Characteristics of Zinc Oxide Film Prepared by Chemical Spray Deposition as a Gas Sensor

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Abstract
Zinc oxide thin films were deposited by chemical spray pyrolysis onto glass substrates which are held at a temperature of 673 K. Some structural, electrical, optical and gas sensing properties of films were studied. The resistance of ZnO thin film exhibits a change of magnitude as the ambient gas is cycled from air to oxygen and nitrogen dioxide.

Keywords
Zinc Oxide, Chemical spray pyrolysis, Gas sensing, Electro-optical properties.

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دراسة خصائص اغشية اوكسيد الزنك المحضرة بطريقة الرش الكيميائي كمتحسس للغازات

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الخلاصة
تم في هذا البحث تحضير عينات من اغشية مركب ZnO وباستخدام طريقة الترسيب بالرش الكيميائي على قواعد زجاجية بدرجة حرارة 673 كلفن . درست بعض الخصائص التركيبية والكهربائية والبصرية والتحسسية للغازات للاغشية المحضرة . مقاومة الاغشية المحضرة تبين تغير بالمقدار عند تعرضها الى غازات الاوكسجين وثاني اوكسيد النايتروجين مقارنة مع الهواء .

Introduction

The gas sensing materials have been widely investigated in order to achieve highly sensitive and selective long-term-operating sensors. Zinc oxide (ZnO) is one of the gases sensing material that has caught much attention. ZnO has a wurtzite hexagonal structure and possesses various interesting properties including wide band gap semiconducting property of 3.3 eV and having a large exciton binding energy of 60 meV. Moreover, ZnO nanostructures have gained attention due to their huge surface-to-volume ratios which are expected to exhibit better sensing properties than gas sensors based on bulk or thin films. ZnO is an n-type semiconductor of wurtzite structure. It has a direct band gap of 3.37 eV at room temperature [1]. Polycrystalline ZnO has found numerous applications, such as surface acoustic wave devices [2], piezoelectric devices [3], varistors, planar optical waveguides [4], transparent electrodes [5, 6], ultraviolet photodetectors [7], facial powders, phosphors [8], gas sensors [9–11], etc. So far ZnO-based elements have attracted much attention as gas sensors because of their chemical sensitivity to different adsorbed gases, high chemical stability, amenability to doping, nontoxicity, and low cost. Thin films of ZnO have been prepared by using several deposition techniques which include chemical vapor deposition, magnetron sputtering, oxidation of an evaporated metallic film, spray pyrolysis, pulsed laser deposition, sol-gel technique etc. [10-16]. Among these methods, the spray pyrolysis technique has several advantages such as simplicity, safety and low cost of the equipments and raw materials. In this technique, a starting solution containing a soluble salt of the cation of interest is sprayed by means of a nozzle assisted by a carrier gas over a hot substrate. When the fine droplets arrive at the substrate, the solid compounds react to become a new chemical compound. The quality and the physical properties of the films depend on the various process parameters, such as substrate temperature, molar concentration of the starting solution, spray rate, type and pressure of the carrier gas and the geometric characteristics of the spray system. Chemical spray ZnO films exhibits higher DC resistivity and a higher optical transmittance. Among these properties, the electrical conductivity is often very sensitive to the adsorption of different gases and vapors onto the ZnO surface. Therefore, the resistivity is a widely used characteristic of ZnO films in sensor technology [17, 18]. The sensitivity of the gas sensor is defined as the capability of the sensor to respond the presence of a given gas concentration. Mathematically, the sensitivity S is defined by the formula [17, 18].

$S = Rg/Rn$ ……………………. (1)

for redactor gas, and

$S = Rn/Rg$ …………………….. (2)

for oxidator gas, where *Rn* and *Rg* is the resistance of the sensor before (air) and after passing the gas and reaches the saturation [18].

In this paper, we report a study on some of physical (structural, optical, electrical and gas sensing) properties of ZnO thin films prepared by spray pyrolysis technique.

Experimental Techniques

Deposition of ZnO thin film on glass substrate and fabrication of aluminum (Al) contact were carried out using spray pyrolysis and thermal evaporation techniques respectively. The films were prepared on clean glass substrates at temperature of 400C, which were placed on the surface of a substrate heater when sprayed. The substrate heater was an electrically controlled block furnace. The spraying solution used was of 0.1 M concentration of high purity $Zn(NO_3)_2$ (Merck, India) prepared in distilled water. The atomization of the solution into a spray of fine droplets was carried out by the spray nozzle, with the help of compressed nitrogen (10^5 N/m^2) as carrier gas. The schematic representation of the spray system is given in figure 1a; b.The substrate temperature was monitored using a K-type thermocouple with the help of a digital multimeter. The reduction leading to the formation of ZnO as follows:

$$2Zn(NO_3)_2 + H_2O \xrightarrow{\text{Heat}} 2ZnO + 4NO_2 + O.$$

Film thickness was determined by the weight-difference method using an electronic precision balance (four digits). The thickness of the films can be calculated according to the following equation:

$T = \Delta m / \rho A$ ……………. (3)

Δm is the mass of the film, ρ is the total density of the film and A is the area of the film. In the present work, prepared ZnO films of thicknesses closed to 400nm, 710nm and 900nm. Diffraction studies are carried out using X- Ray Shemadzu XRD – Diffractrometer (operated at 40 kV an accelerating potential and 30mA with filtered CuKα radiation 0.15418 A^o wavelengths) was performed to identify the crystalline phases present in the deposited films.

The transmittance and absorbance spectrums of the ZnO prepared films were measured using the (OPTIMA-3000 UV-VIS) spectrophotometer. In this experiments the optical measurement were recorded in (300-1100) nm wavelength range. The semiconductor band gap Eg was determined by analyzing the optical data with the expression for the absorption coefficient (α) and the photon energy (hν) [19] using the relation:

$$\alpha = [k (h\nu - Eg)^{n/2}] / h\nu \quad \text{......... (4)}$$

where k is a constant, and n is a constant which is equal to one for a direct-gap material, and four for an indirect-gap material.

The dc resistance of the films as a function of temperature in the temperature range 300–500 K was measured by means of a home-made chamber, connected to heating supply, temperature controller and a low current multimeter. The contacts of electrodes were made by silver paste.

Results and Discussions

The XRD patterns of ZnO films as deposited and thermally annealed at T=873 K for treatment times of 30min. and 60min. are shown in Fig.2. It is observed that there are four characteristics diffraction peaks corresponding to the (002),(100),(101) and (102) reflected at Bragg angles (2θ=34.5,31.7,36.4 and 47.5°) respectively. The peaks of reflections indicate that films are of polycrystalline structure and the intensity of plane (002) reflection is higher than that of other planes, which means that this plan is suitable for crystal growth. The recrystallization of ZnO films occurs, when the films thermally treated and is recognized by the additional increment of plane intensity. The crystallite sizes were estimated using the Scherrer formula [20-22]:

$$D = 0.94\,\lambda / \beta (\cos\theta) \quad \text{..................... (5)}$$

where λ is the X-ray wavelength, θ the Bragg s angle, β the full width of the diffraction line at half of the maximum intensity. For present work, ZnO film deposited at 673 K the corresponding crystallite size (31-34nm).

The optical transmittance and absorbance versus wavelength of ZnO thin films are shown in Fig.3. It obvious from the curve that transmittance is so high (the average transmittance over the range 500-1100nm exceeds 80% with a sharp fall near the fundamental absorption. The ripples in these spectra result from the interference of light, since they show waveforms that are characteristic of the interference of light [13]. After 900nm wavelength, the transmittance is decreased due to the plasma edge. The percentage and peaks of transmittance spectrum of thermally treated films increases and shifted to the longer wavelength respectively compared to the untreated films. This effect could be attributed to the increase in the degree of the crystalinity of films structure by increasing the grains size. The shift of peaks increases with increasing of annealing time and can be attributed to the diffusion of oxygen atoms into band gap. The absorption spectra of the films are shown in Fig.4. These spectra show that films have low absorbance in the visible/near infrared region while the absorbance is high in the ultraviolet region. The absorption edge and optical energy gap have been determined from the plot of absorption coefficient $(\alpha)^2$ vs. photon energy (hν) as shown in Fig.5. The band gap value of (3.2-3.3 eV) was obtained which a good agreement with previous studies [21,22].

The resistance of ZnO films depends on the purity of the original materials and the stoichiometry of compound. The variation in electrical resistance of the films with temperature is shown in Fig.6. The resistance is found to decrease with increasing temperature in the temperature range 300-500 K. Above this range the decrease in resistance is related to the increase in carrier concentration resulting from activation of deep and shallow donors which may arise due to native defects such as interstitial zinc atoms and oxygen vacancies [20].

Resistance of ZnO films exposed to various environmental gases at 473 and 523 K was also measured inside the home-made chamber (Fig.7). A result of resistance change vs environmental gas change represented in Table (1). The resistance measurements of ZnO samples were carried out in the dark, so that photo excitation of carriers should not be significant. The sensitivity was found to increase with increasing of working temperature as shown in Figures (8, 9).

Table 1: Gases sensing measurements

Temperature / K	R_{gas}/R_{air} Air›NO_2	R_{gas}/R_{air} Air › O_2
473	3.1	6.3
523	4.2	8.2

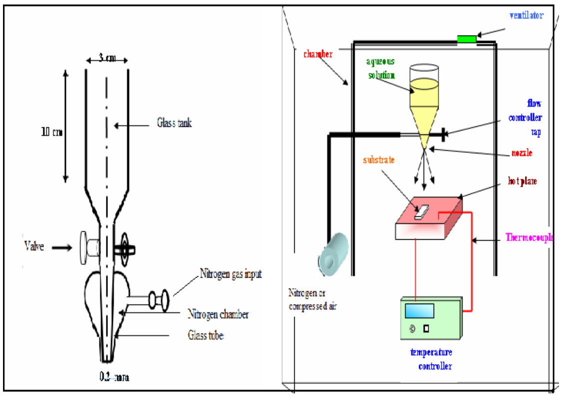

Fig. 1: The schematic representation of the spray system

Conclusions

The XRD analysis, confirmed that the prepared films of ZnO were polycrystalline and the structural properties improved with heat treatment. Direct band gap value which was obtained from optical absorption measurements increases with the heat treatment of prepared ZnO thin films. Prototype ZnO partial pressure sensor has been built

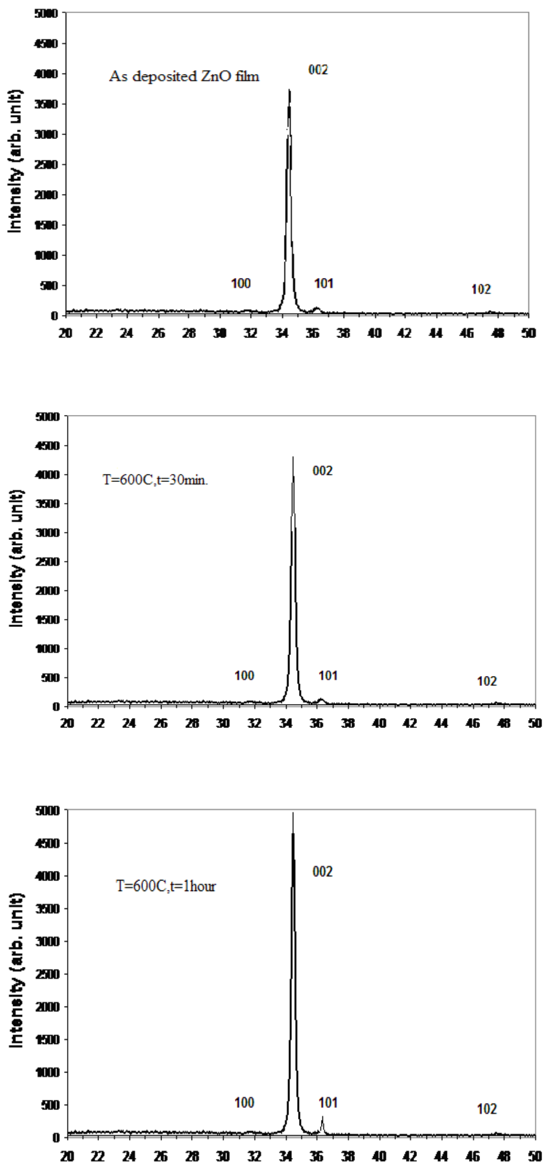

Fig.2: XRD patterns of as deposited ZnO films and thermally treated at 873K.

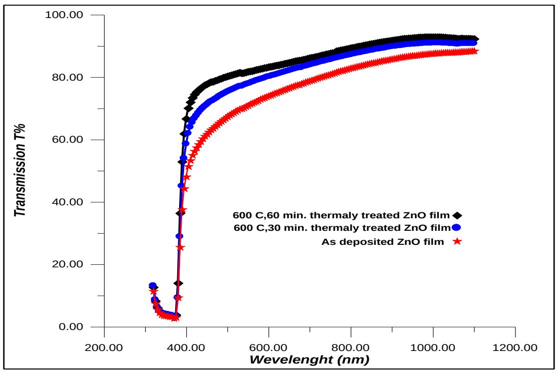

Fig.3: Transmission spectra of the ZnOthin films.

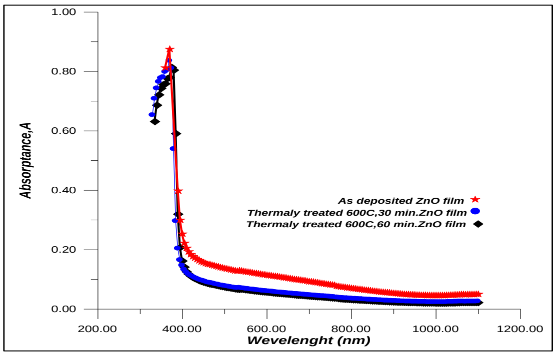

Fig.4: Absorptance spectra of the ZnO thin films.

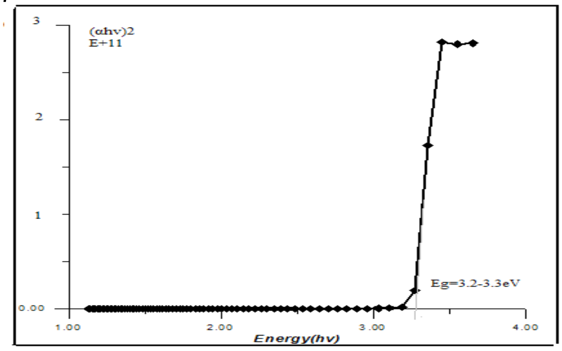

Fig.5: Absorption coefficient as function of photon energy for ZnO thin film.

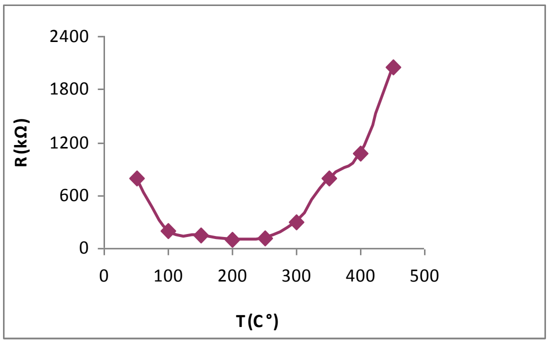

Fig.6: The variation of ZnO thin film resistance with temperature.

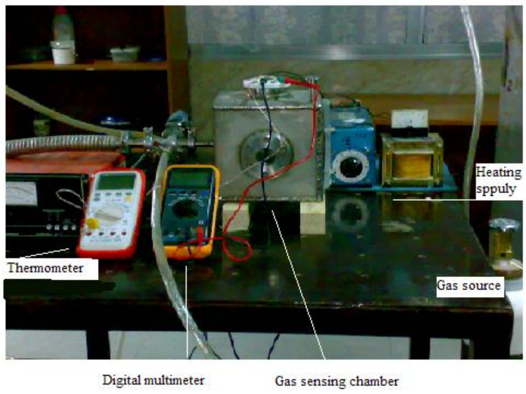

Fig.7: Set-up of gases sensing measurements.

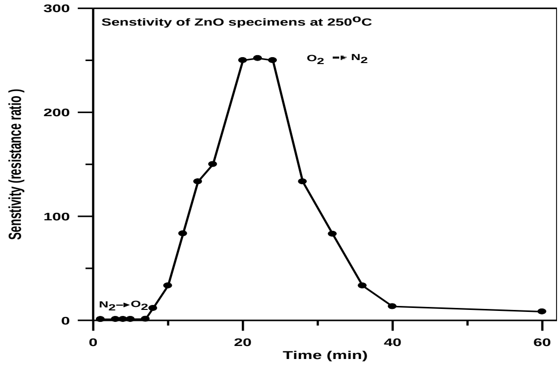

Fig.8: Sensitivity of ZnO Thin Films to O_2

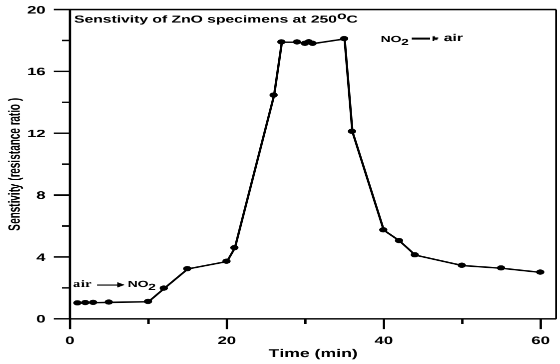

Fig 9 : Sensitivity of ZnO Thin Films to NO_2

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