Synthesis of ZnO: Sb thin films Dropped on glass and Porous Silicon for CO Gas Sensing

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Abstract. Membranes Structural properties have been studied using XRD and compare the different values of the average crystallite size by using correction equations. undoped ZnO and ZnO: Sb for (0.5 - 2) % membranes has been dropped on glass and p-type porous silicon (PS) substrate at 400 °C to use it as a sensor for CO gas. The crystal growth of the films that were deposited on the PS was not uniform due to the nature of the PS surface and due to the breakage of the crystal structure of the membrane material. the sensitivity of membranes dropped on (PS) for CO gas was higher than on glass substrate.

Keywords: ZnO: Sb; PS; membranes; CO.

1. Introduction
Zinc Oxide (ZnO) is a Transparent Conductive Oxide (TCO), has 60 meV exciton energy, an energy gap of 3.37 eV approximately [1-3]. ZnO It is a semiconductor of the negative type (n-type) [1,4]. These specifications attracted scientists to use it in many areas of scientific and industrial research, which made it suitable in manufacturing: optical and electronic devices, solar cells, gas sensors, television screens, manufacture UV lasers and Light Emitted Diodes (LEDs) [5-8]. It is possible to use different elements and add them with ZnO as doping that can affect its properties as Al, Cu, Mg, F, and Ga, which leads to different results in element transparency and conductivity, in other studies the energy gap decreases[1]. Some studies show that doping with Sb, F, As resulted in obtaining substances with good electrical properties, which led to an interest in these elements in doping [8-10]. Several techniques can be used to precipitate inlaid ZnO films, such as chemical vapor, spray pyrolysis, frequency magnetron sputtering, Chemical Vapor Deposition (CVD) [11,12].

2. Materials and method
By using heating analysis at 400 °C of aqueous zinc nitrate solution (Zn (NO₃)₂:6H₂O) with a molar concentration of 0.1 M, the zinc oxide compound can be obtained. PS was manufactured by the electrochemical etching cell, PS was used as bases for deposition of zinc oxide membrane with antimony in ratios (0.5, 1, 1.5, and 2)% in addition to pure zinc oxide, the
following thermochemical decomposition equation shows the precipitation of zinc oxide on porous silicon bases [13]:

\[ 2\text{Zn(NO}_3\text{)}_2 \rightarrow 2\text{ZnO} \downarrow + 4\text{NO}_2 \uparrow + \text{O}_2 \uparrow \quad \text{... (1)} \]

Figure (1, a) shows the electrochemical etching cell used to prepared the PS by applying a current of 35 m Amp. for 25 minutes and hydrofluoric acid at a concentration of 50% plus 50% ethanol. Figure (1, b) clear an optical photograph of the top view of p-PS before and after dropping the undoped ZnO membranes.

3. Results and Discussion
When depositing membranes on the glass substrates, we notice from figure (2, a) that the preferential plane 002 is the plane in which crystal uniformity appears, and this plane is perpendicular to the direction of the substrate on which the films were deposited. The increase in the antimony concentration led to an increase in the crystal size, and it reached its maximum value when the doping ratio was ZnO: Sb (1%) and that means the lower proportions of the antimony lead to improving the crystal structure and filling the gaps within the composition of the material that makes up the membrane. The continued increase in the amount of antimony caused a small decrease in the crystal size, and the reason for this is that the antimony did not continue to increase the improvement of the crystal size, but rather its effect appeared to increase the defects of the material, which led to the breakage of the crystal structure of the membrane material and decreased crystallinity in the preferential direction 002, as shown in the Table (1).

![Fig.1](image1.png)

(a) Electrochemical etching cell, (b) Top view of an optical photograph of p-PS before and after dropping.

![Fig.2](image2.png)

(a) XRD of ZnO and ZnO: Sb for (0.5-2) % deposited on, (a): glass, (b): Porous silicon (PS) substrates.
When the membranes are deposited on the bases of (PS), we notice as shown in figure (2, b) that the undoped ZnO and ZnO: Sb (0.5, 1, 1.5, 2)% membranes have no clear growth, which means that the type of substrate has a clear effect on the growth of preferential planes in the films, and the apparent reflection at the angle (2θ = 28.44 deg.) refers to level (111) for the silicon material that was used in the manufacture of porous silicon, but rather clear, which means that the type of base has a clear effect on the growth of preferential levels in the films, and the apparent reflection at the angle (2θ = 28.44 deg.) refers to the plane (111) for the silicon material that was used in the manufacture of porous silicon [14-18].

The crystallite size $D$ can be calculated by using Sherrer's equation [19]:

$$D = \frac{k\lambda}{\beta_D \cos(\theta)} \quad \ldots (2)$$

Where $k = 2\sqrt{\ln(2)/\pi} = 0.94$ called (Scherer's constant), $(\lambda = 0.15406 \text{ nm})$ is the wavelength of the occurrence beam of XRD, $\beta_D$ is referring to the intrinsic Full Width at Half Maximum (FWHM) of XRD peak, and $\theta$ is the angle of Bragg's diffraction of the own XRD top [20-24].

In the circumstance, measured arc XRD is alike to Lorentz function and income the form $\frac{1}{1+kx^2}$, the improvement is given by the next association, which was so-called (Scherer's correction) [25]:

$$\beta_D = \beta_m - \beta_i \quad \ldots (3)$$

$\beta_m$ is the measured Full Width at Half Maximum of the highest, $\beta_i$ is the instrumental expansion which is equal to 0.11 deg. for the used XRD instrument. By recompense equation (3) in the association (2) we get:

$$D = \frac{k\lambda}{(\beta_m - \beta_i) \cos(\theta)} \quad \ldots (4)$$

In the situation measured XRD curve is comparable to the Gauss purpose which takings the formula $e^{-k^2x^2}$ the correctness to be advanced because of the prodigious resemblance between this meaning and the deflection arcs; it was recommended by Warren in the formula [26]:

$$\beta_D^2 = \beta_m^2 - \beta_i^2 \quad \ldots (5)$$

Eq. (5) is named (Warren Correction). By recompense equation (5) in the relationship (2) we get:

$$D = \frac{k\lambda}{\cos(\theta) \sqrt{\beta_m^2 - \beta_i^2}} \quad \ldots (6)$$

Warren has recommended an affiliation receipt into the version of the geometric sense by multiplying eq. (3) by eq. (5) which is:

$$\beta_D = \sqrt{(\beta_m - \beta_i)(\beta_m^2 - \beta_i^2)} \quad \ldots (7)$$

Recompense equation (7) in the association (2) we get [26, 27]:

$$D = \frac{k\lambda}{\cos(\theta) \sqrt{(\beta_m - \beta_i)(\beta_m^2 - \beta_i^2)}} \quad \ldots (8)$$
Table 1. 2θ, FWHM, and Average crystallite size measured by equations: (2, 4, 6, and 8) for undoped ZnO, ZnO: Sb for (0.5 - 2)% deposited on the glass substrate.

| hkl | Samples   | 2θ (deg.) | FWHM (deg.) | The average crystallite size (nm) |
|-----|-----------|-----------|-------------|----------------------------------|
|     |           |           |             | eq. (2) | eq. (4) | eq. (6) | eq. (8) |
| 002 | ZnO       | 34.4802   | 0.2782      | 31      | 52      | 34      | 42      |
|     | ZnO: Sb (0.5) % | 34.4652   | 0.2032      | 43      | 93      | 51      | 69      |
|     | ZnO: Sb (1) %   | 34.4626   | 0.178       | 49      | 128     | 62      | 89      |
|     | ZnO: Sb (1.5) % | 34.4638   | 0.1808      | 48      | 123     | 61      | 86      |
|     | ZnO: Sb (2) %   | 34.4636   | 0.2085      | 42      | 88      | 49      | 66      |

4. Sensing of CO Gas.

ZnO sensitivity is due to the reduction of gases, such as the absorption of oxygen from the surface of the membrane, which leads to the carbon dioxide molecules interacting with the previously adsorbed oxygen species, as in the equation [28]:

$$\text{CO} + \text{O}^-(\text{ads}) \rightarrow \text{CO}_2(g) + e^- \quad \ldots \quad (9)$$

This leads to a reduction in the oxygen attentiveness in the superficial of the membrane, and the bound electrons are released due to the anions, which causes the membrane resistance to decrease as shown in figure (3) [28]:

![Fig.3. mechanism of the sensitivity to carbon monoxide.](image)

Due to the volume surface of (PS), the substrate is larger than glass, the area of interaction between CO gas and membranes material, the sensitivity for CO gas of the membranes dropped on PS is higher than the sensitivity of the membranes dropped on the glass substrate, as clear in the figure (4).

![Fig.4. sensitivity vs. exposure time of CO gas for undoped ZnO, ZnO: Sb for (0.5 - 2)% deposited on, (a): glass substrate, (b): Porous silicon (PS) substrates.](image)
In figure (4. a), the increase of Sb concentrations led to a smooth increasing of the membranes dropped on the glass substrate, but the sensitivity is jumped rapidly for (1.5 and 2) % of Sb doping concentrations, which clear the influence of doping and surface area of PS.

5. Conclusions:
The average crystallite size of the membranes was Nanostructure, preferential plane 002 is the plane in which crystal uniformity appears in XRD measurements for undoped ZnO, ZnO: Sb dropped on the glass substrate, but there are no uniform growth or crystalline for the membranes which dropped on (PS) due to the breakage of the crystal structure of membranes materials. In general, the sensitivity of ZnO, ZnO: Sb dropped on (PS) substrate for CO gas is higher than the glass substrate.

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