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these nanostructured materials are also discussed.

Growth of zinc oxide nanoflowers by thermal evaporation method

H.I. Abdulgafour*, Z. Hassan, N. Al-Hardan, F.K. Yam

School of Physics, Universiti Sains Malaysia, 11800 Penang, Malaysia

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ABSTRACT

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1. Introduction

Various ZnO hierarchical nanostructures have been fabricated and studied by several groups. Among these, nanoflower, nanofish, and nano multi-tip-like nanostructures possess a fascinating morphology, and may have applications in optical devices, field emission, or other sense devices. The use of semiconductor nanowires [1] is ideal for investigating the physical and chemical characteristics of low-dimensional materials; these can also serve as building blocks for nanoelectronics and nanophotonic devices [2,3]. In both scientific and technological perspectives, it is important to develop a better understanding of the growth mechanisms in order to realize controlled synthesis of nanostructures. One-dimensional (1D) nanostructures, such as nanotubes, nanowires, and nanoflowers, have attracted wide attention for their potential applications in device and interconnect integration in nanoelectronics and molecular electronics [4].

As an important wide-band gap semiconductor, ZnO has a direct band gap of 3.37 eV and a high exciton binding energy of 60 meV, which is stronger than that of thermal energy at room temperature. It is thus a promising material for UV optoelectronic devices and lasers operating at room temperature [5].

In recent years, ZnO nanostructures grown on Si-based substrates have been receiving increased interest due to the main advantages that they offer. Unfortunately, the large mismatches in the thermal expansion coefficients and the lattice constant may lead to a significant stress between the ZnO and the Si substrate. For this reason, several research groups have tried to grow ZnO nanostructures on other substrates.

An alternative method for site-selective growth of ZnO nanostructures that does not use an Au catalyst

or a ZnO thin-film seed layer is presented. Well-aligned ZnO nanoflower structure arrays were directly

fabricated on silicon substrates through zinc powder evaporation, which uses a simple thermal

evaporation method without a catalyst. The collected ZnO nanoflowers were then characterized

through X-ray diffraction (XRD) and scanning electron microscopy (SEM). The optical properties of

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Normally, ZnO is prepared through various methods such as chemical bath deposition, thermal decomposition, hydrothermal synthesis, sol–gel methods, and vapor-phase transport [6].

In spite of various methods of preparing ZnO layers with a nanostructure shape, there is still the need for developing a method that can produce the layers with high repeatability and low cost processes. In this work, we fabricated the hexagonal structure of ZnO nanoflowers at 850 °C through the simple method of thermally evaporating Zn powders without introducing a catalyst. Afterwards, we studied the morphological, structural, and the optical properties of the produced ZnO nanoflowers.

2. Experiments

The process of fabricating the ZnO nanostructure was based on the thermal evaporation process of pure metallic Zn powder (99.9%) without the presence of a catalyst. The synthesis process was carried out in a quartz tube. For this experiment, *n*-type silicon Si(1 0 0) wafers with single polished faces were used as substrates. These substrates were ultrasonically cleaned and placed at the top of an alumina boat with the polished faces toward the Zn powder. The boat was then inserted to the center of a quartz tube furnace. The furnace was slowly heated from 400 °C to 850 °C under a continuous flow of highly pure argon and oxygen gases. A constant flow-rate of 250 sccm was maintained for 1 h. After the evaporation, the alumina boat was slowly drawn out from the furnace and cooled down to room temperature. A white-colored layer formed on the polished face of the Si

^{*} Corresponding author. Tel.: +6017 4961778; fax: +604 6579150; *E-mail address*: hind_alshaikh@yahoo.com (H.I. Abdulgafour).

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substrates. The morphological, structural, and optical properties were investigated through scanning electron microscopy (SEM), X-ray diffraction (XRD), photoluminescence (PL), and Raman spectroscopy.

3. Results and discussions

The XRD pattern of the produced layer is shown in Fig. 1, which shows that the peak positions fall within the Bragg angles between 20° and 80°. The XRD spectrum reveals that the assynthesized layer is polycrystalline. The peaks that appeared at 2 θ of 31.8°, 34.4°, 36.1°, 47.4°, 56.6°, 63.0°, 68.0°, and 69.2° represent the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (1 1 2), and (2 0 1) phases, respectively, of the hexagonal close-packed crystal structure of the ZnO according to JCPDS no. 36-1451. Meanwhile, the peak which appeared at 44.58° could be attributed to the SiO₂ interlayer, which belongs to the (1 0 5) phase (JCPDF no. 46-0570) [7]. There was no evidence of Zn metal in the XRD pattern, thereby confirming the complete conversion of Zn powder to ZnO.

The average grain size in the films can be estimated through the Scherrer formula, which uses the full width at half maximum (FWHM) value of the XRD diffraction peaks. The Scherrer formula is presented as [8]

$$D = \frac{0.9\lambda}{\beta\cos\theta} \tag{1}$$

where *D*, λ , θ , and β are the mean crystallite size, the X-ray wavelength of 0.154 nm, Bragg diffraction angle, and the FWHM of the diffraction peaks for the ZnO nanostructure, respectively. The mean crystallite size is approximately 44.2 nm in the ZnO (1 0 1) plane prepared at a temperature of 850 °C.

The SEM image is shown in Fig. 2. The resulting images of the prepared ZnO depict nanoflower structures. The structures are more than $4-6 \mu m$ long, with a width of about 60-200 nm.

The PL spectra of the ZnO nanostructures were measured using He–Cd laser with an excitation wavelength of 325 nm at room temperature. Fig. 3 shows the PL spectrum of the ZnO nanoflowers with three emitting bands, namely, a strong and broad ultraviolet emission band (at 380 nm), a very weak green band (at 510–580 nm), and an almost negligible blue band (at 440–480 nm). The 380 nm emission pertains to the recombination of free excitons between the conduction and valence bands and is called the near band-edge emission, while the longer wavelength band can be attributed to the radial recombination of a photo-generated hole with electron, which



Fig. 1. The XRD spectra of ZnO grown at 850 °C.

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Fig. 2. The SEM images of ZnO nanoflowers grown at 850 °C.



Fig. 3. Room temperature photoluminescence spectrum from ZnO nanoflowers grown at 850 $^\circ\text{C}.$

belongs to the singly ionized oxygen vacancy in ZnO. The strong UV emission in the PL spectra indicates that the ZnO nanoflowers have good crystal quality with few oxygen vacancies [9–11].

The Raman scattering spectrum is a sensitive and highly useful method for determining crystal perfection and structural defects. In this study, it was used to clarify the structure of ZnO nanostructures. The wurtzite-type ZnO belongs to the space group C^4 (P63mc) with two formula units in the primitive cell. Raman spectra are sensitive to the crystal quality, structural defects, and disorders of the grown products. With the wurtzite hexagonal structure, ZnO belongs to C_{6V}^4 with two formula units per primitive cell. The primitive cell includes two formula units, in which all the atoms occupy the 2b sites of the C_{3V} symmetry. According to the group theory, the single-crystalline ZnO has eight sets of optical phonon modes at the point of the Brillouin zone:

$$\Gamma = A_1 + 2B_1 + E_1 + 2E_2 \tag{2}$$

The A_1 , E_1 , and E_2 modes are Raman active. Furthermore, A_1 and E_1 are infrared active and are, respectively, split into longitudinal optical (OP) and transverse optical (TO) components [12].

The nonpolar phonon modes with symmetry E_2 have two frequencies: E_2H , which is associated with oxygen atoms, and E_2L , which is associated with the Zn sublattice. Among the eight sets of H.I. Abdulgafour et al. / Physica B 405 (2010) 2570-2572



Fig. 4. Typical Raman spectra of the synthesized ZnO nanoflower.

optical modes, A_1 , E_1 and E_2 are Raman active for ZnO single crystal materials. Fig. 4 shows the Raman scattering spectra of the ZnO nanoflowers observed at room temperature.

The Raman spectrum was excited by a 488 nm laser line. The peak at 519 cm⁻¹ can be attributed to the contribution from the oxidized Si substrate, confirming our early observation from the XRD analysis [7,13]. The peaks at 330, 380, 437, and 581 cm^{-1} are assigned to $E_2H - E_2L$, A_1T , E_2H , and E_1L of the bulk ZnO, respectively. As we can see in the spectra, a sharp, strong and dominant E_2H mode of ZnO located at 437 cm⁻¹ could be observed; this is the intrinsic characteristic of the Raman-active mode of wurtzite hexagonal ZnO [14]. This result is also consistent with the XRD analysis. Two very small peaks at 330 and 380 cm⁻¹ were assigned to the $E_2H - E_2L$ (multi-phonon process) and A_1T modes, respectively. A significantly suppressed peak at 581 cm⁻¹ in the spectrum was also assigned to the E_1L mode. The origin of the E_1L mode in the Raman scattering is explained by the impurities and structural defects (oxygen vacancies and Zn interstitials) of the synthesized products [15]. The presence of the high intensity E_2 mode with the suppressed and very weak E_1L peak in the Raman scattering indicates that the synthesized ZnO nanoflowers have good crystal quality and possess the wurtzite hexagonal crystal structure.

4. Conclusion

In summary, the growth of ZnO flowers-like nanostructure arrays on Si substrates has been demonstrated at 850 °C. In this experiment ZnO nanoflowers were synthesized using a zinc powder evaporation process that included the control of growth temperature, gas flow rate, and wet oxygen partial pressure.

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