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FACILE HYDROTHERMAL SYNTHESIS OF FLOWER-LIKE ZNONANORODS WITHOUT CATALYSTS

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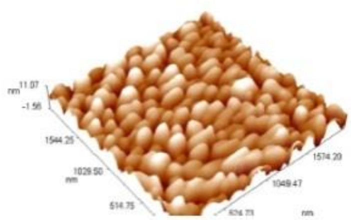
Graphical abstract



Abstract

A very simple hydrothermal method (one step) was used at low temperature to synthesis flower-like ZnOnanorods on glass substrate without any template, catalyst or buffer layer before the reaction. Flower-like ZnOnanorods were synthesized by hydrothermally heating 0.1 M precursor solution of hexahedral zinc nitrate Zn(NO3)2.6H2O, hexamethylenetetramine (HMT) and NaOH were the starting materials for the chemical reaction under stirring. The field emission scanning electron microscopy (FE-SEM) images showed that the flower-like structures were formed in 3.5 h hydrothermally-heated for sample, whereas the experimental pattern of the films by X-ray diffraction show that diffraction peaks can be assigned to the wurtzite hexagonal-shaped ZnO as shown in the (FE-SEM) images, also the morphology of the films studied by atomic force microscope (AFM) shows that the films have high roughness. The energy gap was estimated and optical behavior was investigated.

Keywords: ZnO, Flower-like ZnOnanorods, hydrothermal process

Abstrak

Satu kaedah hidroterma sangat mudah (satu langkah) telah digunakan pada suhu rendah untuk sintesis nanorodsZnO seperti bunga pada substrat kaca tanpa mana-mana template, pemangkin atau lapisan penampan sebelum tindak balas. Bunga-seperti nanorodsZnO telah disintesis oleh pemanasan hidrotermal 0.1 M pelopor penyelesaian berenam segi zink nitrat Zn(NO3)2.6H2O, hexamethylenetetramine (HMT) dan NaOH adalah bahan permulaan untuk tindak balas kimia di bawah kacau. Medan sebaran mikroskop elektron pengimbas (FE-SEM) menunjukkan bahawa imej struktur bunga seperti yang telah ditubuhkan pada 3.5 h pemanasan hidrotermal untuk sampel, manakala corak percubaan oleh filem X-ray menunjukkan bahawa pembelauan puncak pembelauan boleh diberikan kepada wurtzite heksagon berbentuk ZnO seperti yang ditunjukkan dalam (FE-SEM) imej, juga morfologi filem dikaji oleh atom kuasa mikroskop (AFM) menunjukkan bahawa filem mempunyai kekasaran tinggi. Jurang tenaga dianggarkan dan ciri optik telah disiasat.

Kata kunci: ZnO, nanorodsZnO berbentuk bunga, proses hidroterma

1.0 INTRODUCTION

ZnO n-type semiconductor has attracted much attention in the bottom-up engineering of nanostructures technology due to of its various as an excellent nanostructure-former have large surface to volume ratio and its unique electronic properties with a wide band-gap of 3.37 eV as well as a large exciton binding energy of 60 meV at room temperature. In recent years, nanostructured ZnO materials have received considerable interest from researchers due to their remarkable performance in a wide range of high technology applications like surface acoustic wave filters (Emanetoglu *et al*., 1999), solar –cell (Yuan *et al*., 2011), light emitting diodes (Saito *et al*., 2002), short-wavelength UV laser and blue or green optoelectronic devices (H. Cao *et al*., 2000) and gas sensors (Öztürk *et al*., 2014) etc.

The Length, cross-section diameter, orientation, alignment, controlling size and morphology of the nanostructures are a significant challenge to manage the conditions of synthesis process and operations of nanostructure base devices. Also, different nanostructures shapes of ZnO have been reported as flower-like nanorods (Shi *et al*., 2013), nanowire and nanotube (Y. W. Lee *et al*., 2011), nanoparticles (Thareja and Shukla, 2007), nanobelts (Sun *et al*., 2008) and nanocages (Snure and Tiwari, 2007).

ZnO nanostructure have numerous methods to growth it such as pulsed laser deposition (PLD) (Vinodkumar *et al*., 2014), sol-gel method (Talebian *et al*., 2013), magnetic enhanced sputter (J. Lee *et al*., 2002), metal-organic chemical vapor deposition (MOCVD) (Park *et al*., 2002), Liquid phase pulsed laser ablation (LP-PLA) (Singh and Gopal, 2008), and hydrothermal method (Zhang *et al*., 2014).

In this paper, we present simple and low cost hydrothermal methods to synthesis flower-like ZnOnanorods under low temperature growth (110 °C) without using any special devices or catalyst. crystallization of ZnO nanostructure appear wurtzitehexagonal-shaped ZnO as shown in the FE-SEM images and X-ray diffraction and (AFM) shows that the films have high roughness and optical properties of the film was study.

2.0 EXPERIMENTAL

The solution for growing flower- like ZnOnanorods was prepared by dissolved of zinc nitrate hexahydrate ($Zn(NO_3)_2\ 6H_2O$) and hexamethylenetetramine (HMT) in distilled water to give a 0.1M precursor solution, this solution stirred for 30 min to more homogenies. Ammonia (NH_3) was added to the solution dropwise to increase the pH to (10.7). Then, the mixture was transferred to autoclave (glass bottle 120ml and 140 0C). The glass substrates were used to deposited flower-like ZnOnanorods were cleaned by ethanol and acetone with ultrasound bath for 15min, after that substrate was immersed in solutions for growing ZnO nanostructure. The mixture was hydrothermally heated at (110 0C) to (3.5 h). Finally the flower-like ZnOnanorods were successfully grown on the substrate, oven cooled down at room temperature and after that taken the sample out from the solution and the substrate was washed with distilled water and dried at 50 °C to 30min. Structures and morphologies of flower-like ZnOnanorods were characterized by field-emission scanning electron microscope (FE-SEM) and an X-ray diffraction (XRD) technique. Surface morphology of the samples was investigated by atomic force microscopy (AFM) and the optical properties of the flower-like ZnOnanorods was studied using room temperature photoluminescence spectroscopy (PL) with a 360 nm He–Cd laser at 25 mW.

3.0 RESULTS AND DISCUSSION

To study the effect of different precursor concentration on the ZnO nanostructure. The concentrations of solutions were chosen as (0.02 and 0.1 M) respectively. All structure grown on the glass substrate with same temperature (110 0C). Figure 1 (a, b and c) (FE-SEM) images of precursor solution (0.1 M) appeared flower-like ZnOnanorods have larger diameter and length are estimated about (50-400) nm and (70-650) nm respectively. Flower-like ZnOnanorods with larger diameter and length are expected to be beneficial for optical transmittance in UV and VIS region as can be seen in Figure 2. Also, the flower-like ZnOnanorod show hexagonal-shaped ZnO as in the Figure 1 (a, b and c) (FE-SEM) images.

The other concentration did not show any homogenous growth due to low solution concentration value Figure 1(d) image. Also, we can noted semi-alignment for nanorods by this procedure in (EF-SEM) view at (0.1 M).

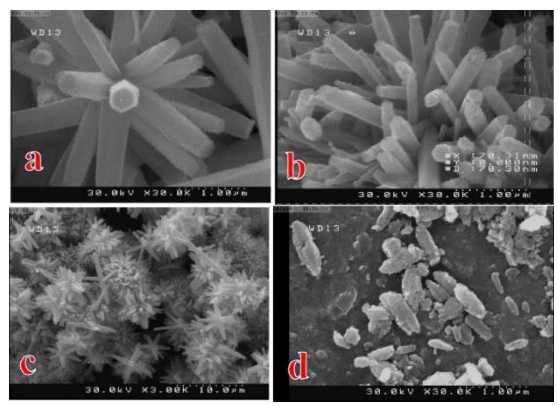


Figure 1 (FE-SEM) images (a,b,c and d) for different solution concentration to Growth ZnO film

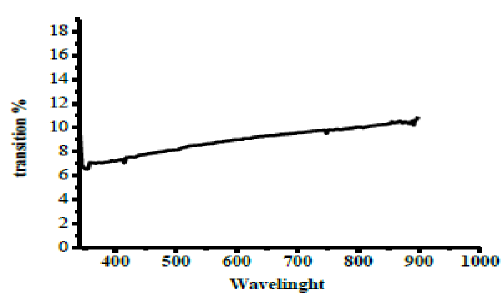


Figure 2 The relationship between transition and wavelength of the grown ZnO film

X-ray diffraction Figure 3 shows polycrystalline structure with major peaks in the direction (100), (002), (101). From the diffraction pattern it's indicate that the growth is dominated in these directions and these diffraction peaks can be assigned to the quartzite hexagonal-shaped ZnO.

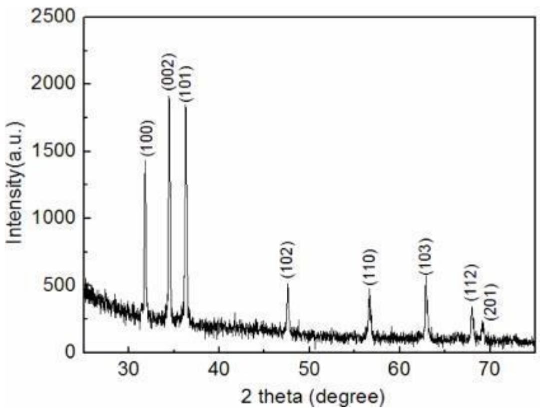


Figure 3 X-ray diffraction of ZnO film

Lattice constant (a and c) for the flowerlike ZnOnanorod film were calculated using the Bragg's law (Lupan *et al.*, 2010) as:

$$n\lambda = 2d\sin\theta \quad (1)$$

Where is the order of diffraction, = 1.5406 A^0 is the X-ray wavelength and is the spacing between planes of given Miller indices h, k, and l. The plane spacing is related to the lattice constants and the Miller indices by the following relation:

$$\frac{1}{d^2_{(hkl)}} = \frac{4}{3}\frac{(h^2+hk+k^2)}{a^2} + \frac{l^2}{c^2} \quad (2)$$

The calculated values for lattice parameters are found a = 3.2389 A and c= 5.206 A°.

Atomic Force microscope (AFM) Figure 4 shows that ZnOnanorods it's thick films have high roughness. This is agreement with cross- section image of FE-SEM Figure 4 were the thickness of the film flower-like ZnO about (7.33 μm).

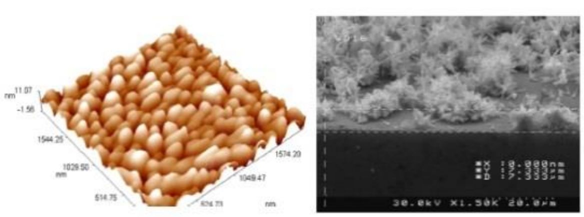


Figure 4 Atomic Force microscope (AFM) of ZnO film and FE-SEM images to ZnO film with (7.33 μm)

The optical behavior of the film was studied with UV–Visible light spectrophotometer. The absorption coefficient is related to the incident photon energy (Ali, 2011).

$$\alpha = A\,(h\upsilon - Eg)^{1/2}\,/h\upsilon \quad (4)$$

Where, A is a constant, Eg is direct band gap of ZnO film. Where, the variation of (ahv)2 with photon energy (hv) is depicted in Figure 5. The direct optical band gap (Eg) of flower-like ZnOnanorods film is determine from extrapolating of the linear part of (ahv)2 vs. (hv) plot on x-axis. The optical band gap found to be about (3.3) eV. The films show high transparence in visible region as shown in Figure 5.

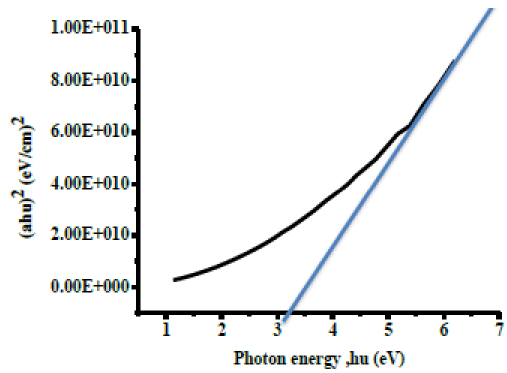


Figure 5 The energy gap of the ZnO film

Figure 6 show the room-temperature PL spectrum of flower-like ZnOnanorod film. The sample has two types of emission peak; at ultraviolet (UV) peak (~344.5 to 399 nm) with fixed intensity and in visible (VIS) range (~ 400 to 481 nm) but with various intensity. The UV emission, which is associated with exciton emission, and another is in the visible emission, which originates from the electron-hole recombination at a deep level, presumably caused by oxygen vacancy or zinc interstitial defects. (B. Cao *et al*., 2007; Liu *et al*., 2006). The intensity ratio of UV to blue emission increased when the quality of ZnO crystallization had been improved (Wang *et al*., 2007).

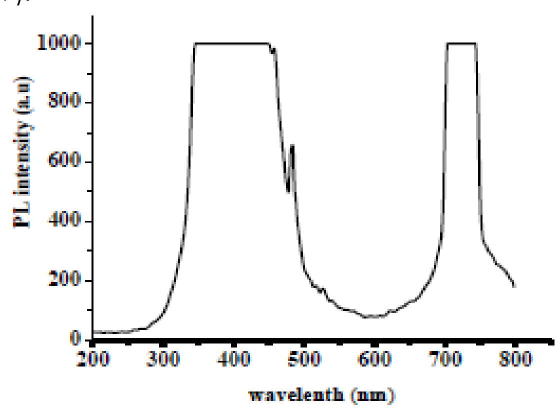


Figure 6 Room-temperature PL spectrum of flower-like ZnOnanorod film

4.0 CONCLUSION

In summary, we successfully growth flower- like ZnOnanorods with hexagonal structure were synthesized by the hydrothermal solution technique. The obtained ZnOnanords like flowers gives high ratio of volume to surface with relatively high roughness both are very effective to improved sensor performance to develop sensing technology.

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