

Defect Driven Emission from ZnO Nano Rods Synthesized by Fast Microwave Irradiation Method for Optoelectronic Applications

Nagendra Pratap Singh^{1,2}, S.A. Shivashankar², Rudra Pratap^{1,2}

¹Department of Mechanical Engineering, Indian Institute of Science, Bangalore-560012, India
²Centre for Nano Science and Engineering (CeNSE), Indian Institute of Science, Bangalore-560012, India

ABSTRACT

Because of its large direct band gap of 3.37 eV and high exciton binding energy (~60 meV), which can lead to efficient excitonic emission at room temperature and above, ZnO nanostructures in the wurtzite polymorph are an ideal choice for electronic and optoelectronic applications. Some of the important parameters in this regard are free carrier concentration, doping compensation, minority carrier lifetime, and luminescence efficiency, which are directly or indirectly related to the defects that, in turn, depend on the method of synthesis. We report the synthesis of undoped ZnO nanorods through microwave irradiation of an aqueous solution of zinc acetate dehydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] and KOH, with zinc acetate dihydrate acting as both the precursor to ZnO and as a self-capping agent. Upon exposure of the solution to microwaves in a domestic oven, ZnO nanorods 1.5 μm - 3 μm and 80 nm in diameter are formed in minutes. The ZnO structures have been characterised in detail by X-ray diffraction (XRD), selective area electron diffraction (SAED) and high-resolution scanning and transmission microscopy, which reveal that each nanorod is single-crystalline. Optical characteristics of the nanorods were investigated through photoluminescence (PL) and cathodoluminescence (CL). These measurements reveal that defect state-induced emission is prominent, with a broad greenish yellow emission. CL measurements made on a number of individual nanorods at different accelerating voltages for the electrons show CL intensity increases with increasing accelerating voltage. A red shift is observed in the CL spectra as the accelerating voltage is raised, implying that emission due to oxygen vacancies dominates under these conditions and that interstitial sites can be controlled with the accelerating voltage of the electron beam. Time-resolved fluorescence (TRFL) measurements yield a life time (τ) of 9.9 picoseconds, indicating that ZnO nanorods synthesized by the present process are excellent candidates for optoelectronic devices.

INTRODUCTION

Zinc oxide (ZnO) is a multifunctional, direct, wide band gap ($E_g=3.37$ eV) semiconductor with a large free-exciton binding energy (~60 meV), rendering excitonic emission processes possible at or above room temperature [1,2,3]. Thus, ZnO is a promising material for UV and blue light emitting devices with several fundamental advantages over GaN, its chief competitor. It is more radiation-resistant than GaN, comparatively inexpensive, and biocompatible [4,5]. Defects in ZnO play a major role in tailoring its optical, piezoelectric, mechanical, electronic and optoelectronic properties [3]. The desired properties of ZnO nanostructures can be tuned with either native defects or foreign atom incorporated defects (doping). Intrinsic point defects in ZnO nanorods give rise to luminescence over a broad range in the visible spectrum. This enables tunable resonant emission in the visible spectral range with a pure ZnO system. Native defect engineering is favorable over doping because foreign atoms usually affect surface morphology as

well as physical, chemical, and optical properties to a greater degree than do native defects. As these are point defects created generally by either oxygen or zinc vacancies, their formation depends on the process of synthesis [6]. Among solution-based processes, microwave-assisted synthesis (MWS) is relatively simple and rapid, and allows control over the growth process through numerous parameters, including the choice of precursor and solvent, and can yield device quality nanomaterial inexpensively compared to other growth processes such as CVD, VLS, PVD, and hydrothermal [7]. We have used simple, surfactant-free chemistry to synthesize high quality ZnO nanorods in the aqueous medium. The tuning of the optical properties is demonstrated with the help of cathodoluminescence (CL) spectra obtained at varying accelerating voltages of incident electrons. The possibility of optical devices requiring fast switching is indicated as a carrier lifetime in these nanorods is found to be less than 10 ps.

EXPERIMENT

To synthesize ZnO nanorods, zinc acetate dihydrate and KOH (in 1:15 molar ratio) is dissolved in 100 ml of de-ionised water (18 MΩ-cm). The solution is stirred for 15 min in a round bottom flask and exposed to microwave radiation at 800 Watt power for 3 minutes in a domestic microwave oven (LG MS 2049, 2.45 GHz). The resulting white precipitate is separated by centrifugation at 4000 rpm and washed in ultra-pure water. The precipitate is then dried in an oven at 75°C. The resulting powder is analyzed using X-ray powder diffraction (XRD), field-emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), photoluminescence (PL, Horiba LabRAM HR), and cathodoluminescence (CL, FESEM-Carl Zeiss Mono). Time-resolved fluorescence lifetime measurement (TRFL, Horiba JobinYvon Fluorocube-01-NL Fluorescence Life time System) was made to determine carrier lifetime at room temperature. A picosecond laser diode (374 nm wavelength) was used as the excitation source.

RESULTS and DISCUSSION

The XRD pattern recorded with a Rigaku powder diffractometer is shown in Fig. 1 (a). All the diffraction peaks can be indexed to zinc oxide of the hexagonal würtzite structure. The XRD data yield lattice constants of $a=3.2478 \text{ \AA}$ and $c =5.2035 \text{ \AA}$ [JCPDS -36-1451]. The Scherrer formula [8] applied to the (101) peak gives the crystallite size of ZnO to be 62.5 nm, equivalent to the diameter of the nanorods. The average crystallite size ($D= 62.5 \text{ nm}$) was calculated using the Scherrer formula,

$$D = \frac{0.9\lambda}{\beta_{hkl}\cos\theta} \dots \dots \dots (1)$$

where β_{hkl} is the full width at half maximum (FWHM) and $\lambda=1.54 \text{ \AA}$.

The Williamson-Hall equation [9] is used to estimate the strain in the ZnO crystallites:

$$\beta_{hkl}\cos\theta = \frac{K\lambda}{D} + 4 \epsilon \sin\theta \dots \dots \dots (2)$$

where ϵ the lattice strain and $K (=0.9)$ is a constant. $\beta\cos\theta$ is plotted against $4\sin\theta$ in Fig. 1 (b). A linear fit to the data yields the crystallite size D through the intercept $\frac{K\lambda}{D}$ and the strain (ϵ) is given by the slope of the straight line from the graph (Fig. 1b). The microstrain $\epsilon = 0.097\%$, which is indicative of the strain due to native defects present in the crystals.

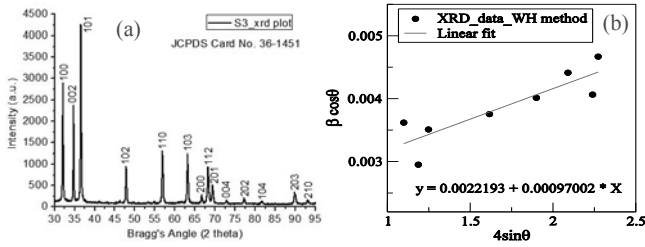


Figure 1 (a) Powder X-ray diffraction pattern of ZnO nanorods, all peaks corresponding to hexagonal ZnO; (b) Williamson-Hall plot derived from the XRD data

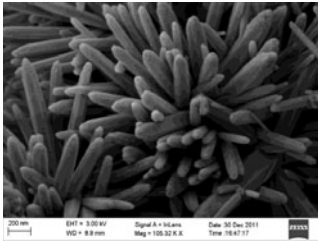


Figure 2 FESEM image of ZnO nanorods

FESEM analysis (Fig.2) reveals clearly that the ZnO sample is made of hexagonal nanorods. It is seen that the rods are well-faceted, but are “tapered” at one end, indicative of the rather gradual termination of the growth process upon microwave power being turned off. They range in length from $\sim 1.5 \mu\text{m}$ to $3 \mu\text{m}$ and in diameter from $\sim 30 \text{ nm}$ to 80 nm . Most rods have relatively large diameters, consistent with the average crystallite size estimated from XRD data. TEM analysis (Fig. 3 (a), 3 (b)), including high-resolution imaging and selected-area electron diffraction (SAED) together reveal that each nanorod is a single crystal of high quality and purity. HRTEM and SAED show also that the ZnO nanorods are oriented in the $\langle 0001 \rangle$ direction.

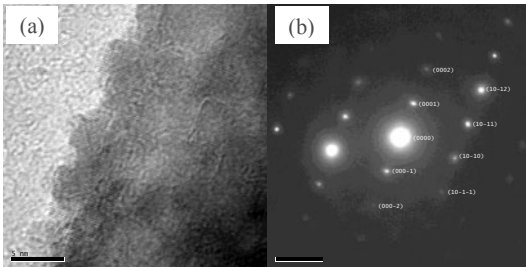


Figure 3 (a) HRTEM image (b) SAED pattern of a ZnO nanorod

The photoluminescence spectrum (Fig. 4a) obtained from an assembly of ZnO nanorods at room temperature through excitation with a He-Cd laser (325 nm) shows that the near-band-edge emission at ~3.27 eV is dwarfed by the strong broadband emission in the green, centred at ~2.20 eV. The components of this well-known emission in ZnO due to native defects are revealed by deconvolution (Fig. 4 (b)). As the schematic band diagram (Fig.4 (c)) shows, the components of the broadband emission are all from deep within the bandgap in the undoped ZnO sample, the Fermi energy being ~1.64 eV. Emission in the green from ZnO is known to be due to oxygen vacancies [10].

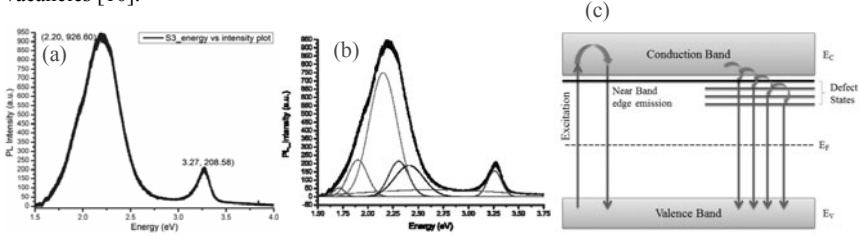


Figure 4(a) Photoluminescence spectrum, (b) Photoluminescence spectrum with de-convoluted peaks and (c) Schematic model for different relaxation processes in ZnO nanostructures

Cathodoluminescence (CL) allows control over emission from native defects through control over such defects provided by the acceleration potential of the electron beam in the SEM. The CL spectra of the ZnO nanostructures obtained with the electron beam accelerated to different voltages are shown in Figs.5 (a) and 5(b). The sample was anchored carefully to a substrate to eliminate artifacts due to heating by the e-beam. A clear – though small – “red shift” of 2.5 nm (between 5 kV and 20 kV of the acceleration potential) in the emission due to the defects as the electron beam is accelerated through higher potentials can be discerned from these spectra. A monotonic increase in the intensity of the broadband emission is seen as the accelerating potential is increased, accompanied by a corresponding monotonic reduction in the intensity of the near-band-edge emission. These changes in intensity together provide evidence that the density of native defects (related to oxygen in ZnO) increases, with an inevitable deterioration in the degree of perfection in the crystals, on which the intensity of the near-band-edge emission depends.

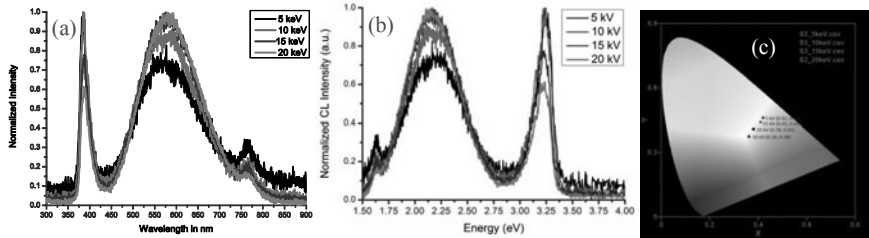


Figure 5(a,b) Cathodoluminescence (CL) spectrum at varying voltages; red shift in the defect peak shows that emission characteristics are tunable with voltage; sample carefully anchored to substrate to avoid heating due to e-beam. (c) CIE color map of CL spectrum.

In a different manifestation of the changes in the ZnO defect structure under electron bombardment, the colour of cathodoluminescence changes steadily as the acceleration potential is increased. This is shown in the CIE colour map (Fig. 5 (c)), with the emission turning from green to orange, with a near-white emission at the acceleration potential of 10 kV.

To examine the process of luminescence from ZnO further, the lifetime of photo-generated carriers was measured by the time-resolved fluorescence technique, with the sample excited by a laser diode emitting at 374 nm, with the lifetime measured at 575 nm.

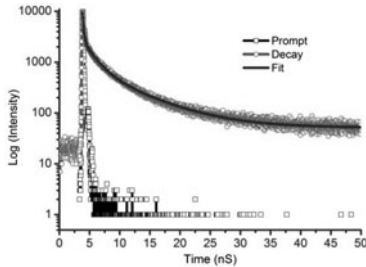


Table 1; Luminescence decay parameters obtained with an excitation wavelength at 374 nm, measured at 575 nm and τ the lifetime and A & B the corresponding relative amplitude

A	B ₁	τ_1 (ps)	B ₂	τ_2 (ps)	B ₃	τ_3 (ps)	χ^2
51.4	33.6	1846.4	49.1	7260.5	17.2	191.1	1.8

Figure 6 Time-resolved fluorescence life time of ZnO nanorods excited by a 374 nm laser diode and measured at 575 nm. Carrier lifetime is calculated to be 191 picoseconds

The intensity of the transient emission (Fig.6) as a function of time (in picoseconds) was fitted to a sum of exponentials [11], according to the equation (1):

$$I(t) = \sum_{i=1}^3 \alpha_i e^{-\frac{t}{\tau_i}} \dots \dots \dots (3)$$

where i is the number of exponentials, and τ_i and α_i are the lifetime and the pre-exponential factor for each component. The TRFL decay spectra of the ZnO nanorods with exponential fits are given in Figure 6 and fitted parameters are listed in table-1. After finding the best fit, we deduce the lifetime of the carriers in the ZnO nanorod to be 191 picoseconds. This indicates fast switching, which shows the potential of this material for applications in memory devices, LEDs, and laser diodes.

CONCLUSIONS

We have synthesized ZnO nanorods by the rapid and inexpensive microwave irradiation method. Structural, morphological, and optical characterization show them to be single-crystalline and of high quality. The tunability of their properties through engineering the defect structures and defect density has been demonstrated by subjecting them to irradiation by electron beams accelerated to different potentials. For example, the colour of emission (in the visible) due to oxygen defects is found to be controllable by just tuning the excitation voltage. Further, carrier lifetime in these nanostructures is found to be in the sub-nanosecond range, which indicates rapid generation and recombination of carriers. Thus, a voltage-controlled, single nanorod-based optoelectronic device appears to be realizable.

ACKNOWLEDGMENTS

This work has been supported by CEN Phase II grant from the Department of Electronics and Information Technology, Government of India. Partial support provided by Centum Electronics, a member of the Industry Affiliate Program, enabling NPS to attend the MRS Fall Meeting, is gratefully acknowledged.

REFERENCES

- [1] A. H. Jayatissa, A. M. Soleimanpour, and Y. Hao, *Adv. Mater. Res.*, **383–390**, pp. 4073–4078, (2011).
- [2] A. Janotti and C. G. V. de Walle., *Reports Prog. Phys.*, **72**, pp. 126501-126530, (2009).
- [3] H. M. and U. Ozgur, *Zinc Oxide: Fundamentals, Materials and Device Technology*, Wiley-VCH Verlag GmbH & Co. 2007, pp. 490.
- [4] Z. L. Wang and J. Song, *Science*, **312**, pp. 242–6, (2006).
- [5] Z. Li, R. Yang, M. Yu, F. Bai, C. Li, Z. L. Wang, *J. Phys. Chem. C*, **112**, pp. 20114–20117, (2008).
- [6] D. F. Wang and T. J. Zhang, *Solid State Commun.*, **149**, pp. 1947–1949, (2009).
- [7] S. Brahma, K. J. Rao, and S.A. Shivashankar, *Bull. Mater. Sci.*, **33**, pp. 89–95, (2010).
- [8] B. D. Cullity, *The Elements of X-Ray Diffraction*, Addison-Wesley, 1978, pp. 102.
- [9] Y. P. and B. D. V.D. Mote, *J. Theor. Appl. Phys.*, **6**, pp. 2–9, (2012).
- [10] A. B. Djuricic and Y. H. Leung, *Small*, **2**, pp. 944-961, (2006).
- [11] E. Sönmez and K. Meral, *J. Nanomater.*, **2012**, pp. 1–6, (2012).