NANOSTRUCTURAL AND OPTICAL PROPERTIES OF HIERARCHICAL ZnO GROWN VIA HYDROTHERMAL METHOD

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Abstract

A simple hydrothermal method was employed to synthesize 3D hierarchical ZnO nanorods deposited on Si (100) substrate at different growth temperatures (110 and 90°C) within 3 h. The structure, mode and composition of hierarchical ZnO nanorods were investigated by XRD, FESEM and EDX spectroscopy. The polycrystalline ZnO nanostructures products were indexed as hexagonal wurtzite structured, while the morphology was urchin like ZnO nanorods with different aspect ratio of nanorods and stoichiometric. The photoluminescence (PL) properties were studied of as-grown ZnO samples dependent on various growth temperatures. The PL results after UV excitation source were shown a single broad Vis emission peak for both samples with absents of UV emission peak. The emission edge of Vis peak was exhibited blue-shift due to increase temperature growth, and that suggest enhancement in hierarchical ZnO nanorods crystallinity. Oxygen deficiency is evidence on the creation various defects types in hierarchical ZnO nanorods. It is responsible on Vis emission bands. The results demonstrate promising future for the hierarchal ZnO nanostructure which could be applied in optoelectronics and gas sensing.

Keywords: Hierarchal ZnO nanorods, photoluminescence, hydrothermal

Abstrak

Satu kaedah hidrotermal ringkas telah digunakan untuk mensintesis hierarki 3D rod nano ZnO yang dienapkan kepada substrat Si (100) pada suhu pertumbuhan yang berbeza (110 dan 90°C) dalam masa 3j. Struktur, mod dan komposisi hierarki rod nano ZnO dikaji menggunakan spektroskopi XRD, FESEM dan EDX. Produk struktur nano ZnO polihabluran telah diindeks sebagai struktur wurtzit heksagon, manakala morfologi rod nano ZnO seperti landak laut dengan nisbah aspek rod nano dan stoikiometri yang berbeza. Sifat-sifat kefotopendarcahayaan (PL) dikaji sebagai sampel ZnO dewasa bersandar kepada pelbagai suhu pertumbuhan. Keputusan PL selepas sumber penguajaan UV ditunjukkan sebagai puncak tunggal luas pancaran Vis untuk kedua-dua sampel tanpa kehadiran puncak pancaran UV. Hujung pancaran Vis dipamerkan sebagai anjakan biru disebabkan oleh peningkatan suhu pertumbuhan, dan ini menunjukkan peningkatan dalam hierarki rod nano ZnO penghabluran. Kekurangan oksigen adalah bukti kepada kewujudan pelbagai jenis kecacatan dalam hierarki rod nano ZnO. Ia bertanggungjawab kepada pancaran jalur Vis. Keputusan menunjukkan potensi hierarki struktur nano ZnO yang boleh digunakan dalam optoelektronik dan pengesan gas.

Kata kunci: Hierarki rod nano ZnO, kefotopendarcahayaan, Hidrotermal

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1.0 INTRODUCTION

Zinc oxide is one of important kinds of metal oxide semiconductor due to its wide band gap of 3.36 eV, large exciton binding energy of 60 meV and a hexagonal wurtzite crystal structure. Undoped ZnO nanostructure is generally exhibited (n-type) properties; this material has good optical and electrical properties and its bio-safety. Because of the unique physical and chemical characteristics of ZnO nanostructure it has potential applications in different fields such as photo-detectors, gas sensors, solar cells, wave resonators and varistors (Cho et al., 2009; Zhang et al., 2014) etc.

ZnO nanostructures have been synthesized via different techniques including pulsed laser deposition, atomic layer deposition, sol-gel, molecular-beam epitaxy, hydrothermal and sputtering method etc. Different dimensions (1D, 2D and 3D) of ZnO nanostructures have been reported such as nanorods, nanosheets and nanoflower etc. However, the hydrothermal solution method is a simple, economic and easily controllable for fabricating ZnO nanostructures. In order to synthesis ZnO nanostructures in liquid solution, the effects of aqueous solution concentration of zinc salt, pH, substrate type, growth temperature, and growth time are the important factors in controlling the ZnO nanostructure properties (Liu et al., 2015; Song and Lim, 2007).

The morphologies of ZnO structures based photoluminescence (PL) spectra are limited in two regions with one or several of the following emission bands: firstly in the UV region centred at around 380 nm and secondly in the visible (Vis) region with green emission band centred at around 510 nm, a red emission band centred at around 640 nm and an IR emission band centred at around 730 nm. The UV emission peak of ZnO nanostructure is attributed to the radiative recombination of excitonic centers. The origin of Vis peak is due to the surface and deep-level defects, such as zinc and oxygen vacancies and oxygen interstitials (Djurisić and Leung, 2006; Tang et al., 2014; Yao et al., 2000).

On the other hand, clarifying the origins responsible on the various type of PL emissions peaks from ZnO nanostructure is an important and a controversial issue, which is need further study (Djurisić and Leung, 2006; Lee et al., 2010). ZnO nanostructures have improvement in the optical properties comparing with the bulk materials due to their large specific surface area to volume ratio, quantum confinement, morphology, and size effect (Djurisić and Leung, 2006; Vinodkumar et al., 2014; Yang et al., 2014).

In this study, the thin film of hierarchical ZnO nanorods was grown by using simple hydrothermal method on silicon (Si) substrate. The PL properties of ZnO nanostructure was studied depending on growth temperature. The structure, mode and composition of ZnO nanostructures were investigated by XRD, FESEM and EDX spectroscopy. Photoluminescence (PL) properties at room temperature of as-synthesis ZnO nanostructures samples were studied by using a photoluminescence spectroscopy (PL) at room temperature.

2.0 EXPERIMENTAL

Zinc oxide precursor solution was prepared by using zinc nitrate, hexamethylenetetramine (HMT) and deionized water as the raw materials to produce a 0.1 M of precursor. All the chemical reagents used in the experiments were analytical grade without further purification. Certain dosage of (NH₃) was added to increase the pH value of precursor solution at 10 values. This solution was stirred for 15 min for homogenization. Later, the mixture of precursor was transferred to autoclave. Si (100) substrates were used to deposit hierarchical ZnO nanorods. The substrates were cleaned by ethanol and acetone with ultrasound bath, prior immersed into solutions for growing ZnO nanostructures. The mixture was hydrothermally heated at (90 and 110°C) for (3 h).

Finally, the hierarchical ZnO nanorods were successfully grown on the substrate and the oven cooled down at room temperature. Next, the samples were washed with ethanol, distilled water and dried at 65°C for 30 min. Structure, mode and stoichiometric ratio of hierarchical ZnO nanorods were characterized by FESEM equipped with an energy-dispersive (EDX) and an X-ray diffraction (XRD) techniques. The optical properties of the hierarchical ZnO nanorods were studied using room temperature photoluminescence spectroscopy (PL) at an excitation wavelength of 350 nm.

3.0 RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of hierarchical ZnO nanostructures dependent on temperature growth (110 - 90°C) and time growth of (3 h). As shown in the figure, the samples were polycrystalline and all diffraction peaks demonstrated as ZnO crystals with a hexagonal wurtzite structure according to the standard card (JCPDS card no.36-1451). In additional, XRD spectra were appeared ZnO samples without any impurity peaks. The variation of growth temperature leads to the intensity of diffraction peaks of the ZnO nanostructure were changed simultaneously. The slightly enhanced in intensity and narrowed spectral width of (FWHM) of oriented in c-axis (002) diffraction peak with increase growth temperature indicating that high crystallinity of the hierarchical ZnO nanorods. The above mentioned properties of hierarchical ZnO nanorods can be attributed to the anisotropic growth of the ZnO crystals, (Hai-Bo et al., 2012; Yang, et al., 2014).
The morphology, composition and size of ZnO nanostructures were characterized by FESEM equipped with an energy-dispersive EDX. Figure 2 (a and b), appear FESEM images of uniform hierarchical shapes like urchin-like ZnO nanorods were samples consisted of different geometry average size about (0.144 - 0.44 μm in diameter and 2.01 to 4.3 μm in length) under different temperatures growth between (90 and 110°C) respectively. FESEM results demonstrated different aspect ratio of nanorods dependent of hierarchical ZnO nanostructures which was affected by changing temperature growth. The diameter and length of ZnO nanorods were increased with increased the temperature of growth from 90 to 110°C. These results are good agreement with previous literature review, (Solís-Pomar et al., 2011; Sorayaie et al., 2015).

Figure 3 (a and b), demonstrate composition of hierarchical ZnO nanostructures films which was grown on Si substrate under different temperatures growth using EDX spectroscopy. The figures confirm the presence of O, Zn, and Si as the elemental compositions, where, Si element can be attributed to substrate. EDX spectra for ZnO samples shows the Zn/O atomic ratios were determined to be approximately 3.03 and 2.88 for ZnO nanostructures grown under different temperature growth (90 – 110°C) respectively. That suggest the oxygen deficiency its presence in the crystal structure of hierarchical ZnO nanorods, and was confirmed by EDX spectra. Thus, creation of different crystal defects with different ratios in hierarchical ZnO nanostructures due to changing in temperature growth of samples.
Figure 3 EDX spectra of hierarchical ZnO nanorods grown with 0.1 M for 3 h at temperature (a) 90°C and (b) 110°C

4.0 CONCLUSION

In present work, hexagonal hierarchical of ZnO nanorods was synthesized via a liquid precipitation route under different low temperatures growth. The change in the temperature growth of ZnO nanostructure was induced to change in the aspect ratio of nanorods-dependent of hierarchical ZnO nanostructures. The temperature growth of the ZnO crystal was proved to play an important role in PL properties of hierarchical ZnO nanorods due to the change in composition ratio of oxygen and zinc atoms. Oxygen deficiency which produces surface defects and defects related to deep level emission in hierarchical ZnO nanostructures were strongest evidence. These defects are responsible on the Vis emission bands. Also, the slightly increase in temperature growth from 90 to 110°C leads to improvement in hierarchical ZnO nanorods crystallinity due to Vis emission intensity increase and blue-shift of the Vis emission edge toward UV region. This work provides a viable and low coast method to control on the morphology dimension and PL properties of hierarchical ZnO nanorods by controlling the crystal temperature growth. These results can be promising future of Hierarchiel ZnO nanorods in different application.

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Figure 4 PL spectra of hierarchical ZnO nanorods grown at (90 and 110°C), 0.1 M and 3 h, curves are the Gaussian fits.
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