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ZNO: AL NANOSTRUCTUR GAS SENSOR BY SPRAY PYROLYSIS

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ABSTRACT

In this work, a study of Structural, electrical, optical and sensing properties are investigated of zinc oxide (ZnO) were deposited on cleaned glass substrates by chemical spray pyrolysis technique using ($ZnCl_2$) as precursor solution. Also, aluminium-doped thin films of ZnO (AZO) were prepared by using ($AlCl_2$) as doping solution for aluminium. The dopant concentration [Al/Zn atomic percentage (at%)] was varied from 0 to 3 at% in thin films of ZnO prepared in different depositions. The X-ray diffraction technique showed that all prepared films are polycrystalline with preferential orientation in the (002) direction, The peaks correspond to a hexagonal wurzite structure,the doping resulted in decreasing grain size i.e deteriorates the crystallinity of the films from (39.38nm)of pure ZnO to (30.22nm) 3% doped. The electrical properties showed the conductivity variation of Al-doped ZnO films with different doping concentrations increase with increased Al concentrations. Maximum electrical conductivity 4.25 ($S.cm^{-1}$)was obtained at a doping concentration of 3% . The films also exhibited distinct changes in their optical properties at different doping concentrations, including a decreasing of bandgap with increasing Al dopant concentration. The gas sensing results show that the sensitivity for detecting 750 ppm ethanol vapor was ~26.5and methanol vapor was ~20 at an operating temperature of 473°k.

KEYWORDS: ZnO:Al, Gas Sensors, Nanostructures

INTRODUCTION

The TCO's thin film is a wide direct band gap compound semiconductor such as In_2O_3, SnO_2 , ZnO , CdO , Cd_2SnO_4 ,… . ,.It is highly transparent in the visible range (more than 80% depends on the deposition technique and thickness) , high stability against heat and high electrical conductivity (about 10^3 ($S.cm^{-1}$)or more) [1]. This material has been used in a wide range of applications in science and technology including solar cells, heat reflecting mirrors, antireflection coating and a variety of electro-optical devices such as flat panel display devices ,sensing and many others different applications depending on the type of material [2] . Doping of various metals with transmission conduction oxide (TCO) films has been demonstrated to be a simple and effective way to enhance the film characteristics and hence efforts have been made in this direction aiming at increasing the conductivity, transmission and stability of various TCOs . Doping is also often used to change the conductivity and sensing properties of oxide films[3]. ZnO is one of the most important TCO materials; it is an intrinsic n-type semiconductor which was regarded one of important transparent conducting oxide with an energy band gap of (3.4eV), is of great use owing to its significant technology applications such as photo-catalysts, solar cells, transparent conductive films and chemical sensors , and so on. ZnO can easily be doped n-type, but is difficult to dope p-type [5]. The electrical conductivity of ZnO thin films increases with increasing temperatures as a result of the semiconductor material nature[6] .ZnO is a II–VI compound semiconductor whose ionicity resides at the borderline between the covalent and ionic semiconductors. The crystal structures shared by ZnO are wurtzite , zinc blende, and rock salt (or Rochelle salt)[7]. Group IIIa elements (Al, Ga, In) have been used to improve the electrical conductivity and thermal stability of ZnO films. For this work,Al^{3+} substitution on Zn^{2+} was chosen due to the small ion size of Al^{3+} compared to that of Zn^{2+} (rAl^{3+} = 0.054 nm and rZn^{2+} =0.074 nm)[8]. Numerous AZO thin film deposition

techniques have been employed: chemical vapour deposition (CVD) [9], radio-frequency magnetron sputtering [10], sol–gel process [11],pulsed laser deposition [12], electro deposition [13] and spray pyrolysis [14]. Compared to the others, the latter technique has many advantages: it is easy, inexpensive, and well adapted for mass fabrication [15]. Gas monitoring devices are in demand for a rapidly growing range of applications. Metal oxidebased chemical sensors have been used extensively for the detection of toxic pollutant gases, combustible gases and organic vapors. The main advantages of chemical sensors are their low price, small size, high sensitivity, and low power consumption[4]. In this paper, we present results of aluminium concentrations on changes in a Structural, electrical, optical and sensing properties of Al doped zinc oxide films deposited by the spray pyrolysis technique.

EXPERIMENTAL PROCEDURE

The films of ZnO were deposited on glass substrates by chemical spray pyrolysis technique as illustrated in figure(1). It is very simple and relatively cost-effective method for preparing films of any desired composition under controlled conditions, involving the spraying of a solution containing a soluble salt of the cation of interest onto a heated substrate. The details of film deposition has been reported elsewhere [16,17]. In the present investigation the ZnO thin films were deposited on properly cleaned glass substrates, all having 2.5 cm × 2.5 cm dimension. The precursor solution used was of (0.1) M concentration of high purity (99.9%) $ZnCl_2$ (Merck, India) prepared in distilled water. ($AlCl_2$) (Merck, India) was used as the source of dopant. The dopant concentration of aluminium (Al/Zn at%) was varied from 0 to 3 at% in different depositions. All the undoped and AZO thin films of three different doping concentrations were prepared separately in different depositions under the same parametric conditions, as given in table 1. During optimization of the process parameters for preparing ZnO thin films, the substrate temperature was found to be the most important parameter influencing the film properties. To obtain good quality ZnO thin films the substrate temperature kept at a constant value of (773 ± 10)◦K. Film thickness was determined by the weight-difference method using an electronic high-precision balance (Citizen, Model: CY 204) . All the film thicknesses were found to be in the range 350–400 nm. The temperature was monitored during the entire deposition process using a pre-calibrated chromel-alumel thermocouple with the help of Motwane digital multimeter (Model: 545).

The structural characterization of the films was performed using atomic force microscopy (AFM, AP-0190) and X-ray Diffractometer is from type (Shimadzu 6000) made in Japan with Cu-Kα radiation (λ = 1.54060 A˚) X-ray source at 40 kV and 30 mA in the scanning angle (2θ) from10◦ to 60◦ with a scan speed of 5.000(deg/min) .For electrical characterization, using vacuum thermal evaporation technique of type (Edward), and by using (Tangiesten W) boat material under pressure (10^{-5}Torr) to Electrodes Deposition, high conducting silver paste was used to make ohmic contacts on both ends of the ZnO thin films. The contacts were properly heated and allowed to dry. The temperature of the film was varied from room temperature (303◦K) to(473◦K) in steps and allowed to equilibrate for some time at intervals of(283◦K). At each stable temperature, The optical transmission spectra for undoped and AZO thin films were obtained in the ultraviolet (UV)/(VIS) region from 200 to 900 nm using (UV-1650PC Shimadzu software 1700 1650, UV-Visible recordig Spectrophotometer), made by (Phillips), Japanese company. The measurements were carried out in the wavelength scanning mode for normal incidence at room temperature using an uncoated glass slide as reference. For Sensing properties of the undoped and AZO films measured by using homemade equipment as illustrated in figure (2). The sensing measurements were carried out by measuring the variation in resistivity resulting from exposing the thin film surface to the chemical vapor ethanol (laboratory reagents 99.9 %) and methanol (laboratory reagents 99.95%) were evaporated by heating them to 473^{o}K, the temperature was recorded by a k-type thermocouple (XB 9208B). The resistivity was recorded by (Fluke Digital Multimeter8845A/8846A) multimeter.

Table 1: Spray Parameters for Film Deposition

Value	Spray Parameter
0.1 M	Concentration of zinc acetate solution
35cm	Nozzle–substrate distance
0.5 ml/min	Solution flow rate
3 kg/cm²	Gas pressure
773 ± 10K	Substrate temperature
5 sec	Spray time
90 sec	Stop time

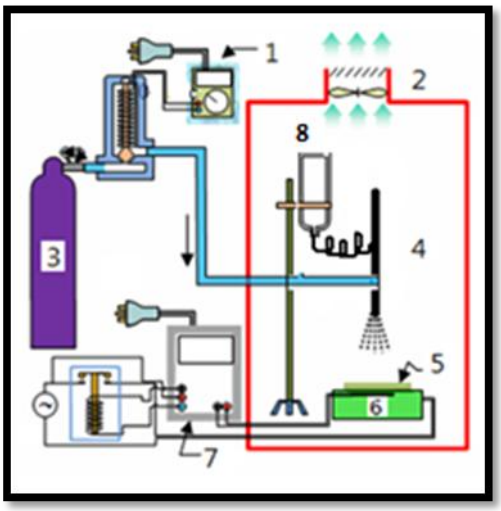


Figure 1: Schematic Representation of the Spray System

The deposition system consists of the following parts: (1) Time controller (2) Hood's ventilation fan(3) N2 gas cylinder(4) atomizer (5) substrate(6) substrate heater (7) substrate temperature Controller(8)Container glass

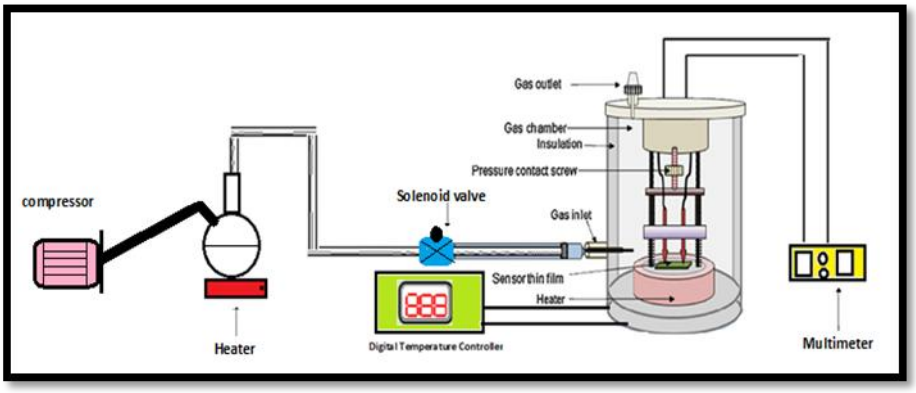


Figure 2: Sensing Measurements System Setting

RESULTS AND DISCUSSIONS

Structural Properties

Figure (3) show the X-ray diffraction pattern of ZnO and AZO films deposited on glass substrates as a function of doping concentration. All films are polycrystalline with a hexagonal wurtzite-type structure. The undoped and doped of ZnO films have preferred (002) orientation. For samples with Al concentration , (101) and (102) reflection peaks of ZnO appear, thus indicating that Al causes a loss of preferential orientation of the films. This result is good agreement with

from almost previous studies[15]. The (002) diffraction peak intensity of AZO films decreased with increased doping concentrations more than 3%. This indicates that an increase in doping concentration deteriorates the crystallinity of the films, which may be due to the formation of the stresses by the difference in ion sizes between zinc and the dopant. The effect of doping concentrations on the average grain size is illustrated in table (2) the result ,shows that the increasing of concentration decreased the grain size up to 3% this result is in good agreement with [19]. The surface morphology of the films measured by AFM is shown in Fig (4). From the AFM surface morphology measurement of the ZnO and AZO, the RMS roughness is found decreasing from 9.46 nm to 4.12 nm and the surface roughness of the films decreases with increasing the aluminium concentration in the films(table 2).

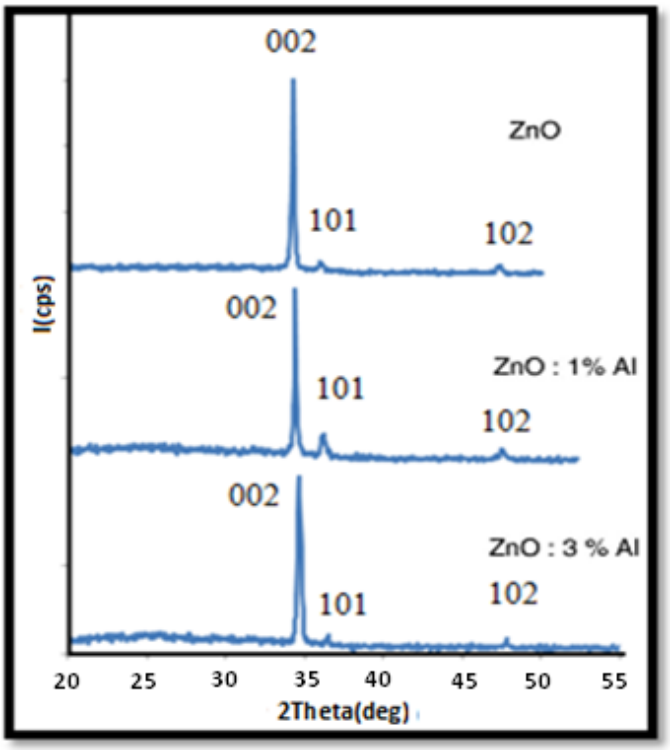
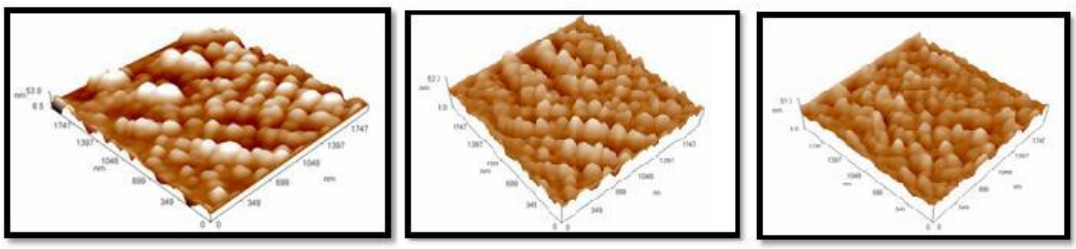


Figure 3: XRD ZnO and AZO

Table 2: Grain Size and RMS for AZO

RMS	Grain Size	Doping
9.46	39.38	ZnO
5.37	38.86	AZO 1%
4.12	30.22	AZO 3%



(a) **(b)** **(c)**

Figure 4: AFM (a) ZnO (b)AZO1% (c)AZO3%

Optical Properties

Figure (5) show the optical transmission as a function of wavelength in the range (300 – 900 nm) for undoped and doped thin films. The maximum transmittance observed for undoped ZnO was almost (90%), while for the doped films was maximum transmittance equal (85 ±3 %) for AZO. The optical transmission values are decrease with the increase aluminium concentration this behavior is may be due to the increase in free electrons with the increase in aluminium concentration. The figure show that the transmittance for all films has a high value (more than 80%) at (λ>500nm), i.e. in visible and near infrared regions. Our result is in good agreement with [15][18].

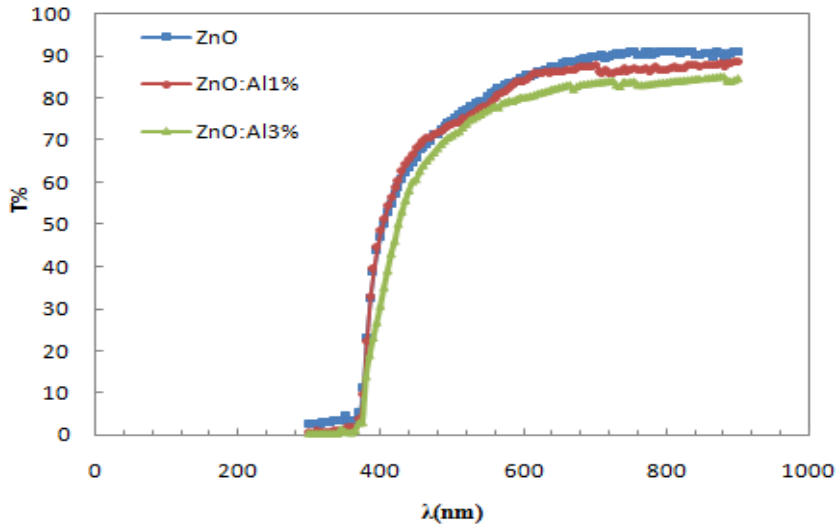


Figure 5: Transmittance (%) versus Wavelength for AZO Films

Figure (6) show the change of the absorption coefficient of undoped and doped films as a function of incident photon energy. It is observed that the absorption coefficient (α) increases gradually with the incident photon energy, and that value is greater than ($2\times10^{4}cm^{-1}$) which indicates the strong possibility of direct electronic transitions. It can be noticed from this figure that the absorption coefficient (α) increases with increasing doping . This behavior is attributed to the increasing of absorbance with doping which lead to the decreasing of energy gap with doping.

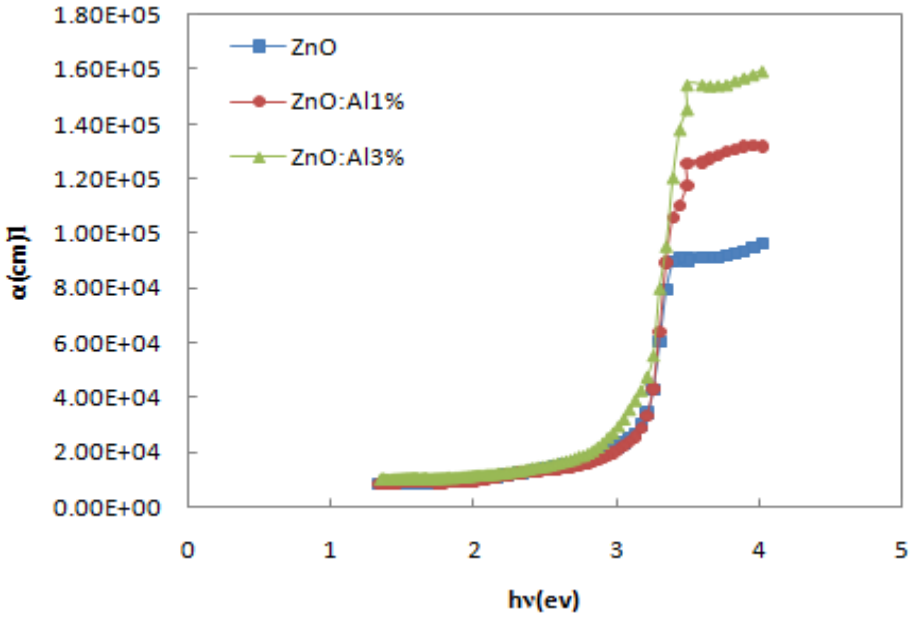


Figure 6: Absorption Coefficient versus Photon Energy for ZnO and AZO Films

The relation are drawn between $(\alpha h\upsilon)^2$and photon energy as show in figure(7) The values of band gap can be determined by extraplotting the linear portion of the curve to $(\alpha h\upsilon)^2=0$. The direct band gap was found to decrease with the increasing of doping from (3.3 ev) at 1% to (3.1 ev)at 3%) this result is in good agreement with [19],this effect happens in semiconductors, the Fermi level lies below the conduction band edge and above the occupied donor states, Where with increase the doping more and more, Fermi level moves in to the conduction band, this result is in good agreement with [20].

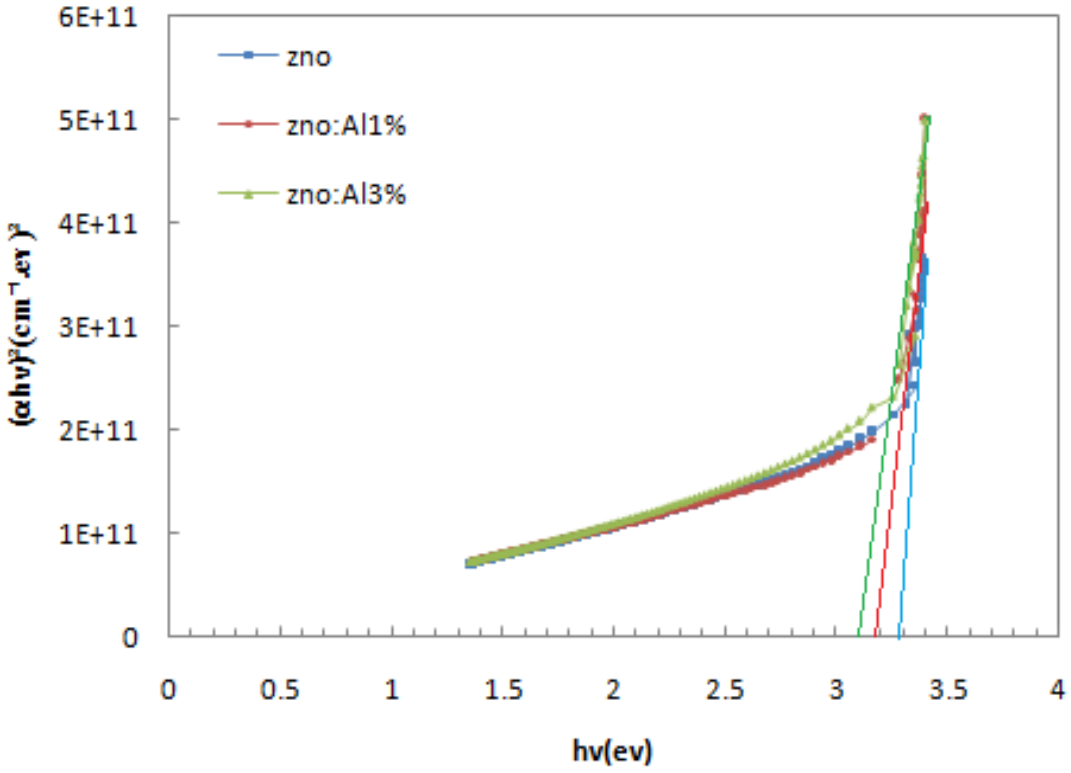


Figure 7: $(\alpha h\upsilon)^2$ versus Photon Energy for ZnO and AZO

Electrical Properties

Electrical conductivity for ZnO and AZO films had been measured for temperature range (303 – 423 K). It has been noticed that in general and in all films that the electrical conductivity is increases as the temperature increases exponentially, the maximum electrical conductivity 4.25 ($S.cm^{-1}$)was obtained at a doping concentration of 3% , and this represents common semiconductors property, which is related to the charge carriers' concentration, which increases when the temperature increases.

The electrical activation energy of AZO films were calculated from (Ln σ) versus (1/T) plot as shown in figure (7) .The activation energy depends on the doping and it will be decreased with increasing doping until 3%, The activation energy is illustrated in table (3).

Table 3: Activation Energy and Electrical Conductivity at Room Temperature

Doping	σ($S.cm^{-1}$)	Ea_1	Ea_2
ZnO	2.43	0.08	0.6
ZnO:Al 1%	3.28	0.06	0.5
ZnO:Al 3%	4.25	0.04	0.3

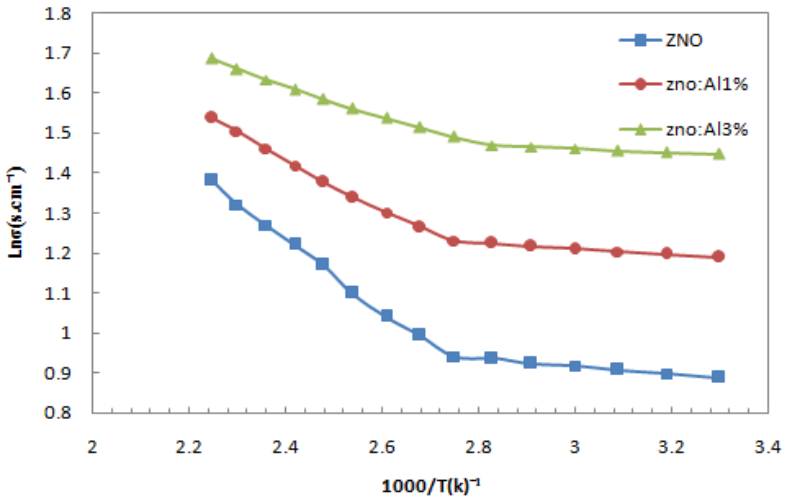


Figure 8: Activation Energy for ZnO and AZO

Sensing Properties

The Sensitivity of ZnO and AZO to vapors (ethanol and methanol) with increasing time operation at temperature of 473 °K with concentrations of about (750 ppm) in figures(9) and(10) ,We noticed the sensitivity for all samples including ethanol and methanol vapors is increasing with Al doping. AZO 3% has the maximum sensitivity of (26.5%) to ethanol and (20%) to methanol this result is in good agreement with [21] ,the sensing results for ethanol is a little bit higher than methanol. this because the similar constitution for ethanol and methanol. The characteristic behavior of the sensitivity When the (ethanol and methanol)vapors were introduced into the test chamber, the sensitivity of the sensor increase and soon afterwards it became saturated. When the gas was turned-off, the sensitivity of the sensor decreased. and it can be seen that the sensitivity decreased After many tests, which may be due to the sample became saturated. The response time is defined as the time taken by the sensor to attain 90% of the maximum increase in resistance on exposure of target gas and recovery time as the time to get back 90% of the maximum resistance when exposed to clean air. The variation of response times with different doping of AL concentrationat temperature 473 K is represented in Figure (11). The response time decreases from 400 to 310 s for ethanol and 420 to 330 s for methanol with increasing AL doping. The decreasing in response time may be due to large availability of vacant sites on thin films for gas adsorption[22].

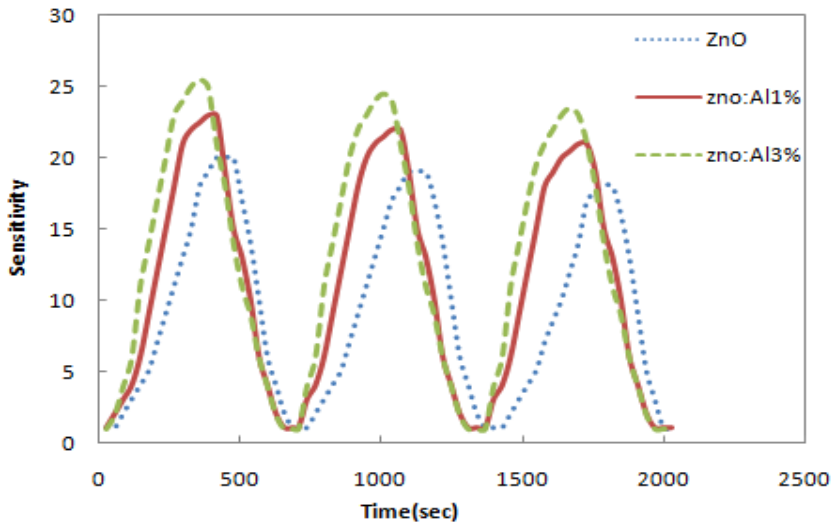


Figure 9: Sensitivity of ZnO and AZO to Vapors Ethanol with Increasing Time Operation at Temperature of 473 °K with Concentrations of (750 ppm)

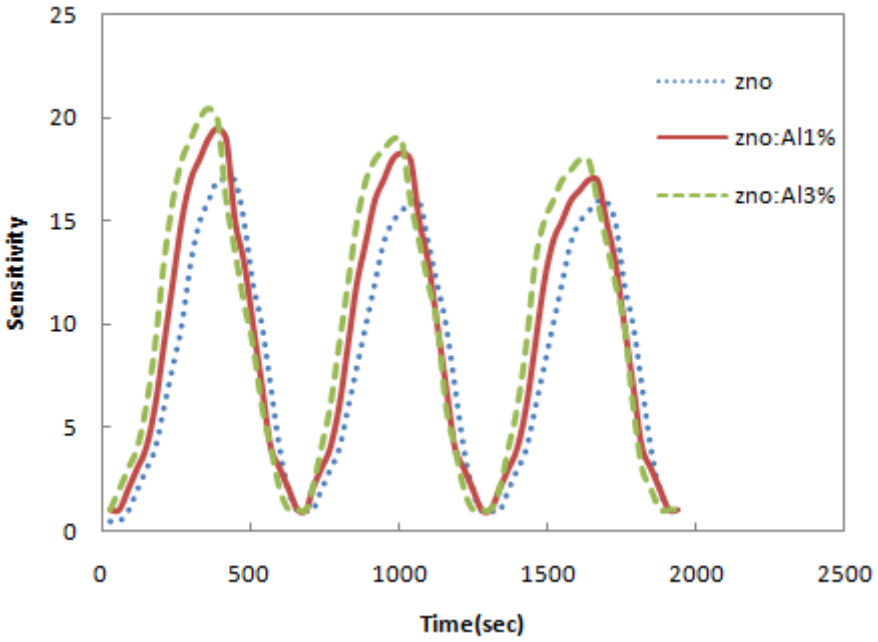


Figure 10: Sensitivity of ZnO and AZO to Vapors Methanol with Increasing Time Operation at Temperature of 473 °K with Concentrations of about (750 ppm)

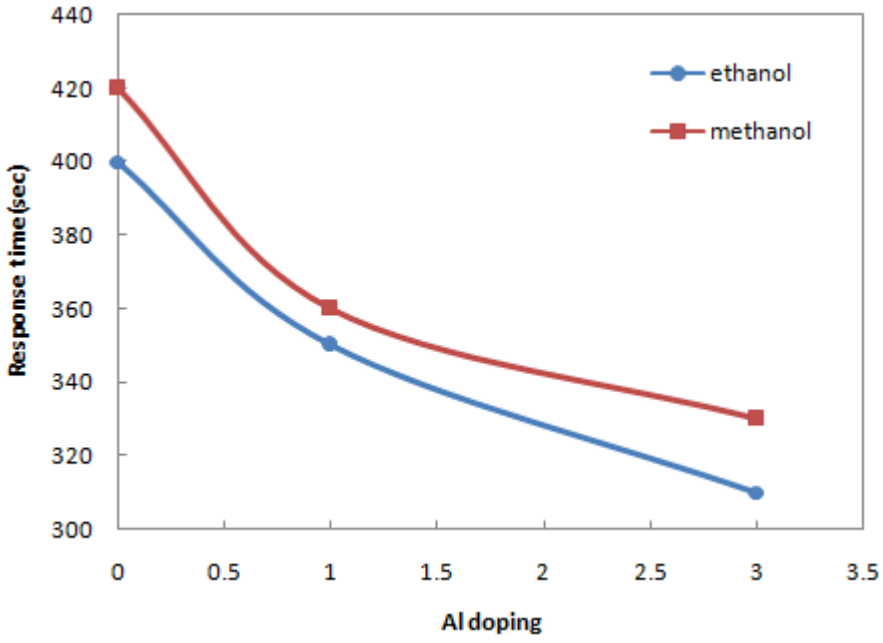


Figure 11: Response Time of ZnO and AZO Sensor to Vapors (Ethanol and Methanol) with Increasing Time Operation at Temperature of 473 °K with Concentrations of (750 ppm)

CONCLUSIONS

The structural, optical electrical and sensing properties of Al-doped zinc oxide thin films prepared by the chemical spray pyrolysis was studied in this paper. The structural analysis confirmed the prepared films to be ZnO. these films are polycrystalline showing a preferential orientation in the (002) direction. Our studies revealed that there was a slight change in crystallite size which occurred with increasing doping concentration of Al. The electrical investigation revealed that with Al-doping the conductivity of the ZnO film. The optical transmittance was high in visible range, the band gap decrease with increasing Al-dopant concentration. The sensitivity for all samples including ethanol and methanol vapors is

increasing with Al doping, AZO 3% has the maximum sensitivity of (26.5%) to ethanol and (20%) to methanol at temperature of 473 °k with concentrations of about (750 ppm).

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