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Structural, Morphological, Optical and Hydrogen Gas Sensing Properties of ZnO Thin Film

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Abstract: ***The objective of this study is to improve the hydrogen gas detection capabilities of thin films of zinc oxide (ZnO). The sol - gel method was employed to synthesis ZnO thin films, which were then manufactured using the spin coating technique. These films were subsequently analyzed using X - ray diffraction (XRD), Scanning electron microscopy (SEM), AFM, and UV - Vis spectroscopy to assess their structural, morphological, and optical features. The gas sensing performance was assessed by subjecting the films to varied quantities of hydrogen gas. The gas sensing behavior was identified by observing the resistance change following exposure to hydrogen gas, using computer - controlled, domestically built hydrogen gas sensing equipment.***

Keywords: ZnO, XRD, SEM, AFM, and hydrogen gas sensor

1. Introduction

ZnO is one of the most studied materials now being used and investigated as a potential material for a variety of applications. ZnO is one of the most important metal oxides at room temperature. ZnO is an inorganic compound that is white, powdery, and insoluble in water. It is found as the zincite mineral on the earth's surface [1, 2]. It's usually found in powder form in paints, ointments, lubricants, batteries, rubber, cosmetics, etc [3, 4]. One - dimensional nanostructures have a large aspect ratio and surface area, allowing electrons to conduct directly. ZnO has a bandgap of 3.37 eV and a high exciton binding energy of 60 meV. ZnO has hexagonal wurtzite structure. Because of its non - stoichiometric defected structure ZnO has electrical properties that vary with chemical composition. ZnO has traditional n - type semiconductor properties [5, 6]. ZnO is a piezoelectric material with a wide band gap. Because of these qualities, ZnO has gained a lot of attention for its potential applications in electrical and optoelectronic systems, sparking a lot of interest in the previous 15 years. Because of its low cost and ease of preparation, ZnO is one of the most widely studied metal oxides for gas sensing applications [7, 8]. Several deposition methods have been reported to deposit ZnO on substrates, including radio frequency (RF) sputtering [9], Pulse laser deposition (PLD) [10], Sol - gel method [11].

For detailed structural analysis, the prepared samples were characterized using XRD, SEM, AFM and Uv - Vis. We intended to investigate the impact of ZnO thin film on gas sensing properties in this study. Furthermore, the ZnO was utilized as a gas sensor to sense the gases like H_2, NO_2, SO_2, and methanol. The ZnO thin film was found to be good gas sensor for H_2 gases.

2. Experimental Procedure

The creation of an aqueous Zinc Oxide, solution 2M zinc acetate dehydrate dissolved in the 2 - Methoxy Ethanol and HCL. Subsequently, Mono Ethanolamine (MEA) was incrementally introduced into the solution as a stabilizing agent clear solution during a 3.5 hour period at 65°C. Then the solution was put onto the pre - cleared glass substrate, which was then spun for 40 seconds at room temperature at 2500 rpm. The solvent was then removed from the films by drying them over a hot plate for 10 minutes at 105 °C followed the procedure of spin coating deposition, until the necessary film thickness for processing had been obtained, the process of drying were repeated. The generated multilayered ZnO films were annealed in muffle furnace for about 1.30 hours at temperature 650°C.

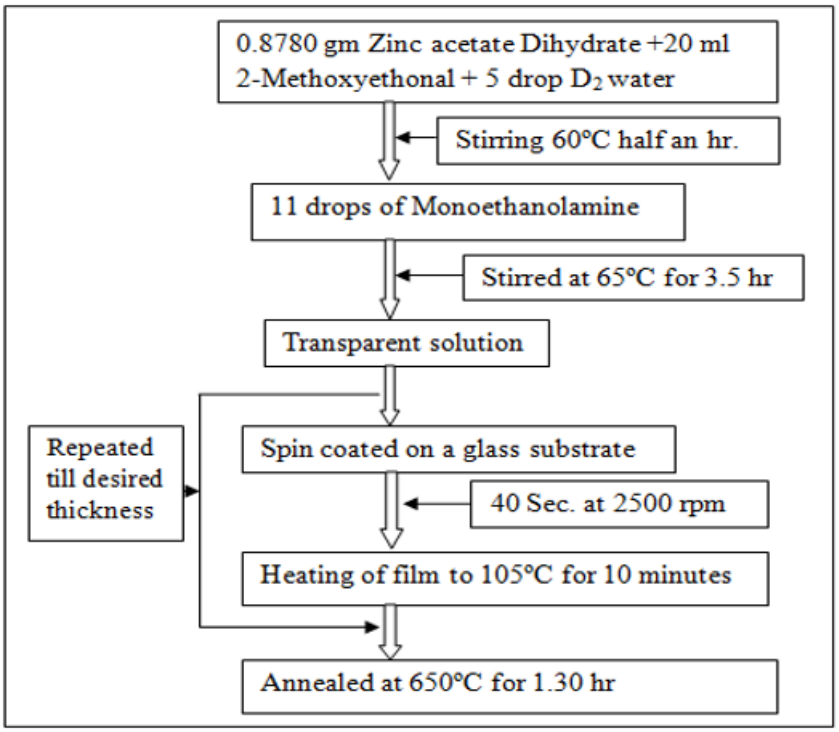

Figure 1: Flow chart for ZnO thin films deposition procedure

3. Structural Properties

3.1 XRD analysis

Fig. 2 depicts the XRD pattern of ZnO, which confirms the formation of hexagonal crystal lattice zinc oxide based on the obtained XRD data. We characterized all the prepared materials using X - ray diffraction spectroscopy with a Braggs scanning angle of 20 - 70°. The MoKα_1 radiations having wavelength 1.54 A^0 were used to produce the X - rays. Compare picks with JCPDS card no.00 - 036 - 1451.

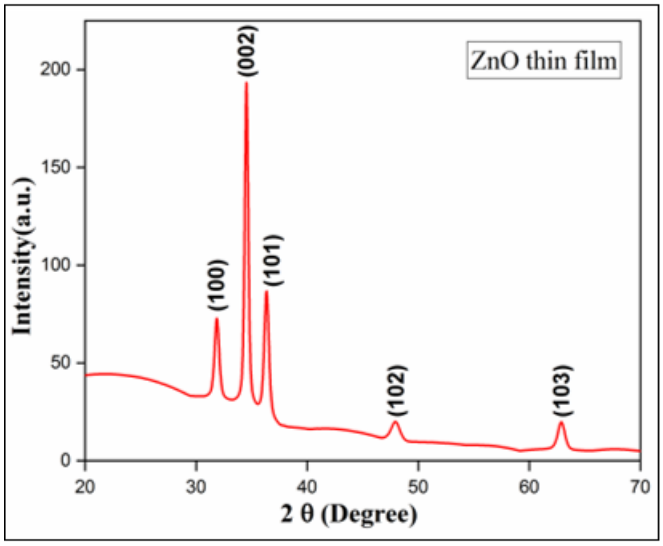

Figure 2: XRD pattern for Zinc Oxide thin films

The XRD of Zinc Oxide shown in fig.2, samples exhibited varying diffraction peak intensities. This indicates strong orientation peak of (002) in XRD pattern and other peaks (100), (101), (102) and (103) also belongs to Zinc Oxide. The difference in intensity of the diffraction peak might indicate the difference in crystal size.

The diffraction peak was estimated from the FWHM of (002) using the Scherrer formula to understand the crystalline ZnO particles. [12]:

$$d=0.9\lambda/\beta cos\theta \quad \ldots\ldots\ldots . (1)$$

Where λ denotes the x - ray wavelength of 1.54 Å, θ represents the Bragg diffraction angle of the (002) peak, and β signifies the full - width at half - maximum (FWHM) of θ (002) at around 34.5069, respectively.

Table 1: The XRD Table of zinc oxide thin films.

Pos. [°2Th.]	Height	FWHM [°2Th.]	d - Spacing (A°)
31.8419	28.30	0.4723	2.81045
34.5069	116.48	0.3542	2.59926
36.3139	44.47	0.4723	2.47396
47.9165	7.03	0.9446	1.89853
62.8289	10.04	0.7085	1.47909

Table 1 shows the peak position with peak height, FWHM, and d - spacing values.

4. Surface Morphology Properties

4.1 SEM Analysis

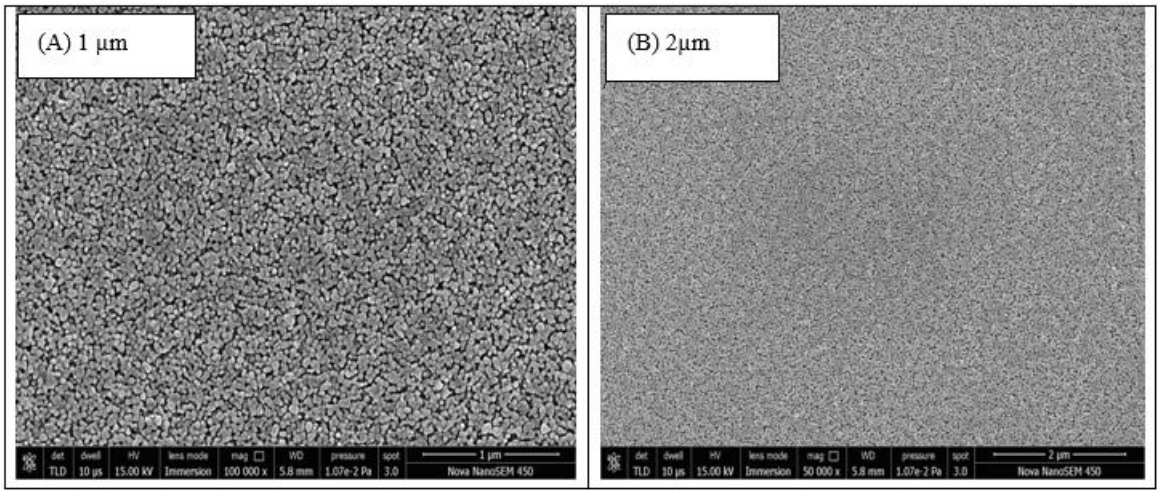

Figure 3: SEM pictures for ZnO Thin film

Figure 3, presents SEM images of the surface of ZnO thin films that were prepared using a spin - coating technique at 2500 rpm, followed by a preheating step at 105 ℃ for 10 minutes and a post - heating process at 650 ℃ for 1.5 hours.

The examination of surface morphology in ZnO thin films is essential because of its considerable influence on the electrical and optical properties of optoelectronic devices. This is a favorable condition for gas sensors, as larger surface areas provide a larger reason for their use. The average value of the crystalline size 1µm and 2µm is 122.885 nm and 142.792 nm, respectively for ZnO thin film.

4.2 AFM Analysis

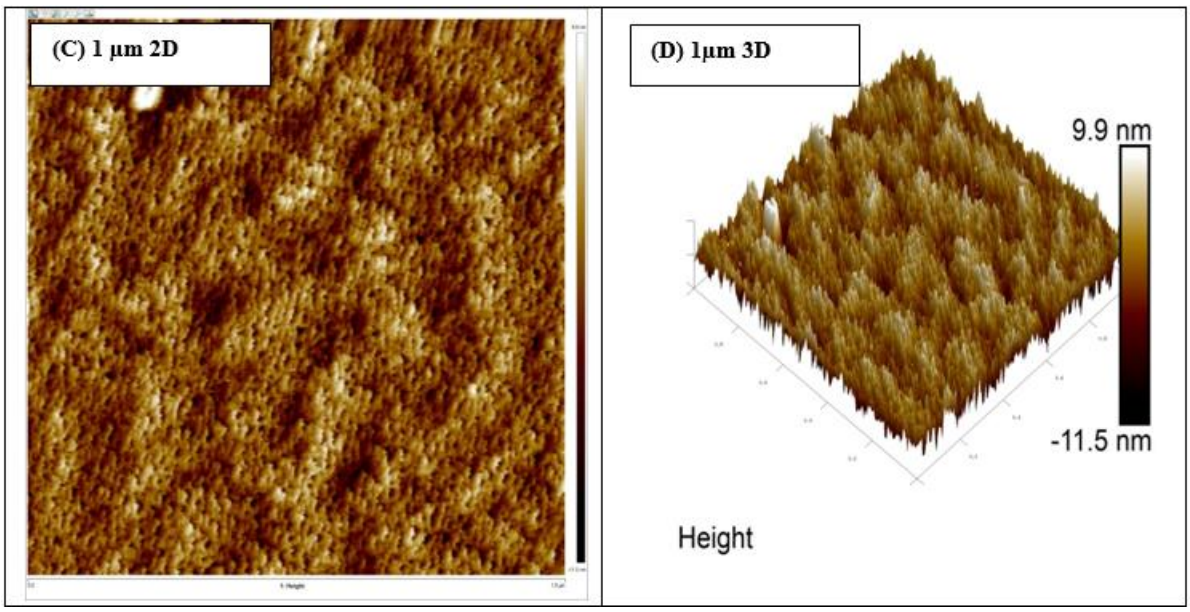

Figure 4: AFM images of ZnO thin film annealed at 650 ºC.

Surface morphology of ZnO films annealed at 650 ºC was shown in Figure 4. The films generated through spin coating exhibit homogeneity, as demonstrated by AFM images in both 2D and 3D captured at 1µm. The pictures were acquired by atomic force microscopy (AFM) measurement. We observed that as the annealing temperature increased, the ZnO films' surface morphology and roughness also improved. The value of RMS roughness and Mean roughness are 289.6 nm, 270 nm respectively.

5. Optical Properties

5.1 UV - Visible spectroscope

This part specifies all the foundations of mathematics for optical constants using UV - Vis measurements. The Famous Tauc formula is applied to calculate the energy band gap value:

$$(\alpha h\nu)^2 = A(h\nu - Eg)^n \quad \ldots\ldots (2)$$

where n is the index density of the states with A, h and v as the absorption Constant, Plank constant and Frequency respectively of incoming light and Eg is the energy gap.

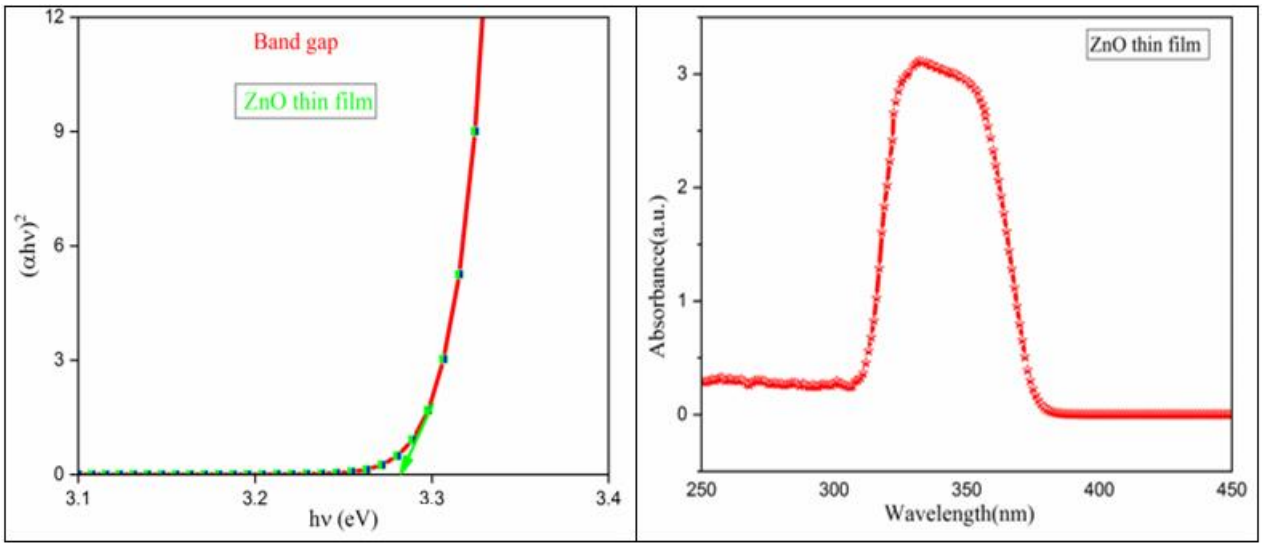

Figure 5: Absorbance and Band gap of Zinc Oxide Thin film

According to Fig.5, ZnO thin film, the absorption spectra rises with increasing wavelength and this Fig. Depicts the relation between $(\alpha hv)^2$ and hv, where hv is the energy of the incident photon and α represents the optical absorption coefficients. The band gap determined using Eq. (2) was 3.28 eV for ZnO thin film. The ZnO thin films observed a band gap, seen in Fig.5. [13].

Hydrogen (H_2) sensing mechanism -

Gas sensors were developed using figure type Cu - integrated electrodes with a width and gap of 0.5 mm, which were applied to epoxy glass substrates. Thin films of sensitive materials, such as ZnO, were applied to the substrates using the spin coating technique at a rotation speed of 2500 rpm. The prepared sensors were strategically placed within a meticulously designed gas sensing chamber. Two high - quality copper wires were attached to an LCR meter (Aplab - MT 4080D) following their application to the sensor electrodes with silver paste.

This enabled the observation of the sensing signal through the measurement of resistance changes in the sensitive thin film upon exposure to hydrogen gas at concentrations between 0 to 2500 ppm. To record the I - V curves and resistance variations, we used a Keithley electrometer in conjunction with the Aplab - MT 4080D LCR meter. Following extended exposure to hydrogen gas, the ZnO - based sensing films showed remarkable stability and repeatability as gas sensors, displaying a reliable response pattern.

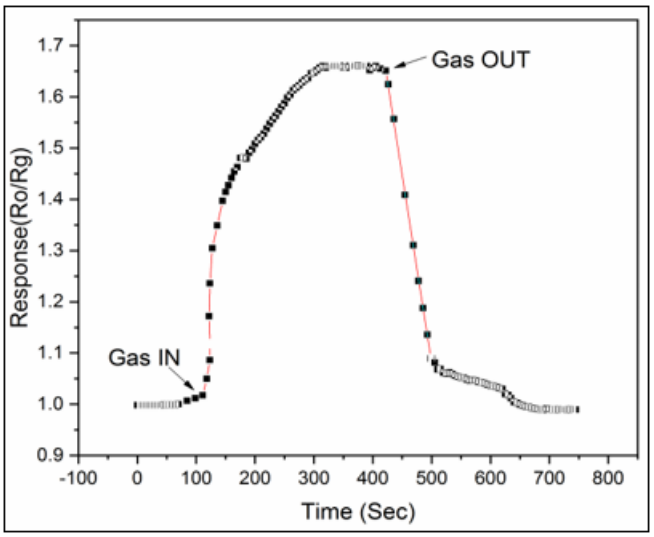

Figure 6: Response and Time - based sensors after exposure to H_2 gas for ZnO Thin film

We observed that the resistance of the sensing films varied when exposed to hydrogen or air, indicating their n - type semiconductor behavior. The sensing response to hydrogen gas was calculated using the following equation:

Response = R_o/R_g

Here:

- R_o is the initial resistance of the sensing film
- R_g is the resistance of the sensor when exposed to hydrogen gas

The calculated maximum response for hydrogen gas at room temperature was ~1.66 for ZnO thin film (Figure 6).

The transient time, an essential parameter in sensing technology, was established at 210 seconds to attain the optimal response. Following exposure to hydrogen gas, the gas sensor's initial state was restored by purging the chamber with air. [14, 15].

After an extended duration of hydrogen exposure, the developed sensor exhibited a stable response magnitude, highlighting its dependability and appropriateness for H_2 gas

detection at room temperature. The prepared sensor consistently exhibited a notable response throughout a prolonged exposure to hydrogen, underscoring its dependability and appropriateness for detecting H_2 gas at ambient temperature.

6. Conclusions

Sol - gel was used to create ZnO thin films, which were then spin - coated on a glass substrate. The influences of annealing treatment on furnaces effect on structural, morphological, and optical properties of ZnO thin films were investigated for gas sensing properties. XRD studies discovered the hexagonal structure of prepared analyzed ZnO thin film.

According to the SEM image the calculated average value of the crystalline size 1µm and 2µm were 122.885 nm and 142.792 nm, respectively for ZnO thin film. By AFM image we observed the value of RMS roughness and Mean roughness were 289.6 nm, 270 nm respectively. The band gap values for all produced film was obtained to be 3.28 eV for ZnO thin film. The determined peak response for hydrogen gas at ambient temperature was ~1.66 for ZnO thin films.

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References

[1] Q. A. Drmosh, Z. H. Yamani (2016). Hydrogen sensing properties of sputtered ZnOmfilms decorated with Pt nanoparticles, Ceram. Int.42 12378e12384.
[2] Bagul, V. R., Bhagure, G. R., Ahire, S. A., Patil, A. V., Adole, V. A., & Koli, P. B. (2021). Fabrication, characterization and exploration of cobalt (II) ion doped, modified zinc oxide thick film sensor for gas sensing characteristics of some pernicious gases. *Journal of the Indian Chemical Society*, *98* (11), 100187.
[3] Kim, Kyu - Bong & Kim, Young & Lim, Seong & Roh, Taehyun & Bang, Du & Choi, Seul & Duck Soo, Lim & Kim, Yeon & Baek, Seol - Hwa & Kim, Min - Kook & Seo, Hyo - Seon & Kim, Min - Hwa & Kim, Hyung & Lee, Joo & Kacew, Sam & Lee, Byung. (2017). Risk assessment of zinc oxide, a cosmetic ingredient used as a UV filter of sunscreens. Journal of Toxicology and Environmental Health, Part B.20.155 - 182.
[4] Restelatto, D., Bortoluz, J., Sartori, P., Guerra, N. B., Cid, C. C., Cruz, R. C., Gately, N. M., Devine, D. M., Giovanela, M., Roesch - Ely, M., & Crespo, J. S. (2024). Cosmetic gloves from natural rubber latex for upper limb prostheses: Preparation and physicochemical, mechanical and biological characterization. *Biomedical Engineering Advances*, *7*, 100126.
[5] Sonali, S., Jena, I., & Rout, S. K. (2019). A comparative study of synthesis of ZnO nano particles: Hydrothermal and modified combustion routes. *Materials Today: Proceedings*, *33*, 4966 - 4970.
[6] N. Lavanya, C. Sekar, E. Fazio, F. Neri (2017). Development of a selective hydrogen leak sensor based on chemically doped SnO2 for automotive applications, Int. J. Hydrogen Energy 42 10645e10655.
[7] Xu, X., Chen, Y., Zhang, G., Bian, H., Zhao, M., & Ma, S. (2018). Optical properties and the band - gap variation in diverse Zn1 - xSnxO nanostructures. *Superlattices and Microstructures*, *123*, 349 - 357.
[8] Bhati, V. S., Hojamberdiev, M., & Kumar, M. (2020). Enhanced sensing performance of ZnO nanostructures - based gas sensors: A review. *Energy Reports*, *6*, 46 - 62.
[9] Tchenka, Abdelaziz & Agdad, Abdelali & Samba Vall, Cheikh & Hnawi, Salma & Narjis, Abdelfattah & Nkhaili, Lahcen & Ibnouelghazi, E. & Ech - chamikh, Elmaati. (2021). Effect of RF Sputtering Power and Deposition Time on Optical and Electrical Properties of Indium Tin Oxide Thin Film. Advances in Materials Science and Engineering.
[10] Tsoutsouva, Maria & Panagopoulos, C. & Papadimitriou, D. & Fasaki, Ioanna & Kompitsas, Michael. (2011). ZnO thin films prepared by pulsed laser deposition. Materials Science and Engineering B - Advanced Functional Solid - State Materials.176.480 - 483.
[11] Kamalasanan, M., & Chandra, S. (1996). Sol - gel synthesis of ZnO thin films. *Thin Solid Films*, *288* (1 - 2), 112 - 115.
[12] Bhardwaj, R., Bharti, A., Singh, J. P., Chae, K. H., Goyal, N., & Gautam, S. (2018). Structural and electronic investigation of ZnO nanostructures synthesized under different environments. *Heliyon*, *4* (4), e00594.
[13] Terán, C. L., Calderón, J. A., Quiroz, H. P., & Dussan, A. (2021). Optical properties and bipolar resistive switching of ZnO thin films deposited via DC magnetron sputtering. *Chinese Journal of Physics*, *74*, 1 - 8.
[14] Adachi, Y., Watanable, K., Stito, N., and Suzuki, T (2016). Gas Sensing properties of C - axis - oriented Al - incroporatedZnO films epitaxially grown on (112 - 0) sapphire substrates using pulsed laser deposition. Journal of the Ceramic socity of Japan 124 [6], 668 - 672.
[15] Al - Salman, H. S., Abdullah, M., & Al - Hardan, N. (2013). ZnO thin film nanostructures for hydrogen gas sensing applications. *Ceramics International*, *39*, S447 - S450.