Study the Effect of Annealing Process on Nanorods and Nanonails ZnO Thin Films Prepared by Hydrothermal Technique.

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Abstract: Wurtzite hexagonal Zinc oxide (ZnO) nanorods and nanonails arrays have been successfully fabricated and deposited on glass substrates pre-coated with ZnO seed layer using a simple hydrothermal method. The influence of annealing temperatures on the morphological, structural and optical properties was studied. The size and shape of the nanostructures and the band gap energy depend on the deposition temperature of ZnO thin films have been studied. The optical energy band gaps of ZnO were calculated to be 3.25 eV and 3.26 eV for the samples annealed at 300°C and 350°C respectively. The XRD results show the formation of wurtzite hexagonal ZnO structures for nanonails and nanorods arrays with prominent (002) orientation. The c/a ratio of 1.6033 is close to the ideal value for hexagonal cell around 1.633. The transmittance of the films is about 80% in the visible range. The (EDX) analysis identified the pure ZnO phase with a ratio of Z:O = 1:1.

Keywords: ZnO nanostructures, Annealing temperature, FE-SEM, XRD, Optical Band gap, Transmittance.

1. Introduction

Due to their unique electrical, optical, photonic and mechanical properties, semiconductor nanomaterials have been a rapidly growing area of research [1, 2]. One dimensional nanostructure such as nanonails appeared the most appealing sensing materials for developing gas sensor devices, since 1D, ZnO possess a good sensitivity and fast response time [3]. Nanowire, nanotubes and nanoribbons [4] have been widely studied for their important applications due to their unique optical and electrical characteristics. ZnO nanostructure is an important II–VI semiconductor, and it possesses a high electron-hole binding energy of 60 meV, with a direct band-gap about 3.37 eV, and as a result they have been used in sensors, lasers, displays, solar cells, field emissions, and photocatalysis [5–9]. Various techniques such as precipitation process, spray pyrolysis [10], thermal decomposition [11] and hydrothermal process [12] have been used to fabricate ZnO nanorods [13]. ZnO could be easily grown; and it is suitable for industrial and medical applications due to its diverse properties which depend on their morphology [14]. The well-adjusted arrays of ZnO rods were grown by a simple hydrothermal method on glass substrate using autoclave, and the samples are post annealed at different annealing temperatures. It is familiar that hydrothermally grown ZnO nanostructures have many imperfections due to
their growth temperatures [15]. Therefore, the qualities of ZnO nanostructures have been improved by reducing the defects via thermal treatment process of the synthesized thin films. The results illustrate the well-oriented ZnO nanorods and nanonails arrays grown directly on glass substrate, as well as the effect of annealing temperature on ZnO nanostructures, size, shape and band gap energies with the use of seed layers as pre-coating layers without any catalysts or surfactants at high temperature of 180 °C of the autoclave.

2. Experimental

2.1. Preparation of ZnO Seed Layers
The solution prepared from mixing of Zinc acetate dehydrate (CH₃COO)₂.H₂O with a concentration of (10mM) into 50 ml ethanol and stirred ultrasonically for 15 minutes. The solution was deposited by drop casting on top of cleaned glass substrates and dried on a hot plate at 80°C for 2 minutes. Finally, all the films were annealed by using a hot plate in air at 350 °C for 30 minutes to improve the film adhesion to the substrate. Vertical alignment of ZnO nanonails and nanorods were also improved by annealing process of ZnO seeds. ZnO film growth was conducted by using hydrothermal process.

2.2 Growth of ZnO nanonails and nanorods
After ZnO seed layer deposition, the seeded substrates were placed vertically in an autoclave which contained a growth solution at 180 °C for 6 hours in an oven; taking into account that the seed layers substrates were facing downward. The growth solution prepared from mixing each of hexamethylenetetramine and Zinc nitrate hexahydrate of the same molarity of (25 mM) into 50 ml deionized water and the mixture stirred ultrasonically for 15 minutes. After the growth operation, the samples were rinsed by deionized water (DW), to remove the inorganic residuals from the surface of the films. Finally, all the films were annealed by using a hot plate at 300 and 350°C for 90 min.

2.3 Characterization
The structural composition of the films was examined by using X-ray (6000 XRD, Cu-kα beam of λ=1.54). The morphologies of all samples were inquired by field emission scanning electron microscopy (FE-SEM; Model Mira3-XMU, TESCAN, Japan). And the thin films composition was analysed by EDX technique. 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. XRD analysis
Fig.1 represents X-ray pattern for zinc oxide nanostructure prepared by hydrothermal route. Annealed samples have polycrystalline hexagonal (wurtzite) structures. 2θ has three strong peaks observed at 31.76°, 34.45° and 36.25° attributable to ZnO (100), (002) and (101) crystal planes, respectively, (in agreement with ICDD card No. 036-1451 for ZnO). The strong ZnO diffraction peak (002) agrees with the highly oriented c-axis growth along this direction which was observed in the FE-SEM images to be shown later. From Fig. 1, we also observe that the intensity of (002) peak decreased with increasing annealing temperature up to 350°C, which means that the sample annealed at 300°C has better crystal quality than that annealed at 350°C. This is due to the heat treatment the films were exposed to which is compatible with the previous study[16].
Figure 1. XRD patterns of the annealed ZnO nanonails and nanorods at annealing temperatures 300 and 350°C respectively.

Table 1. Estimated structure parameters with dislocation density of (002) peak position

| Annealing Temperature (°C) | D (nm) | ao (Å) | co (Å) | Ratio co/ao | Dislocation Density δ x 10¹⁴ (line²/m²) |
|----------------------------|--------|--------|--------|-------------|-----------------------------------------|
| 300                        | 43.097 | 3.2498 | 5.2104 | 1.60329     | 5.3840                                  |
| 350                        | 43.519 | 3.2505 | 5.2117 | 1.60335     | 5.2801                                  |

Table 1 compares two samples annealed at 300°C and 350°C which estimate the structure parameters with dislocation density for the most prominent peak position (002).

The lattice parameters (ao and co) are calculated from the relation [17]

\[ d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2} \cos^2 \theta} \]  

Crystal lattice parameters for thin films annealed at a temperature of 300°C are ao = 3.2498 Å, co = 5.2104 Å, and the ratio of co/ao is 1.60329, while for thin film annealed at 350°C ao = 3.2505 Å, co = 5.2117 Å and the ratio of co/ao is 1.60335. The ratio co/ao for both annealed temperatures has the values very close to each other, while the ideal value for hexagonal cells is co/ao = 1.602 [18]

Scherer's formula is applied for grain size calculation:

\[ D = \frac{K \lambda}{\beta \cos \theta} \]  

where D is stand for a grain size, λ is applied wavelength (1.5406 Å), β: Full Width at Half Maximum of the peak (FWHM), θ: diffraction angle

The thin film undergoes dislocations in its structure due to the heat treatment process. Therefore, the dislocation density is calculated by the equation [19], which decreased slightly with increasing temperature for 50°C.

\[ \delta = \frac{1}{D^2} \]  

3.2. FE-SEM study

The morphology of the synthesized ZnO nanorods and nanonails was examined by FE-SEM. Fig.2 shows the top view images of the films annealed at two different annealing temperatures. From fig.2
(a), It is observed that the surface structure of the films is made up of nanorods form as groups of highly dense nanorods and crystallized along the direction of c-axis of ZnO, were all arranged in vertical direction on the surface of the glass substrates. They covered the entire surface, and they were relatively smooth, had uniform surface, and were characterized by hexagonal structure and symmetrical shapes, except for the nanonails film fig. 2 (b) which annealed at 350°C is consisting of a shank-nanorod and a lotus-shaped head [20]. The process of the growth in such a structure can be described in two steps. First, the nanorod grows along the c-axis by alternating the atomic layers (O) and (Zn), and secondly the head or upper face growth in the c-axis direction and its diagonal growth accelerates, leading to the formation of a hexagonally shaped nanonail head, and this in itself has many applications like photovoltaic, etc [21].

![Figure 2](image)

Figure 2. FE-SEM Surface morphologies (a) ZnO nanorods annealed at 300 °C, (b) ZnO nanonails annealed at 350 °C

It was also observed that the nanorods were vertical to the substrate, and on the upside, it appeared slightly tilted. The length and alignment of the nanorods were related to the seed growth mechanism. The (ZnO) nanorods mean diameter was calculated by use of Image J software. This clearly shows that when the annealing temperature increased from 300 °C to 350 °C, the average diameter nanorods also increases from 47 nm to 71 nm respectively. Figure 3(a, b) shows the spectrum of the energy dispersive x-ray, of both samples annealed at 300°C and 350 °C. A representation of the elements percentage in the matrix films is shown in the inset tables. The amount of these elements is represented by the intensity of the peaks, and distinctly shows the 1:1, Z:O elements. No element contamination detected in the films structure. The analysis of the samples by (EDX) technique notably show that the films prepared by hydrothermal method had pure Zinc oxide phases, and the quantitative analysis data was close to that of bulk ZnO [22].
Figure 3. EDX results of  a) ZnO nanorods annealed at 300°C    b) ZnO nanonails annealed at 350°C.

4. Optical study of ZnO nanorods and nanonails
Fig. 4 shows the optical transmittance spectrum in the UV-Visible region of (200 – 900) nm of the zinc oxide nanorods and nanonails annealed at 300˚C and 350˚C for 30 minutes. The transmittance is slightly more than 80% in the range (450 nm to 850 nm) for both films. At 360 nm there is acute absorption edge, which is resulting from the direct band gap of ZnO [23].

![Transmittance spectrum](image)

**Figure 4.** Transmittance spectrum for samples with variations annealing temperature of 300˚C and 350 ˚C.

Zinc oxide, ZnO nanorods and nanonails are evaluated by extrapolation of the linear connection between $(\alpha h\nu)^2$ and $h\nu$ which is consistent to the equation below [24]

$$\alpha h\nu = A(h\nu - E_g)^n$$  \hspace{1cm} (4)

where $\alpha$, and $h\nu$, are the absorption coefficient and the photon energy respectively. $E_g$ is the optical band gap and $A$, a constant. Fig. 5 describes the graph of $(\alpha h\nu)^2$ against $h\nu$. The direct optical band gap value $E_g$ of the films is estimated from the curve interception of $(\alpha h\nu)^2$ vs $h\nu$ plot. The existence of a single slope in the curve implies that the ZnO film has direct and allowed transition. The annealed ZnO nanorod and nanonails band gap value at temperatures of 300˚C and 350˚C was found to be (3.25 and 3.26) eV, respectively. This is due to increase the annealing temperature which accelerates the formation of crystals and slightly increases its band gap [25].

![Graph](image)

**Figure 5.** The relation between $(\alpha h\nu)^2$ and $(h\nu)$ for ZnO nanorods (a) annealed at 300˚C, (b) annealed at 350 ˚C

5. Conclusions
The hydrothermal process is a simple and efficient method. It has received an increased attention due to its implicitly. In this paper, we presented the synthesis, structure characterization, and properties of nanorods and nanonails structure arrays for ZnO thin films prepared by hydrothermal technique and annealed at temperatures of 300˚C and 350˚C. Highly preferential growth of ZnO nanorod and nanoails
along the c-axis orientation was observed with hexagonal wurtzite structure. The average diameter of the ZnO nanostructure obtained from the FE-SEM by using image J analysis increased clearly from (42 nm to 71 nm) for nanorods and nanonails respectively with increasing annealing temperature from 300 °C to 350 °C. The intensity of (002) peak was decreased by increasing the annealing temperature while the transmittance and the optical band gaps (3.25 and 3.26 eV), were slightly increased. The energy dispersive x-ray (EDX) analyses of the samples obviously show that the films synthesized by hydrothermal method have pure zinc oxide phases. It is evidence from the results that the nanostructure properties like size, shape structural characterization and optical band gaps can be tuned according to the synthesis temperature which leads to tuning the nanostructure materials properties for a certain applications.

6. References
[1] Singh M, Hlabana kk, Singhal S and Devlal K 2016 Grain-size effects on the thermal conductivity of nanosolids J.Taibah Univ. Sci. 10 375-380.
[2] Mehr A and Emami F 2014 Effects of structural factors on filtering operation of photonic band gap air bridges with circular and square shape holes Optik 125 2625-2632, 2014.
[3] Lin J, Chen Z, He X and Xie W 2017 Detection of H2S at room temperature using ZnO sensors based on Hall effect Int. J. Electrochem. Sci. 12 6465–6476.
[4] She GW 2008 Controlled synthesis of oriented single-crystal ZnO nanotube arrays on transparent conductive substrates Appl. Phys. Lett. 92 5311.
[5] Jiang Y, Meng X, Liu J, Xie Z, Lee C and Lee S 2003 Hydrogen-assisted thermal evaporation synthesis of ZnS nanoribbons on a large scale Adv. Mater., 15 323–327.
[6] Huang H, Shao I, She GW, Wang M, Chen S and X.-M. Meng XM 2012 Catalyst-free synthesis of single crystalline ZnO nanonails with ultra-thin caps Cryst. Eng. Comm. 14 8330–8334.
[7] Muchuweni E, Sathiaraj T and Nyakotyo H 2017 Hydrothermal synthesis of ZnO nanowires on rf sputtered Ga and Al co-doped ZnO thin films for solar cell application J. Alloys Comp. 721 45-54.
[8] Wang ZL and Song J 2006 Piezoelectric nanogenerators based on zinc oxide nanowire arrays Science 312 242–246.
[9] Liu XY, Shan CX, Wang SP, Zhang ZZ and Shen DZ 2012 Electrically pumped random lasers fabricated from ZnO nanowire arrays Nanoscale 4 2843–2846.
[10] Kumar NS, Bangera KV and Shivakumar GK 2014 Effect of annealing on the properties of zinc oxide nanofiber thin films grown by spray pyrolysis technique Appl. Nanosci. 4 209–216.
[11] Lin CC and Li YY 2009 Synthesis of ZnO nanowires by thermal decomposition of zinc acetate dihydrate Mater. Chem. Phys. 113 334–337.
[12] Van Duy L, Hanh NH, Son DN, Hung PT, Hung CM, Van Duy N, Hoa ND and Van Hieu N 2019 Facile Hydrothermal Synthesis of Two-Dimensional Porous ZnO Nanosheets for Highly Sensitive Ethanol Sensor J. Nanomater. 2019.
[13] Byrappa K and Yoshimura M 2012 Handbook of hydrothermal technology. William Andrew.
[14] Osman DAM and Mustafa MA 2015 Synthesis and characterization of zinc oxide nanoparticles using zinc acetate dihydrate and sodium hydroxide J. Nanosci. Nanotech. 1 248-251.
[15] Zhao QX 2009 Effects of thermal annealing temperature and duration on hydrothermally grown ZnO nanorod arrays Appl. Surf. Sci. 255 5861–5865.
[16] Kareem MM, Khodair ZT and Mohammed FY 2020 Effect of annealing temperature on Structural, morphological and optical properties of ZnO nanorod thin films prepared by hydrothermal method J. Ovonic Res. 16 53–61.
[17] Lupal O 2010 Effects of annealing on properties of ZnO thin films prepared by electrochemical deposition in chloride medium Appl. Surf. Sci. 256 1895–1907.
[18] Klingshirn CF 2007 ZnO: material, physics and applications Chem. Phys. Chem. 8 782–803.
[19] Kahraman S, Çetinkara HA, Bayansal F, Çakmak HM and Güder HS 2012 Characterisation of ZnO nanorod arrays grown by a low temperature hydrothermal method Philos. Mag. 92 2150–2163.

[20] Liu J and Motta N 2014 The nanonail flower Mater. Today 17 307–308.

[21] Kar S, Dev A and Chaudhuri S 2006 Simple solvothermal route to synthesize ZnO nanosheets, nanonails, and well-aligned nanorod arrays J. Phys. Chem. B 110 17848–17853.

[22] Al-Owais AA 2013 Synthesis and magnetic properties of hexagonally packed ZnO nanorods Arab. J. Chem. 6 229–234.

[23] Amakali T, Daniel L, Uahengo V, Dzade NY and De Leeuw NH 2020 Structural and Optical Properties of ZnO Thin Films Prepared by Molecular Precursor and Sol–Gel Methods Crystals 10, 132.

[24] Muchuweni E, Sathiaraj TS and Nyakotyo H 2017 Low temperature synthesis of ZnO nanowires on GAZO thin films annealed at different temperatures for solar cell application Mater. Sci. Semicond. Process. 68 80–86.

[25] Narayanan GN, Ganesh RS and Karthigeyan A 2016 Effect of annealing temperature on structural, optical and electrical properties of hydrothermal assisted zinc oxide nanorods Thin Solid Films 598 39–45.