

Study of Structural and electrical Properties of WO_3 as Thin Films

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Abstract
Three thin films were prepared by PVD starting from WO_3 powder with thicknesses (998.7, 1620, 2240 nm) respectively on glass substrates under limited thermal and pressure conditions, studied their I-V characteristics and calculated the sensitivity for 100 ppm of ethanol vapor adsorption (The temperature of the films have been changed from 25°C to 350°C). A comparison among them was achieved at 300 °C as an operating degree and found that the 1620 nm WO_3 has more sensitivity and has more power to adsorb for ethanol vapor on it. The crystal structure of the prepared WO_3 thin films were characterized by X-ray diffraction, then the comparison of the development which happened on the crystal structure reasons of deposition were studied. the crystal size has been calculated from patterns X-ray diffraction depended Scherrer Equation
Keywords: Tungsten Oxide WO_3, Ethanol Vapor, Sensing properties, thin film.

1. INTRODUCTION

Thin film considers the most important invention in twenty century cause we use this technique to prepare and study the materials in micro or even in nano dimensions; without any errors depends on crystal defects or that huge surface of a bulk material….etc, in addition ; low cost; friend of environment and small size, all of these give thin film a rapid extensive in common photoelectrical and electronic industry.

By the time thin film get more attention specially in semiconductor in several technical and industrial application like as: corrosion protection, optical filter, anti-reflection coating, solar cells, anti-scratched layer, and sensors [1].

Nano-Technology

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].

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[8,9]

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 our research is to prepare thin film of WO_3 by PVD, and study of its I-V characteristics in air and in 100 ppm of ethanol vapor by using KEITHLEY 237, then find which thickness has the best sensitivity to ethanol vapor.

Experimental Procedure

2.1. Substrate and cleaning procedure [10]:

We used glass substrates Soda-lime that has 13% Na_2O which dissolved in water and converting to NaOH as a thin film making a collapse in preparing procedure so we have to etch this film by washing the substrate with distilled water and apply the cleaning procedure as follows:

1. Put the substrate in 3% solution of normal detergent ultrasonically 5-7 min.
2. Immerse it in HCl 2M for 15 min
3. Washed with distilled water for 20 min
4. Dry it by hot air for 5 min

2.2. preparation of thin film by PVD

Three types of thin films prepared by PVD (Elltroava, Italy) with thickness 998.7, 1620, 2240 nm respectively, so we put a cleaned glass substrate in its location in the apparatus and vacuumed the chamber into $5x10^{-4}$ mbar then we evaporated the substance to get a desired thickness. Table .1 shows the thicknesses and preparation conditions:

Table .1 preparation conditions of thin films (998.7, 1620, 2240 nm)

Substance of the film	Method of deposition	The temperature during process	The pressure in the chamber	The rate of evaporation
WO_3 (powder)	PVD	400°C	5×10^{-4} mbar	32 A°/sec

We choose evaporation rate 32 A°/sec as a suitable velocity, and 400°C as a temperature of the substrate for deposition to eliminate all any other factors may cause problems on the prepared film.

3. Results and Dissection

3.1. I-V Characteristics for prepared films

The conductivity measurements are carried out in a pressure-controlled chamber during heating the thin films in a gas flow apparatus equipped with an external controlled heating facility. The resistances of the thin films are measured by the two-probes method with sliver-copper electrode deposited on the films by chemical painting method. The nature of the contact is verified to be ohmic by I–V Characteristics. A thermocouple was attached to the thin films holders for monitoring and controlling the operation during conductance measurements. The resistance of the sensors in the presence of either pure air (R_{air}) or the different pollutants (R_{gas}) at different concentrations is monitored and stored in a PC. All films prepared from powdered metal oxides used underwent for the same conditions and the measurement of electrical parameters applied to the device KEITHLEY 237using the following parameters which shown in the table (2).

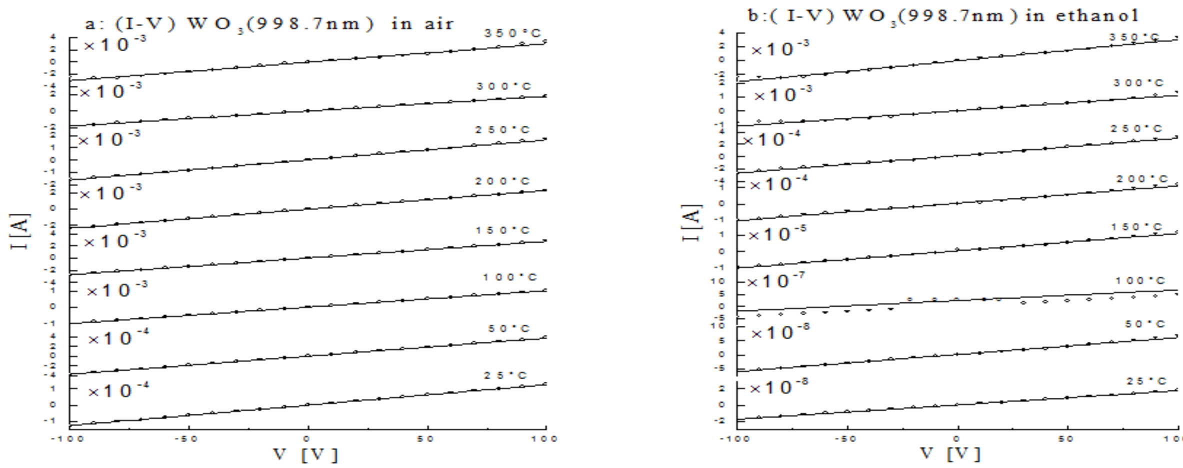
Table .2 Parameters for KEITHLEY 237 for I-V Characteristics

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 [11,12].

The I-V characteristics for each prepared film is studied in air and in 100 ppm of ethanol vapor at different temperature (25-350 °C) drawn as follows:

3.1.1.I-V characteristic for 998.7nm thickness WO_3 thin film:



a b

Figure 1. . I-V characteristic for 998.7nm thickness WO_3 thin film
a: in air, b: in 100 ppm of ethanol vapor

3.1.2. I-V characteristic for 1620 nm thickness WO_3 thin film

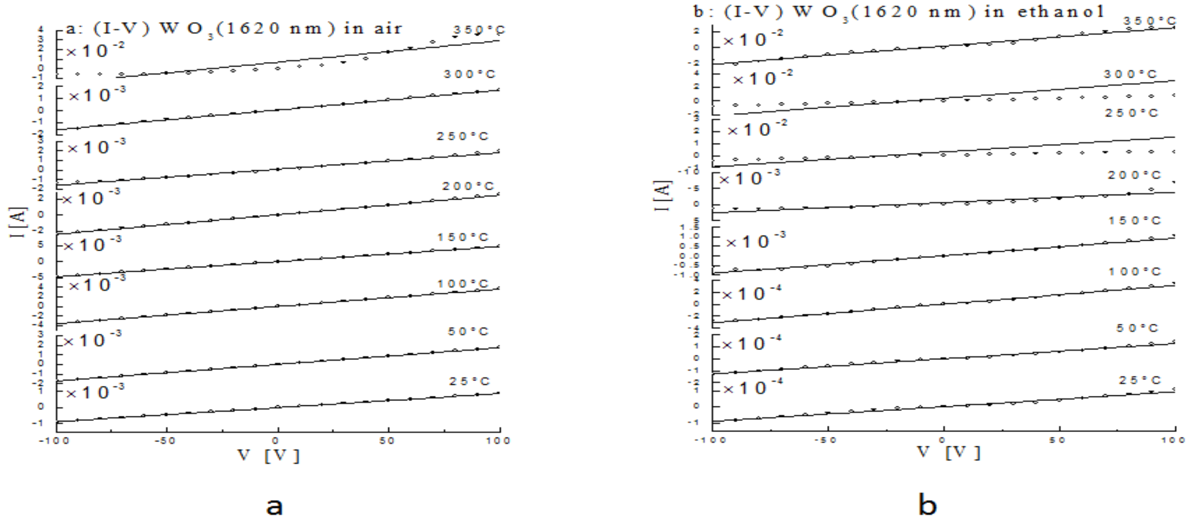


Figure 2. . I-V characteristic for 1620 nm thickness WO_3 thin film
a: in air, b: in 100 ppm of ethanol vapor

3.1.3. I-V characteristic for 2240 nm thickness WO_3 thin film:

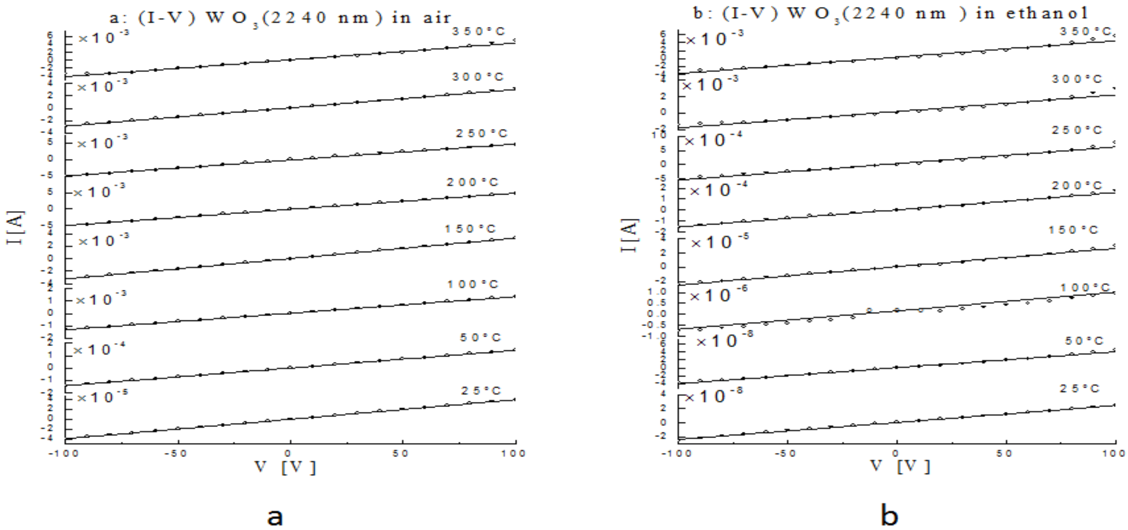


Figure 3. . I-V characteristic for 2240 nm thickness WO_3 thin film
a: in air, b: in 100 ppm of ethanol vapor

We notice from the previous figures that all thin 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 25°C to a few parts of mA at 350°C, and from these figures we can calculate the resistance in air and in 100 ppm of ethanol vapor as follows:

Table .3 Resistance for 998.7 nm WO_3 in air and in 100 ppm of ethanol vapor

T[°C]	25	50	100	150	200	250	300	350
R_{air}[Ω]	7.99E+05	2.71E+05	9.94E+04	3.66E+04	4.32E+04	6.09E+04	5.49E+04	3.29E+04
R_{gas}[Ω]	5.75E+09	1.64E+09	6.44E+07	9.44E+06	9.35E+05	3.50E+05	8.92E+04	3.28E+04

Table .4 Resistance for 1620 nm WO_3 in air and in 100 ppm of ethanol vapor

T[°C]	25	50	100	150	200	250	300	350
R_{air}[Ω]	1.14E+05	5.78E+04	2.77E+04	2.12E+04	4.10E+04	5.89E+04	6.06E+04	3.82E+03
R_{gas}[Ω]	1.07E+06	7.80E+05	3.18E+05	1.07E+05	2.55E+04	2.62E+04	1.32E+04	4.25E+03

Table .5 Resistance for 2240 nm WO_3 in air and in 100 ppm of ethanol vapor

T[°C]	25	50	100	150	200	250	300	350
R_{air}[Ω]	2.54E+06	7.02E+05	7.48E+04	3.04E+04	2.04E+04	2.06E+04	3.38E+04	2.33E+04
R_{gas}[Ω]	4.17E+09	2.48E+09	8.21E+07	3.84E+06	6.40E+05	1.68E+05	4.78E+04	2.35E+04

3.2. Calculating of Sensitivity for WO_3 thin film toward Ethanol vapor:

We calculate the Sensitivity for WO_3 thin film toward Ethanol vapor from the equation: $S = \frac{R_{air}}{R_{gas}} \times 100$ [8, 13]

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 WO_3 thin films by change of temperature

T[°C]	S[%]WO_3(998.7nm)	S[%]WO_3(1620nm)	S[%]WO_3(2240nm)
25	0.01	10.7	0.06
50	0.02	7.40	0.03
100	0.15	8.70	0.09
150	0.39	19.82	0.79
200	4.62	160.63	3.18
250	17.41	224.55	12.31
300	61.55	458.72	70.74
350	100.24	89.78	99.22

When we draw the sensitivity as a function of temperature for three thin films (998.7, 1620, 2240 nm) as follows:

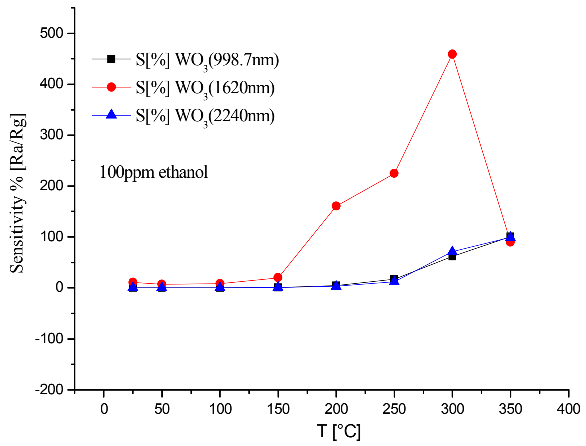


Figure 4. sensitivity as a function of temperature for three thin films of WO_3

We notice that the sensitivity of WO_3 thin film which has 1620 nm as a thickness was increasing by increasing of temperature to reach a high value 458.72% at 300 °C then it was decreasing by increasing of temperature so, we can say that a 300 °C is an operating degree for this film, but the others WO_3 (998.7 and 2240 nm) have as increase of temperature as increase of sensitivity till 350°C but not over 100%.

We found that the 1620 nm WO_3 thin film has a high sensitivity where the thickness, and the defects play a big role in sensitivity, so we get more defects on the surface at 1620 nm and these defects decrease by increasing the thickness to 2240 nm [14].

3.3. Structural Properties for prepared WO_3 thin films

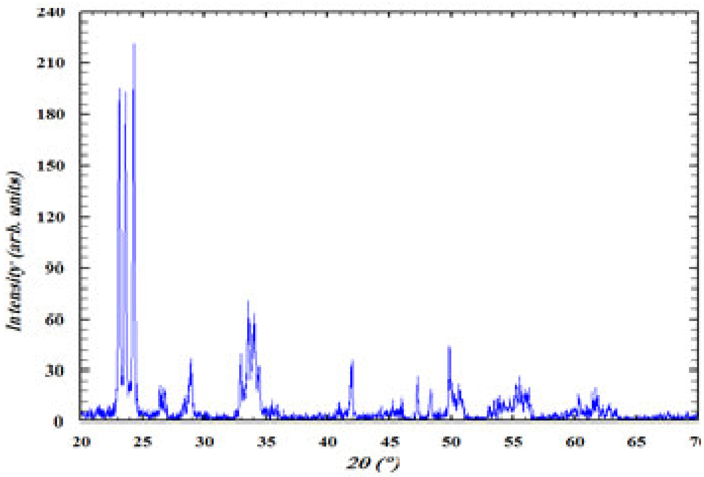


Figure 5. X- ray diffraction pattern for the WO_3 powder which uses in deposition

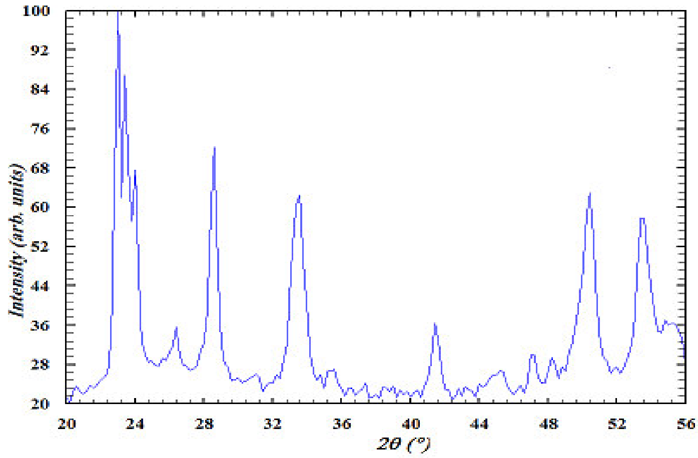


Figure 6. X- ray diffraction pattern for the WO_3 thin film which has thickness (998.7nm).

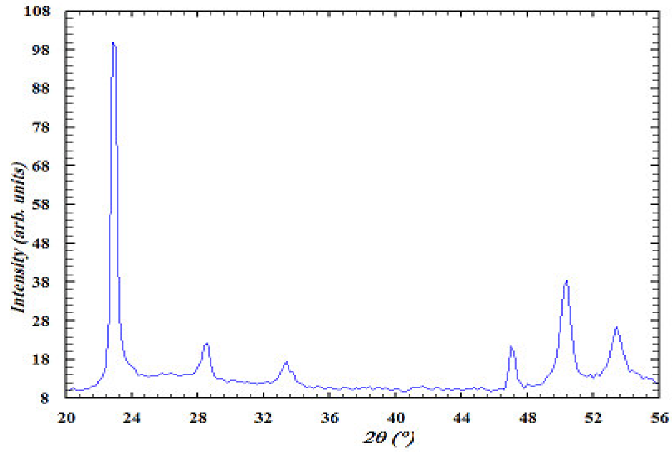


Figure 7. X- ray diffraction pattern for the WO_3 thin film which has thickness (1620nm)

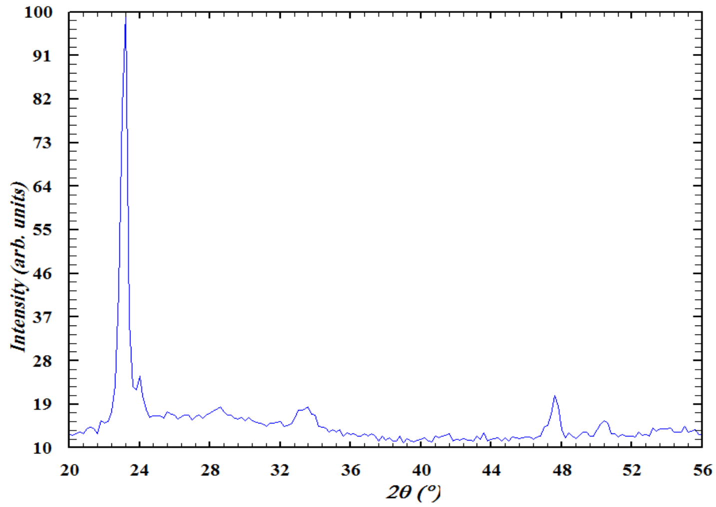


Figure 8. X- ray diffraction pattern for the WO_3 thin film which has thickness (2240nm)

We notice from X- ray diffraction patterns for WO_3 thin films high intensity Bragg peaks for WO_3 thin film which has thickness 998.7nm and low intensity for WO_3 thin films which have thickness (1620, 2240nm) and disappear some peaks but X- ray diffraction patterns for the WO_3 thin films which have thickness (998.7, 1620, 2240nm)) have Triclinic crystal structure this mean that the crystal structure for WO_3 dos not change result the deposition the average of the crystal size was evaluated by using Scherrer Equation, and their mean values were adopted as an average crystal size (diameter D).

$$D = \frac{K \times \lambda}{\beta \times \cos\theta} \qquad [15]$$

Table .7 values of crystal size for WO_3 thin films

WO_3(998.7nm)			WO_3(1620nm).			WO_3(2240nm).		
2θ°	β[rad.]	D[nm]	2θ°	β[rad.]	D[nm]	2θ°	β[rad.]	D[nm]
28.50	5.7×10^{-3}	27.834	22.96	8×10^{-3}	19.65	23.14	7.75×10^{-3}	20.3
33.44	9.6×10^{-3}	16.75	28.39	5×10^{-3}	31.76	47.60	4.3×10^{-3}	39.37
50.24	8×10^{-3}	19.238	50.28	8.4×10^{-3}	20.15			Average=29.835
		Average=21.2			Average=23.85			

We notice that WO_3 thin film which has thickness 1620nm and has high sensitivity towards ethanol vapor has not the smallest crystal size and the play big role in sensitivity of WO_3 thin film which has thickness its thickness as we remember above

4. CONCLUSION

Three thin films were prepared by PVD starting from WO_3 powder (998.7, 1620, 2240 nm), studied the I-V characteristic and calculated the sensitivity at 100 ppm of ethanol vapor and in comparison among them at 300 °C as an operating degree and found that the 1620 nm WO_3 has more sensitivity and power to adsorb an ethanol vapor on it. Then we found from X- ray diffraction patterns for three WO_3 thin films that the thin film which has the smallest crystal size has not the high sensitivity

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