

Fabrication and Characterization of ZnO Gas Sensor

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ABSTRACT

In this paper thin films of zinc oxide ZnO was prepared by spray pyrolysis method with thickness were about ($0.1 \pm 0.05 \mu\text{m}$) on n-type silicon substrates at different deposition temperature ($300, 400, 500$) $^{\circ}\text{C}$, from zinc chloride at concentrations (0.05, 0.1) M as a sensor for pollutant gases like CO_2 , NO_2 , and H_2S related with oil manufacture. The crystallinity and morphology of the films were characterized by XRD, and optical microscopy was done on prepared films, addition to sensitivity to polluting gases previously mentioned at different test temperature ($10-50$) $^{\circ}\text{C}$.

Result shows that the crystallization increased by increasing deposition temperature (substrate temperature), and the sensitivity increased by rising both of the gas concentration or temperature.

Keyword: ZnO thin film, gas sensor, spray pyrolysis, pollutant gases, XRD.

تصنيع و توصيف كاشف غازي ZnO

الخلاصة:

تم في هذا البحث تحضير أغشية من اوكسيد الزنك ZnO بطريقة الرش الكيميائي الحراري و بسمك حوالي ($0.1 \pm 0.05 \mu\text{m}$) على قواعد من السليكون نوع السالب , و بدرجات حرارة ترسيب مختلفة بلغت ($300, 400, 500$) $^{\circ}\text{C}$ لمادة كلوريد الزنك و بتراكيز (0.05, 0.1) M ككاشف للغازات الملوثة مثل (CO_2 , NO_2 و H_2S) المرتبطة مع الصناعة النفطية.

تم تشخيص التبلور و تشكل سطح الأغشية المحضرة (مورفولوجية) بواسطة حيود الأشعة السينية XRD و المجهر الضوئي لها , بالإضافة إلى الحساسية للغازات الملوثة المذكورة عند درجات حرارية اختباريه مختلفة ($10-50$ $^{\circ}\text{C}$).

أظهرت النتائج زيادة في التبلور مع زيادة درجة حرارة الترسيب (درجة حرارة القواعد) علاوة على زيادة الحساسية مع زيادة كل من تركيز الغاز و درجة الحرارة.

INTRODUCTION

Low-cost deposition techniques (incorporation) have been developed drastically and several deposition improved methods have been investigated for fabrication of sensitive device at high deposition rates (0.9 to 2.0) nm/s, such as hot wire CVD, high frequency and microwave PECVD, and expanding thermal plasma CVD. Parallel to these improvements, vacuum conditions and chemical processes cost increased the manner that serial fabrication becomes sometimes limited. Nowadays, it is expected that low processing temperature allow using a wide range of low-cost substrates such as glass sheet, polymer foil or metal[1]. These features have made the second-generation low-cost metal-oxides thin-film promising candidates for many applications[1], the adsorption of gas on the surface of a semiconductor can bring about a significant change in the electrical resistance of the material, there has been a sustained and successful effort to make use of this change for purposes of gas detection [2].

Detection of toxic and flammable gases is a subject of growing importance in both domestic and industrial environments. Simple metal oxides such as SnO_2 , WO_3 and ZnO are well known for their high sensitivity due to changes in the surrounding gas atmosphere[2].

It is also recognized that semiconductors layered films technology, in reducing production costs, should rapidly expand high-scale commercialization. Despite the excellent achievements made with the earliest used materials, it is also predicted that other materials might be, in the next few decades, have advantages over these front-runners. The factors that should be considered in developing new materials include: band gaps matching the solar spectrum, low-cost deposition/incorporation methods, abundance of the elements, non toxicity and environmental concerns. Transparent conducting oxides as ZnO , SnO_2 as well as doped oxides could be good alternative candidates[3].

ZnO was used as sensor, N. Khoang et al.[4] fabricated On-chip growth of wafer-scale planar-type ZnO nano rod sensors for effective detection of CO gas using combined lithography and chemical hydrothermal techniques The ZnO NR sensors grown at 6 h exhibited the highest response to CO and NH_3 gases with sensitivities of 0.37 and 0.05 %ppm, respectively.

L. Wang et al.[5] fabricated Controllable and enhanced HCHO sensing performances of different-shelled ZnO hollow micro spheres by a simple green chemistry routes at low temperature. X. Xue et al.[6] studied Surface free-carrier screening effect on the output of a ZnO nano wire nano generator and its potential as a self-powered active gas sensor and demonstrated its sensitivity to H_2S to a level as low as 100 ppm. Many method to fabricated ZnO gas sensor like microwave hydrothermal method low-temperature sono chemical method, sol gel and spray pyrolysis[7].

The goals of this paper is to fabricating ZnO thin film by spray pyrolysis technique, and study some of their structural properties and sensitivity to some Pollutant gas.

Experimental Work

The work includes steps;

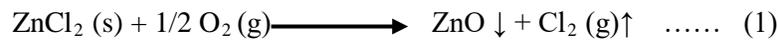
The first step: preparation of ZnO film from an aqueous solution of zinc chloride (ZnCl_2). The concentrations were (0.05 & 0.1 M), the acidity was maintained to be ≈ 5 pH during spraying. The preparing of the thin film is made by spray pyrolysis technique. The

spraying apparatus was manufactured locally in the university laboratories. In this technique, the prepared aqueous solutions were atomized by a special nozzle glass sprayer at heated collector glass fixed at thermostatic controlled hot plate heater as shown in figure (1).

Air was used as a carrier gas to atomize the spray solution with the help of an air compressor. The substrate temperature was maintained at 300-500 °C during spraying , the thickness (0.2) cm.

Atomization rate was about(1 nm/s) with (0.5 ml/min) of feeding rate. The distance between the collector and spray nozzle was kept at (20±1 cm) the volume of spray solution was 50 ml.

The spray of the aqueous solution yields the following chemical reaction [8]:



The second step: preparing specimens substrate with dimension for (1*1 *0.2) cm³ n-type Silicon wafer (99.9%)

The third step: deposition of thin film by spraying the solution on the surface of n/Si and at three different temperatures (300,400,500°C).

The Forth step : is the measurement which include:

1- X-ray diffraction with diffractometer type CuKα (λ = 1.5406 Å). This test is carried out in Advanced Materials Research Center at the Technology and Science Ministry, the scanning speed was 3% .To determine the (a- lattice constant) from X-ray spectrum were using the following formulas were used for hexagonal crystal system [9]which is a relationship between the d-spacing and lattice constants:

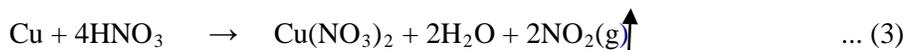
$$1/d^2 = (4/3) [(h^2+hk+k^2)/a^2] + l^2/c^2 \dots\dots (2)$$

Where h, k, and l, are known as the Miller indices (hkl) and are used to identify each lattice plane.

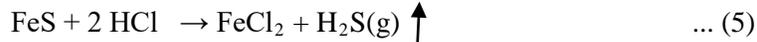
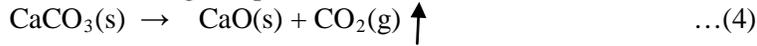
2- The optical microscopic test of the prepared film using a microscope type (permable) 100X can be used to characterize information on the structural morphology of the film. The test was carry out in Nanotechnology and Advanced Materials Research Center / the University of Technology.

3- The gas-sensing experiments were carried out by introducing the thus prepared devices into a home-made test cell, which was consist of a cylinder with cover to restrict prepared gas as in figure (2) .

The gas was obtained from reaction solution to escalate predicted gases. Pollutant gases that prepared nitrogen dioxide gas as will be explained in the following equation[8,10]:



In addition to CO₂ and H₂S gases produce from reactions :



The dilution were (0.01) M concentration , and solution was fixed at 5ml, the same concentration of gas was expected to be produced.

The gases -sensing properties were determined at different temperature by measurement of the D.C. electrical conductivity of the samples was exposed to various concentration of the gases (10, 50,100) ppm_v.

The sensor response was deined using the following equation[11,12 ,13]:

$$\text{Sensor response (\%)} = [(\text{Ra}-\text{Rg})/\text{Ra}] \times 100\% \quad \dots(6)$$

where Ra and Rg are the electric resistance in air and test gas, respectively.

Results and Discussion

Figure (3) Low-magnified images of ZnO, shows the homogeneity of the fine structure and soft cover most of the surface area and the effect of concentration and temperature Molar deposition as well as not clear when the structure of the softest and highest temperature so as to increase the rate of nucleation on the surface growing and grain size[14,15].

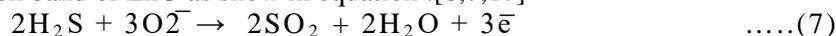
The results of X-ray diffraction are shown in figure (4) a correspond with the standard value (ASTM card No. 36-1451) ZnO have a hexagonal system , and clear increasing in the values of the peaks intensity and the half width of the Bragg peaks decreases with increasing in deposition temperature due to increasing in regularity of film structure and the substrate temperature provides the required energy to ensure occurrence regularity[16].

Peak intensity change with deposition temperature and decreases the intensity upwards from the [hkl] plane [100] to [002] instead of increasing it and this is consistent with many of the research for zinc oxide coating[15,16], as Clarify in table (1).

Lattice parameters are shown in table (2) illustrates the values change with temperature and low lattice constants by increasing the rate of nucleation with the heat and as explained previously.

For the investigation of the gas sensing properties of the ZnO films , the optimum operation gas temperature should be determined at the very first, it has been selected the highest temperature deposition and concentration to achieve the highest levels of crystallization .

Resistance and sensitivity to H₂S gas is shown in figures (5,6).Resistance change with the concentration of gas and different operating temperatures and found to decrease with increasing concentration of gas ,that's when the device is exposed to hydrogen sulphide gas with a strong reducing characteristic, the oxygen ions adsorbed on the surface of ZnO will react with H₂S molecules and release the captured electrons flowing back into the conduction band of ZnO as show in equation :[6,7,17]



Sensitivity of ZnO thin film is shown in figure (6) , it increases with temperature and less time required to respond, by increased gas concentration sensitivity will be increased due to reaction and so more electrons released. Growth of acidity of the ZnO surface has the opposite effect causing difficulties for a heterolytic break of the H – S bond in the H₂S molecule and a decrease of the H₂S adsorption[18]. The semi stability of the plots at high gas concentrations may be due to incomplete desorption of SO₂ or formation of sulphate groups on the semiconductor surface, which could occupy some adsorption sites and lead to a decrease of the sensor response[18].

In the presence of NO₂ in air the sample's resistance and sensitivity is shown in figures (7,8) respectively, resistance increases due to acceptor gas adsorption[18] :



where NO (gas) is the NO₂ molecule in the gas phase, e⁻ an electron from the conduction band of the semiconductor, NO_{2(ads)}⁻ adsorbed form of NO₂ on the semiconductor surface. This indicates the role of the electronic factor in the sensor sensitivity. After the adsorption on the surface the NO₂ molecule acts as an electronic trap, profoundly depleting the electron density in the conduction band and leading to a significant decrease of the nano crystalline material conductance , according to equation 8, and this indicates the role of the electronic factor in the sensor sensitivity[6].

So, an increase of concentration of electrons, which have enough energy to overcome the electric barrier resulting from the negative charging of the surface, favours reaction that leads to an increase of the sensor signal.

It is worth mentioning environmental humidity also an important factor influencing the performance of metal oxide gas sensors, water molecules act as a barrier against gas adsorption.

Resistance and sensitivity are set out in the figures (9 ,10) respectively. As shown in the figures, when O₂ molecules are adsorbed on the surface of metal oxides, they would extract electrons from the conduction band E_c and trap the electrons at the surface in the form of ions, differences in the nature of the interaction with different gas CO₂ from NO₂ gas on the one hand the length of the bond, and enthalpy and also the influence of the crystallite which found in sensitivity[6,18].

This will lead a band bending and an electron depleted region. The electron-depleted region is so called space-charge layer, of which thickness is the length of band bending region. Reaction of these oxygen species with reducing gases or a competitive adsorption and replacement of the adsorbed oxygen by other molecules decreases and can reverse the band bending, resulting in an increased conductivity. O⁻ is believed to be dominant at the operating temperature which is the work temperature for most metal oxide gas sensors [19] . In general sensitivity with the gas temperature (thermal energy) increasing developed activate sensor respond ,for all tested gas[19,20].

Conclusions

Gas sensor can be prepared from ZnO film on n- type silicon and be acceptable sensitivity at different temperatures and be appropriate for pollution resulting from oil industry applications, ZnO response for oxide gas more than reducing gases.

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Table (1) Results of XRD

$2\theta_{ASTM}$	300 C°	400 C°	500 C°	Hkl
	$2\theta_M$	$2\theta_M$	$2\theta_M$	
ZnO				
31.769	31.76	31.761	31.762	100
34.421	34.385	34.401	34.409	002
36.252	36.241	36.242	36.248	101
47.538	47.528	47.53	47.531	102
Si				
39.892	39.892	39.892	39.891	111

Table(2) Lattice constants of ZnO

Temp. C°	a A°	c A°
ASTM	3.249	5.206
300	3.2505	5.212
400	3.0077	5.2096
500	3.0070	5.2084

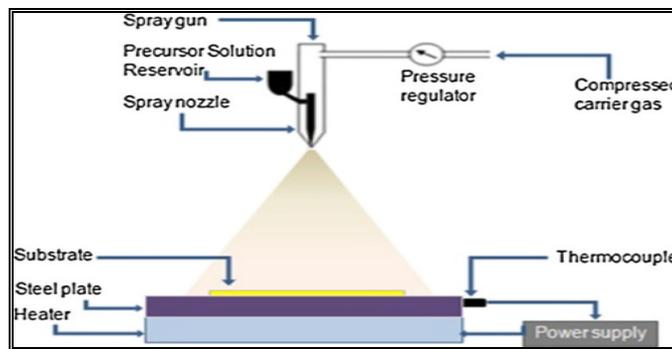


Figure (1) Spray pyrolysis set up.

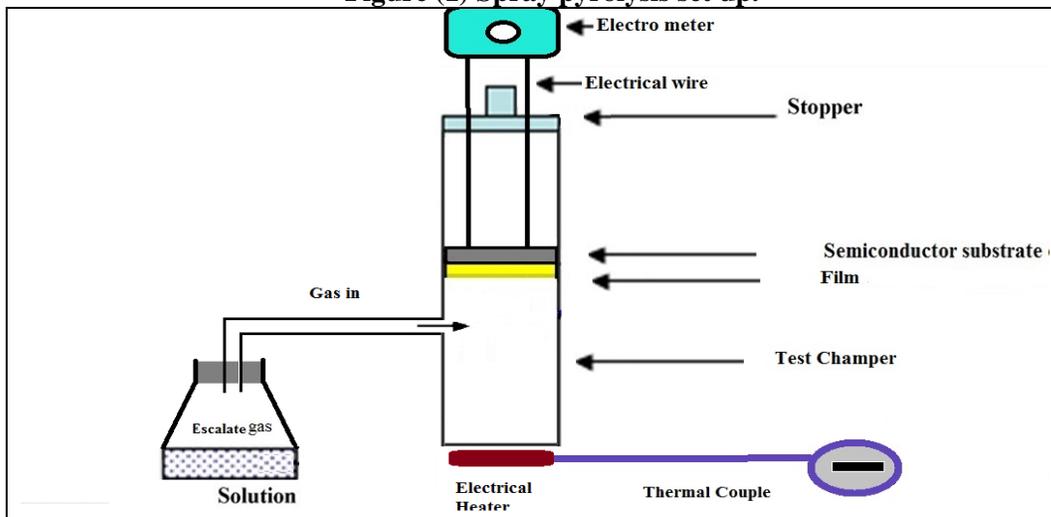


Figure (2) Detection set up.

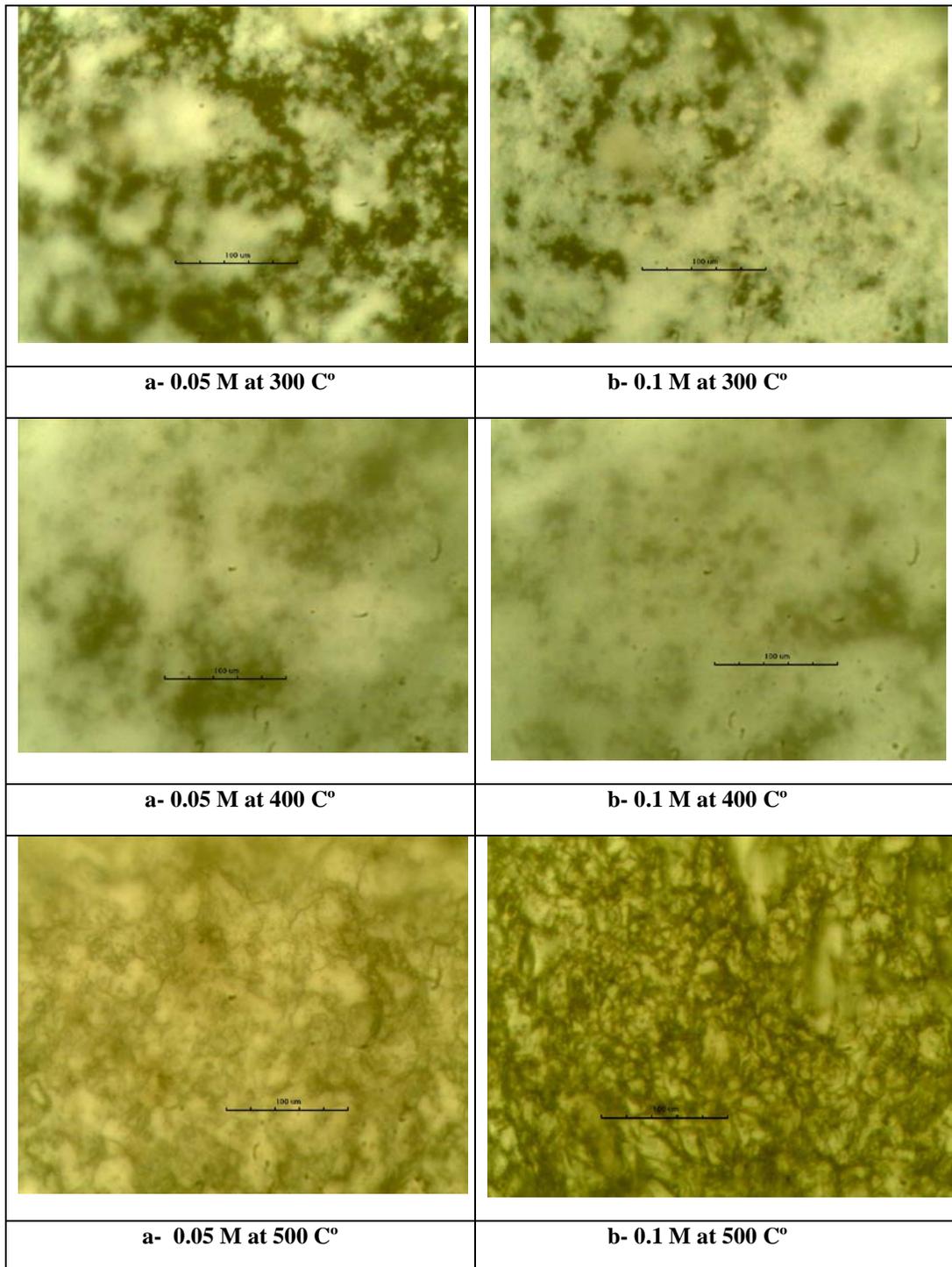


Figure (3) Optical microscope images of ZnO (X100), as a function of concentration and temperature.

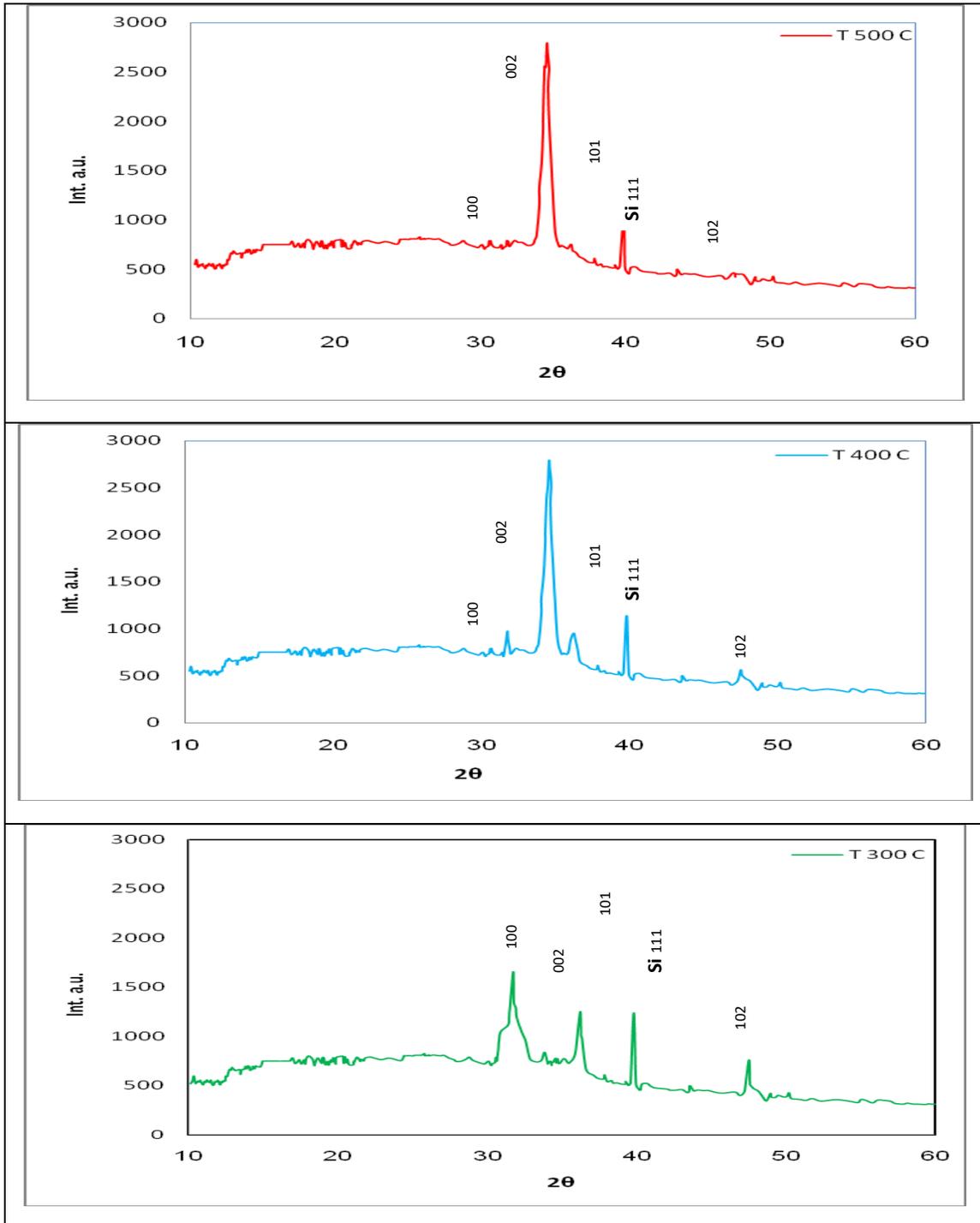


Figure (4) XRD result of ZnO thin film at 0.1 M

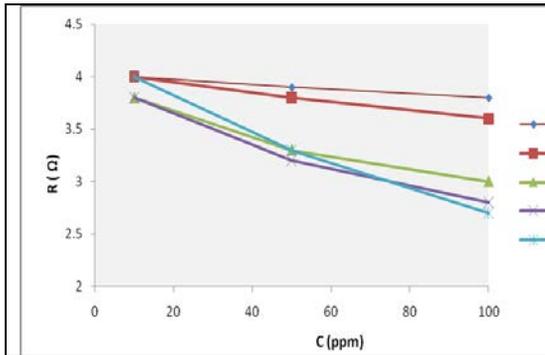


Figure (5) Resistance of ZnO thin film to H₂S gas .

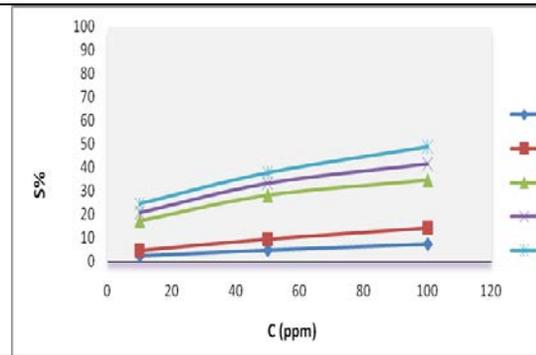


Figure (6) Sensitivity of ZnO thin film to H₂S gas.

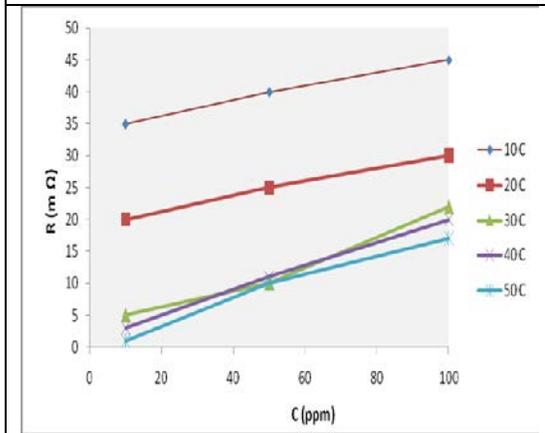


Figure (7) Resistance of ZnO thin film to NO₂ gas .

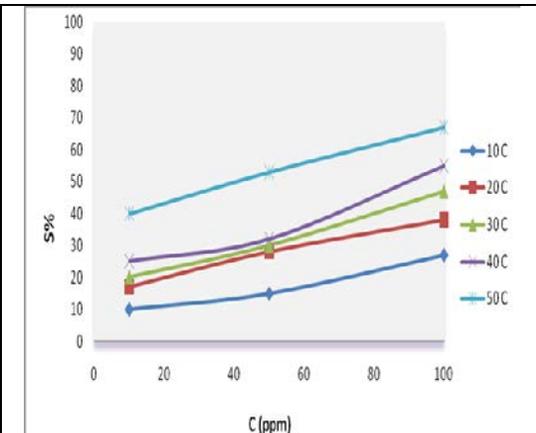


Figure (8) Sensitivity of ZnO thin film to NO₂ gas.

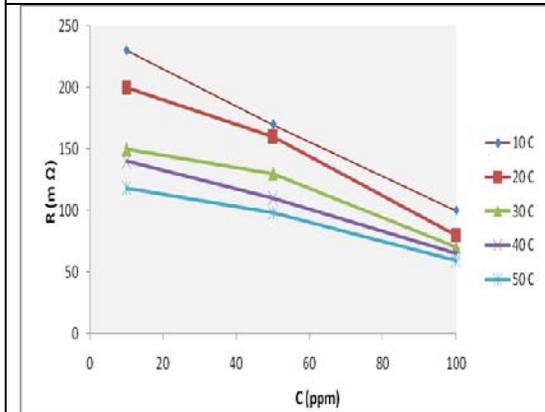


Figure (9) Resistance of ZnO thin film to CO₂ gas .

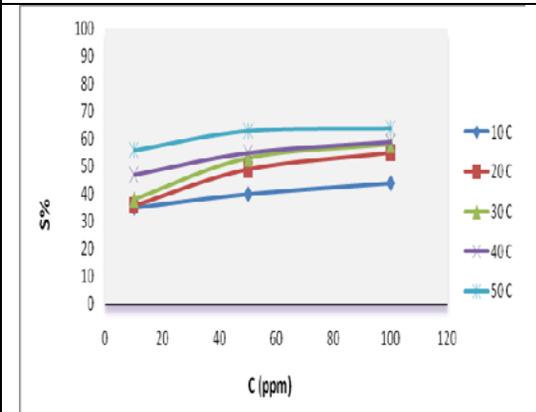


Figure (10) Sensitivity of ZnO thin film to CO₂ gas.