

Effect of Annealing Time on the Optical and Structural Properties of ZnO Nanorods

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(Received 13 August 2019; revised manuscript received 05 December 2019; published online 13 December 2019)

Zinc oxide nanorods (NRs) are successfully synthesized by simple chemical precipitation method using zinc nitrate hexahydrate and sodium hydroxide as the precursors. The effect of annealing at 400 °C for 2 h and 4 h on the ZnO sample is investigated by UV-Vis spectroscopy, emission spectrum and XRD analysis. The band gap of NRs decreased from 3.86 eV to 3.54 eV and Urbach energy increased from 1.33 eV to 1.75 eV under heat treatment. Strong excitonic related UV emission at 381 nm, 399 nm, 394 nm and defect related emissions in the visible regions are observed from ZnO NRs. X-ray diffraction study revealed that the ZnO NRs are highly crystalline and have a pure hexagonal phase. The results revealed that grain size increases and strain decreases after annealing the ZnO NRs. Well crystalline ZnO NRs with aspect ratio of about 4.25 and bright diffraction spots are observed from TEM and SAED patterns.

Keywords: ZnO nanocrystals, Band gap, Emission spectrum, XRD, TEM.

DOI: [10.21272/jnep.11\(6\).06003](https://doi.org/10.21272/jnep.11(6).06003)

PACS numbers: 78.66.Bz, 81.40.Vw

1. INTRODUCTION

The advent of nanoscience and applied science has accelerated the evolution of various materials with several exceptional size-dependent properties for various optoelectronic and industrial applications. Zinc oxide (ZnO) may be an important II-IV direct band gap semiconductor with wide band gap (bulk band gap is 3.37 eV at 300 K) and enormous exciton energy of 60 meV at room temperature. Being a multifunctional direct band gap semiconductor having wonderful size dependent reasonable optical property, ZnO has necessary applications within the nanoscience primarily based on drug delivery, solar cell, semiconductor based optoelectronic devices, gas sensing, bio-imaging, bio-sensing and medical specialty analysis [1] thanks to its wonderful properties, there is a broad variety of potential applications, e.g., in ultraviolet (UV) light weight emitters, electricity devices, wave guides, optical device diodes and gas sensors, chemical sensors [2, 3]. It has sensible transparency, high electron mobility of $\sim 2000 \text{ cm}^2/(\text{V s})$ at eighty K and it is arguably the richest single semiconductor material in terms of form of different nanostructures like nanorods (NRs), nanoflakes and nanoneedles [4]. Several ways for fabrication of nanosized ZnO particles with uniform morphology and controlled particle size, as well as the hydrothermal technique, sol-gel technique, and direct precipitation ways, are reported [5, 6]. Amongst these synthesis techniques, the chemical precipitation technique represents an easy suggestion for big scale production at low price while not requiring valuable raw materials or difficult instrumentality. Chemical precipitation technique synthesis may be a widely used chemical synthesis technique attributable to its simplicity, repeatability, cheapness, and dependableness. Thermal hardening is widely utilized to boost the crystal quality and to check the struc-

tural defects of nanomaterials. Elaborate investigations of area unit needed to elucidate the grain size impact on the temperature dependent behaviour that is extremely a lot of essential from the technological perspective as a result of the particle size and annealing temperature have a detailed relation [7, 8]. Annealing process may be responsible for the occurrence of dislocation and adsorption/decomposition on the surface, thus the structure of the material would change. There are few reports on the effect of annealing temperature on zinc oxide nanostructure [9, 10]. In the work presented herein, the structural, morphological, and optical properties of nanosized ZnO particles synthesized by a chemical precipitation method were investigated. In the chemical precipitation method, zinc nitrate hexahydrate was used as precursor. The effect of different annealing time on the structural and optical properties of the ZnO NRs was studied and is reported herein.

2. EXPERIMENTAL

2.1 Growth of ZnO NRs

The used chemicals are supplied from MERCK. We used zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and sodium hydroxide (NaOH) for the growth of ZnO NRs. Initially we prepare two separate solutions: in one solution 7.44 g of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in deionized water to prepare 100 ml of solution, in another solution 0.4 g of sodium hydroxide (NaOH) was dissolved in deionized water to prepare 100 ml of NaOH solution. This $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solution was then put under vigorous stirring at room temperature (30 °C) in a conical flask using a magnetic stirrer (SPINOT make). The previously prepared NaOH solution was added dropwise to the zinc nitrate hexahydrate solution for 30 min. The mechanical stir-

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ring was continued for 4 h. The pH of the solution was 11. A white precipitate was deposited at the bottom of the flask. The precipitate was then filtered and washed 3-4 times with distilled water. The final powder sample was separated into three parts and they also were collected separately. One sample is denoted as 'after growth' (sample 1). The second sample is annealed at 400 °C for two hours. After annealing it is cooled to room temperature. This sample is denoted as 'annealing 2 h' (sample 2). The third sample is annealed at 400 °C for four hours. After annealing it is cooled to room temperature. This sample is denoted as 'annealing 4 h' (sample 3). These collected three different samples are further used for different characterizations.

2.2 Absorption Spectrum

We studied the optical properties of the prepared three samples by absorption spectrum shown in Fig. 1A. The absorbance maxima occur at 362.53 nm, 377.87 nm, and 379.06 nm for samples 1, 2, and 3 respectively. We observe a red shift in the absorbance maxima and the blue shift in the energy band gap due to increase in the annealing temperature of the grown ZnO NRs. The band gaps of samples 1, 2, and 3 are determined from the Tauc's formula [11]: $(ahv)^2 = c(hv - E_g)$. The plots of $(ahv)^2$ vs. (hv) for three different samples (1, 2, 3) are shown in Fig. 1B. The calculated band gaps are 3.86 eV, 3.67 eV, and 3.54 eV for samples 1, 2, and 3 respectively. The increase in the red shift in the absorption maxima leads to decrease in the band gap. Zak et al. also observed a red shift in the absorbance maxima due to annealing [12]. The absorbance maxima arise below 400 nm for all three ZnO nanosamples due to the electron transitions from the valence band to the conduction band ($O_{2p}-Zn_{3d}$) within the intrinsic band gap absorption. This shift and band gap changes occur probably due to size and microstructure changes. The size and strain determination discussed in the XRD section supports this shift and band gap change. The Urbach energy (E_U) is also determined from the following formula energy [13]:

$$\alpha = \alpha_0 \exp\left[\frac{h\nu}{E_U}\right].$$

The plot of $\ln\alpha$ vs. $h\nu$ is shown in Fig. 1C. The average Urbach energy (E_U) values are 1.33 eV, 1.53 eV, and 1.75 eV for samples 1, 2, and 3 respectively. Our results are slightly greater than other reported values [14]. This change in the E_U may be the cause of microstructure change, size changes and the crystal disorder. The results clearly indicate that band gap and Urbach energy of semiconductor ZnO NRs may change by changing ZnO microstructure and size with the effect of heat treatment. Increase in the annealing time reduces the band gap and enhances the Urbach energy.

2.3 Emission Spectrum

The emission spectroscopy is an effective method to investigate the presence of defects in semiconductors. Fig. 2a shows the emission spectra of ZnO NRs after

growth and after annealing under different time at 400 °C. The excitation wavelength for the entire three samples is 330 nm. It is observed from Fig. 2 that ZnO NRs exhibit a strong excitonic related UV emission positioned at 381 nm, 399 nm, and 394 nm for samples 1, 2, and 3 respectively. The change in the UV peak position is associated with the grain and crystal orientation. The annealing condition may change the grain boundaries and number of surface particles, the number of non-radiative transitions and deep level defects. The emission of sample 1 (after growth) (Fig. 2a) shows two defect related blue and green emission peaks at 486.75 nm and 549.45 nm respectively. The emission of sample 2 (annealing 2 h) (Fig. 2b) shows three defect related emission peaks at 452.03 nm (blue emission), 484.04 nm (blue emission) and 528.99 nm (green emission). The emission of sample 3 (annealing 4 h) (Fig. 2c) shows five defect related emission peaks: (i) violet emission at ~ 420.02 nm, (ii) violet emission at ~ 445.91 nm, (iii) blue emission at ~ 458.84 nm, (iv) cyan emission at ~ 486.76 nm, (v) green emission at ~ 525.58 nm. The defect related emissions are observed for sample 2 (annealing 2 h) and sample 3 (annealing 4 h) due to the formation of Zn_i (zinc interstitials) and V_O (oxygen vacancies) [15].

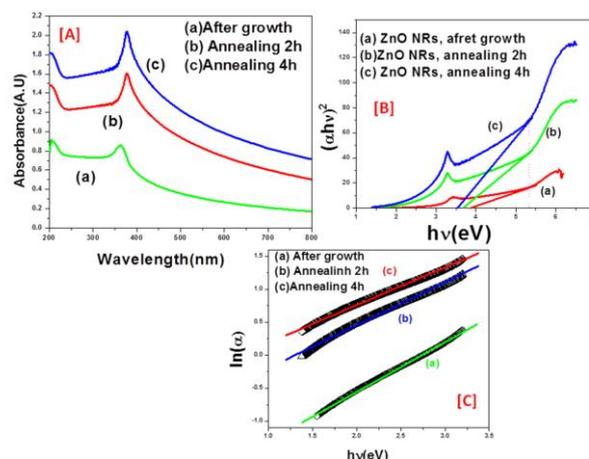


Fig. 1 – Absorption spectroscopy of ZnO NRs [A]: after growth (a), after annealing 2 h (b), after annealing 4 h (c); Bandgap determination plot of ZnO NRs [B]: after growth (a), after annealing 2 h (b), after annealing 4 h (c); Plot of $\ln\alpha$ vs. photon energy $h\nu$ of ZnO NRs [C]: after growth (a), after annealing 2 h (b), after annealing 4 h (c)

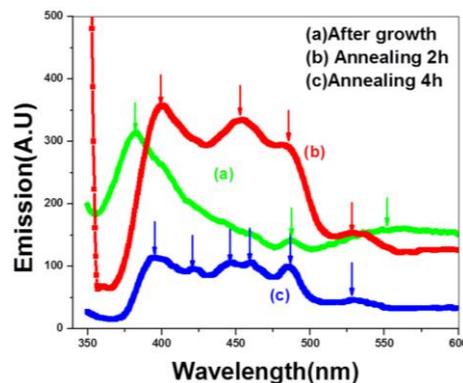


Fig. 2 – Emission spectrum of ZnO NRs: after growth (a), after annealing 2 h (b), after annealing 4 h (c)

2.4 XRD Analysis

The XRD spectra of the synthesized ZnO NRs after growth and annealing for 2 h and 4 h are shown in Fig. 3a, c, e for the samples after growth, after annealing 2 h, and after annealing 4 h respectively. The average crystallite size and strain of the synthesized ZnO NRs and NRs after annealing was calculated by applying the Scherrer formula [16]:

$$R_{hkl} = \frac{0.89\lambda}{\beta \cos \theta}$$

The diffraction peaks appear at the same positions (2θ) for all three samples, but intensities are changed. The XRD patterns of all three samples show the presence of the (100), (002), (101), (102), (110), (103), (200), (112), (201), (004) and (202) peaks corresponding to hexagonal wurtzite phase of the ZnO nanocrystal. First six peaks are fitted with Gaussian equation [$y = y_0 + (A/(\beta \cdot \sqrt{\pi/2})) \cdot \exp(-2 \cdot ((x - x_c)/\beta)^2)$], and the corresponding half widths (β) are determined. The variations of half widths with respect to different diffraction peaks are shown in Fig. 3b, d, f for samples 1, 2, and 3 respectively. The average crystal sizes are 26.91 nm, 34.25 nm, and 33.25 nm for sample 1 (after growth), sample 2 (annealing 2 h), sample 3 (annealing 4 h) respectively. It was observed that the grain size increased in the range from 26.9 nm to 34.25 nm due to increasing annealing time, which might be due to recrystallization of the sample. The decrease in average full width at half maximum (FWHM) within the XRD peak leads to increase in the crystallite size. This decrease in FWHM with increasing annealing temperature could be due to grain coalescence at higher annealing temperature. The intensity of the maximum peaks gets sharpened and increases with increasing annealing time. Primarily, the increase in the peak intensities is attributed to increase of the crystallinity and crystallite size. In general, for ZnO there are many dangling bonds related to the zinc and oxygen defects at the grain boundaries. As a result, these defects are favourable for the merging process to form larger ZnO grains when increasing the annealing time. The average crystal strain is also calculated from the following formula:

$$\text{Strain} = \frac{\beta}{4 \tan \theta}$$

The calculated strains are 0.21333, 0.1667, and 0.171265 for samples 1, 2, and 3 respectively. The crystal strain decreases due to increase in the crystal size.

2.5 TEM Analysis

The TEM image of the grown ZnO sample (sample 1 i.e. after growth) is shown in Fig. 4a. TEM image is the direct visualization of the shape and size of the nanocrystals [17]. TEM image clearly shows the formation of ZnO NRs. In the image, single NR is clearly observed. The diameter and length of the clearly observed nanorod is ~ 25.5 nm and ~ 108.5 nm respectively. The aspect ratio of the NR shown in the inset of Fig. 4a is ~ 4.25 . The corresponding selected area (electron) diffraction (SAED) pattern clearly shows the crystalline

nature of ZnO NRs. The SAED pattern of the NR is shown in Fig. 4b. The SAED pattern of the ZnO NRs shows well crystalline nature of the NRs with the diffraction spot corresponding to (100), (002), (101), (102), (110), (103), (200), (112) planes which match with the XRD peaks.

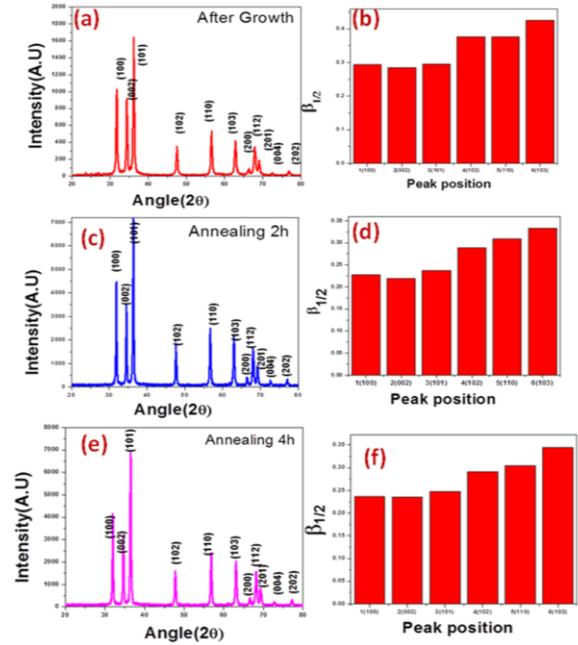


Fig. 3 – XRD spectroscopy of ZnO NRs: after growth (a), after annealing 2 h (c), after annealing 4 h (e); Variation of $\beta_{1/2}$ with different diffraction peaks: after growth (a), after annealing 2 h (c), after annealing 4 h (e); Variation of $\beta_{1/2}$ with diffraction peaks of ZnO NRs: after growth (a), after annealing 2 h (b), after annealing 4 h (c)

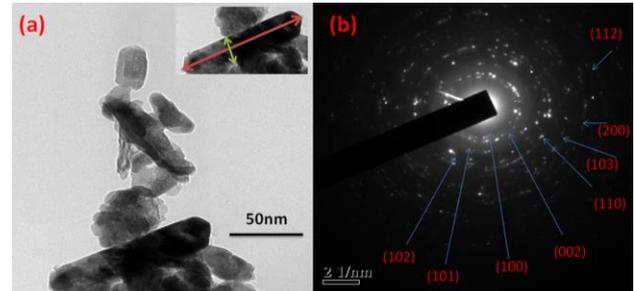


Fig. 4 – TEM image of ZnO NRs (a), SAED pattern obtained for ZnO NRs (b)

3. CONCLUSIONS

UV-Vis spectroscopy of our synthesized ZnO NRs showed a red shift in the absorbance maxima after annealing the NRs. The absorbance maxima for the ZnO NRs and NRs after annealing at 400 °C for 2 h and 4 h showed excitonic formation below 400 nm. The calculated band gaps from the Tauc's formula are 3.86 eV, 3.67 eV, and 3.54 eV for the ZnO NRs and NRs after annealing at 400 °C for 2 h and 4 h respectively. The band gap of NRs decreased from 3.86 eV to 3.54 eV and Urbach energy increased from 1.33 eV to 1.75 eV under heat treatment. The ZnO NRs and NRs after annealing showed strong excitonic related UV emission

Table 1 – Characterization parameters

Sample	Absorption peak	Band gap	Urbach energy (E_U)	Size from XRD	Strain	Size from TEM
After growth	362.53 nm	3.86 eV	1.331 eV	26.91 nm	0.21333	25.5 nm
Annealing 2 h	377.866 nm	3.67 eV	1.533 eV	34.25 nm	0.1667	–
Annealing 4 h	379.06 nm	3.541 eV	1.752 eV	33.25 nm	0.171265	–

around ~ 381 nm, ~ 399 nm, and ~ 394 nm. The number of defect related emission peaks increased after annealing the ZnO NRs. X-ray diffraction study revealed that the ZnO NRs are highly crystalline and have a pure hexagonal wurtzite phase. The results revealed that grain size increases and strain decreases after annealing the ZnO NRs. The average crystal sizes are 26.91 nm, 34.25 nm, and 33.25 nm for the sample 1 (after growth), sample 2 (annealing 2 h), and sample 3 (annealing 4 h)

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Вплив часу відпалу на оптичні та структурні властивості нанострижнів ZnO

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Нанострижні окису цинку успішно синтезуються простим хімічним методом осадження, використовуючи гексагідрат нітрату цинку та гідроксид натрію як прекурсори. Вплив відпалу при 400 °C протягом 2 і 4 годин на зразок ZnO досліджується за допомогою спектроскопії в УФ та видимому діапазонах, спектру випромінювання та рентгенодифракційного аналізу. Заборонена зона нанострижнів зменшилася з 3,86 eV до 3,54 eV, а енергія Урбаха зросла з 1,33 eV до 1,75 eV при термічній обробці. Сильне ексітонне ультрафіолетове випромінювання при 381 nm, 399 nm і 394 nm та випромінювання у видимих областях, пов'язане з дефектами, спостерігаються від нанострижнів ZnO. Рентгенодифракційне дослідження виявило, що нанострижні ZnO висококристалічні і мають чисту гексагональну фазу. Результати показали, що розмір зерна збільшується, а деформація зменшується після відпалу нанострижнів ZnO. Висококристалічні нанострижні ZnO із співвідношенням сторін приблизно 4,25 та яскравими дифракційними рефlekсами спостерігаються на TEM та SAED зразках.

Ключові слова: Нанокристали ZnO, Заборонена зона, Спектр випромінювання, XRD, TEM.

respectively. The TEM image and SAED pattern of the synthesized ZnO NRs (after growth) showed well crystalline single ZnO NR formed with aspect ratio of ~ 4.25 . Our results showed that thermal annealing is important to boost the crystal quality and to check the structural defects of nanomaterials. We successfully report the relationship between particle size and annealing temperature. Our synthesized ZnO NRs and NRs after annealing are good optical materials that are/and very important for technological purpose.

ACKNOWLEDGEMENTS

The authors are grateful to the Department of Physics and Technophysics of Vidyasagar University. The authors are also thankful to CRF, IIT Kharagpur for measurement facilities. Author AKB is thankful to the Department of Physics, Government General Degree College at Gopiballavpur-II.