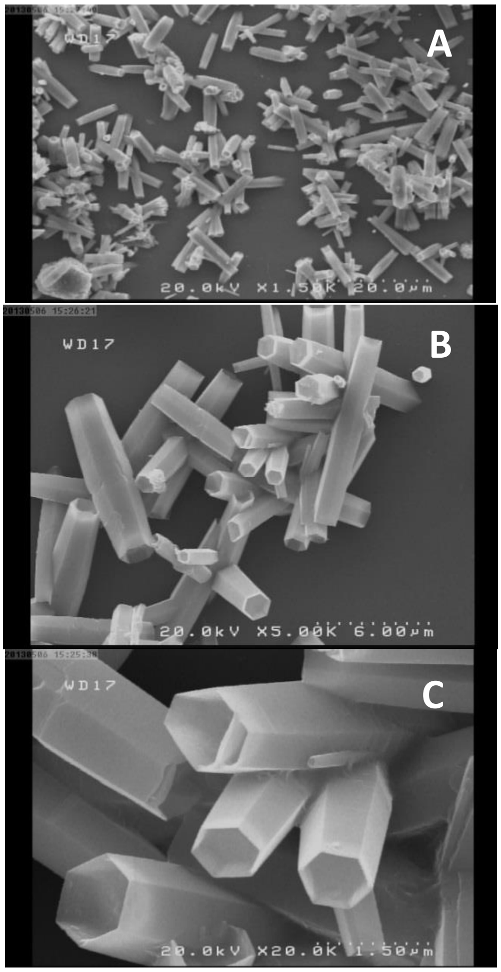

Fig. 4: SEM images of the hexagonal nanotube depositions at different magnifications: A) 1.5k; B) 5.0k, and C) 20.0k

The hexagonally faceted providing strong evidence that the single hexagonal nanotube grows along the c-axis direction. The ZnO hexagonal nanotubes have a hexagonal wurtzite structure confirmed by the XRD result (Yanhong Tong, *et al*., 2006), The final morphology and dimension of the nanostructures are determined by a competition between adsorption and desorption of the precursor molecules, or in other words crystal growth and dissolution processes (Yanhong Tong, *et al*., 2006; Sheng Xu, *et al*., 2010; Guang-Wei She, *et al*., 2008).

hexamethylenetetramine $C_6H_{12}N_4$ (HMT) is a reactants materials can hydrolyze and decrease the concentration of H^+ ions for the nucleation and growth of ZnO nanostructures, as well as HMT tetradentate ligand and tends to bind metal ions in different coordination modes including the monodentate and μ_n-bridging modes (Yanhong Tong, *et al*., 2006) On the other hand, ammonium salts tend to bind with Zn^{2+} ions generating Zn^{2+} amino complexes. They primarily adsorb on the six prismatic side planes slowing down the growth velocity of the side surfaces. This is a key point for the formation of the ZnO nanotube. Zn^{2+} amino complexes play an important role in the whole process. However, it is not absolutely necessary for the formation of the 1D solid ZnO structure but determinative for the formation of hollow structure, these complexes play an indispensable role in the process of forming the tubular ZnO nanostructure Additionally, the polarity of ZnO is a necessary factor for the 1D solid and hollow structure in the whole growth process according to the growth mechanism of ZnO nanotubes mentioned above. (Yanhong Tong, *et al*., 2006)

Optical properties:

The behavior of the films show high transparence with low absorption (A) in visible region as shown in figure 5, this behavior depends on the thickness of the prepared films.

The optical absorption coefficient was calculated for film using The Lambert's formula.

$$\alpha = (1/t)ln(1/T) \tag{5}$$

Where, t = is the film thickness.

T = is a transmittance of the film.

The absorption coefficient is related to the incident photon energy:

$$\alpha = k(hv - Eg)^{n/2}/hv \tag{6}$$

Where, k is a constant, Eg is the optical band gap. ZnO is one of the well-known material have direct optical band gap, therefore the value of (n) equal to 1. The optical band gap was determined from Fig. 6 and found to be 3.42 eV.

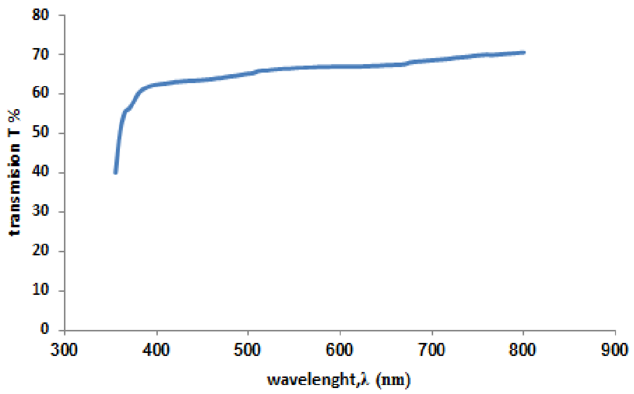

Fig. 5: Transparency of the ZnO film for visible wavelength region.

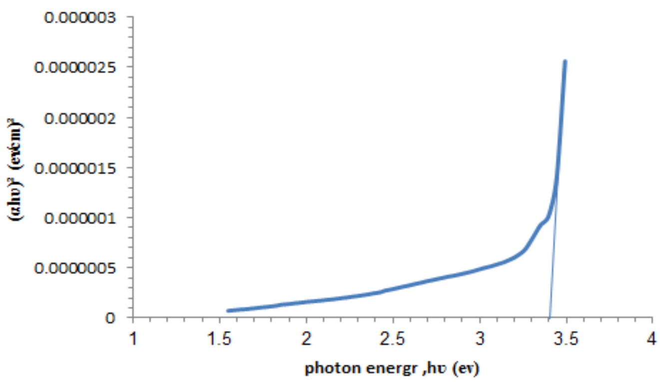

Fig. 6: Energy gap of the prepared ZnO film.

It is well known that the photoluminescence PL of nanostructural ZnO generally presents two typical emission bands peaked at ultraviolet and visible regions (Xu, C.X., *et al*., 2006), the room-temperature (PL) spectrum of the as-grown ZnO hexagonal nanotube was investigated with the excitation wavelength of 325 nm as shown in figure 7, The spectrum of the ZnO hexagonal nanotubes consists of two emission bands the first strong ultraviolet emission at around 368 nm ,the second weak and broad blue-green emission band centered at 472.1 nm is associated with oxygen vacancies, The former is originating from the exitonic recombination corresponding to the band-edge emission of the intrinsic wide band gap of ZnO ,From this figure it can be seen that the UV emission have a blue shift in comparison with the band gap of bulk ZnO (at around 380 nm) (Hu, J.Q. and Y. Bando, 2003; Xiaobao Li, Wei Dou, Ningzhong Bao, 2012), this may be related to quantum confinement effect, The ratio of peak intensities of the UV and blue-green components (I_{UV}/I_{BG}) in the PL spectra of the as-grown ZnO hexagonal nanotube is 3.87, implying that the nanotubes are of substantially higher crystal quality.

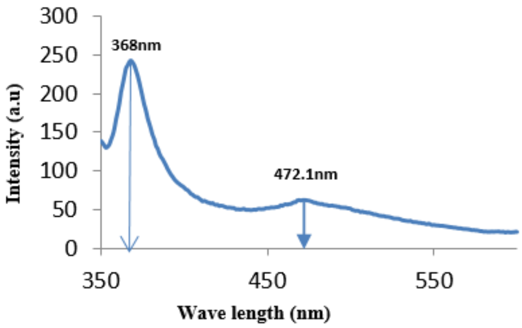

Fig. 7: PL spectrum of ZnO nanotube at Exaction wave length 325 nm.

Conclusions:

It was successfully synthesized ZnO hexagonal nanotubes by a very simple method without complex reagents and use of vacuum.in this work The formation of the hexagonal nanotubes structure is exceedingly related to the polarity of ZnO and the selective adsorption effect of Zn^{2+} amino complexes. In the word the PH of the solution play important role in the formation of the tube also this work suggest that the cooling time contributed in ethching process to form the tube shape. The obtained ZnO hexagonal nanotubes possess high ratio of volume to surface which could be very effective in sensing applications, the strong UV peak and high (I_{UV}/I_{BG}) ratio, suggests that the material could be employed in photoluminescent devices. We can also anticipate potential applications in the areas of optoelectronic applications.

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