

Study of Effect Concentration of Ethanol Vapor on Sensing Properties of Nano Powders Zinc Oxide Films

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Abstract
The purpose of this research is study the effect concentration of ethanol vapor on Sensing Properties of nano powders Zinc Oxide thick films. So three thick films have been prepared by the chemical painting method from Zinc Oxide nano powders as the source compound their dimensions of particle about (166.47, 34.7, 36.23nm), nano powders of Zinc Oxide 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 sensitivity depends 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. .The films have been investigated for their sensing properties relating to 200ppm ethanol vapor adsorption using the (I–V) characteristics in air and in the presence of ethanol vapor using KEITHLEY 237 device .The temperature of the films has been changed from 50°C to 350°C we note improving in sensitivity of three films with increasing temperature until specific temperature degree, then we note that the film which dimensions 34.7nm has high sensitive among three films at 250°C .We note that improves the sensitivity of the film with an increased concentration and the operating temperature of film has decreased with increased concentration
Keywords: Zinc Oxide (ZnO), Ethanol Vapor, Sensing properties.

1.1. Nano Technology:

In the current materials science research, great emphasis has been placed on the nano materials in order to study the unique physical properties. The surface-to-bulk ratio for the nano materials is much greater than that for coarse materials, in nano materials, a large fraction of the atoms is present at the surface, and hence, the surface properties become paramount. Another important factor associated with the depth of charge region and the surface space is affected by the relation between gas adsorption and the particle size. These features of nano particles make the materials particularly good for their applications as gas sensors [1].

Nanotechnology studies the molecules and compounds with dimensions not more than 100 nanometer as a grain size and has an accurate control in producing these materials and in inner reaction to direct these molecules to get a desired substance.

Nanotechnology gets a huge antecedence as the most cleaned produced technology for decreasing the industrial garbage, less industrial pollution, and more efficiency in all of electronic, agricultural, medicine, water treatment, and environment industries[2,3].

Gas sensors considers as one of the best output of nanotechnology specially that made from metal oxide [4,5] for their properties like: sensitivity, working at high temperature (200-400°C), good chemical flexibility, low cost, small size, low energy desperation, low limit detection (a few of ppm), stability, in addition that we can make it to detect more than one gas at the same time[6], so, we find that it is important to study sensors and their sensitive properties for organic vapors which that is very important in many industrial fields[7]. 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 20 ± 2 nm with uniform potentials across the particulates [8].

1.2. Principal of sensors working:

The principal of sensors working depends on a variation of resistance or electrical conductivity for metal oxide when some of pollutant gas particles affection on it[9,10] . Gas sensors depend on physical or chemical adsorption and desorption reactions on the surface of the sensor material which caused some physical unique variation that is detected by series of several principals like conductivity, electrical polarization,….etc.

The aim of the research is to prepare thick films of ZnO nano powder by painting chemical method, and study of its I-V characteristics in air and in 200 ppm of ethanol vapor by using KEITHLEY 237, then comparative with its I-V characteristics in 100 ppm of ethanol vapor.

1.3. Materials:

Ethanol: a hydrocarbon belong to alcohol compounds, readily miscible with water, has the molecular formula C_2H_5OH. Zinc Oxide: white powder slightly bluish, turns yellow on heating, and returns to its original colour by cooling, it is a fluctuating oxide and overcome by its basic features, it decomposes in acid forming zinc salts also decomposes in alkaline to form zincates (ZnO_2^{2-})

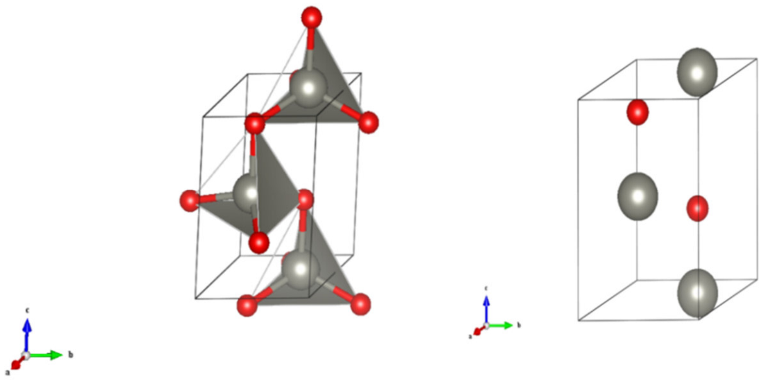


Figure 1: the crystal structure of zinc oxide.

2. Experimental Procedure:

2.1. Preparation of ZnO Nano-powders:

In a previous study, the preparation of nano-powder was explained in details using the high energy ball grinder [10], ZnO powders were milled by (Activator 2S, Russia) system during time from 1 to 18 h with step at 3 h. The milling conditions and the material compositions are summarized in Table.1.

Table 1. Milling conditions in the high energy ball mill.

Raw materials	Materials of jars & balls	Ball to powder weight ratio	Volumes of jars	Ball diameters	Jar speed	Disc speed
ZnO	WC	1:2	80[ml]	10[mm]	320 [rpm]	640[rpm]

2.2. Preparation of thick films:

Nano-powder was used in the preparation of the thick films in this present study We used painting chemical method to prepare thick films. 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 C0. This thick films preparation method was chosen to prevent any change in the crystalline structure of zinc oxide powders [17]. 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 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.

The following parameters which shown in the table (2) point to Parameters for KEITHLEY 237 for I-V Characteristics [10].

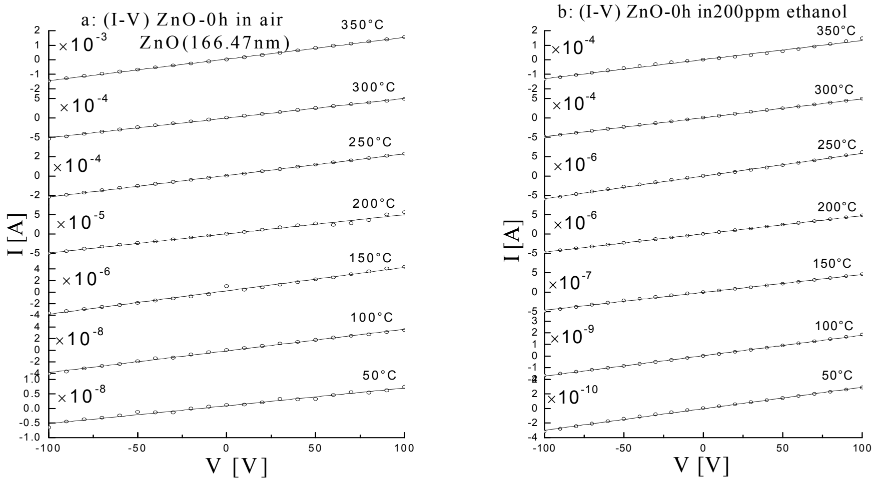
Table .2 Parameters for KEITHLEY 237 for I-V Characteristics

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

This way was used from the other for many materials to measure the sensitivity for humidity ,gases, and vapor for many organic solvents [12,13]. The I-V characteristics for each prepared film is studied in air and in 200 ppm of ethanol vapor at different temperature (50-350 °C) drawn as follows:

3. Results and Dissection :

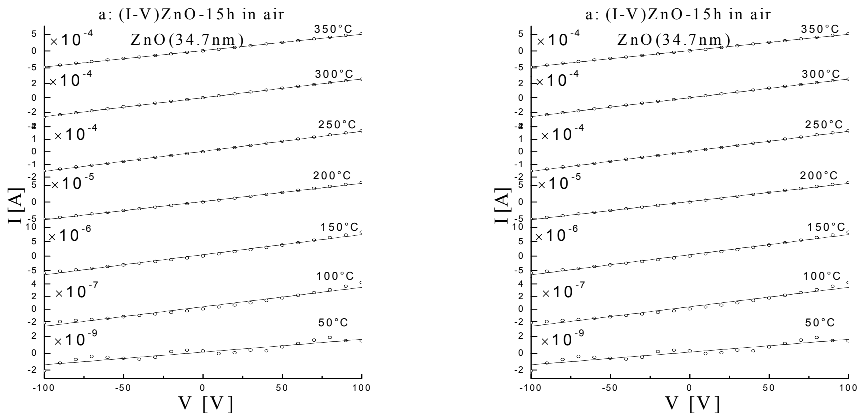
3.1.1. I-V characteristic for ZnO has granular size 166.47nm (before milling):



A B

Figure 2. I-V characteristic for ZnO has granular size 166.47nm
a: in air, b: in 200 ppm of ethanol vapor.

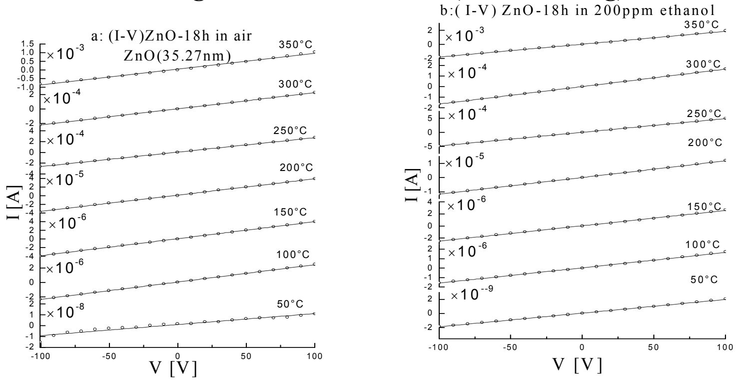
3.1.2. I-V characteristic for ZnO has granular size 34.7nm (at 15h milling):



a b

Figure 3. I-V characteristic for ZnO has granular size 34.7nm
a: in air, b: in 200 ppm of ethanol vapor

3.1.3. I-V characteristic for ZnO has granular size 36.23nm (at 18h milling):



a b

Figure 4. I-V characteristic for ZnO has granular size 36.23nm
a: in air, b: in 200 ppm of ethanol vapor

We notice from the previous figures that all thick films are affected by change of applied temperatures during the measurements, and have an ohmic resistance, as increasing the temperature as increasing the current from µA at 50°C to a few parts of mA at 350°C, and from these figures we can calculate the resistance in air and in 200 ppm of ethanol vapor as follows:

Table .3 Resistance for ZnO (166.47nm) in air and in 200 ppm of ethanol vapor

T[°C]	50	100	150	200	250	300	350
R_{air}[Ω]	1.60E+10	2.68E+09	2.47E+07	2.00E+06	4.49E+05	1.97E+05	6.72E+04
R_{gas}[Ω]	9.25E+11	4.65E+10	2.37E+08	1.16E+07	2.06E+06	8.67E+05	4.36E+05

Table .4 Resistance for ZnO (34.7 nm) in air and in 200 ppm of ethanol vapor

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]	3.16E+11	5.69E+08	1.05E+07	9.67E+05	2.10E+05	1.30E+05	9.61E+04

Table .5 Resistance for ZnO (36.23nm) in air and in 200 ppm of ethanol vapor

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]	3.49E+10	6.35E+07	2.47E+07	1.41E+06	1.59E+05	1.55E+05	5.73E+04

3.2. Calculating of Sensitivity for ZnO thick films toward Ethanol vapor:

We calculate the Sensitivity for ZnO thick films toward Ethanol vapor from the equation:

$$S = \frac{R_{air}}{R_{gas}} \times 100$$

so: R_{air}: Resistance for thin film in air (Ω)
R_{gas}: Resistance for thin film in 100 ppm of ethanol vapor (Ω)
S: Sensitivity %

Table .6 Sensitivity for ZnO thick films by change of temperature

T[°C]	S[%]ZnO(166.47nm)	S[%]ZnO(34.7nm)	S[%]ZnO(36.23nm)
50	1.73	18.46	26.38
100	5.76	55.30	65.50
150	10.41	135.57	102.03
200	17.26	190.51	188.72
250	21.74	299.23	234.87
300	22.75	295.47	288.32
350	15.41	213.29	189.77

When we draw the sensitivity as a function of temperature for three thick films (166.47, 34.7, 36.23nm) as follows:

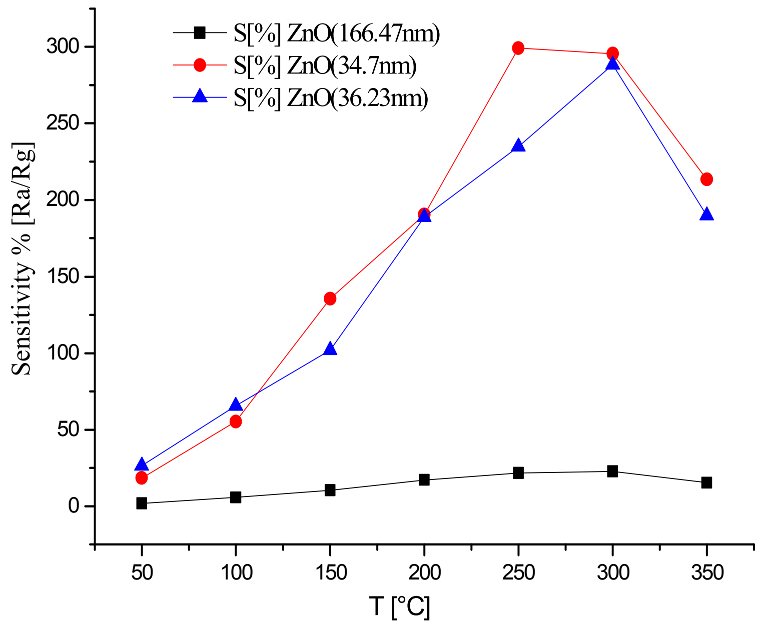


Figure 5. The sensitivity S =[(R_{air}/R_{gas})×100] to 200 ppm of ethanol as a function of temperature for three films of ZnO

We note from figure 5 improving in sensitivity of three films with increasing temperature until specific temperature degree due to increasing constitute of self-defects on the surface of the film which formed from the indiscriminate expulsion of oxygen which leads to formation of oxygen gaps that gas atoms can be stabilized place then by progressing and increasing of expulsion process with high temperature to get a maximum number of defects at a specific temperature degree that called critical temperature, which the sensitivity be as high as possible, this temperature degree can be called as an operating temperature for the sensor [15]. So the temperature is an important factor in gas sensors of semiconducting metal oxides, the sensitivity is increasing and arriving up to high limits at specific temperature degree then decreasing with increasing the temperature degree this agree with scientific paper [13,16], among these three films we show that the film which has the smallest granular size 34.7nm has a high sensitivity, so we can say that the responsible of the marked advance the sensitivity toward methanol vapor is the nano structure according to scientific paper [15].

3.3. Study Of The Effect Of Ethanol Vapor Concentration On The Sensitivity Properties Of ZnO Films Nanoparticles:

In previous study [17] we study the sensitivity properties of the ZnO thick films nano particles towards 100ppm of ethanol vapor and here we will make a comparison of the sensitivity properties of the film with a granular size 34.7nm towards 200ppm of ethanol vapor.

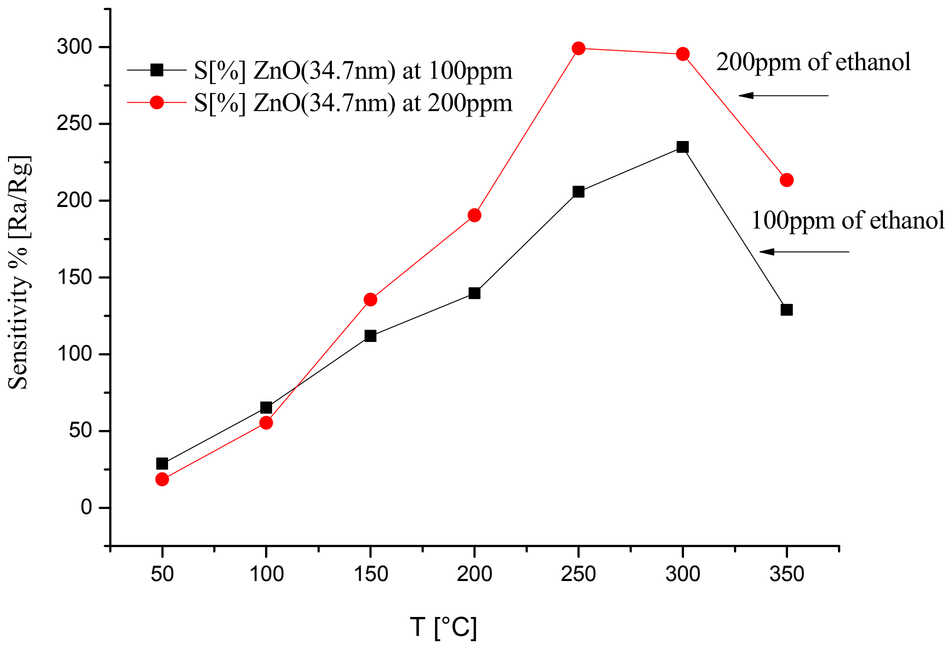


Figure 6: Comparison of the sensitivity ZnO has granular size 34.7nm towards 100ppm and 200 ppm of ethanol vapor as a functionof temperature

We note from the previous figure that improves the sensitivity of the film with an increased concentration and The operating temperature of film has decreased with increased concentration because the presence of low concentration of gas make the effective sites of the surface of the sensors remain empty This mean that the effective surface area of sensors became smaller, With the increased concentration these empty sites are filled with gas molecules and become the effective surface area of sensors became largest. And previous studies it shows that with the increased focus of more than a certain limit Sensitivity does not increase to a large extent because it becomes all the sensitive surface completely filled with gas molecule and formed more than a layer of gas On the sensitive surface And we have become a surplus of gas molecules These molecules remain idle And cause obstruction to the interaction of the gas molecules with the sensitive surface of the particles [18].

4-Conclusion:

1-In this study, films from nano ZnO powder were prepared, and placed on glass sample holders under specific heating conditions by chemical plating method.

2-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.

3-The effects of changing the particulate size on the sensitivity was studied. It was found that the sensitivity towards the ethanol vapor increases as the particulate size decreased. The sensitivity of the three films with different particulate sizes was compared at 250 C,. It was found that the 34.7 nm particulate size ZnO film has the greatest efficiency and ability to adsorb ethanol vapor, and this was due the changes of the nano structures – acquired large surface area.

4-It was concluded that the structure of the film material determined the properties of the prepared films, such as gas sensitivity and electrical conductance.

5-We note improves the sensitivity of the film with an increased concentration and The operating temperature of film has decreased with increased concentration.

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