

## Boron doped Zinc Oxide for Ethanol and CO Gas Sensing

Huda J. Ali

Department of Physics, College of Science, Mustansiriyah University, IRAQ  
Correspondent Author Email: hudaphysics2017@gmail.com

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### Abstract

Properties of ZnO and ZnO:B deposited at 723K on glass substrates by chemical spray pyrolysis (CSP) with thickness ( $150\pm 5$  nm) as a gas sensor for vapor ethanol and CO gases are studied. The structure of ZnO:B films has been found to exhibit the hexagonal wurtzite structure. The increase of boron concentration caused to decrease the grain size. The structural details were obtained from X-ray diffraction. The surface morphology of the films was studied by using the Scanning Electron Microscopy (SEM), and the Transmission electron microscopy (TEM). Sensitivity of the films is increasing with the increase of boron concentration and substrate temperature.

**Keywords:** ZnO:B nanostructures, boron doped, hexagonal wurtzite structure.

### الخلاصة

تم في هذا البحث دراسة خصائص اغشية اوكسيد الزنك ZnO و ZnO:B المرسية على قواعد زجاجية بدرجة حرارة 723K والمحضرة بطريقة التطل الكيميائي الحراري (CSP) وكان سمك الاغشية بحدود ( $150\pm 5$  nm) كمتحسس غازي لغاز الايثانول وغاز اول اوكسيد الكربون. اظهرت فحوصات حيود الاشعة السينية (XRD) ان لاغشية ZnO:B تركيب سداسي كتركييب كبريتيد الزنك. ان زيادة تركيز البورون تسبب نقصان الحجم الحبيبي. تم دراسة مورفولوجية السطح للاغشية باستخدام المجهر الالكتروني الماسح (SEM) والمجهر الالكتروني النافذ (TEM). تزداد تحسسية الاغشية بزيادة نسبة التشويب للبورون وزيادة درجة حرارة القواعد.

### Introduction

Zinc Oxide has been shown to be useful material for monitoring a lot of pollutant gases as CO, benzene, NH<sub>3</sub> and NO<sub>x</sub>. Zinc oxide is an n-type semiconductor with a wide direct band gap (3.3 eV) [1], ZnO has been the subject of research for several applications for the past years. Where the conduction band bottom is formed from the 4s levels of Zn<sup>2+</sup> and the top of the valence band is contains of the 2p orbitals of O<sup>2-</sup>[2]. It has strong ionic bonding and exciting binding energy of 60 meV [3], high transparency and Low resistivity in the visible range [3] [4]. ZnO has increasing attention as a potential material for devices of optoelectronic such as low threshold lasers, light emitting diodes (LEDs), solar cells, sensors, display devices and photodetectors [5] [6] [7]. The synthesis of nanostructures has become investigated cell nucleus from the cell surface or from cytoplasm; hence it is effective in single cell killing. Gallium-67 emits rays with energies

ranged from 91 to 394KeV, which is suitable to be detected by gamma cameras [4]. For single photon imaging in Positron Emission Tomography (PET) scan [5]. Ga-68 ( $t_{1/2} = 68$ min,  $\beta^+$ : 89.1%; EC: 10.9%) have distinctive characteristics that made it used in PET scan imaging and in tumor diagnosing[6]. The aim of the present work is to highly developed to the technological and scientific interest due to the structural properties and unusual chemical and physical properties [4]. ZnO can be synthesized by several methods such as electron beam evaporation technique [5], chemical spray pyrolysis technique [1], RF thermal plasma evaporation [6] and precipitation [1] [7] methods. ZnO has been used in products for many years. Besides these established applications, ZnO and its ternary alloys are now also being considered as potential materials for the applications of optoelectronic, such as light emitting diodes, photovoltaic, sensors, displays, etc. [8] [9].

## Materials and Methodology

Films of ZnO, ZnO:B prepared using the spray pyrolysis deposition (SPD) technique in air from zinc nitrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) its molecular weight (297.4 g/mole), and boric acid ( $\text{H}_3\text{BO}_3$ ) diluted with distilled water to molarities concentration equal 0.075 M. Figure 1 shows the schematic diagram of the thermal chemical spray pyrolysis deposition system. The solution of spray is sprayed onto heated substrates held at 723K. The time of the deposition is three second for each 42 sec; compressed nitrogen is used as a gas. Film thickness is ( $t=150 \pm 5$  nm) was determined using (TFProbe<sup>TM</sup> Spectroscopic Reflectometer film thickness measurement system). Diffraction studies were created out by X- Ray Shemadz XRD Diffractometer (operated at 40 KV with filtered  $\text{CuK}\alpha$  radiation 0.15406 nm wavelengths).

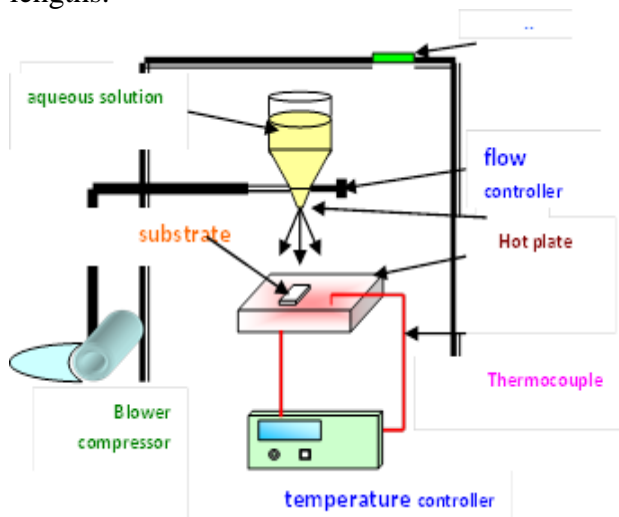


Figure 1: General schematic of a spray pyrolysis deposition process.

## Results and Discussion

The XRD graphs of ZnO:B nanostructure films are shown in Figure 2. 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. The grain size decreases with the increase of boron concentration from 21.9 to 10.8 nm.

TEM shows the average size of the grains more than the XRD. This difference in the grain size

refers to this fact that "TEM shows the particles size and XRD shows the crystallites size" [10] [11] [12] [13]. The presence of ZnO spherical nanoparticles along with a few nanorods was observed as shown in Figure 3. The grain sizes of spherical particles were found to be in the range of 6.5–23 nm.

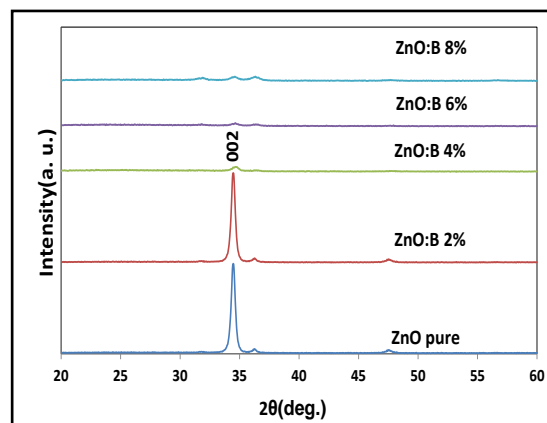


Figure 2: X-ray diffraction pattern of ZnO and ZnO:B nanostructure with concentration (2, 4, 6 and 8)%.

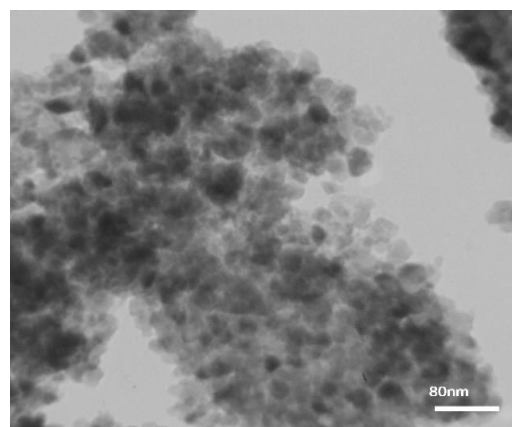


Figure 3: TEM image of undoped ZnO.

The surface morphology of the ZnO:B nanostructures is observed using scanning electron microscope (SEM) as shown in Figure 4. The change in the morphology of ZnO:B nanostructure films is due to the difference in ionic radius between  $\text{B}^{3+}$  (0.041 nm) with  $\text{Zn}^{2+}$  (0.074 nm) [14] [15] [16].

The grain size measured using SEM decreases with the increase of boron doping from 43.4 to 17.1 nm. It can be summarized Sensing properties of vapor ethanol and CO gases as follow:

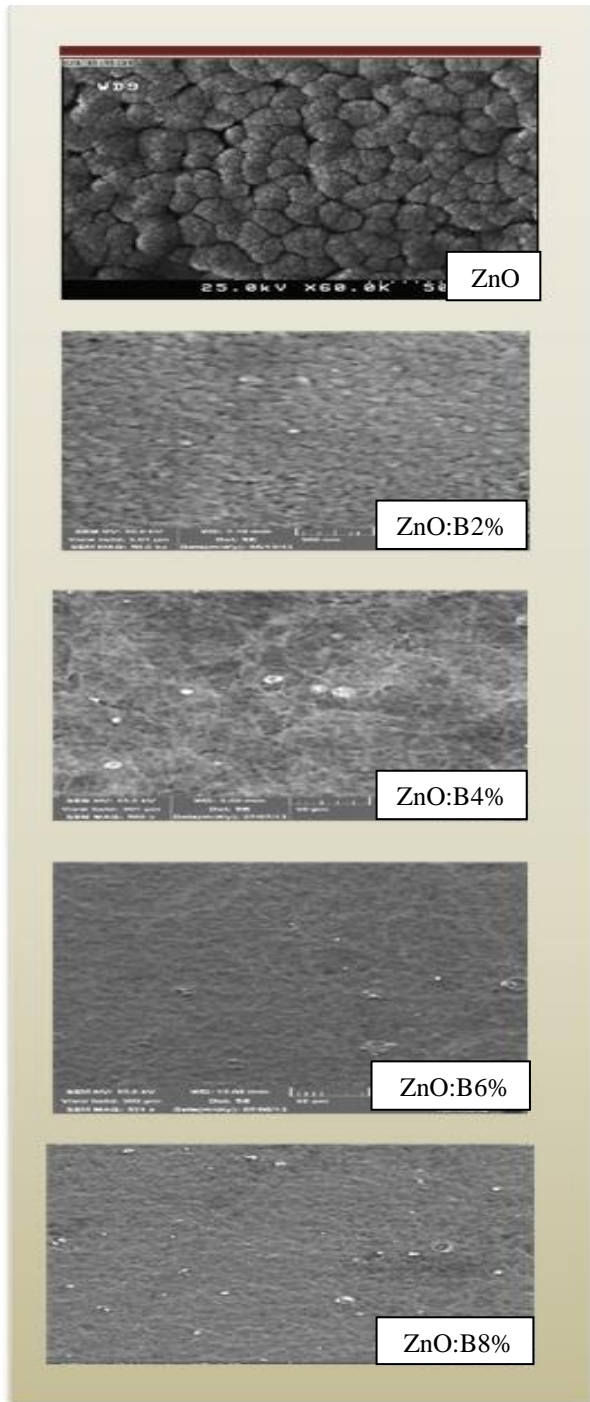
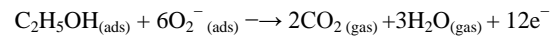


Figure 4: SEM image of ZnO and ZnO:B nanostructure with concentration(2, 4, 6 and 8)%.

When the gas target such as ethanol ( $C_2H_5OH$ ) adsorbed in the surface area, it causes an oxidation process. Some  $O_2^+$  ions will be removed from the surface and release the bound electrons of atoms O. These electrons will flow back to the conduction band. This condition will cause the value of the resistance to be de-

creased. Potential barrier under these conditions is reduced. Electrons from the surface of the thin film will react with oxygen from the environment to form oxygen ions; this causes the value of resistance to be decreased. The response to vapor ethanol at the tested range of temperature can be explained by the following reactions [17] [18]:



Ethanol molecules can interact mainly with the Zn atoms or with oxygen species previously adsorbed, the main oxygen species at ZnO surface is  $O^{-2}$ .

Figure 5 shows the sensitivity as a function of operating time for vapor ethanol gas with the concentration (50 ppm) at room temperature for ZnO and ZnO:B films prepared at 723K. During the adsorption of oxygen species on the surface of sensing element, capturing of electrons from conduction band and the associated decrease in the charge carrier concentration ( $e^-$ ) leads to an increase in the resistance of the n-type sensing element until it attains equilibrium.

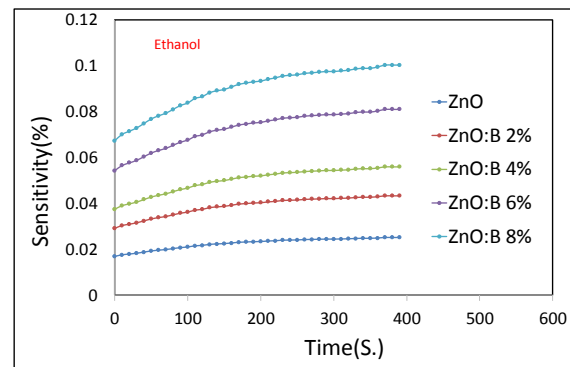


Figure 5: Sensitivity for ZnO and ZnO:B with doping concentration(2, 4, 6 and 8)%. Deposited on glass as a function of operating time for vapor ethanol gas with 50 ppm concentration.

Figure 6 shows the sensitivity of ZnO and ZnO:B nanostructure thin films deposited on glass substrate for vapor ethanol gas with concentrations of 50ppm and substrate temperature, the sensitivity increases with increasing of substrate temperature until reach to highest

sensitivity at 423K, then decrease above this temperature.

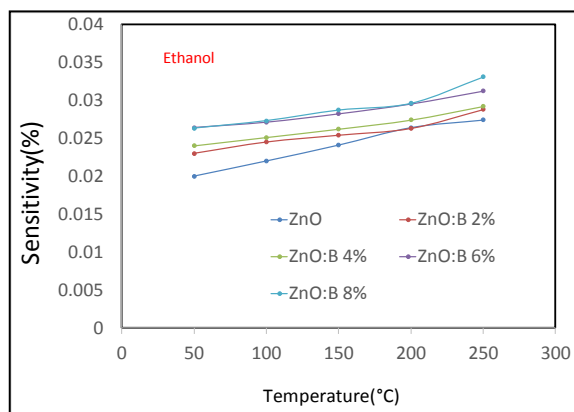
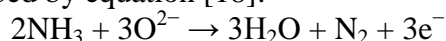


Figure 6: Sensitivity for ZnO and ZnO:B with doping concentration (2, 4, 6 and 8)% deposited on glass as a function of operating time for vapor ethanol gas with 50ppm concentration at R.T.

It is known that the sensing mechanism of ZnO towards  $\text{NH}_3$  gas depends on the interaction between the reducing gas and the negatively charged  $\text{O}^{2-}$  ions on the ZnO thin film surface, thereby causing a variation in conductance, as described by equation [18]:



So that, by the electrons released back into the ZnO conduction band and increasing the carrier doped in the ZnO active layer, the resistance of the sensor is decreased upon exposure to a reducing gas [19]. Figure 7 shows the sensitivity as a function of operating time for  $\text{NH}_3$  gas at room temperature for ZnO and ZnO:B deposited on glass substrate prepared at 723K. As shown in the Figure 8, the sensitivity is increase with the increase of boron concentration.

## Conclusions

It was found that the increase of concentration of B in ZnO due to decrease of grain size and increase of roughness, so that the interaction area of the films increases and the sensitivity of the films increase with doping concentration. The increase of the substrate temperature due to increase of the sensitivity of the films for  $\text{NH}_3$  gas and be in optimum value in 423K for vapor ethanol gas.

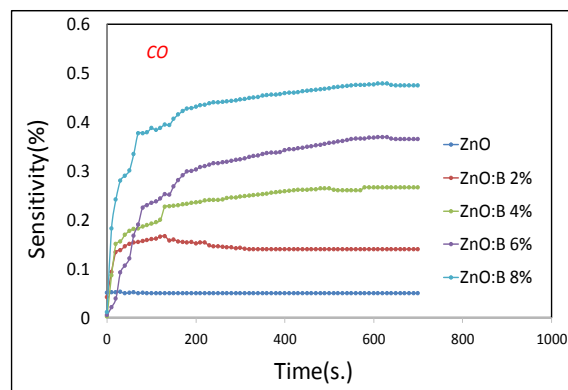


Figure 7: Sensitivity for ZnO and ZnO:B with doping concentration(2, 4, 6 and 8)% deposited on glass as a function of operating time for  $\text{NH}_3$  gas with 50ppm concentration at R.T.

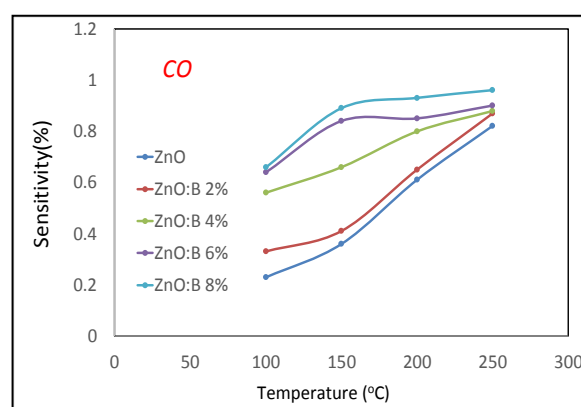


Figure 8: Change of sensitivity with temperature for undoped ZnO and ZnO:B with doping concentration (2, 4, 6 and 8) % deposited on glass substrate for  $\text{NH}_3$  gas with 50ppm concentration.

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