Study of the Effect of Annealing Temperature on the Response of Nano-Films of ZnO to Ammonia Gas Sensor

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Abstract: Zinc oxide (ZnO) nanoparticles were prepared by sol-gel method and deposited on the substrates (glass gliders and platinum electrodes) by a rotation coating at 2000 rpm. The coated substrate was calcined at 500, 550 and 600 °C for 1 hour. The films were determined by XRD and UV, where the results showed their compatibility with the global measurements, and through the results of the test of sensitivity to the membranes of the stomach, we obtained that the film is heat at a temperature of 550 high sensitivity, depending on the surface area of the surface. The ZnO thin films were exposed to NH3 gas with a different concentration of 50 ppm – 4000 ppm and the resulting resistance transient was recorded at different operating temperatures (500, 550, 600 °C).

Keywords: Zinc oxide (ZnO), sol-gel, spin coating, Nano-thin film, sensitivity.

1- Introduction

Zinc oxide (ZnO) is at the forefront of semiconductor compounds II-VI with potential applications due to the high optical transmittance in the visible region due to its large band gap and electrical conductivity at room temperature; these characteristics make it an ideal candidate for applications such as transparent conductive electrode, window layers in the solar cell applications and gas sensors[1]. The nanoscale structure of zinc oxides plays an important role in the devices performance, as an example in gas sensor devices because the large area will enhance the properties of gas sensors and, moreover, have safe biological properties (as a non-toxic substance) which makes ZnO very attractive for vital applications. The simple preparation methods of producing ZnO thin films give them the potential to be studied. ZnO can be applied as thin layers in transistor applications[2], and is considered a rotational electronic material[7]. Zinc oxide films can be prepared using various techniques, including lamination, chemical vapor, sol-gel and pyrolysis spray. Recently, due to its excellent physical properties and potential technological applications, ZnO has attracted considerable attention. ZnO is an n-type semiconductor with wurtzite structure of hexagonal crystals as shown in Fig.1(A). O2− crystals can be described as tetrahedral and Zn2+ ions consist of alternately flat, stacked [3]. On the other hand, carbon based materials such as multi-walled carbon nanotubes (MWCNTs) which has significant applications in the field of sensors as well as other electronic devices due to the large area; the MWCNT includes a plurality of tubes in a concentric cylinder as
shown in Fig.1(B)[4]; the number of concentric walls can range from 6 to 25 or more. The diameter of the MWCNT can be about 30nm compared to 0.7-2.0 nm for a typical SWCNT. The unique properties of carbon nanotubes make it possible for a wide range of novel applications and existing performance improvements. UndopedZnO has high conductivity due to the crystalline defects that contribute to a number of secondary levels between the valence and conduction bands. On the other hand, doping ZnO is to improve the stability of ZnO and further increase the electrical conductivity, as an example, doping with MWCNTs. Such thin film has high permeability in the visible region of the spectra and low resistance; the optical energy gap can be controlled by the concentration of doping material added to the ZnO [5]. The latter enhancement can be used in improving the characteristics of different applications such as solar cells, coatings and chemical sensor devices [6].

Figure 1 (A) Wurtzite structure of ZnO, and (B) Multi-walled carbon nanotubes

2- Experimental section:

2.1. Sol-gel preparation of ZnO

First, the isopropanol engine mode was 4 ml, and then 50 μL of ethanolamine (MEA) was added by performing a mixed solvent treatment at 60 ° C for 30 minutes. Then, zinc acetate was added to the solvent mixture with stirring and the process was maintained at 60 ° C for 1 hour. The final solution was kept in a sealed flask (paraffin paper was used to prevent the penetration of colloidal dust and moisture into the solution). Viscous liquids are transparent and uniform for 24 hours at room temperature under laboratory conditions.

2.2. Preparation of samples

After soaking in ethanol for half an hour, using clean (slides, interdigitated electrodes), the sections were placed in a heating oven and dried at 50 ° C, and then washed three times with distilled water. ZNO was prepared on pre-cleaning (glass substrate, interdigitated electrode) using spin coating. The solution is deposited on the sedimentation substrate during deposition. The sample was then raised and placed on a hot plate at 60 ° C until the solvent and film dried. The sample is then placed in an oven at (500°,550°, 600°)C)
2.3. Gas sensor

The gas sensing performance of ZnO thin films prepared by using spin coating method and deposited on platinum interdigitated electrode was evaluated by measuring the changes in the electrical resistance with respect to the variation in the Ammonia (NH₃) gas concentrations (50 ppm to 4000 ppm at equal intervals) at different operating temperatures (500, 550, 600) °C. The gas sensing measurements of ZnO thin film sensors were taken in a home-built computer-controlled static gas sensing system that consists of an airtight stainless steel test chamber having a volume capacity of 5306.6 cm³; it has an inlet for allowing the test gas to flow in and an air admittance valve to allow atmospheric air after evacuation. Another third port is provided for vacuum gauge connection. A multi-pin feed through at the base of the chamber allows for the electrical connections to be established to the heater assembly as well as to the sensor electrodes via spring loaded pins. The heater assembly consists of a hot plate and a k-type thermo-couple inside the chamber in order to control the operating temperature of the sensor [7].

The thermocouple senses the temperature at the surface of the film exposed to the analyte gas. PC-interfaced digital multimeter of type (UNI-T UT81B), and laptop PC, is used to register the variation of the sensor conductance (reciprocal of resistance) exposed to predetermined air – gases ratio [8].

The chamber can be evacuated using a rotary pump to a rough vacuum. A gas mixing manifold is incorporated to control the mixing ratios of the test and carrier gases prior to being injected into the test chamber. The film sensor was placed on the heating plate in the test chamber. After that, using the needle valves the flow rate of the carrier and test gases flow meters is adjusted, next, the gas of known concentration in chamber is allowed to flow to the test chamber by opening the valve, measurement of the electrical resistance variation with the time of the sensor for the known concentration of test gas ratio is observed by the PC – interfaced digital multimeter of type (UNI-UT81B). The sensitivity (S%) of sensors can calculate depending on the electrical resistance of the films by using the equation [9].

\[
(S\%) = \frac{\Delta R}{R_a} = \left| \frac{R_a - R_g}{R_a} \right| \times 100\% \quad (1)
\]

Where: \( R_a \) is the thin film electric resistance in the air, and \( R_g \) is the electric resistance of the thin film in gas presence.

XRD:

X-ray powder diffraction (XRD) was used to characterize the zinc oxide powders. Particle size of the samples was determined using X-ray diffraction technique. XRD patterns were collected using Bruker, D8 advance-taflux diffraction meter using CuK radiation and \( \lambda = 1.5406A° \). Crystallite size is calculated using Scherrer equation [10].

\[
CS = \frac{0.9\lambda}{\beta \cos\theta} \quad …………………3.4
\]

Where, CS is the crystallite size, \( \beta \) is full width at half maximum (FWHM) of an hkl peak at \( \theta \) value.25
3. Results and Discussion

3.1. X-Ray Diffraction Analysis

The XRD pattern of ZnO thin film fabricated by sol-gel method on quartz substrates is shown in Figure 6. All the peaks of the ZnO thin films correspond to the peaks of standard ZnO (JCPDS S6-314). For all the samples, (100), (101) and (002) diffraction peaks are observed in the XRD pattern, showing the growth of ZnO crystallites along different directions. Strong preferential growth is observed along (002) plane indicating that the films are oriented along c-axis [11]. The typical hexagonal wurtzite structure of thin films is inferred from the XRD pattern. The crystallites sizes (D) of the films are estimated using the Scherer formula [12]:

### 3.2. X-Ray Diffraction

X-ray diffraction (XRD) was used for crystal phase identification for ZnO thin films prepared by sol-gel technique, Figure 1 represent X-ray pattern of ZnO thin film prepared by using dip coating method.

From Figure 1, the film has polycrystalline of hexagonal structure with one sharp peak and two small peaks; (002), (101), and (102) appear at 2θ = 34.45°, 36.23° and 47.55° respectively, as listed in Table 1. The results are in agreement with the American Standard of Testing Materials (ASTM) and with [10]. Figure 2 shows that the film has amorphous structure with three pronounced ZnO diffraction peaks; (100), (002), and (101) appear at 2θ = 31.8°, 34.4° and 36.2° which are very close to wurtzite ZnO ones and in agreement with (ASTM), as listed in Table 2.

| Table 1. The value of (hkl), 2θ, and d for all peak of ZnO thin films prepared by dip coating technique. (hkl) |
|---|---|---|---|
| d (Å) (XRD) | d (Å) (ASTM) | (2θ) Degree | Table 1. The value of (hkl), 2θ, and d for all peak of ZnO thin films prepared by dip coating technique. (hkl) |
| 2.601 | 2.602 | 34.45° | (002) |
| 2.478 | 2.476 | 36.23° | (101) |
| 1.9106 | 1.911 | 47.55° | (102) |

1-The results of the tests (AFM) of the nano films for pure (P3HT) and doped with different ratio of (MWCNTs) films which prepared by spin coating which showed a uniform granular surface morphology, as in Figures (9, 10, and 11). Where it can be note that the roughness increased with increasing the ratio of doped. As well the root mean square (RMS) increased with increasing of doped ratio, the average grain diameter also it exhibits the same behavior. This indicates improved crystalline structure with an increased proportion of carbon nanotubes resulting in
increased particle size and increased roughness, as in Table 4.3. This is consistent with the findings of the researchers [13].

3.3. Gas sensing characteristics of the thin films

Before exposing the Ammonia (NH₃) to the samples allowed to stable electrical resistance. The stabilized the electrical resistance was noted as resistance in air (Ra). Then (50 - 4000 ppm) of NH₃ was injected in gas testing chamber and change in the electrical resistance was measured function of time at different operating temperatures (500, 550, 600 °C). The resistance was calculated resistance in NH₃ gas is Rg. We note the variation of resistance as function of time for both cases open and closed gas, we show that the resistance decreases in opened the gas case and increases rapidly in closed gas because NH₃ is reducing gas when applied on the Zno films (n-type semiconductor) and adsorb to oxygen ion on the surface at the grain boundaries so that charge carrier concentration (electrons) will increase so the conductivity will increase too [14].

![ZNO at 500 °C](image1)

**Fig (2)** Transient sensitivity characteristics in presence of Zno at 500 °C.

![ZNO at 550 °C](image2)

**Fig (3)** Transient sensitivity characteristics in presence of Zno at 550 °C.
Fig (4) Transient sensitivity characteristics in presence of ZnO at 600°C.

Fig (5) Transient response characteristics in presence of ZnO at (500, 550, 600) °C.

Figure (6): XRD pattern of ZnO nanoparticles at 500 °C
Figure (7): XRD pattern of ZnO nanoparticles at 550 °C

Figure (8): XRD pattern of ZnO nanoparticles at 600 °C

Figure (9): AFM images of ZnO with ratio 500 T
4. Conclusion:

In this work, Figure(2) , (3) and (4) showing the variation of the sensitivity of the tested Zno films as time at different operating temperatures (500, 550, 600) °C respectively. It can be observed that the sensitivity decreases as opened the gas case because Rg< Ra, whereas the sensitivity increases rapidly in closed gas and recovers almost to its initial value after the NH3 flow is switched off this leading to Rg> Ra, this agreement with study[15]. On the other hand, Figure(5) show the variation of the response of the tested films as a function of different concentration of NH3 gas [16-20]. It can be observed that the response increases as different concentration the temperature increases from 500 °C to 600°C. Over 600°C, sensor response decreases with the increasing temperature. The response increasing is attributed to the thermally activated carriers at high temperature. For simulation, other methods can also be used [21-28].
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