Study the Sensing Properties of Nano-Powders Zinc Oxide Films Towards Ethanol Vapor

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Abstract
Thick Films have been prepared by the chemical painting method from Zinc Oxide nano powder as the source compound, which are prepared by milling in a high energy ball mill for various spans of time (1-18h) on cleaned glass substrates under limited thermal conditions. The temperature of the films has been changed from 50°C to 350°C. The films have been investigated for their sensing properties relating to 100ppm methanol vapor adsorption, using the (I–V) characteristics. The effect of the grain size and the thermal conditions on the sensing properties of the ZnO thick films to methanol vapor adsorption, as well as the correlations between The electrical conductivity of the ZnO thick films and the grain size of the material films are reported. The response time for films which have particle size about 34.7nm is defined at 300°C.
Keywords: Zinc Oxide (ZnO), Methanol Vapor, Sensing properties.

Introduction:
The science of nanotechnology emphasis on the basic principles for molecules and compounds that has the dimension within or below 100 nm range, therefore this science precisely govern the production of materials through the control of the reacting molecules in the reaction and utilize these molecules to produce specific products or materials, the nano-material can be accordingly classified into three groups; one-dimension 1D, two-dimension 2D, and three-dimension 3D, then these groups can be farther assigned accordingly into several different shapes depending on the preparation method. They can be prepared in the shape of this films or fibres or wires or rods or particles (thin powder).The nanotechnology has created a huge advancement in the clean production technology represented by the reduction of industrial effluents and consequently the removal of industrial pollutants, and the efficient use of the available economical resources. Research groups have concentrated on how to use the nanotechnology in the electronic industry, agriculture, medicine, pharmaceutical industries, treatment of waste water and the environment in general.[1-2].The sensors are considered as an important result of the nanotechnology, as the use of nano-materials rapidly become one of the major materials used in research centres interested in gas sensors. [3-4].The nano-particles are considered of metallic oxides such as SnO_2 , ZnO, TiO_2 , and WO_3 that posses the properties of semi-transition metals, these materials are commonly and symbolically used in the manufacture of nano layers of specific sensors for monitoring and recording the gases in air, which work in temperatures between 200 – 400 C^0.

The sensors made from semi-transition metal oxides were applied in many fields such as protective layers, solar filters, chemical preventive/protection layers, and chemical sensors, because of their important characteristics [5], relative high sensitivity, credibility, good chemical stability, low production cost, minute size, strong structure, low decimation of energy, long period of stability, their limit of gas detection could reach parts per million ppm. Additionally, the possibility of manufacturing these sensors in a way that several kinds of gases can be detected at the same time[6].Thus huge benefits can be gained in studying the properties of sensitivity for these films, particularly its sensitivity to vapours of organic compounds, it is necessary and important to determine the exact contents of these vapours in various environments for application in several industrial processes. For these reasons scientists paid more attention in studying and manufacturing gas sensors from the semi-transition metal oxides. In 2009, Jin Huang et al, presented a detailed report on the recent advancements in gas sensors from semi-transition metal oxides that have 1 D nanostructures, and they referred to several challenges that might face the practical application of these sensors in the future [7]. Afterwards in 2011, A Khorsand et al synthesize nano particulates of ZnO using the Sol-Gel technique, starting with Zinc Acetate as a basic material and acetic acid, and the nano particulates are formed at 650 C^0 or 750 C^0 for 1 hour, the formed nano particulates were characterized using TEM and XRD techniques, the results from XRD indicated that the sample product was a crystalline with Wurtzite phase, and Hexagonal symmetrical structure, also the High Amplification Electron Microscope showed that the particulate were 1 D nano crystal with a possibility circular cross-section. Also, images of the TEM have shown that the formed nano particulates at 750 C^0 the mean diameter for the particulate volume was around 2 nm ± 20 with uniform potentials across the particulates [8]. Consequently these sensors appear to be more promising devices amongst the gas sensors, however despite all the advantages of these group of sensors they are not studied well enough.

Chemical Sensors:
The chemical sensors are known as devices that transfer chemical state into electrical signal, and the chemical

states here describe the concentrations or molecular vapour pressures for the ions or the molecules in the gaseous or liquid or solid phase, basically the sensor can be considered as black box, and its significance is the relation between the input signal and the output signal [9].

Gas Sensing Mechanism:
Gas sensors depend on adsorption reactions and chemical or physical desorption, and photo absorption reactions, and chemical reactions that occur on the surface or within the sensor material. These reactions lead to specific physical changes in the sensor which can be analyzed. This identification process can be carried out using several different principles such as conductivity, electrical polarography, electrochemical activity, photo and magnetic properties, and electrical isolation properties.

Sensor Operating Parameters:
Sensitivity, Response Time, Recovery Time, Low Detection Limit, Operation Temperature. [10].

Factors Affecting the Sensitivity:
chemical structure , surface substitution by using particles of rare metals, moisture , temperature . [10]

Aim of Research:
The aims of this study is to prepare thick films of nano zinc oxide ZnO powder, this is done using the chemical plating method on glass surfaces, and studying the current – voltage I-V characteristics in air and in the presence of methanol vapour using KEITHLEY 237 device. Also, studying the effects of changing the conditions of the applied heat, and the particulate size of the prepared film material on its sensing properties towards the methanol vapour, moreover the activation energy of the films and the response time to give a significance change in I – V characteristics were determined.

Materials & Methodology:
Methanol , Zinc Oxide .

Research Methodology:
Preparation:
In a previous study, the preparation of nano-powder was explained in details using the high energy ball grinder [14], this nano-powder was used in the preparation of the thick films in this present study. An appropriate amount of the nano-zinc oxide powder was mixed with distilled water to form a dough, which was then placed on a clean glass sample holders as thick films with 1 cm x 2 cm dimension, silver electrodes were immersed in the thick films and heated to approximately 30 C^0. This thick films preparation method was chosen to prevent any change in the crystalline structure of zinc oxide powders [15]. Afterwards the films were left to dry in the air. For the measurements of electrical resistance, to adopt a locally made gas measuring chamber was used (GS-Cha1-L16-F3), this chamber is dark, that can control the light intensity, and can perform under vacuum up to 10^{-3} mbar using a rotary pump, it basically works by expelling noble gases and relatively heavy gases, also types and pressures of gases entering the chamber can be controlled, this chamber is connected to a device for measuring the current-voltage characteristic curves – KEITHLEY 237, which can measure a current sensitivity in the order of pico ampere (pA), also connected with a heating device for the films holders, the resistance of the thick films were measured by the correct connection was checked, and showed that it was ohmic by the measurement of I – V. The heating couple was connected to the thick films holders to control and observe the process during the measurement steps. The sensors resistance was monitored in the presence of air (R_{air}), and 100 ppm methanol vapour (R_{gas}), and the results were recorded in a computer for analysis.

Figure (1) shows a schematic diagram for the electrical measuring device (curve characteristics), and gas chamber with holders and heaters..

Table (1) KEITHLEY 237 device applied parameters during the study of the Current – Voltage characteristics.

Start Value (V) =	-100
Stop Value (V) =	+100
Steps Count =	20
Current Limit (A) =	0.1
Time Interval (ms) =	500
Bias (v) =	0

Results & Discussion:

The study of the change in Current – Voltage characteristics for the prepared films from ZnO powder :

The sensitivity of these films to 100 ppm methanol vapour has been studied, by monitoring the change in the Current – Voltage characteristics of the films surfaces at different temperatures, a similar method was used to study the sensitivity for many nano-structure materials to humidity, gases, and vapours of other organic compounds by many groups [16].

166.47 nm Particulate Size Film (ungrind) with Temperature:

Figure (2) shows the effects of temperature change (50 – 350 C^0) on the Current – Voltage characteristics of the prepared film from ZnO powder having a particulate size 166.47 nm.

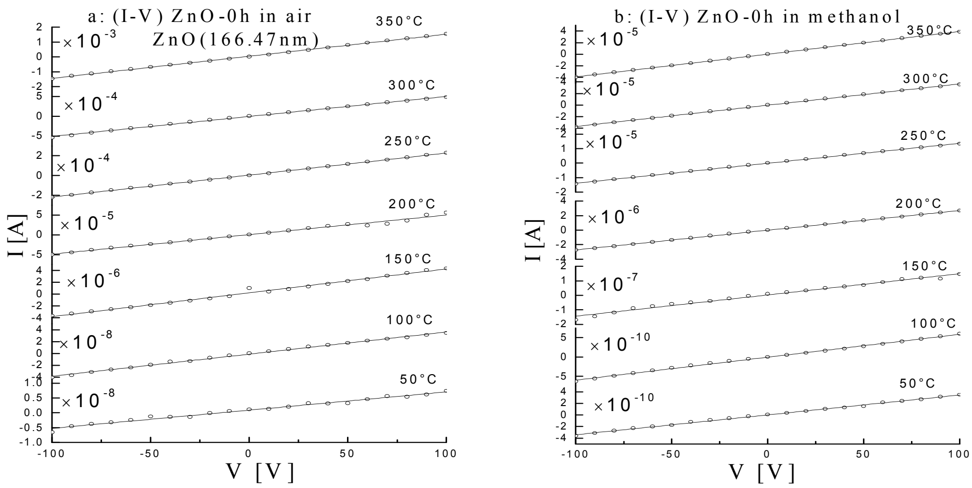

Figure (2) changing of I – V characteristics for ZnO film (166.47 nm) (a) in air (b) in atmosphere contains 100 ppm methanol vapour.

Particulate Size 34.7 nm Film (ground 15h) with Temperature

The sensitivity of this film to 100 ppm methanol vapour was studied.

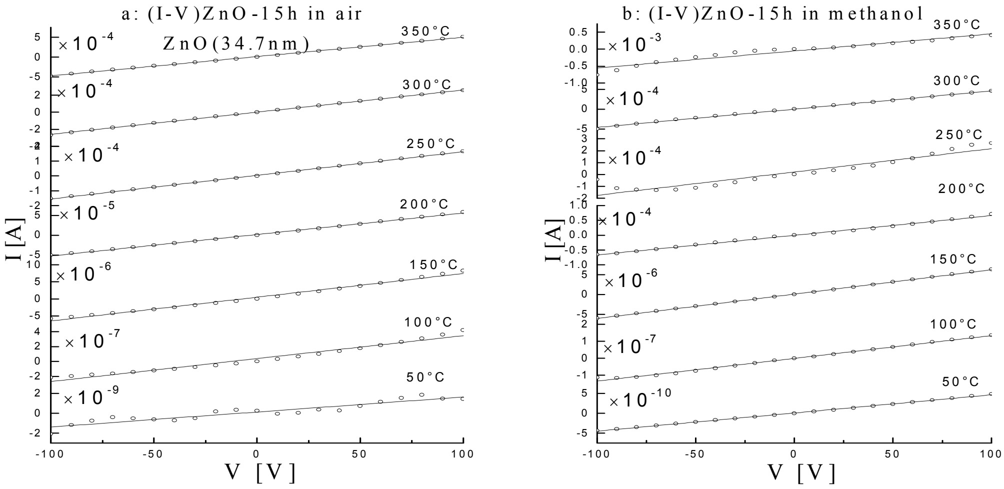

Figure (3) : changes in I – V characteristics for a ZnO film (34.7 nm) (a) in air (b) in an atmosphere containing 100 ppm methanol vapour.

Particulate Size 36.23 nm Film (ground 18h) with Temperature

The effects of different temperatures (50 – 350 C^0) on the I – V characteristics of the prepared film from ZnO powder having a particulate size of 36.23 nm was shown in Figure 4.

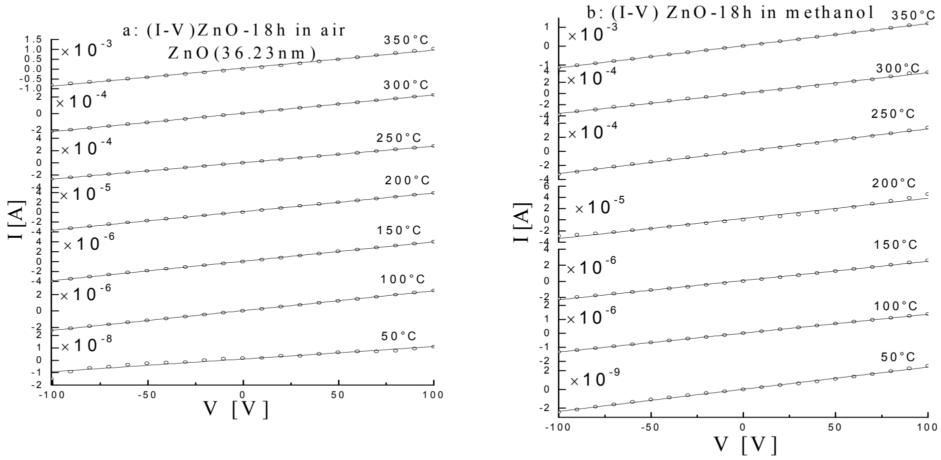

Figure (4) : changes in I – V characteristics for ZnO film (36.23 nm) (a) in air (b) in an atmosphere containing 100 ppm methanol vapour.

From the figures 2, 3, and 4 it can be seen that the I – V characteristics are clearly affected with the applied temperatures during the measurements in the presence of methanol vapour or without the methanol vapour (air). Also, that all these characteristics proceed in an ohmic behavior, and that as the temperature rises the intensity of the current increases, changing its values from parts in micro ampere μA at 50 C^0 to parts in mille ampere mA at 300 C^0.

From the characteristic curves, we can calculate the resistance for the three films in air and in the presence of methanol vapour, as shown in tables 2, 3, and 4.

Table 2 : resistance values of the ZnO film (166.47 nm) in air and in the presence of 100 ppm methanol vapour.

T[°C]	50	100	150	200	250	300	350
$R_{air}[\Omega]$	1.60E+10	2.68E+09	2.47E+07	2.00E+06	4.49E+05	1.97E+05	6.72E+04
$R_{gas}[\Omega]$	2.91E+11	1.69E+11	6.74E+08	3.68E+07	7.26E+06	2.73E+06	2.56E+06

Table 3 : resistance values of the ZnO film (34.7 nm) in air and in the presence of 100 ppm methanol vapour.

T[°C]	50	100	150	200	250	300	350
R_{air}[Ω]	5.83E+10	3.15E+08	1.42E+07	1.84E+06	6.28E+05	3.83E+05	2.05E+05
R_{gas}[Ω]	2.18E+11	7.42E+08	1.62E+07	1.50E+06	4.57E+05	2.16E+05	1.88E+05

Table 4 : resistance values of the ZnO film (36.23 nm) in air and in the presence of 100 ppm methanol vapour.

T[°C]	50	100	150	200	250	300	350
R_{air}[Ω]	9.21E+09	4.16E+07	2.52E+07	2.66E+06	3.74E+05	4.47E+05	1.09E+05
R_{gas}[Ω]	4.21E+10	7.42E+07	4.16E+07	2.74E+06	3.13E+05	2.74E+05	8.46E+04

Calculation of the ZnO Film Sensitivity Towards the Methanol Vapour

The calculation of the ZnO films sensitivity towards the methanol vapour by using the relation :

$$S = \frac{R_{air}}{R_{gas}} \times 100 \qquad (10,17)$$

R_{air} is the resistance of the film in the presence of air measured in Ω
R_{gas} is the resistance of the film in the presence of methanol vapour measured in Ω
S is the percentage sensitivity

Table 5: The sensitivity values for the three prepared ZnO films in the presence of 100 ppm methanol vapour with T

T[°C]	S[%]ZnO(166.47nm)	S[%]ZnO(34.7nm)	S[%]ZnO(36.23nm)
50	5.51	26.79	21.85
100	1.59	42.41	56.06
150	3.66	87.34	60.60
200	5.44	122.47	96.85
250	6.19	137.21	119.48
300	7.23	177.02	163.10
350	2.63	109.19	128.64

To explain the relation of the sensitivity of the prepared ZnO films with temperature, we draw figure 5.

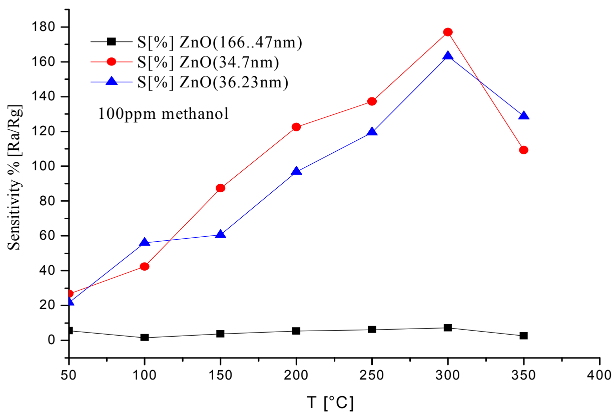

Figure 5 : Variation of the sensitivity for the three prepared ZnO films with the applied temperatures.

From figure 5, it can be seen that the sensitivity of the three prepared films in general are enhanced as the temperature is increased, this was due to the increase in the formation of self-deformations on the film surface initiated from the random expulsion of oxygen atoms , which led to the formation of oxygen holes, the expulsion of oxygen atoms increases and continue as the temperature rises, until the concentrations of the deformations reaches a maximum level at a specific temperature. Consequently the sensitivity increases, this was due to the positioning of the gas molecules in the oxygen holes on the surface of the semi-transition metal oxide film [18, 19].

Also it is observed from the previous figure that the film sensitivity of the 34.7 nm particulate size increases with the increase in temperature and reached a maximum value 177.0 % at 300 C^0, and then afterwards decreases as the temperature continue to increase above 300 C^0, which indicate that the efficient functioning temperature is 300 C^0, also for the film of 36.23 particulate size, where its maximum sensitivity reached 163.1 % at 300 C^0, and then decreased gradually as temperature increases above 300 C^0, also it can be seen that the sensitivity of the 166.7 nm particulate size film was very low. Therefore, temperature constitute an important factor in the metal oxides gas sensors, as the sensitivity increases and reaches its maximum limit at specific temperature, then decreased rapidly with increase in temperature, and these observations agrees with most previous studies in general [20].

To explain the effect of the particulate size of the film material on the sensitivity, a diagram of the change in sensitivity of the three ZnO films in the presence of methanol vapour virsus particulate size at 300 C^0 was drawn , see figure 6.

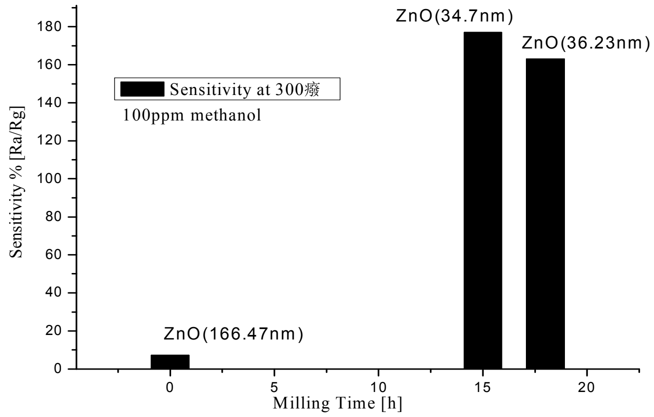

Figure 6 : Variation of the sensitivity of the three prepared films according to its particulate size from the milling time in hours.

It can be seen that the maximum sensitivity appears for the 34.7 nm particulate size film, these results indicate that every change in the nano-structure is responsible for the observed progress in the response of methanol vapour, and according to the study in reference [18], the minute particulate size plays an important role in the sensing properties of the prepared films, the smaller the film particulates the greater the deformation of the crystalline, in addition the crystalline acquires a large typical surface, which enables it to sense the gas much better.

Measurement of the Response Time for the 34.7 nm ZnO Film in the Presence of 100 ppm Methanol Vapour.

The response time for the sensitivity of the 34.7 nm ZnO film in the presence of 100 ppm methanol vapour was measured at 300 C^0, because it posses the maximum sensitivity at this temperature. This was done by measuring the film resistance every 10 seconds for a period of two minutes using KEITHLEY 614 ELECTROMETER device to follow the change in resistance, and the response time will be the required time to obtain a significant change in the film resistance in the presence of 100 ppm methanol vapour, and the results are shown in table 6.

Table 6 : Resistance values of the 34.7 nm ZnO film in the presence of 100 ppm methanol vapour.

T[Sec]	0	5	10	20	30	40	50
R[KΩ]	360	357	357	357	357	357	357.5
T[Sec]	60	70	80	90	100	110	120
R[KΩ]	358	358.5	359	359.5	360	360.5	360.5

A diagram was drawn to explain the variation in the electrical resistance for the 34.7 nm ZnO film in the presence of 100 ppm methanol vapour for a period of two minutes, see figure 7.

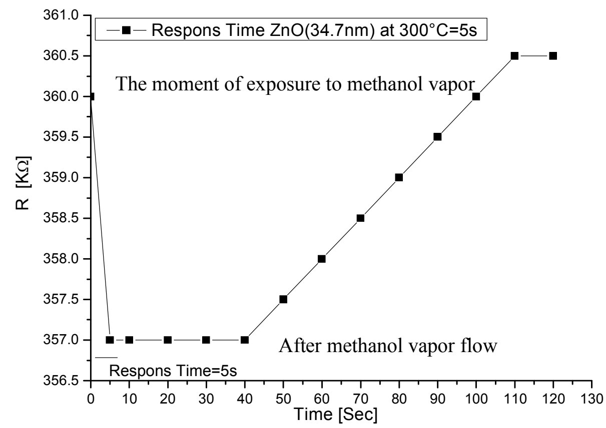

Figure 7 : Change in Electrical Resistance for the 34.7 nm ZnO film at 300 C^0, in the presence of 100 ppm methanol vapour.

As it can be seen in figure 7, there is a significant change of the film resistance from the start of the introduction of the 100 ppm methanol vapour at zero second, this was indicated by the sharp drop in the film resistance until it levels off after 5 seconds, therefore it can be concluded that the response time is 5 seconds.

Conclusion & Recommendation:

The sensitivity was studied by using the I – V characteristics for the prepared films using KEITHLEY 237 device it was found that the characteristics changes as the temperature changes during the measurements. The effects of changing the particulate size on the sensitivity was studied. It was found that the sensitivity towards the methanol vapour increases as the particulate size decreased. The sensitivity of the three films with different particulate sizes was compared at 300 C^0,. It was found that the 34.7 nm particulate size ZnO film has the greatest efficiency and ability to adsorb methanol vapour, and this was due the changes of the nano structures – acquired large surface area. It was concluded that the structure of the film material determined the properties of the prepared films, such as gas sensitivity and electrical conductance. The response time for the 34.7 nm particulate size ZnO film in the presence of 100 ppm methanol vapour at 300 C^0, was measured and found to be 5 seconds.

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