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Original Article

# Characteristics of B doped ZnO thin films deposited on n and p-type porous silicon for $NH_3$ and CO gas sensing

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## ABSTRACT

ZnO and ZnO:B thin films properties were studied. These films were deposited at 450 ˚C on n-type and p-type porous silicon (PS) substrates using spray pyrolysis deposition (SPD) technique with a thickness of (250±10 nm) as a gas sensor for $NH_3$ and CO gases. Boron increasing led to increasing the roughness and decreasing the grain size. The structural details were obtained by using (XRD), (SEM) and (TEM). The sensitivity of the films for $NH_3$ and CO gas increased by increasing boron doping.

**Keywords:** ZnO:B, $NH_3$, CO, gas Sensing, boron-doped, porous silicon.

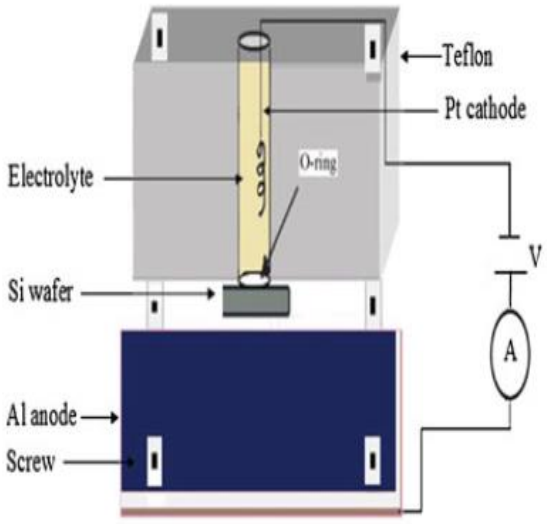
## Introduction

Zinc oxide is useful for several pollutant gases such as CO, $NH_3$. Zinc Oxide is approximately 3.3-3.4 eV direct band gap [1]. ZnO semiconductor is one of the most important materials of II-VI for several applications in the last decades. The binding energy of Zinc Oxide was 60 meV which was a strong ionic bonding material. At the visible region, ZnO had high transparency [2, 3]. Zinc Oxide has been used for many applications in the devices of optoelectronic, sensors, solar cells and photodetectors [4- 6]. The nanostructured materials has had important applications in chemical, physical and structural properties so that the nanostructure thin films can be used as gas sensors [7]. ZnO can be deposited as a thin film by several methods such as electron beam evaporation technique [4], chemical spray pyrolysis technique [1], RF thermal plasma evaporation [5] and precipitation methods [8-10].

## Experimental:

ZnO thin films and ZnO:B have been prepared using the SPD technique in the air from zinc nitrate ($Zn(NO_3)_2.6H_2O$) and boric acid ($H_3BO_3$) diluted with distilled water to molarities' concentration equal to 0.1 M. Its molecular weight was (297.4 g/mole). The solutions were sprayed on the heated substrates held at 450 ˚C.

Porous silicon (PS) sheet of different thicknesses was made on the surface of n-type and p-type silicon substrate using two methods; Electrochemical Etching (ECE) used for p-type silicon substrate and Photo Electro-Chemical Etching (PECE) used for n-type silicon substrate as shown in figure (1) by using the halogen lamps of (100 W) applied on silicon substrate for electron excitation. The PS was prepared by two etching of 30 mA for 30 minutes.




**(a)**

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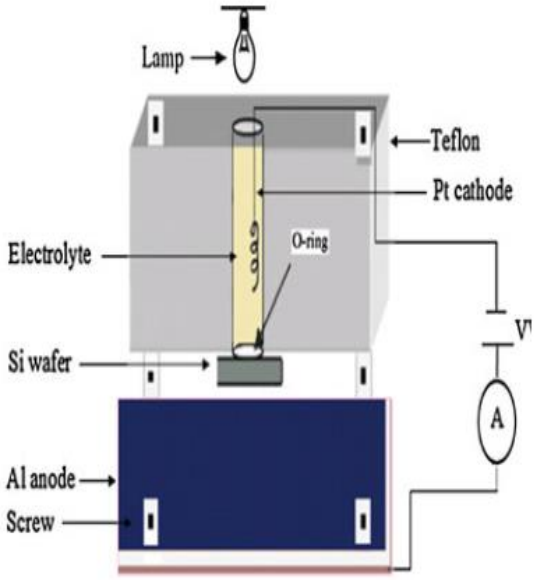
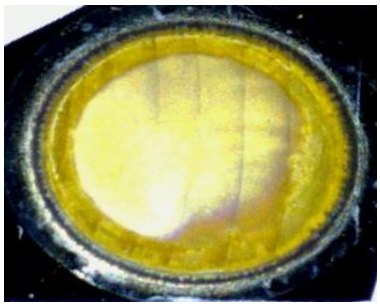



**(b)**

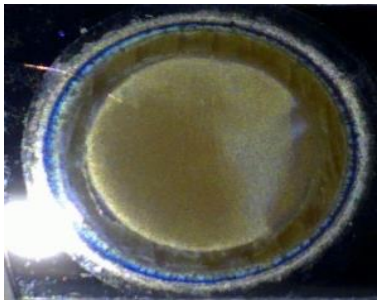
**Figure 1:** (a) electrochemical etching (ECE) cell set-up and (b) photo electrochemical etching (PECE) cell set-up.

Figure (2) shows optical photographs of the samples of n-type and p-type PS before and after the deposition of ZnO and ZnO:B thin films, the different color of the samples of n-type and p-type was unrecognizable after the deposition of the thin films.

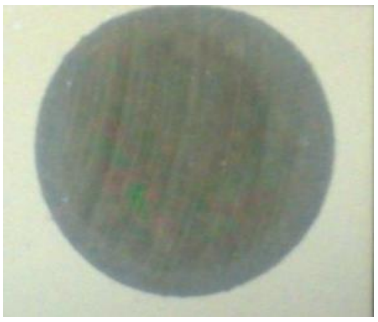


n-type(before)

n-type(after)



p-type(before)



p-type(after)

**Figure 2:** Optical photograph top view of n-PS and p- PS before and after the deposition of ZnO and ZnO:B thin films

## Result and Discussion:

### Structural properties:

The X-ray diffraction graphs of ZnO:B nanostructured thin films have been shown in figure (3). The nanostructured film had polycrystalline structure. The X-ray diffraction intensity of pure ZnO and ZnO:B 2% nanostructures film were larger than the intensity of ZnO:B nanostructure for (002) plane due to decreased crystallite size, where the crystallite size decreased with the increase of boron concentration due to the difference in ionic radius between $B^{3+}$ (0.041 nm) and $Zn^{2+}$ (0.074 nm) [8-11].

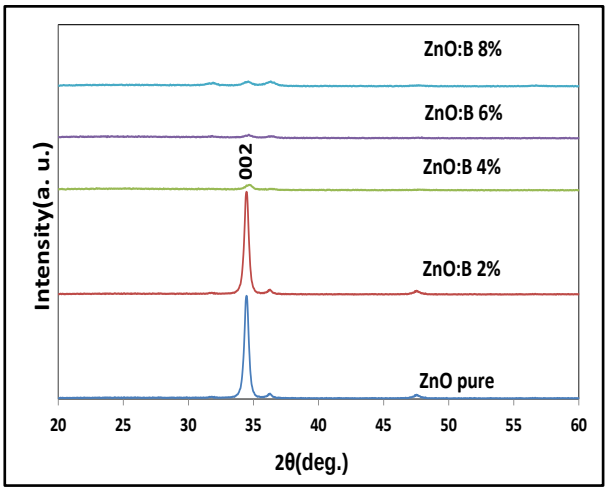



**Figure 3:** X-ray diffraction pattern of ZnO and ZnO:B nanostructure with concentration (2, 4, 6, and 8)%.

### Surface Morphology

Transmission Electron Microscopy (TEM) showed the average size of the grains in a clearer view than the X-ray diffraction. This difference in the grain size referred to this fact that "TEM shows the particles size and XRD shows the crystallites size" [12-15]. The image of the particles showed that the ZnO is a spherical nanoparticle lengthways with insufficient other neighbor nano rods experientially clear in figure (4). The grain sizes of spherical particles measured by TEM were found within the range of (6.5–23) nm.

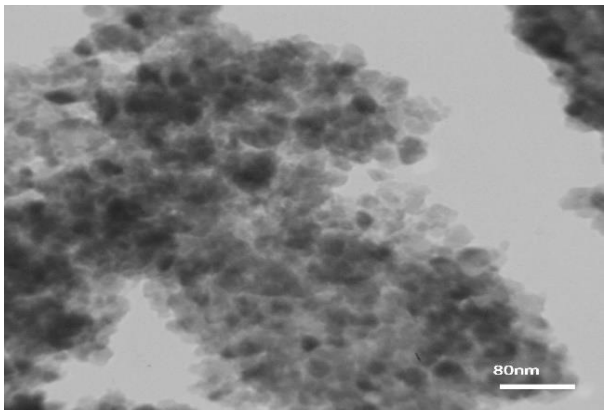
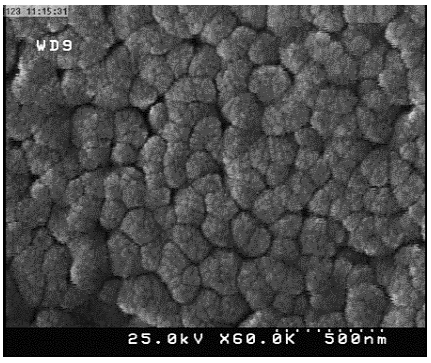
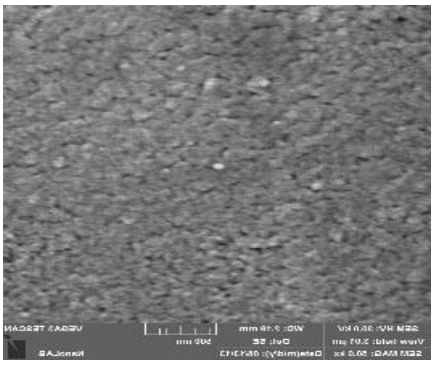



**Figure 4:** TEM image of pure ZnO.

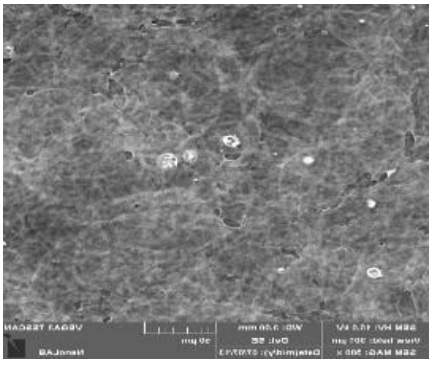
The thin films surface measured by (SEM) showed the upper view morphology of ZnO:B films as shown in images of the figure (5). The grain size of the films decreased with increasing boron doping concentration. The grain size of ZnO:B nanostructured thin films measured by SEM were within the range of (18-37) nm [16, 17].



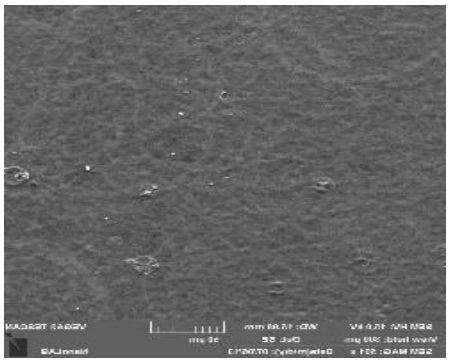

ZnO



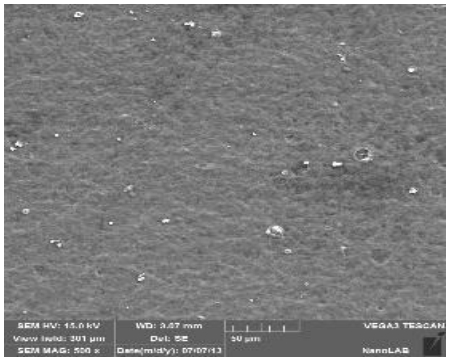
ZnO:B 2%



ZnO:B 4%



ZnO:B 6%



ZnO:B 8%

**Figure 5:** SEM image of ZnO and ZnO:B nanostructures with concentrations of 2, 4, 6 and 8%.

## Sensing properties of NH3 gas:

New materials and treatment processes for applications of gas sensing that can detect gaseous molecules have attracted increasing attention for several years. Several types of gases, such as $H_2$, $NH_3$, $CO_2$, and $NO_2$, are toxic, flammable, or harmful. Among these gases, $NH_3$ is the most common and is used in food processing, agriculture, environmental remediation, and medical diagnostics.

The mechanism of sensing of ZnO to $NH_3$ gas depended on the interactions between the reducing gas and the negatively charged $O^{2-}$ ions on the surface of ZnO thin films, thereby causing a variation in conductance, as described by the following equation [10]:

$$2NH_3 + 3O^{2-} \rightarrow 3H_2O + N_2 + 3e^- \quad (1)$$

By the electrons released back into the ZnO conduction band and increasing the carrier-doped in the ZnO active layer, the resistance of the thin film was decreased upon exposure to a reducing gas. Figure (6) shows the sensitivity of ZnO and ZnO:B as a function of operating time for $NH_3$ gas at the room temperature with the concentration of (300 ppm) at R.T. prepared on a p-type porous silicon substrate at 450 °C.

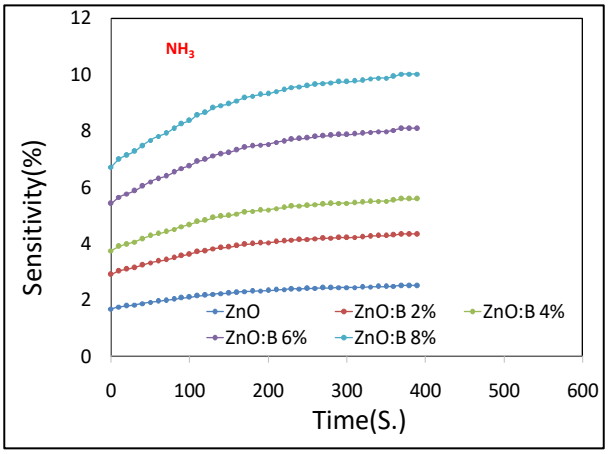



**Figure 6:** Sensitivity for ZnO, ZnO:B with doping concentration 2, 4, 6 and 8%. Deposited on the p-PS substrate as a function of operating time for $NH_3$ gas with a concentration of 300 ppm at R.T.

Figure (7) shows the sensitivity of ZnO and ZnO:B as a function of operating time for $NH_3$ gas at the room temperature with the concentration of (300ppm) at R.T. prepared on n-type porous silicon (n-PS) substrate at 450°C. The sensitivity of the films deposited on n-PS was higher than the sensitivity of the films deposited on p-type porous silicon p-PS due to the negative charge of n-PS. The sensitivity increased with the increase of the concentration of boron due to the increase of electrons in the thin films.

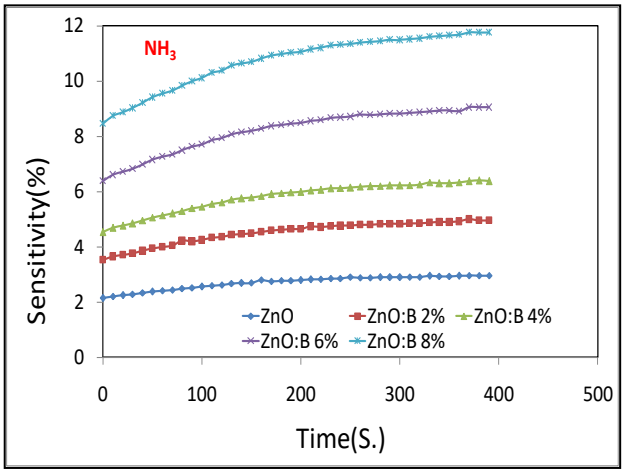



**Figure 7:** Sensitivity for ZnO, ZnO:B with doping concentration (2, 4, 6 and 8) %. Deposited on the n-PS substrate as a function of operating time for $NH_3$ gas with the concentration of 300ppm at R.T.

## Sensing properties of CO gas:

The sensing mechanism of ZnO towards CO gas depended on the interaction between the reducing gas and the negatively charged $O^{2-}$ ions on the ZnO thin films surface, thereby causing a variation in conductance, as described by equation [18]:

$$CO_{(gas)} + O^-_{(ads)} \rightarrow CO_2 + e^- \qquad (2)$$

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 was decreased upon the exposure to a reducing gas [19, 20]. Figure (8) shows the sensitivity of ZnO, ZnO:B thin films of doping concentrations of (2, 4, 6 and 8)% deposited on the p-PS substrate as a function of operating time for CO gas with the concentration of 300 ppm at room temperature. The sensitivity increased with the increase of Boron concentration due to the increase of boron electrons in the thin films, so that the increase of Boron-doped led to improve the sensitivity [21].

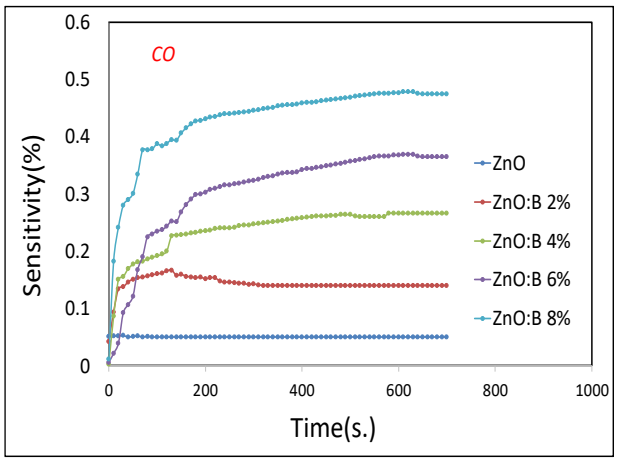



**Figure 8:** Sensitivity for ZnO, ZnO:B with doping concentration 2, 4, 6 and 8%. Deposited on the p-PS substrate as a function of operating time for CO gas with the concentration of 300ppm at R.T.

Figure (9) shows the Sensitivity of ZnO, ZnO:B thin films of doping concentrations of 2, 4, 6 and 8% deposited on the n-PS substrate as a function of operating time for CO gas with the concentration of 300 ppm at R.T. The sensitivity was increased with the increase of Boron concentration due to the increase of Boron electrons in the thin films, so that the increasing of Boron-doped led to improve the sensitivity.

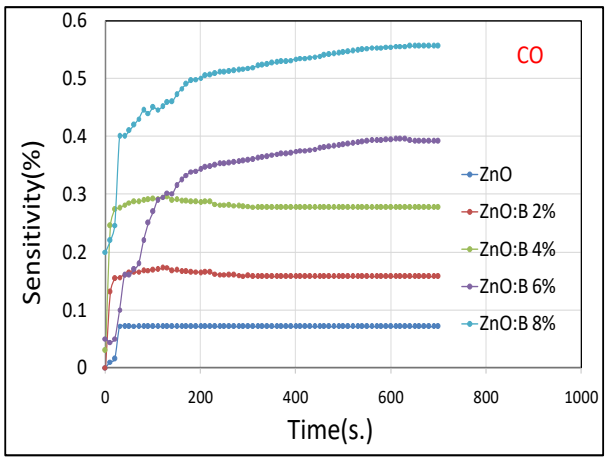



**Figure 9:** Sensitivity for ZnO, ZnO:B with doping concentration (2, 4, 6 and 8) %. Deposited on the n-PS substrate as a function of operating time for CO gas with the concentration of 300 ppm at R.T.

## Conclusions

It was found from the results that the increasing of boron concentration in ZnO decreased the grain size and increased the roughness so that the surface area of the interaction of the films increased. The increase of boron concentration increased the sensitivity of the films. The sensitivity of the thin films deposited on the n-PS substrate was higher than the p-PS.

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