# EFFECT OF ANNEALING TEMPERATURE ON STRUCTURAL, MORPHOLOGICAL AND OPTICAL PROPERTIES OF ZnO NANOROD THIN FILMS PREPARED BY HYDROTHERMAL METHOD

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The hydrothermal process is considered as one of the simplest and cheapest methods applied to prepare zinc oxide nanorods (ZnO-NRs) to be arranged on glass substrates. Each glass substrate was pre-coated by ZnO seed layer. The grown nanostructures were annealed in air at temperatures of 200, 250 and 400 °C. The effect of annealing process on structural, optical and morphological properties has been studied. The X-ray diffraction (XRD) tests confirmed that all synthesized samples are polycrystalline structures that possess hexagonal shapes and preferable orientation plane of (002), along with c-axis coordination which is also evident from FE-SEM image. The intensity of (002) peak was most prominent at 250 °C. Due to the increase in crystals size with annealing temperature at 250 °C, the full width at half maximum (FWHM) has been decreased. The energy dispersive spectroscopy test (EDS) showed that the Zn:O atomic ratio for all samples was nearly stoichiometric. The atomic force microscopy (AFM) image show that the root mean square (RMS) decreases when the temperature increases up to 400 °C. The optical transparency and band gap of (ZnO-NRs) decreased with the increase of annealing temperature.

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### **1. Introduction**

Zinc oxide is an eminent n-type semiconductor for its unique properties such as large band gap (3.37 eV), excitation binding energy of (60 meV), and chemical stability [1,2]. The onedimensional (1D) ZnO nanostructures include nanotube, nanowires, and nanorods [3,4]. They can serve as keystones for the integration of nano-devices, as they provide a direct conduction pathway for charge carrier transport [5,6]. The morphology of one dimensional structures is particularly suitable for vertically-stacked devices such as short-wavelength laser, diodes, and light emitting diodes (LEDs). The doped metal oxide nanoparticles are valuable for a wide range of implementation[7,8]. Various methods have been developed for the growth of well-arranged metal oxide (ZnO, SnO<sub>2</sub>, In<sub>2</sub>O<sub>3</sub>)nanorods. The pulsed laser deposition(PLD)[9], the chemical vapor deposition under air ambient[10], spray pyrolysis technique, and anodic alumina membrane as template are the most commonly used methods [11,12]. Due to the complexity and high cost of most methods mentioned above, the hydrothermal process can be considered as the preferable approach [13,14]. An autoclave which is sealed steel cylinder that can resist at high temperature and pressure for a long duration is used to achieve the hydrothermal process [15]. The hydrothermal route appears to be a promising method for ZnO nanostructure growth due to its cost effectiveness, simplicity and high growth rate [16]. However, the hydrothermally grown ZnO NRs have numerous defects due to the low formation energies. Some of these defects in caused by incorporation of unknown elements in Zno matrix, which can be solved by heat treatment. The annealing process is an effective method to improve the crystallinity of organic materials. The properties of ZnO NRs such as morphology, defect concentration, surface area, and structure can

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be affected by the annealing conditions (temperature, time, atmosphere, etc.) [17]. The major challenge in ZnO NRs through the annealing process is obtaining high crystal-quality nonrod. High annealing temperature often increases intrinsic defects by sintering between the NRs. Hence, the annealing temperature needs to be optimized in order to achieve high crystallinity and low defect concentration without morphological change. In this study, ZnO NRs were synthesized on glass substrate using a hydrothermal method, and annealed at different temperatures (200–400 °C). Furthermore, the effect of annealing temperature on the crystallinity structure, morphology and optical properties has been studied in detail.

#### 2. Materials and methodology

Typically two steps were used in hydrothermal procedure for ZnO thin film preparation. The ZnO nanorods were grown on ultrasonically cleaned microscope glass substrates of dimensions ( $2 \text{cm} \times 1.5 \text{cm}$ ). The seed layers or precursor of the nanostructures were prepared by mixing (10mM) Zinc acetate dehydrate (CH3COO)2.H2O in ethanol to form the seed layer solution. glass substrates are pre-cleaned before the deposition process in pure ethanol and are treated ultrasonically for 15 minutes to remove any organic materials that may be adhered to the surface of the substrate. Finally, the substrates are blown dried by nitrogen gun. For the preparation of seed layer solution, 20  $\mu$ L of the prepared solution is drop-casted on the glass substrates which, later, placed on a hot plate to soft-bake at 80 °C. Finally, the substrates were annealed in air ambient on hot plate at 350 °C for 30 minutes, to complete the ZnO seed growth. In order to prepare the ZnO nanorods over the seed layers for Hydrothermal method, an equimolar precursor solution mixture of (25 mM) Zinc nitrate hexahydrate and hexamethylenetetramine was added in DI- water, a solution finally spilt into a stainless steel Teflon-lined autoclave. The substrates with seed layers were submerged in the solution which was kept at 180 °C for 6 hr in an oven. The autoclave was taken out of the oven and cooled down to room temperature. The produced films were taken out and washed in distilled water and then dried in air. The prepared films then annealed on hot plate in air at 200, 250, and 400 °C for 1.30 hr. The grown films were characterized by the distinction of the effect of annealing process on ZnO nanostructure properties.

#### 2.3. Characterization

The structural composition of samples was investigated by using X-ray diffraction (6000 XRD, Cu- $k_{\alpha}$  radiation,  $\lambda$ =1.54 Å. The morphologies of all samples were inquired by field emission scanning electron microscopy (FE-SEM; Model Mira3-XMU, TESCAN, japan), and atomic force microscopy (AFM) (Auto probe type, USA with software: nanotech electronica) Day Petronic company –Iran, has been utilized to estimate the roughness of prepared films. The optical transmittance of the samples was evaluated in the wavelength range of 200–900 nm by double beam UV- visible spectroscopy -2600 from Shimadzu Co. Japan

## 3. Results and discussion

### 3.1. Structural characterization

The XRD patterns of the ZnO nanostructure annealed at different temperatures which are a polycrystalline hexagonal (wurtzite) structure. as shown in Fig. 1. The diffraction peaks at 31.76°, 34.45°, 36.25° and 62.86°, indicate the (100), (002), (101) and (103) planes in sequence. The XRD patterns of ZnO structure were compared with ICDD card No. 036-1451.



Fig. 1. XRD patterns of the annealed ZnO NRs with different annealing temperatures.

All prepared samples possessed a high and sharp intense (002) plane, which referred to the preferable orientation of nanorods in the c-axis direction, normal to the substrate surface. The peak intensity of the plane (002) increased with the annealing effect up to 250 °C and then decreased at 400 °C, which refer to promotion in degree of crystallinity up to 250 °C .Later it decreased at 40 °C which is compatible with the previous study [18]. To give the atoms enough activation energy and consequently to occupy the energetically convenient site in the ZnO crystal lattice, higher annealing temperature was achieved. The outcome was grains with less surface energy and bigger size [19,20]. This leads to higher intensities of (002) peak of ZnO with theprogress of aligned nanorods.. Faint diffraction peaks related to the (103) were also observed for the ZnO nanorod annealed at 400 °C. Additionally, as the temperature rose, molecular motion gained more strength and this lead to the growth in other directions as observed at 40 °C. Any peaks related to the impurity phases were not observed on the XRD patterns pointing to the high purity of the ZnO nanorods.

The lattice constant c, texture coefficient and grain size of ZnO NRs were calculated from (002) peak using relations (1) and (2) [21] respectively:

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

$$c = \frac{\lambda}{\sin\theta} \tag{2}$$

where *D* stands for the crystallite size,  $\lambda$  is the wavelength of the applied x-ray (0.15406 Å),  $\beta$  is the full width at half-maximum (FWHM) of the peaks,  $\theta$  is the diffraction angle of (002) peak, *c* is the lattice constant. The lattice parameters are tabulated in table 1. The FWHM value mirrors the crystallinity of the annealed films. The FWHM reduced sharply with the increase of annealing temperature up to 250 °C which clearly shows the crystallinity of the film with annealing process. The crystallite size increased with increasing annealing temperature up to 250 °C due to the recrystallization of the atoms of ZnO into wurtzite lattice structure due to thermal energy generated by annealing process. This energy helps atoms to align themselves into the plane with lowest free surface energy, and small crystallites were aggregated after annealing to form larger crystallites. As the temperature increased to 400 °C, the grain size decreased. This may be due to the cleavage of Zn–O bond [22].



*Fig. 2. The crystallite size and full width at half maximum of ZnO nanorods in the 200, 250 and 400 °C as a function of the annealing temperature.* 

Table 1. Shows XRD analysis of (002) peak position, FWHM, crystallite size, and lattice parameter  $C_o$ .

Annealing Temperature (°C)	<b>2θ(°</b> )	FWHM(°)	D (nm)	c <sub>o</sub> (Å)
200	34.3821	0.1856	44.808	5.2124
250	34.4203	0.1414	58.820	5.2068
400	34.4304	0.1911	43.524	5.2069

The texture coefficient  $(T_c)$ , which describe the most prominent direction can be calculated from XRD data by using the following expression [23]

$$T_c = \frac{\frac{I_{(hkl)}}{I_o(hkl)}}{N^{-1} \sum_N \frac{I_{(hkl)}}{I_o(hkl)}}$$
(3)

where  $T_{C (hkl)}$  stands for the texture coefficient of the reflection peak,  $I_{(hkl)}$  is the relative diffraction intensity of (h k l) diffraction peak which its data were collected experimentally and  $I_o$  (hkl) is the standard peak intensity for the reflection (h k l) according to the ICDD: card number 036-1451.

The inset of (Fig. 4-b) shows that the values of  $TC_{(002)}$  and  $TC_{(103)}$  for ZnO nanorods annealed at 400 °C are 88% and 12% respectively. The supreme value of  $TC_{(002)}$  worth the maximum.

Table 2. The calculated values of texture coefficient for annealed at different temperatures.

	Annealing temperature (°C)	<u>Texture coefficient</u> (100) (002) (101)		<u>nt</u> 01)	(103)	
4	200	0.25	2.60	0.142		-
2	250	-	2.43	0.28	2 -	
4	400	-	21.2	-	0.296	



*Fig. 3. Shows texture coefficient of sample annealed at 400 °C.* 

#### 3.2. FE-SEM study

Fig. 4 (a),(b) shows FE-SEM images for the surface morphologies of annealed ZnO NRs with various temperatures. All the FE-SEM images reveal that the NRs were grown vertically on substrates and had good uniformity with the hexagonal pillar shape. The preferential growth direction of the c-axis is probably due to the high surface energy of the polar (002) plane [24]. The diameter of the nanorods is distributed in the range of 46-66 nm with an average value of 55 nm and the range of 35-71 nm with an average value of 52 at annealing temperature 200 °C and 400 °C respectively.



*Fig. 4. FE-SEM micrographs of ZnO nanorods prepared by hydrothermal process with annealing temperature of 200 °C for( a,b) and 400 °C for( C,d).* 

#### 3.3. EDS study

Fig. 5 shows the spectrum of (EDX) and the atomic structure of the ZnO-NRs for the samples annealed at 200 °C and 400 °C. The description of the atomic structure of the elements in the ZnO-NRs samples is presented in percentages, in an inset table inside figure 5. It was

confirmed by the Zn:O average atomic percentages that the nanorod samples tended to be more similar to stoichiometric ZnO, also the elements of Zn and O were detected in all samples [25].



Fig. 5. EDX spectrum of ZnO nanorods samples that annealed at 200 °C and 400°C respectively.

#### 3.4. AFM study

The surface morphology of the films was also studied by atomic force microscopy (AFM). Fig. 6 shows the three dimensional (3D) and two dimensional (2D) AFM images for the annealed ZnO NRso that were obtained from the peak force tapping mode over the scan area of 2.5  $\mu$ m × 2.5  $\mu$ m. Moreover, no cracks were observed over the surface of prepared samples while they showed an acceptable level of uniformity with a flat surface. what is more, the roughness's root mean square (RMS) for the surface has decreased evidently from (48-41) nm for the sample annealed at (200, 400) °C, respectively [26]. This could refer to the previously reduction in RMS surface roughness and island coalescence which resulted in an increase in grain growth [27].



Fig. 6. AFM images of ZnO nanorods (a) annealed at 200°C, (b) annealed at 400 °C .

#### 4. The optical properties:

Fig. 7 shows the (ZnO) nanorod's optical transmittance at different annealing temperatures (200, 300 and 400  $^{\circ}$ C). The optical transmittance evidently decreases in the visible region, however in UV region it increased with the increase of annealing temperature. Furthermore, the optical transmittance for the (ZnO) nanorod that annealed at 400  $^{\circ}$ C decreased in the visible region compared to the one annealed at 200  $^{\circ}$ C [28]. Also, it was observed that the optical transmission for ZnO nanowire annealed in the air was decreased in the visible region.



Fig. 7. The optical transmittance spectra of the ZnO nanorod as a function of the annealing temperature.

The optical band gap of the nanofilms was calculated according to the extrapolation of the linear part of  $(\alpha h \upsilon)^2$  versus the photon energy (h $\upsilon$ ). The result of the calculations for each sample is shown in Fig. 8. To estimate the direct transition, the following equation was used [29].

$$\alpha h \upsilon = A (h \upsilon - \mathbf{E}_g)^n \tag{4}$$

where n = 1/2 for the direct band gap,  $E_g$  is the optical band gap, A is a constant,  $\alpha$  is the absorption coefficient, and h is the Planck constant. Optical band gap of the samples is achieved using the linear region extrapolation. The results clearly show that the optical band gap for the annealing temperature at 200 °C is about 3.28 eV. Moreover, with the increase of annealing temperature, the optical band gap changes, however, the optical band gap remains at the value of 3.22 eV even when annealing process reaches 400 °C.



Fig. 8. The  $(\alpha h \upsilon)^2$  vs. photon energy plot of the (ZnO) nanorod annealed at different temperatures (200, 250, 400 °C).

The calculation of absorption coefficient for the annealed ZnO nanorod was calculated by a primitive method from transmittance spectra [30]:

$$\Gamma = \exp\left[-\alpha_{(\lambda)} d\right] \tag{5}$$

where T is the optical transmittance ,  $\alpha_{(\lambda)}$  is absorption coefficient, and d is the thickness of ZnO film. It is clear from Figure 9 that the absorption coefficient at different annealing temperature is a function of the wavelength. Furthermore, it decreases with the increase of wavelength. The absorption coefficient for a certain wavelength increases in the visible region, while it decreases in the UV region when the annealing temperature is increased. Figu. 9 also reveals that the absorption coefficient shows an exponential dependence on the photon energy near the band edge.



Fig. 9. The absorption coefficients of the (ZnO) nanorod annealed at different annealing temperatures (200,250,400 °C).

### 5. Conclusions

Zinc oxide NRs structures were grown vertically on glass substrates with a hexagonal pillar shape and exhibited the polycrystalline wurtzite phase. ZnO NRs were annealed at different temperatures. The crystal size of the nanorods decreased as the annealing temperature increased to 400 °C as a response to the thermal energy generated by the annealing process.

It is concluded that RMS roughness of ZnO nanorod decreased with the increase of annealing temperature. The absorption coefficient ( $\alpha$ ) decreased as the wavelength increased which clearly dropped off in the visible region, and kept on decreasing in the ultraviolet region with increase of annealing temperature. The band gap energies (E<sub>g</sub>) slightly decreased with the increase of wavelengths for annealing temperatures.

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