

Characteristics of controllable-shape well-aligned zinc oxide nanorods synthesised by microwave-assisted heating

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A microwave-assisted heating method for growing well-aligned zinc oxide (ZnO) nanorods on the ZnO/silicon (Si) substrate is developed. For ZnO nanorods growth, a thin ZnO seed layer was deposited on an Si substrate by sputtering technique. The ZnO nanorods grown on the ZnO/Si substrate were synthesised in aqueous solution mixed with zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) under microwave heating. The scanning electron microscopy (SEM) images and X-ray diffraction results exhibit that the ZnO nanorods with hexagonal phase, single crystalline, and highly oriented along (002) plane are obtained successfully. SEM images also show that the morphology and diameter of the synthesised ZnO nanorods can be controlled by adjusting the molar ratio of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to HMTA. The Raman scattering results evidence the vertical well-aligned ZnO nanorods with larger diameter are strain-free. The investigations of the photoluminescence spectra suggest that the ultraviolet emission peak of the synthesised ZnO nanorods depending on its controllable diameter would be applicable for various nanodevice fabrications.

1. Introduction: Recently, one-dimensional (1D) semiconducting nanostructures have attracted much attention due to their unique electrical and optoelectronic properties [1, 2]. Among semiconductor materials, zinc oxide (ZnO) having direct wide bandgap and large exciton binding energy are considered to be one of the most important semiconducting nanomaterials for fabricating nanodevices [3–5].

So far, various synthesis approaches have been developed for preparing 1D ZnO nanomaterial such as vapour–liquid–solid growth [6], chemical vapour deposition [7, 8], electrochemical deposition [9], and the hydrothermal solution synthesis [10, 11]. Comparing with the gas phase approaches, the hydrothermal solution synthesis is an economical synthesis approach to produce ZnO nanorods at low temperature and atmospheric pressure over large scale on different types of substrates [10, 11].

However, a problem associated with hydrothermal synthesis is the required processing time from several hours to days [4, 10, 11]. To decrease the processing time, microwave heating has been considered to be the rapid synthesis of ZnO nanostructures [12, 13]. Since microwave energy can transform into heat inside material to reduce the energy consumption and provide rapid and controllable volumetric heating with a particular temperature distribution, the high-performance nanostructured can be achieved [12, 13]. Thus, the microwave-assisted synthesis has advantages over other hydrothermal approaches such as low cost, rapid heating, thermal uniformity, and energy efficiency.

In this paper, we report on the use of microwave heating for growing well-aligned ZnO nanorods on the silicon (Si) substrate. We present the feasibility of controlling morphologies of well-aligned ZnO nanorods under various synthesis conditions confirmed by scanning electron microscopy (SEM). In addition, the crystalline quality and optical properties of the well-aligned synthesised ZnO nanorods are investigated by using X-ray diffraction (XRD), Raman scattering, and photoluminescence (PL) spectroscopy.

2. Experimental procedures: We used a two-step method including substrate pretreatment and microwave heating process to grow well-aligned ZnO nanorods on the Si substrate. First, the ZnO seed layer with a thickness of about 300 nm was deposited on the Si substrate by sputtering technology. Then, the prepared ZnO/Si substrate was suspended in the mixed aqueous solution of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine (HMTA). In this paper, the concentration of HMTA is fixed as 0.005 mol/l (M) and the molar ratio of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to HMTA was controlled to be 1:1, 3:1, 5:1, and 7:1, which are named W1, W2, W3, and W4, respectively, for the synthesised ZnO samples. Then, the obtained well-mixed precursor solution was placed into a microwave oven and heated at the temperature of 95 °C with magnetic stirring within two hours at atmospheric conditions. During the reaction process, the $\text{Zn}(\text{NO}_3)_2$ solution provided Zinc ion (Zn^{2+}) to react with Hydroxyl Ions (OH^-) dissociated from the HMTA ($\text{C}_6\text{H}_{12}\text{N}_4$) solution to form ZnO nanorods [13, 14]. Finally, the samples were removed from the growth solution, and then rinsed with deionised water and dried at room temperature in the atmosphere.

The morphology and size of the synthesised ZnO nanorods were investigated by field emission scanning electron microscope (FE-SEM) (JSM-6701F, JEOL, Japan). The crystal structure of the synthesised ZnO nanorods were observed by XRD spectrometer (Shimadzu XRD-6000) with a $\text{Cu K}\alpha$ line of 1.5405 Å. Raman scattering spectra were recorded by using the Renishaw System (inVia Raman microscope) to analyse the variation of stress in the synthesised ZnO nanorods. Raman spectra were excited with the 514.5 nm line of an Argon ion (Ar^+) laser at an incident power of 10 mW at room temperature. The PL measurements were conducted under the excitation with a 5 mW/cm² of a micro-chip laser (266 nm). The luminescence was collected with a spectrometer (Zolix omni- λ 500) with a 1200 grooves/mm grating and detected using a gallium arsenide photomultiplier tube. The PL signal obtained from the photomultiplier was analysed by the lock-in technique and recorded in a computer.

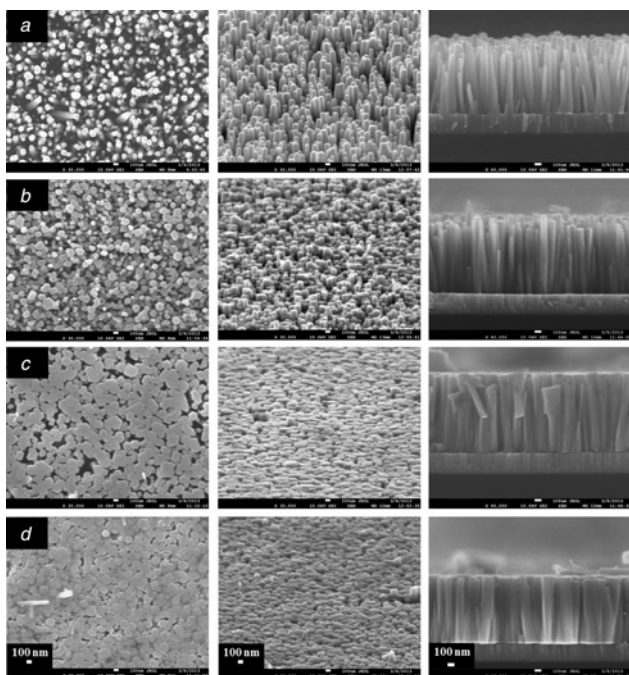


Fig. 1 SEM images of the synthesised ZnO nanorods samples named
 a W1
 b W2
 c W3
 d W4
 Left, middle, and right images are the top, tilted 45°, and cross-sectional views, respectively

3. Results and discussion: Figs. 1a–d show the SEM images of ZnO nanorod grown on the ZnO/Si substrate for the samples labelled W1–4, respectively. For each sample, the left image is the top view, the middle image is the tilted view of 45°, the right image is the cross-sectional view, and the scale bar is shown in Fig. 1d for each column. In Fig. 1a, the top view clearly exhibits the individual ZnO nanorod revealing a typical hexagonal surface with the tapered tips and the estimated average diameter is about 100 nm. The tilted 45° and cross-sectional view reveals that well-aligned ZnO nanorods have been grown successfully on the ZnO/Si substrate. On the other hand, the non-uniform diameter and length of the synthesised ZnO nanorods would form a manifestation of waviness on the top of W1 sample. Fig. 1b presents that the W2 sample synthesised with the molar ratio of 3:1 has a higher density of ZnO nanorods and the average diameter is increased to about 120 nm with clearer hexagonal morphology. With increasing the molar ratio, the estimated average diameter for the W3 and W4 samples is increased significantly to about 200 nm.

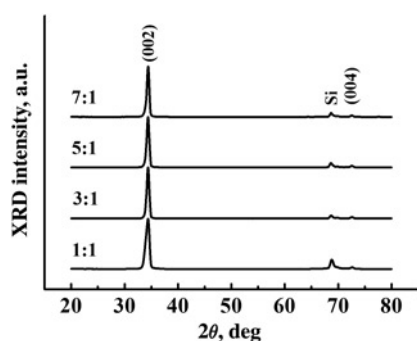


Fig. 2 XRD patterns of the synthesised ZnO nanorods. The presented ratio is the molar ratio of precursor

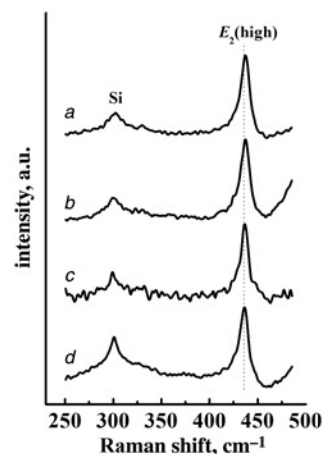


Fig. 3 Room temperature Raman spectra of the synthesised ZnO nanorods samples named
 a W1
 b W2
 c W3
 d W4

Fig. 2 presents the XRD spectrum scanned in the degree range from 20° to 80° for the ZnO nanorods synthesised with different molar ratios of precursors. For all samples, only the strong (002) peak and weak (004) peak along with the Si signal can be observed, indicating that the ZnO nanorods are well oriented along the normal direction of the substrate surface [15, 16]. The XRD results are in good agreement with the SEM images, which reveal that the synthesised ZnO nanorods perpendicularly grows on the ZnO/Si substrate.

Fig. 3 shows the Raman scattering spectra recorded over the range of 250–480 cm^{-1} . For all samples, the peak at higher frequency is attributed to the E_2 (high) mode of ZnO, but the peak at about 300 cm^{-1} is assigned to the Si substrate. The E_2 (high) mode exhibits a relative high intensity compared with the signal of Si substrate, which also evidences that the synthesised samples are highly c -axis oriented [17]. In addition, the peak position of the E_2 (high) mode is studied to clarify the residual stress in the synthesised ZnO nanorods because the frequency shift of the E_2 (high) mode is sensitive to the strain variation [17, 18]. Comparing with the Raman peak at 437 cm^{-1} in the stress-free ZnO bulk crystal, the downshift and upshift are attributed to the tensile and compressive stresses, respectively. Thus, the positions of the E_2 (high) mode of the W1 and W2 samples are at 436.2 and 436.7 cm^{-1} , respectively, implies a tensile stress existing in the synthesised ZnO nanorods [19]. On the other hand, the position of the E_2 (high) mode of W3 and W4 samples is at about 437.2 cm^{-1} , which can consider the synthesised samples as stress-free [18].

The 12 and 300 K PL spectra of the ZnO nanorods synthesised with different molar ratios are shown in Figs. 4a and b, respectively. It is noted that the PL spectra in the ultraviolet (UV) region are presented to discuss the appearance of UV emission, which are directly related to crystal quality and morphology of ZnO nanostructure. The UV emission has been assigned to the near-band-edge emission, which results from the recombination of the free-exciton through an exciton–exciton collision process [19, 20].

For the samples W1 and W2, the UV emission peaks are centred at about 3.33 eV at 12 K and 3.29 eV at 300 K. For the samples W3 and W4, the UV emission peaks slightly shift to 3.30 and 3.27 eV at 12 and 300 K, respectively. As a result, the UV emission energy shifted to low energy should be attributed to the increased average diameter of the synthesised nanorods. Previously, Yang *et al.* [21] reported the UV emission energy shifting to the high energy as reducing the size of ZnO nanostructure and indicated

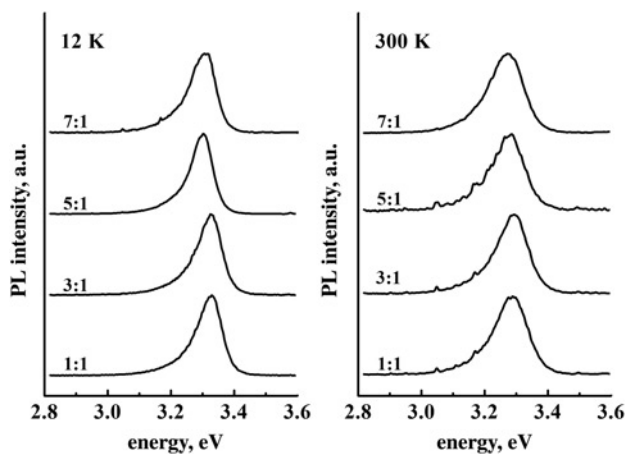


Fig. 4 PL spectra of the ZnO nanorods

the blue-shift starting to appear when the diameter of the ZnO nanostructure is smaller than 200 nm. Additionally, our experimental data can be well described by their theoretical model for predicating the UV emission energy as a function of the diameter of ZnO nanostructure.

4. Conclusion: In summary, we have presented an efficient method of microwave heating to synthesise vertically aligned ZnO nanorods on the Si substrate. This method enables the control of the size and morphology of the ZnO nanorods by adjusting the molar ratio of precursors. Our work illustrates that the diameter-dependent appearance of the UV emission of the synthesised ZnO nanorods can be widely applied to a variety of nanodevices.

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6 References

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