HYDROGEN GAS SENSORS BASED ON ZnO THIN FILMS

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ABSTRACT

Nanocrystalline (ZnO) thin films were synthesized by chemical spray pyrolysis technique, a 0.1 M Spray solution is prepared by dissolving Zinc Chloride (ZnCl₂) in 100 ml distilled water were deposited on glass substrates heated 450 °C. The crystal structure and morphology of synthesized films were characterized by X-ray diffraction (XRD) and Atomic Force Microscope (AFM). The crystallite size was evaluated to be 48.599 nm by using Scherrer’s equation and the optical absorption spectra were taken to determine the band gap 3.2 nm eV increase in band gap energy is revealed that nanostructure films. The gas sensing properties of the ZnO films were investigated towards the reducing gas such as H₂. The sample showed the maximum gas sensitivity (64.65%) at operating temperature 300 °C with fast response time 6 s and recovery time 57 s respectively.

KEYWORDS: Spray Pyrolysis, ZnO Thin Films, H₂ Gas Sensing, Sensitivity

INTRODUCTION

Zinc Oxide is one of the compound semiconductors of the II-VI family with a direct band gap of 3.37 eV at room temperature, and a large excitation binding energy (60 meV) [1]. ZnO Posses potential material for many devices application such as gas sensor, solar cells, high density data storage devices, UV detectors, optoelectronic devices, photoluminescent devices [2-4]. Several deposition techniques have been used to grow ZnO thin films. These include sputtering, spray pyrolysis, sol-gel process, pulse laser deposition, plasma enhanced chemical vapour deposition, vacuum evaporation, electron beam evaporation, low pressure metal organic chemical vapour deposition (MOCVD) [5,6]. In 1962 Seiyama et al discovered that the electric conductivity of ZnO changed dramatically by the presence of reactive gases in the air [7]. Thin films of ZnO are expected to exhibit a high degree of gas sensitivity, because the sensing mechanism involves chemisorptions followed by charge transfer at the surface leading to a change resistance of the sensor element [8]. Generally, ZnO sensors provide a wide variety of advantages, such as low cost, short response time, easy manufacturing, and small in size, compared with the traditional analytical instruments [9]. Among the semiconductor metal oxides ZnO was one of the earliest discovered and is the most widely applied oxide gas sensing materials due to its high mobility of conduction and good chemical and thermal stability under operating condition. ZnO gas sensor have been fabricated in various forms, including single crystals, sintered pellets, thick films, thin films, and heterojunctions which were studied to detect H₂, NO₂, NH₃, CH₄, O₂, CO, and ethanol [10].

In this work, a hydrogen gas sensing device has been designed, fabricated by using chemical spray pyrolysis deposition technique on glass substrates and tested for H₂ gas sensing. X-Ray diffraction (XRD) and Scanning Probe Microscope (SPM) and resistance measurement are used to characterize the microstructure and electrical properties of ZnO gas sensor.
Experimental Work

The ZnO thin films were prepared by chemical spray pyrolysis technique. The films were deposited on glass substrates heated to (450°C). A 0.1 M Spray solution is prepared by dissolving Zinc Chloride (ZnCl$_2$) of 98% purity in 100 ml distilled water. The above mixture solution was placed in the flask of the atomizer and spread by controllable pressurized nitrogen gas flow on the heated substrats. The spraying time was 4 seconds, which is controlled by adjustable solenoid valve. The heated substrate was left for 20 sec after each spraying run to give time for the deposited (ZnO) layer. The optimum experimental conditions for obtaining homogeneous ZnO thin film at (450°C) were determined by the spraying time, the drying time and the flashing gas pressure [11]. The preparation of Zinc Oxide thin films depends on surface hydrolysis of metal chloride according to the following chemical reaction equation [12].

\[
\text{ZnCl}_2 + H_2O \rightarrow \text{ZnO (Films)} + 2 \text{HCl} \uparrow
\]  

(1)

Optical interferometer method is used for measuring the thickness of the film by employing He–Ne laser (0.632 µm) wavelength with incident angle 45°. This method depends on the interference of the laser beam reflected from thin film surface and the substrate. The structural of the thin films were examined by X-ray diffractometer (6000-Shimadzu) using CuK$_\alpha$ radiation with a wavelength, $\lambda$=1.54060 Å, voltage 30 kV, current 15 mA. The morphological of the films were analyzed using scanning Probe Microscope (SPM, model AA3000 Angstrom Advanced. Inc). The optical absorbance of the films was measured using UV-visible spectrophotometer (SP-3000 Optima) in the wavelength range 200-1200 nm at room temperature. Interdigitated Aluminum ohmic metal contacts are deposited on the ZnO films using vacuum evaporation technique. The mask of (1mm) electrode spacing was used to deposit the electrical electrode on the ZnO layer surface. The gas sensing chamber had been employed for testing of these films to gases. A fixed voltage of 6 V was applied across the films. The current was measured using a Scope digital multimeters (UT81).

RESULTS AND DISCUSSIONS

The X-ray diffraction (XRD) pattern of the 400 nm thick ZnO thin films were deposited on glass substrates heated to (450°C) is shown in figure 1. From this figure, the well –crystallized diffraction peaks were observed with crystal planes (002), (101), and (102). The film is crystallized in the hexagonal wurtzite phase and presents a preferential orientation along the c-axis indicated by the plane (002). The result is a good agreement with data mentioned in the literature (JCPDF card no 36-1451) [13]. The strongest peak, observed at $2\theta = 34.1387^\circ$ can be attributed to the (002) plane of the hexagonal ZnO. Another major orientations like (101) and (102) at $2\theta = 36.2587^\circ$ and $47.4424^\circ$. The mechanism of formation of the c-axis preferentially oriented ZnO thin films can be suggested that the value of surface energy is minimum for the ZnO (002) plane at the growth stage [14]. The grain size (D) of film is 48.599 nm were calculated by using the Scherrer’s equation [15].

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  

(2)

Where $\lambda = 0.154$ nm is the wavelength of the X-Ray radiation used, $\theta$ the Bragg diffraction angle of the XRD peak and $\beta$ is the measured broadening of the diffraction line peak at an angle of 20, at half its maximum intensity (FWHM) in radian.
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Figure 1: XRD Patterns of ZnO Thin Films (d= 400 nm) Deposition at Temperature 450 °C

The surface morphology of the samples was investigated using AFM and shown in Figure 2. The image (micrograph) is taken over scale of 2 x 2 µm². It is observed that particles on the surface are irregular and inhomogeneous nature, with some voids which arises from the aggregation of grains due to the movement of grain boundaries [16]. The root mean square (rms) of the film surface roughness is 0.206 nm, the surface of ZnO film becomes smoother again. The higher sensitivity results from an increase in the roughness of the sensing film [17]. The grain value 89.93 nm is found to be larger than the grain size calculated from XRD data. This may be due to the aggregation of smaller grains which from bigger clusters on the surface of the films.

Figure 2: AFM Surface Morphology of ZnO Film (Scan Area 2 x 2 µm²) Deposited on Glass Substrat

Figure 3 Shows the transmission spectra in the wavelength range of 350 to 1000 nm. From the spectra, it is clear that film exhibit a transmission of about 85% in the visible range. Transmission however falls very sharply in the UV region due to onset of fundamental absorption. The optical transmittance of film is known to depend strongly on its surface.
morbidity [16].

The optical energy bandgap $E_g$ of the films were derived assuming a direct transition between the edges of the valence and the conduction band, using the tauc relationship as follows [18].

$$(\alpha \nu) = A(\nu - E_g)^n$$

Where $\alpha$ is the absorption coefficient, $A$ is a constant, $h$ is planck’s constant, $\nu$ is the photon frequency, the value of $n$ is 1/2 or 2 depending on presence of the direct and indirect allowed transitions. Figure 4. Shows the plot of $(\alpha \nu)^2$ on the y-axis versus photon energy ($h\nu$) on the x-axis gives the value of band gap $E_g$. An extrapolation of the linear part of the above plot $(\alpha \nu)^2 = 0$ gives the energy gap value of ZnO film, which was found to be about (3.2 eV), at room temperature, Which is agreement with Shingo et al [19].

Figure 3: Optical Transmittance Spectra of ZnO Thin Film on the Glass Substrate

However, the band-edge of ZnO nano particle was blue-shifted by quantum confinement effect.

Figure 4: Plots of $(\alpha \nu)^2$ versus $h\nu$ of ZnO Thin Film on the Glass Substrate
For gas sensing was used a vacuum–tight stainless steel cylindrical test chamber of diameter 21.8 cm and of height 16.4 cm with the bottom base made removable and of O–ring sealed. The sensor was inserted in the central portion of the cylinder with a 6 V bias voltage was applied across the films. The gas sensitivity tests at room temperature by introducing 2% H₂: air mixing volume ratio show no variation on the film resistance, the increase in the operation temperature leads to an improvement of the films sensitivity. Figure 5. It is seen that the film maximum conductance goes through a maximum on changing Temperature, with the best operating temperature at around 300°C. The maximum peak values at certain temperature called optimal temperature and then decreases with further increase in temperature. The increase of conductance (the left of the maximum) results from an increase in the rate of surface reaction of the target gas, while the decrease of conductance (the right side) results from a decrease in the utility of the gas sensing layer. At the maximum conductance (response),

\[ S = \frac{(R_A - R_g)}{R_A} \]  

(4)

Where, \( R_A \) is the resistance of the film in the air and \( R_g \) is the resistance of the film under exposed gas. It is evident from the figure that the maximum value of sensitivity is (64.65%) at 300°C with a fast response time of 6s and a baseline recovery time of 57s.

**Figure 5: The Variation of Sensitivity with the Operating Temperature of ZnO Gas Sensors with 2% H₂: Air Mixing Volume Ratio and 6 Volt Bias Voltage**

The target gas molecules have optimum penetration depth into the gas sensing grain i.e., optimum reactivity for diffusion in the whole sensing layer, as well as for exerting sufficiently large interaction with surface. This explains the correlations between conductance or sensitivity and temperature take a volcano shape for semiconductor gas sensors [20]. Figure 6. Shows that the gas sensing characteristics of the as-sprayed ZnO films are carried out for H₂ reducing gas which was kept constant at 2% in atmospheric air with different operating temperatures. The sensitivity \( S \) of the sensor was calculated after the response had reached steady state condition by using equation [3].

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The response time was defined as the time taken for sensor to attain 90% of maximum change in resistance or conductance upon exposure to H₂. The time taken by the sensors to get back 90% of original resistance or conductance is the recovery time, \( T_{\text{rec}} = |t_{\text{test}} - t_{\text{rest}}| \) [21].

![Figure 6: The Variation of Sensitivity versus Time at Different Operating Temperature of ZnO Gas Sensors with 2% H₂: Air Mixing Volume Ratio and 6 Volt Bias Voltage](image_url)

The gas sensing mechanism depends on the surface reaction between chemisorbed oxygen and reducing gases. Adsorption of O₂ on ZnO films the oxygen molecules extracts electrons from the conduction band to form oxygen ions. That may lead to the formation of an electron depletion region near surface, which can greatly increase the resistance due to the decrease of net carrier density. In the presence of a reducing gas as H₂ a chemical reaction between gas molecules and negatively charged adsorbed oxygen species \( O^-, O^{2-} \) leads to electron transfer back into the surface, the released electrons will reduce the thickness of the depletion region, and decrease the resistance of the semiconductors. The fundamental sensing mechanism of metal–oxide based gas sensor relies upon this change in electrical conductivity in ambient gases. These processes are generically expressed by the reactions below [22].

\[
\frac{1}{2} O_2 (g) + e^- (cb) \leftrightarrow O^- (ad) \tag{5}
\]

\[ H_2 (g) + O^- (ad) \leftrightarrow e^- + H_2O (g) \tag{6} \]

Figure 7 shows the response of ZnO thin film towards hydrogen gas of different mixing ratios has been explored. It is apparent from figure, the sensor current to hydrogen gas increases linearly with H₂ test gas mixing ratio. The sensitivity tends to saturate in the high gas concentration. This may be due to a saturation of adsorption of H₂ atoms at the Al electrode / ZnO nanofilm interface and lack of adsorbed oxygen ions at the nanofilm surface to react with gas molecules [23]. The variation of sensor sensitivity S, with test mixing ratio is illustrated in figure 8. The figure displays that the maximum sensitivity obtained is 58.55% at 3% H₂ gas concentration.
CONCLUSIONS

ZnO thin films were successfully synthesized by chemical spray pyrolysis. The XRD studies revealed the formation of nanocrystalline in the hexagonal wurtzite phase and presents a preferential orientation along the c-axis indicated to the plane (002). AFM investigations that the average grain size is found to be larger than the grain size calculated from XRD data. This may be due to the aggregation of smaller grains which from bigger clusters on the surface of the films. The hydrogen gas sensing results show the sensitivity of the films increases with temperature, reaches a maximum value at 300°C and then decreases.

ACKNOWLEDGMENTS

The author would like to thank the members of Material Physics & Chemistry Research Establishment labs at the Ministry of Science and Technology of Iraq.

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