Structural properties of borondoped zinc oxide nanostructure films depositon Glass Substrate

Rashid Hashim Jabbar1, Abdulhussein K. Elttyayef1, Ashwaq A. Jabor1, Abdulkareem H. Hashim2

1Center of Applied Physics, 2Center of advance materials, Ministry of Science and Technology, Baghdad, Iraq

Abstract
This paper presents the structural properties of boron doped ZnO nanostructures ZnO:B deposited at 450 °C on glass substrates by chemical spray pyrolysis in thickness(150±5 nm). The structure of ZnO:B nanostructure films has been found to exhibit the hexagonal wurtzite structure. The increase of Boron concentration caused to decrease the grain size, interplaner spacing in the ZnO:B(4%) be in the maximum value for (100) plane and the minimum value for (002 and 101) planes. The structural details and microstructure were obtained from X-ray diffraction.

Keywords: ZnOnanostructures, boron doped, structural properties.

1. Introduction
Semiconductor ZnO has been the subject of research for many applications for the past several years, because the material is nontoxic, bio-safe, chemically stable, and biocompatible. ZnO has a direct wide bandgap of around 3.2-3.37 eV at room temperature 300K[1,2,], where the bottom of the conduction band is formed from the 4s levels of Zn2+ and the top of the valence band is built from the 2p orbitals of O2-.. It has strong ionic bonding and exciton binding energy of 60 meV[3], low resistivity and high transparency in the visible range and high light trapping characteristics [3]. [4] ZnO has attracted increasing attention as a potential material for optoelectronic devices such as low threshold blue/UV lasers, solar cells, LEDs, sensors, display devices and photodetectors[5-7]. The synthesis of nanoparticles has become a highly developed field owing to the scientific and technological interest due to the structural peculiarities and unusual physical and chemical properties they may lead to[4]. In recent years, it has been found that ZnO can be synthesized by various routes such as electron beam evaporation technique [5], chemical spray pyrolysis technique [1], RF thermal plasmaevaporation [6], sol-gel method [3, 7], and precipitation[1, 7] methods. Among these methods, precipitation has many advantages over the other methods, for example, it is unsophisticated and a low cost method[4, 8, 2]. ZnO pure has been used in a wide range of products for many years, including, among others, varistors, surface acoustic wave devices and cosmetics. Besides these established applications, ZnO and its ternary alloys are now also being considered as potential materials for optoelectronic applications, such as light emitting diodes, photovoltaics, sensors, displays, etc[9].

2. Experimental:
Nanostructure films of ZnO: ZnO:B prepared by spray pyrolysis deposition (SPD) technique in air from zinc nitrate (Zn(NO3)2.6H2O), and boric acid (H3BO3) diluted with distilled water to concentration of molarities equal 0.075 M, Zn(NO3)2.6H2O is a solid material which has a white color and its molecular weight (297.4 g/mole). The deposition method involves the decomposition of an aqueous solution of zinc nitrate. The spray solution is sprayed onto heated substrates held at 450°C. The time of the deposition is 3 sec. each 42 sec., Compressed air is used as a gas carrier and it is fed with the solution into a spray nozzle at a predetermined constant atomization pressure. Film thickness(τ=150±5 nm) was determined by(TFProbe™ Spectroscopic Reflectometer film thickness measurement system). Diffraction studies are carried out using X-Ray Shemadz XRD – Diffractometer (operated at 40 kV an accelerating potential and 30 mA with filtered CuKα radiation 0.15406 nm wavelengths) was performed to identify the crystalline phases present in the deposited films.

3. Result and discussion:
3.1. Structural analysis:
The XRD graphs of ZnO:B nanostructure films are shown in fig.1. It is obvious the nanostructure film is polycrystalline and all the samples have hexagonal wurtzite structure. The intensity of ZnO pure nanostructure film is more than the intensity of ZnO:B nanostructure for (002) plane.

Figure 1. X-ray diffraction pattern of ZnO:B nanostructure with concentration: 0.0 to 8 at.%.
The values which measured by XRD instrument of diffraction angle(20), Interplaner spacing(d) and Full Width at Half Maximum (FWHM) are in table(1).

**Table 1:** XRD patterns, inter-planar spacing and angular full width at half maximum for ZnO:B nanostructure films deposited at substrate temperature 450 °C on glass substrates.

<table>
<thead>
<tr>
<th>hkl</th>
<th>Doping(%)</th>
<th>2θ(de g.)</th>
<th>d(Å)</th>
<th>FWHM(de g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>2</td>
<td>31.808</td>
<td>0.28</td>
<td>0.57</td>
</tr>
<tr>
<td>100</td>
<td>4</td>
<td>31.716</td>
<td>0.28</td>
<td>0.45</td>
</tr>
<tr>
<td>100</td>
<td>6</td>
<td>31.829</td>
<td>0.28</td>
<td>0.58</td>
</tr>
<tr>
<td>100</td>
<td>8</td>
<td>31.785</td>
<td>0.28</td>
<td>0.91</td>
</tr>
<tr>
<td>002</td>
<td>0</td>
<td>34.475</td>
<td>0.25</td>
<td>0.40</td>
</tr>
<tr>
<td>002</td>
<td>2</td>
<td>34.577</td>
<td>0.25</td>
<td>0.48</td>
</tr>
<tr>
<td>002</td>
<td>4</td>
<td>34.659</td>
<td>0.25</td>
<td>0.67</td>
</tr>
<tr>
<td>002</td>
<td>6</td>
<td>34.621</td>
<td>0.25</td>
<td>0.69</td>
</tr>
<tr>
<td>002</td>
<td>8</td>
<td>34.557</td>
<td>0.25</td>
<td>0.81</td>
</tr>
<tr>
<td>011</td>
<td>0</td>
<td>36.246</td>
<td>0.24</td>
<td>0.39</td>
</tr>
<tr>
<td>011</td>
<td>2</td>
<td>36.281</td>
<td>0.24</td>
<td>0.51</td>
</tr>
<tr>
<td>011</td>
<td>4</td>
<td>36.410</td>
<td>0.24</td>
<td>0.59</td>
</tr>
<tr>
<td>011</td>
<td>6</td>
<td>36.375</td>
<td>0.24</td>
<td>0.66</td>
</tr>
<tr>
<td>011</td>
<td>8</td>
<td>36.317</td>
<td>0.24</td>
<td>0.86</td>
</tr>
</tbody>
</table>

The Average grain size $d_g$ was calculated by Scherer equation [10]:

$$d_g = \frac{\lambda}{\beta \cos \theta}$$ (1)

Where $\kappa = 2 \sqrt{\frac{2}{\pi}} = 0.94$ called(Scherer's constant), $\lambda$ is the wave length of incident X-ray radiation , $\beta$ is the intrinsic full width at Half Maximum of the peak , and $\theta$ is the Bragg's diffraction angle of the respective XRD peak .Assumes the world Warren that the mathematical representation of curves resulting from the X-ray diffraction (XRD) depends primarily on the amount of similarity between these curves and functions of each of the Cauchy and Gauss, inthe case considered curve X-ray diffraction is similar to function Cauchy and take the form of $\frac{1}{\sqrt{\pi \beta}}$ the correction is given by the following relationship, which was called (Scherer's correction):

$$\beta_{eq} = \beta_1 - \beta_0$$ (2)

Where $\beta_{eq}$ is the measured full width at Half Maximum of the peak, $\beta_0$ is the instrumental broadening[11],where $\beta_0 = 0.11$ for the used instrument.Compensation equation (2) in the relationship (1) we get:

$$d_g = \frac{\lambda}{\beta_{eq} \cos \theta}$$ (3)

In the case considered X-ray diffraction curve similar to the function Gauss which takes the form $(e^{-x^2})$ the accuracy to be higher because of the great similarity between this function and the diffraction curves; it was suggested(Warren correction) form:

$$\beta_{eq}^2 = \beta_1^2 + \beta_0^2$$ (4)

This correction called (Warren’s Correction). Compensation equation (4) in the relationship (1) we get:
\[ D_g = \frac{k\lambda}{\beta_{2n}^2 - \beta_l^2 \cos^2(\theta)} \quad \ldots \ldots \quad (5) \]

Since the output line shape does not resemble the Gauss curve and Cauchy curve completely, so these relations have limited operation values. If the intensity curve does not sharp may be used (Scherer’s correction) or (Warren’s Correction) former because the difference between the values given by relations (3) and (5) is not large, which means that the decrease of the curve breadth (an increase of sharpness) means that the effect of the amount \( \beta \) is significant, since the width of the curve in the half intensity (FWHM) is inversely proportional with grain size according to equation (1), the decrease in (FWHM) leads to increase in the grain size, which means that few crystal defects are present in the sample. Moreover, Warren was suggested a relationship takes into account the geometric meaning which is [12, 13]:

\[ \beta_{2n} = \sqrt{\beta_{2n}^2 - \beta_l^2} \sqrt{\beta_{2n}^2 - \beta_l^2} \quad \ldots \ldots \quad (6) \]

Compensation equation (6) in the relationship (1) we get:

\[ D_g = \frac{k\lambda}{\beta_{2n}^2 - \beta_l^2 \cos^2(\theta)} \quad \ldots \ldots \quad (7) \]

The grain size of (100), (002) and (101) planes using equations (1, 3, 5 and 7) is in the table (2).

<table>
<thead>
<tr>
<th>( h ) ( k ) ( l )</th>
<th>Doping(%)</th>
<th>Grain size(nm)</th>
<th>eq.(1)</th>
<th>eq.(3)</th>
<th>eq.(5)</th>
<th>eq.(7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 0 0</td>
<td>0</td>
<td>21.9</td>
<td>30.4</td>
<td>22.8</td>
<td>26.3</td>
<td></td>
</tr>
<tr>
<td>0 0 0</td>
<td>2</td>
<td>18.0</td>
<td>23.3</td>
<td>18.5</td>
<td>20.8</td>
<td></td>
</tr>
<tr>
<td>0 0 0</td>
<td>4</td>
<td>12.9</td>
<td>15.4</td>
<td>13.1</td>
<td>14.2</td>
<td></td>
</tr>
<tr>
<td>0 0 0</td>
<td>6</td>
<td>12.7</td>
<td>15.1</td>
<td>12.9</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>0 0 0</td>
<td>8</td>
<td>10.8</td>
<td>12.5</td>
<td>10.9</td>
<td>11.6</td>
<td></td>
</tr>
<tr>
<td>0 0 2</td>
<td>10</td>
<td>22.2</td>
<td>30.8</td>
<td>23.1</td>
<td>26.7</td>
<td></td>
</tr>
<tr>
<td>0 0 2</td>
<td>2</td>
<td>17.0</td>
<td>21.7</td>
<td>17.5</td>
<td>19.5</td>
<td></td>
</tr>
<tr>
<td>0 0 2</td>
<td>4</td>
<td>14.9</td>
<td>18.3</td>
<td>15.2</td>
<td>16.7</td>
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</tr>
<tr>
<td>0 0 2</td>
<td>6</td>
<td>13.2</td>
<td>15.8</td>
<td>13.4</td>
<td>14.5</td>
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</tr>
<tr>
<td>0 0 2</td>
<td>8</td>
<td>10.1</td>
<td>11.6</td>
<td>10.2</td>
<td>10.9</td>
<td></td>
</tr>
</tbody>
</table>

Fig.2. Shows the difference among the equations 1, 3, 5 and 7 to the plane 002, where the median value represent the geometric meaning of Warren correction i.e.(eq.7).
The dislocation density ($\sigma$) which represents the defect in the film was determined from the formula[16]:

$$\sigma = \frac{1}{D^2} \quad \ldots \ldots (8)$$

Using eq.(7) and eq.(8), the grain size and dislocation density for (101, 002 and 100) plane are shown in figure(3).

The lattice parameters $a$ and $c$ were calculated from the XRD pattern using the equation[14,15].

$$\frac{1}{d^2} = \frac{4}{3} \left[ \frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \right] + \frac{2}{c^2} \quad \ldots \ldots (9)$$

The microstrain ($\varepsilon$) can be calculated from the relation[16]:

$$\varepsilon = \frac{[C_{XRD} - C_{CALC}]}{C_{CALC}} \times 100\% \quad \ldots \ldots (10)$$

Fig.(4) shows the micro strain of ZnO: nanostructure films Using eq.(9) and (10).

XRD measurements of the interplaner spacing (d) for (100, 002 and 101) planes as shown in fig.(5) where in the ZnO:B(4%) the maximum value of (d) for (100) plane and the minimum value for (002 and 101) planes.

3.3. Surface morphology

The surface morphology of the ZnO:B nanostructures is observed using scanning electron microscope (SEM) as shown in figure(6). The change in the morphology of ZnO:B nanostructure films is due to the difference in ionic radius between B3+ (0.041 nm) with Zn2+ (0.074 nm)[17]. The pictures of morphological structure of ZnO:B nanostructure films were obtained by using an atomic force microscopy are shown in Figure(7).
4. Conclusions
ZnO:B nanostructures of different shapes have been synthesized on glass substrate using a low cost spray pyrolysis deposition. It was found that the increase of concentration of B due to decrease of grain size in general and varying the morphology, (002 and 101) plane has the minimum value of interplaner spacing in the ZnO:B(4%).

References

AUTHOR

Rashid Hashim Jabbar, Ph.D student. Presently, M.Sc. in Physics Science degree in 2009, Al-Mustansiriya University, College of Science, Dept. of Physics, and BSc. in Department of Physics College of science in 1989, from University of Baghdad, a researcher at the Applied Physics Center and member of thin films application Department, Ministry of Science and Technology, Baghdad, Iraq.

Abdulhussein K. Elttayef is currently a professor of physics at the Applied physics center, Baghdad, Iraq. He received his Ph.D Degree from Heriot–Watt University (U.K) in 1990. His current research Interests include the preparation of nano films (semiconductors and polymers) by different methods for applications of gas sensors, solar cells and optical detectors. He has written 40 scientific publications in this area.

Ashwaq Abdul Hussienjabar, M.Sc.in physical Chemistry Department of Science, University of Baghdad, 2003. B.Sc.chemistry college of science University of Baghdad 1990, a researcher at the Applied Physics Center and member of thin films application Department, Ministry of Science and Technology, Baghdad, Iraq.

Abdulkareem H. Hashim, professional of X-ray Diffraction for ten years, Center of advance materials, Ministry of Science and Technology, Baghdad, Iraq.