Synthesis of ZnO:B thin films Dropped on Porous Silicon for H₂ Gas Sensing

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Abstract
Porous Silicon PS has been prepared so as to use it a substrate to dropped ZnO:B thin films with different boron concentrations additions (2-8) % dropped at 450°C through used the chemical spray pyrolysis (CSP) technique in approximately 150nm thicknesses. Crystallite and Grain size decreases with adding more of boron as a doping for zinc oxide films which dropped on the negative type (n-type) and positive type (p-type) of PS. Surface morphology study for the obtained the ZnO:B thin films and for the n-PS and p-PS was studied by TEM, SEM and AFM. Sensing properties of ZnO:B thin films for H₂ gas showed that the increases of boron leads to increases of the thin films sensitivity, measured sensitivity of the n-PS substrate was more than p-PS.

Keywords: H₂ Gas sensor; porous silicon; thin films; ZnO:B.

Introduction
Zinc oxide, is an significant substantial for the last decades according to the truth that it reveals semiconducting and piezoelectric twofold belongings, ZnO is one of the significant multifunctional materials used for several applications of transparent conductive oxide (TCO) due to the good performance (1). The semiconductor-based sensors possess several characteristic advantages, results in practical measurements, such as low cost, high permanency, and transportability (2). The energy bandgap of ZnO is 3.371 eV, high conductivity of thermal and mobility of electron, 60 meV exciton of energy binding and good chemical stability material (3-6), from the beginning of using zinc oxide as a gas sensor, good efforts from researchers have been completed to improve the performance of the sensitivity of ZnO films (2, 8). ZnO thin films applications are proper for electronics strategies like LED, solar cell gas sensing, windows, and photodetectors (9, 10). A porous silicon (PS) material has a significant characteristic to study and investigation and use it as a substrate to the thin films (11, 12).
The typical mechanism of gas sensing in metal oxides is the interaction of oxygen atoms and the surface of thin films material (13, 14).

**Aim of the research:**

The aim of this research is to prepare thin films of ZnO:B deposit on porous silicon synthesized by using photo-electro-chemical etching), and to use the thin films for H2 gas sensing applications.

**Materials and method:**

ZnO has a white color which preparing by chemical heat analysis of solution of nitrate of Zinc (Zn (NO₃)₂.6H₂O) by using 0.075M concentration by using chemical spray pyrolysis (CSP). The resistivity values of used silicon is between 0.05 Ω.cm to 0.1 Ω.cm. the silicon sample dimensions thickness is approximately about 500 μm and (111) orientation used to prepared sample dimensions (2 × 2 cm²). This material is employed to synthesis porous silicon (PS) by using the photochemical etching method. Magnetic stirring requires (10-15) min to enable competition solution insolvent. The thin films prepared on the substrates at 450 °C. Factors affecting thin film thickness are the sprays number and the solutions concentration. Three seconds time of solution spray that continued through the experimentation followed by stop for forty seconds so as which it is sufficient kept the substrate temperature to reaching for 450°C again. Normalization distances between each of spray nozzles, and substrate fixed in (28cm). The nanostructured film synthesis for pure ZnO and ZnO doped with 2% - 8 % of boron doped concentration in the the solution. The drop of zinc nitrate solution leading to the construction of ZnO by heat analysis as show in the relation (15, 16):

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

The etching of electrodeless method means no base voltage used in the etching processes. These processes supported using conventional light source. The simplicity of the preparation method our experiment have been utilized for the etching of photochemical techniques. Fig. 1 illustrated experimental setups. This setup involves a lamp made by Tungsten Halogen of 100 W through weak etching acid which consist by Hydrofluoric acid and ethanol. Thin homogenous of Porous Silicon layers by used different thicknesses are which is formed on frontal surfaces by used electrochemical (EC) material and photoelectrons chemical (PEC) methods. Porous Silicon layers prepared through halogen lamps for PEC processes characterized by different structures and properties. Porous silicon which synthesizes using 30 mA current in 30 min , through the electrochemical and photo electrochemical etching.
From Fig. 2 above, the optical photos of prepared thin films of each n-PS and p-PS types in case of ZnO un deposited and with deposited ZnO doped with B thin films, that’s difference in color of (n and p) type is could not be a distinction when thin films deposition on the PS substrate.

Results and Discussion:
Structural Properties

Fig. 3 illustrated the X-ray diffractions analysis of ZnO film, and boron for 2% - 8% concentration doped ZnO deposited on (p-type) of porous silicon.
The Fig. 3 shows the existence of one peak of pure ZnO and ZnO:B 2% corresponding to (002) directions plane of the preferred orientation. This analysis means that films have polycrystalline and hexagonal wurtzite structural comparing with the standard (ASTM) of the ZnO card. Imbalance of ions size of the B$^{3+}$ (r=0.041nm) interstitial in Zn$^{2+}$ (r= 0.074 nm) which leads to many defects such as stress and dislocation in the thin films (3, 17). The interplanar spacing (d) decreases due to the smaller ionic size of boron as shown in table (1). For the doping concentrations (4, 6 and 8) %, the high crystal distortion caused by these doping (as shown in fig. 3) illustrates the fact that the crystallite size is small for these doping's as shown in Table 1.

Table 1. forms of XRD of ZnO:B thin films.

| Doping (%) | 2θ (deg.) | d (nm) | FWHM (deg.) | Crystallite size (nm) |
|------------|-----------|--------|-------------|----------------------|
| 0          | 34.475    | 0.25994| 0.40        | 21.9                 |
| 2          | 34.577    | 0.25920| 0.48        | 18.0                 |
| 4          | 34.659    | 0.25861| 0.67        | 12.9                 |
| 6          | 34.621    | 0.25888| 0.69        | 12.7                 |
| 8          | 34.557    | 0.25935| 0.81        | 10.8                 |

Scherer equations which calculated ($D_0$, average grain size (18, 19):

\[
D_0 = \frac{K \lambda}{\beta \cos(\theta)} \quad 2
\]

Where: k is Scherer's constant, \(\lambda\) is the wave length of incident XRD beam, \(\beta\) is the fundamental of full width at the half maximum (FWHM) of the XRD peak, and \(\theta\) is the angle of Bragg's diffraction.

**PL Properties**

Fig. 4 shows the silicon layer which is formed on the n-type region has (111) orientation by using the (\(\lambda=325\) nm) of xenon lamp at Room Temperature.
Energy band gaps $E$ (eV) of silicon layers which can be calculated from PL peaks equal (2.397 eV). So that (d) is average pore diameter for Pours Silicon layers can be deposited on the (111) p-type Silicon wafer is 4.83 nm, eq.3 used for calculated energy gap value $^{(20)}$:

$$E(eV) = E_g + \frac{\hbar^2}{8d^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) \quad \text{... 3}$$

Where: energy gap ($E_g$) of c-Si, $\hbar$: constant of Planck which equal (4.13×10^{-15} eV·s.), while $m_e^*$, and $m_h^*$: are the effective mass of electron and hole effective respectively (at 300 K).

**Surface Morphology**

TEM results illustrated mean grains size, over XRD. The different size between TEM and XRD, where TEM illustrate particles size while XRD illustrate crystallites size $^{(13)}$. ZnO nanoparticles have many spherical shapes with little nanorods as noted in Fig. 5. Average grain sizes is between (6.4 – 24 nm) of spherical nanoparticles. This results obtained and the images of TEM of the prepared the films is good agree of results with $^{(21)}$.

Figure 5. images of TEM for undoped ZnO thin film.
Fig. 5 demonstrate of n-PS and p-PS of PS images arranged within half a clock at 30mA/cm² etched the density of current earlier and later dropping the ZnO at 450 °C, grain size that determines by SEM which showed in the table.1 above. This results in good agreement with previous reports (22).

Fig. 6. SEM images of: (a) ZnO/p-PS, (b)ZnO:B 2%/p-PS, (c) ZnO:B 4%/p-PS, (d) ZnO:B 6%/p-PS, and (e) ZnO:B 8%/p-PS deposited at temperature 450°C.

Fig. 7. dimensions image of AFM: (a) ZnO/p-PS, (b)ZnO:B 2%/p-PS, (c) ZnO:B 4%/p-PS, (d) ZnO:B 6%/p-PS, and (e) ZnO:B 8%/p-PS dropped at temperature 450°C.

Fig. 7, AFM measurements illustrate the inverse relationship between average grain size and different concentration doped of boron, the range of grain size lies between (15.6 - 41.2) nm. As well as increased surface roughness with an increase of doping levels within range between (7.40-11.47 nm).

SEM and AFM images of each undoped ZnO and ZnO:B films precipitation on PS for each of n-PS and p-PS shows the average grain size is decrease according to increasing of increasing concentrations of boron in the solution. The thin films roughness of the surfaces is increased according to the growth of boron doping concentrations, as reveals in Table 1.

Table 1. Average grain size measured by SEM and AFM instruments, and average of roughness for undoped ZnO and ZnO:B films.

| Sample    | $D_{AFM-PS}$ (nm) | $D_{SEM-PS}$ (nm) | Sa(roughness average)(nm) |
|-----------|-------------------|-------------------|---------------------------|
| ZnO       | 41.2              | 31.4              | 7.40                      |
| ZnO:B 2%  | 35.7              | 22.5              | 8.34                      |
| ZnO:B 4%  | 31.4              | 19.4              | 9.16                      |
| ZnO:B 6%  | 20.3              | 17.2              | 11.04                     |
| ZnO:B 8%  | 15.6              | 11.3              | 11.47                     |
Sensing of H₂ Gas

Sensitivity of the undoped ZnO for H₂ gas rely on interactions between each of reducing gas with O²⁻ ions on the external surface of ZnO films, thus caused a decreasing of the thin films conductivity, as clear from chemical interaction (21):

\[ \text{H}_2(\text{ad}) \rightarrow 2\text{H}^+ + 2e^- \quad \ldots \ 2 \]

Releasing of an electrons are backing into the ZnO and ZnO:B thin films conduction bands, this leads to increasing of carrier-doped interactive layer of the thin films, the sensor conductivity decreased onto exposure to a reducing gases (9, 22).

Figure 8. Relation of sensitivity vs. operating time of 50 ppm H₂ gas of undoped ZnO, and ZnO: B 2%- 8% concentration at R.T. on n-type.

As revealed in the Fig. 8, the sensitivity is increases according to boron concentration caused by boron electrons increased, so that increase boron concentration leads to improve the sensitivity. Fig. 9 indications the relation of the sensitivity of the prepared thin films dropped on the n-PS and p-PS substrate, as clear from the figure, the sensing of the thin films dropped on n-PS is more than p-PS substrate, that because of the carriers of an electrons of the n-type of PS substrates. Carrier of an electron is increases according to the increasing of boron concentration, This result is because of the substitutional combination of B³⁺ ions at the sites cation of Zn²⁺ ions, or due to the combination of B³⁺ ions in the places of interstitial (23).

Figure 9. Sensitivity vs. time for ZnO, and ZnO doped with B concentrations 2, 4, 6 and 8 % on the n-type as a function of operating time for H₂ gas with concentration 50 ppm at R.T.
Fig. 10 reveals the relationship between the sensitivity vs. operating time for ZnO and ZnO:B thin films dropped on p-PS for 50ppm concentrations of H₂, the sensing is rising up according to the temperature applied on thin films which dropped on the substrate until reach to the highest sensitivity at 150°C, and then decrease above this temperature.

![Figure 10. Relation of Changing sensitivity vs. the temperature of H₂ gas for the pure ZnO and ZnO: B for doping concentration equal 2%- 8% dropped on p-PS.](image)

As clear from Fig. 11, the high sensitivity for the films deposited on n-type of PS comparing with p-type substrate for 50 ppm concentration of H₂ rising up to 150°C of substrate temperature.

![Figure 11. Relation of Changing sensitivity vs. temperature for H₂ gas for the pure ZnO and ZnO: B for doping concentration equal (2- 8)% dropped on n-PS.](image)

**Conclusions**

ZnO nanostructured films and boron doped ZnO illustrated increasing the doped concentrated caused decreased of grains size. The direct interaction between each of roughness and doped concentrations by boron, denominate direct relation between thin films sensitivity for H₂ gas, and increasing boron concentrations. The proportional more obviousness in n–type porous silicon comparing with p – type. The reason of high sensitivity of the thin films dropped on PS is due to the large area of the surface of PS, which means high interaction between the thin films surface and H₂ gas.

**Conflicts of Interest:** The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.
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