

The influence of precursor concentration on the crystallinity and morphology of ZnO nanorods grown on printed circuit board substrate

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Abstract. In this work, the influence of precursor concentration on the surface morphologies, and the crystallinity of ZnO nanorods (NRs) grown on printed circuit board substrates (PCBs) is presented. It was shown that by implementing a galvanic cell structure in an aqueous solution of equimolar concentration of zinc nitrate hexahydrate ($\text{Zn}[\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$), ZnO NRs can directly grow on the PCBs substrate without the assistance of a seed layer. It has been shown that the vertical growth and the crystallinity of the ZnO NRs can also be significantly improved by increasing the equimolar precursor concentrations. The morphologies of the ZnO nanorods were investigated by scanning electron microscope (SEM) and X-ray diffraction (XRD). The crystallinity properties were characterized by Raman spectroscopy and photoluminescence (PL) spectroscopy.

1. Introduction

Nowadays, semiconductor nanostructures have attracted a lot of interest and are widely used in the construction of optoelectronic devices. Zinc oxide (ZnO) has been recognized as one of the most important *n*-type II–VI semiconductors, with a direct wide band gap (3.37 eV) and has large exciton binding energy (~ 60 MeV). ZnO nanostructures have been intensively applied in a wide range of applications such as: in dye-sensitized solar cells, chemical and biological sensors, piezoelectric, and thermoelectric devices [1–5]. In fact, the properties of optoelectronic devices based ZnO nanostructures were strongly affected by their parameters like morphology, size, crystallinity, defects, and impurity contents [6][7].

In general, the fabrication of ZnO nanostructures can be done by using different techniques such as spray pyrolysis, sputtering, MOCVD, and hydrothermal method. The hydrothermal method has been widely used in producing ZnO nanostructures by using a simple, safe and low-cost technique on different kinds of substrates such as GaN, Si, sapphire, ITO and FTO. Recently, ZnO nanorods (NRs), nanotubes were successfully grown on Printed circuit board (PCB) substrate [8–10] which is cost-effective, and commonly used in electronic circuit and optoelectronics devices. In this work, a seedless hydrothermal method was elevated by implementing a galvanic cell structure in non-saturated equimolar aqueous solutions of zinc nitrate hexahydrate ($\text{Zn}[\text{NO}_3]_2 \cdot 6\text{H}_2\text{O}$) and hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) [9]. In this work, the galvanic cell structure created between a scarifying Al thin film and PCB substrate assisted the formation of a buffer layer on top of the substrate. As a result, ZnO NRs and nanotubes can grow directly on the PCBs without the adhesion of

a seed layer. However, in these works the influence of precursor concentrations on the surface morphology, crystallinity and optical properties of the as-grown ZnO NRs was not studied yet.

In this paper, ZnO NRs have been successfully synthesized using a simple seedless hydrothermal method to investigate the influence of equimolar precursor concentrations on the surface morphology, crystallinity and optical properties of ZnO NRs grown on PCB substrates. The synthesized samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical properties were studied using Raman spectroscopy and photoluminescence spectroscopy (PL).

2. Experimental

ZnO NRs were grown on PCB substrates by a hydrothermal growth technique which was described elsewhere [8,9]. The substrates was polished with SiC sandpaper and then ultrasonically cleaned with acetone, ethanol, and deionized (DI) water sequentially. After being cleaned, the surface oxide was removed by dipping the substrates in low concentration HCl, followed by an ultrasonic rinse in DI water. In order to create a galvanic cell structure, Al foil was used to cover the edge of the substrates. The uncovered area is where ZnO NRs would be grown. Afterwards, the as-prepared substrates were dipped into a mixture of equimolar concentration solution of zinc nitrate hydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and hexamethylenetetramine ($C_6H_{12}N_4$), which was placed in a sealed vitreous bottle isolated by an oil bath. The substrates were suspended facing downwards in the solution for 3 h with the temperature of the oil bath maintained at 90°C. After 3h, the Al layer was then removed and the substrates were again rinsed with DI water to remove residual salts from the surface before being air-dried.

In this work, different equimolar concentrations of $Zn(NO_3)_2 \cdot 6H_2O$ and of $C_6H_{12}N_4$ were chosen to investigate the influence of precursor concentration on surface morphology, crystallinity and optical properties of the as-grown ZnO NRs.

The crystal structure of the ZnO NRs was characterized by X-ray diffraction (X-ray Powder Diffraction System D5000 Siemens) and Raman spectroscopy (Labram Hr800, Horiba). The morphology of the sample surface was examined by scanning electron microscopy (SEM) (Nova NanoSEM 450). Photoluminescence (PL) measurements were performed using a continuous wave HeCd laser operated at 325 nm as an excitation light source.

3. Results and discussion

The chemistry of the hydrothermal growth of ZnO nanocrystals is well reported elsewhere [11–13]. Zinc nitrate salt provide Zn^{2+} ions required for building up the ZnO NRs while hexamethylenetetramine hydrolyzes to produce formaldehyde and ammonia. Ammonia further hydrolyzes into OH^- and NH_4^+ . The OH^- ion forms a complex compound with Zn^{2+} and then it decomposes into ZnO under given reaction conditions. The chemical reactions are summarized as follows:

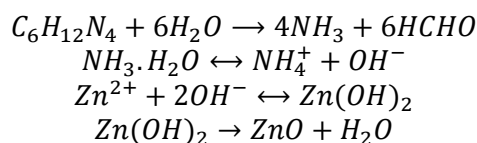


Figure 1 shows the room temperature PL spectra of the ZnO NRs with different equimolar concentrations of $Zn(NO_3)_2 \cdot 6H_2O$ and of $C_6H_{12}N_4$. Generally speaking, a PL spectrum of ZnO normally contains a narrow UV emission peak (384 nm) and a weak broad green emission band. The UV emission peak attributes to the near-band-edge emission resulting from the recombination of free excitons through an exciton–exciton collision process [14]. The broad green emission band of the visible region is generally associated with various point defects, intrinsic defects and extrinsic defects, e.g., oxygen vacancies, zinc interstitials and the incorporation of hydroxyl groups in the crystal lattice located at the surface of the material [14,15]. The higher the intensity ratio between the UV emission and green emission band indicates the better crystallinity of ZnO. As seen from the figure, the crystallinity of the as-grown ZnO was significantly improved when the precursor concentration was increased from 0.025 M to 0.08 M. Note that, in previous works in which a seed layer of ZnO or a thin layer of Au or Pt was foremost used for assisting the growth and for increasing the crystallinity of ZnO NRs, the concentration of 0.025 M was most commonly used [5,16]. However, in this work, the 0.025

M results in a very poor crystallinity with the intensity ratio of only 2.3. Since the precursor concentration was increased to 0.05 M, the intensity ratio is significantly increased to 9.8. The highest intensity ratio between UV and green emission band is obtained with the saturated concentration of 0.08 M.

The morphologies of the as-grown ZnO NRs with different equimolar concentrations shown in Figure 2. It can be seen that the ZnO NRs underwent a morphological evolution with respect to precursor concentration. When the concentration was of 0.025 M, both the lateral growth and vertical growth occur. It is due to the big lattice mismatch between ZnO and the copper layer of the PCB substrate. When the equimolar aqueous solution was of 0.08 M, ZnO NRs can grow vertically on the substrate. This is probably attributed to the fact that when the solution is saturated, the number of ion Zn^{2+} and OH^- is drastically increased. This resulted in the significant enhancement of ZnO nuclei which then formed a thin layer of ZnO on the surface. This thin layer can act as a seed layer to release the elastic strain resulted from the lattice mismatch between ZnO and the PCB surface. Subsequently, ZnO NRs began to grow up along c-axis preferentially on the surfaces without strain and defect. With this precursor concentration value, vertically aligned ZnO NRs can be obtained without implementing an additional ZnO seed layer.

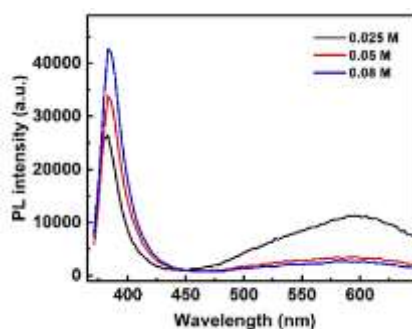


Figure 1. Room temperature PL spectra of different precursor concentrations of ZnO NRs ranging from 0.025 M to 0.08 M.

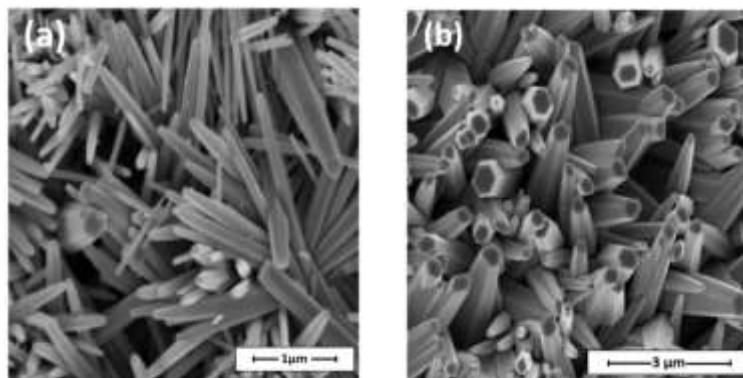


Figure 2. SEM images of ZnO NRs on PCB substrates at different concentrations of (a) 0.025 M and (b) 0.08 M.

Figure 3 presents the Xray pattern of as-grown ZnO NRs with precursor concentrations of 0.025 M and 0.08 M. As seen in the figure, the preferential growth of the ZnO NRs in the (002) direction is noticeable in the case of 0.08 M precursor concentration. With this concentration, the highest ratio between the (002) peak and two lateral peaks denoted the best vertical orientation was also obtained.

The crystallinity of the as-grown ZnO NRs can also be studied with Raman spectroscopy. Figure 4 shows the Raman spectra of the ZnO NRs grown which exhibit main peaks at 98 cm^{-1} and 437 cm^{-1} , corresponding to the optical phonon E_2 (low) and E_2 (high) of the ZnO, respectively [15,17,18]. The stronger and sharper the two peaks indicate the higher crystallinity of the as-grown ZnO NRs. The figure also denotes the significant enhancement in crystallinity of the as-grown ZnO NRs with respect to the increase of precursor concentrations. The best crystallinity was obtained with samples of 0.08 M.

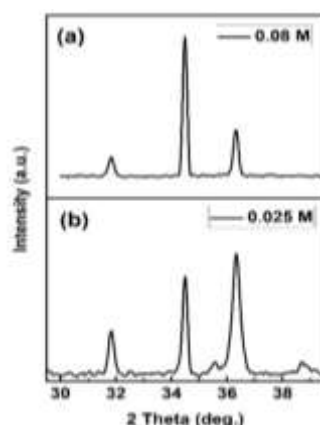


Figure 3. X-ray patterns of the as-grown ZnO NRs with different concentrations of (a) 0.025 M and (b) 0.08 M.

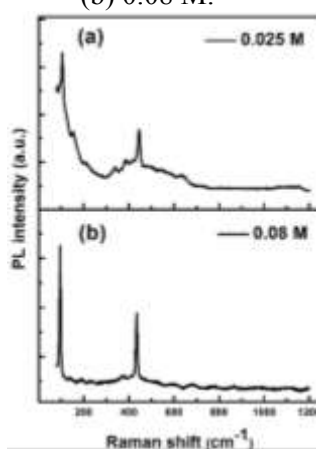


Figure 4. Raman scattering spectra of the as-grown ZnO NRs with different hydrothermal time.

4. Conclusion

In this study, high-crystallinity, high-density and well-aligned ZnO NRs grown on low-cost effective PCB substrates were obtained by using a seedless hydrothermal method together with galvanic effect. The structural, morphological and optical properties of ZnO NRs synthesized at different equimolar concentrations of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and of $\text{C}_6\text{H}_{12}\text{N}_4$ have been investigated. The SEM, XRay, Raman and PL spectra have confirmed the improvements in both vertical alignment and crystallinity since the precursor concentrations of increased from 0.025M to 0.08M. The best results were obtained with saturated concentration of 0.08M.

5. Acknowledgements

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6. References

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