Effect of doping and temperature on (NO_2) gas sensing properties for Mg_xZnO_{1-x} heterojunction

Abdulazeez O. Mousa[*], Saleem H. Trier[**]
[*]Department of Physics, College of Science, University of Babylon, P.O. Box 4, Babylon, Iraq
[**]Department of Environment, College of Science, University of Al- Qadisiyah, Diwaniya, Iraq
E-mail address: [*]Azizliquid_2005@yahoo.com, [**]Salemhamza79@yahoo.com

Abstract

In this paper was prepared ZnO/n-Si, and dopant $Mg_{0.05}ZnO_{0.95}$/n-Si films using a chemical spraying pyrolysis (CSP) technique. The grow doped solutions $Mg_{0.05}ZnO_{0.95}$ volumetric ratio (5)% from MgO and deposited on silicon substrates and at different temperatures (400,450,and 500)°C was installed thickness by installing a number of sprays. The thickness of all the films ranges between (80 ±5) nm, was used as a gas holder nitrogen. The crystal structure was examined by using X-ray diffraction(XRD) technique. The results showed that all the films prepared polycrystalline, showing improvement in the crystal structure in terms of increasing the intensity of the peaks, by change of temperature. As was studied the topography of the surface of the films prepared using field emission scanning electron microscopy (FESEM), and energy dispersive X-ray (EDS), and atomic force microscope (AFM), and granular size for the ZnO depends on the ratio of Mg-content volumetric, where decreases grain size with adding Mg-content. As well as that add MgO in the films lead to a decrease in surface roughness. Also, (EDS) showed films contain elements (Si, N, O, Zn, and Mg) as expected. The sensitivity of the prepared films to (NO_2) gas in air ambient has been measured in the gas sensing system. All samples were tested at a ratio (3% NO_2:air) and bias voltage (6Volt). The best ratio dopant of the Mg-content is (5)% , best operating temperature is (200)°C, and best temperature of the silicon substrate is (400)°C. The maximum sensitivity is (90.80)% and fast response time is((6.3s) and recovery time is (44.1s).

Keywords: Gas sensing, NO_2, operating temperature, response and recovery time

I. Introduction

The mechanism of sensing by the oxide thin films is based on electrical conductance change upon surface reduction-oxidation (redox) reactions with gas species [1]. The effect of grain boundary in the polycrystalline thin film metal oxide sensors was studied and showed that it limits the repeatability and long term stability [2], and the crystalline structure also can be affected the sensitivity of the chemical sensor [3] ,the gas sensing depending on the variation of resistivity of ZnO thin film prepared by atomic layer deposition (ALD) technique was studied [4] ,the measured values showed that sensitivity was extremely high for ultrathin ZnO films. Mg_xZnO_{1-x} belong to the class of transparent conductive oxides (TCOs). TCOs are a unique class of materials, because they exhibit both, transparency and electronic conductivity, simultaneously[5]. Usually, conductive materials, such as metals, are not transparent, while transparent materials, such as insulators, are not conductive. TCOs combine these two properties due to their large band gap (≥3 eV), leading to the transparency in the visible spectrum of the light, and a low effective mass of the electrons, which can be attributed to the high dispersion and the s-type character of the conduction band, explaining the high conductivity[6,7]. The gas sensing characteristics of the materials can be improved by incorporating some additives into oxide films. Catalysts like (In, Pt, Pd, Ag, Au, and Cu) often added to the based material to improve the gas sensitivity and selectivity[8].The adsorption and desorption gas sensing mechanism of semiconductor gas sensor is the simple resistivity change. The surface morphology is controlled by varying the deposition parameters. The control of the surface morphology is of particular interest for gas sensor applications where a porous morphology is desired to increase the adsorption and implicitly the sensor response to specified gas [9]. Resistive sensors have been used to measure a wide variety of physical and chemical properties and are among the most common and cheap sensors commercially available. There are for example photoresistive sensors, which use materials that change conductivity with light absorption; thermoresistive sensors in which resistivity variation is controlled by the temperature, piezoresistive sensors, that use the change in resistance with mechanical stress, magnetoresistive sensors based on the resistivity change in the presence of an external magnetic field and chemoresistive that measure the resistivity change produced by the interaction of a chemical substance with the sensing material. The aims of this paper is to determine the optimum ratio for $Mg_xZn_{1-x}O$/n-Si heterojunction which used as gas sensor, and determine best operating temperature.

2. The theoretical part

Some metal oxides are intrinsically n-type semiconductors, the stoichiometeric excess being due to oxygen vacancies. The conductivity of the surface has revealed to be much less than that of the bulk [10]. This has been attributed to the formation of surface oxygen ions that trap electrons, inducing a surface depletion layer and thus the development of Schottky barriers at interparticle contacts. The surface barrier height $\emptyset_s$ is given by:

$$\emptyset_s = \frac{e(N_s\theta')^2}{2\varepsilon_r N_D} \quad (1)$$

Where $N_s$is the number of the surface states, $\theta'$is the fractional occupancy, N_D is the number of donor states per unit volume in the bulk, and ε_r the relative permittivity of the film material. In the case of n-type metal oxides, since the electrons come from ionized donors via the conduction band. The charge carrier density at the interface is thereby reduced and a potential barrier to charge transport. It is due to the adsorption of oxygen ions at the surface, the resistance at the junction between the grains of the solid will be changed leading to depletion layer. In the presence of a reactive gas or chemical vapor, the surface coverage of adsorbed oxygen ions might be decreased and the resistance will be decreased as a consequence of the reduction in the surface potential-barrier and depletion length, so the depletion layer width will be [11].

$$w = \frac{Q_s}{N_D e\bar{A}} \quad (2)$$

Where Q_s is the charge associated with oxygen surface coverage, $\bar{A}$ area of the sensor [12]. The sensitivity of sensors is defined as the relative variation of the resistance of the sensitive thin film in percent per ppm of applied gas concentration [13].

$$s = \left|\frac{(R_g - R_a)}{NR_a}\right| \times 100\% \quad (3)$$

Where R_a and R_g are the electric resistance of the sensor in air and in presence of gas respectively and N is the gas concentration. Although it can be calculated from conductance as in relation:

$$s = \frac{G_{gas}}{G_{air}} \quad (4)$$

Where G_{air} is the conductance of the sensor in pure and dry air and G_{gas} is the conductance of the sensor in the air containing a given concentration of reducing gas [14].The conductance of the sensor will be changed with the change of the resistance as in relation:

$$G_{gas} = \frac{1}{R_{gas}} \quad (5)$$

At a given temperature, the conductance will be proportional to the gas pressure as:

$$G_{gas} \cong \left(P_{gas}\right)^{y} \quad (6)$$

Where P_{gas} is the partial pressure of the reducing gas in the air and y is the characteristic exponent, lower than (1), depending on the kind of gas and composition of gas sensitive layer.

3. The experiment part

The $Mg_{0.05}ZnO_{0.95}$ thin films were prepared by chemical spray pyrolysis (CSP) technique under ambient atmosphere. An $Mg_{0.05}ZnO_{0.95}$ thin film was fabricated by doping a mixture of MgO (99.99%) and ZnO (99.99%) solutions at different substrate temperatures (400, 450,and 500) ^{o}C in air ambient. The n-Si substrates were cleaned in an ultrasonic bath with de-ionized water ,acetone, and (HF:H_2O) (2:10) respectively. The distance between the n-Si substrate and the nozzle was about (31) cm. The spray pyrolysis chamber was cleaned before the beginning of the spraying process. The gas pressure in the system was kept at (4.5) bar. The substrate temperature was controlled through digital control system in the chemical spray pyrolysis technique during the spraying process. The thickness of the shotcrete films it was fixed by installing a number sprinkles. The structural characterizations of the $Mg_{0.05}ZnO_{0.95}$ thin films were carried out by X-ray diffraction (XRD) with a λ=(0.154) nm line of Cu Kα as the radiation source. The X-ray scans are performed between 2θ values of (20°-60°). The FESEM study carried out by (S-4300 of Hitachi, S-4700 FESEM in Islamic republic of Iran/ university of Tehran/ Razi foundation) scanning electron microscope equipped with (EDS). The use of an atomic force microscope (AFM), in order to observe the surface roughness and topography of deposited thin films, typical data have been taken from (AFM) height images include root mean square (RMS) roughness and grain size. The sensing measurements were carried out $Mg_{0.05}ZnO_{0.95}$ by measuring the variation in resistivity resulting from exposing the thin film surface to the gas (NO_2), the temperature was recorded by a k-type thermocouple (XB 9208B). The bias voltage was supplied by (FARNELL E350) power supply. The resistivity was recorded by (Fluke Digital Multimeter 8845A / 8846 A).

4. Results and discussion

The results and discusses the effect of doping, on the characterization structural and sensing properties of the $Mg_{0.05}ZnO_{0.95}$ films the deposited by (CSP), also the structural and sensing measurements such as, X-ray diffraction (XRD), surface morphological features by (FESEM) and (AFM). The sensing measurements by using homemade equipment.

4.1 X-ray diffraction (XRD):

Fig.1shows the XRD spectrum of ZnO/n-Si, and doped $Mg_{0.05}ZnO_{0.95}$/n-Si thin films with different substrate temperatures (400,450,and 500) ^{o}C, for range from (20^{o}-60^{o}) in 2θ, at nitrogen pressure (4.5) bar, and constant thickness. It can be seen that the film is less crystallized at T_s=(400)^{o}C. There are three prominent diffraction peaks viz. (100), (002), and (101) which corresponding to different angle (31.65^{o}, 34,5^{o}, and 36.31^{o}) , respectively belong to the hexagonal wurtzite structure of ZnOas shown in Fig.(1a). The XRD measurements revealed that the ZnO/n-Si film show a peak (002) with a full width at half maximum FWHM equal to (0.28), and average grain size is (32.7). When Mg dopant with ZnO by volumetric ratio (5)% and at the temperature of (400) °C decrease of average grain size to become (31.8)nm, and decreases the intensity of diffraction peaks as shown in Fig.(1b). At a temperature of (450) ^{o}C, we note that the average grain size an increases of the $Mg_{0.05}ZnO_{0.95}$/n-Si film for become (33.24)nm, and decrease the grain boundaries, and this refers to the improvement of the crystal structure (i.e., decrease of crystalline defects) as shown in Fig.(1c). When increasing the temperature to (500) ^{o}C, we note that the grain size increases more to become (44.3)nm. This refers to the decrease of grain boundaries of the $Mg_{0.05}ZnO_{0.95}$/n-Si film, and improve the crystal structure and that shown in Fig.(1d).

4.2 Field emission scanning electron microscopy (FESEM):

ZnO, and dopant $Mg_{0.05}ZnO_{0.95}$/n-Si films were measured nanostructure in the Islamic republic of Iran/university of Tehran/Razi foundation. Surface morphologies of (FESEM) images and their corresponding (EDS) spectra at different substrate temperatures (400, 450 ,and 500) ^{o}C are shown in Figs.(2A,2B,2C, and 2D) respectively, were all fixed thickness of the films (80) nm. The morphology of the surface of pure ZnO is a nanostructure cannot determine its kind, as this irregular in shape, as shown in Fig.(2A). From the (FESEM) images the grain size value are found to be in the range of (30-63)nm for ZnO/n-Si. At a temperature of (450)°C, we note increased average grain size of the (33-67.34) nm as in Fig.(2B). At a dopant $Mg_{0.05}ZnO_{0.95}$ /n-Si films, when a temperature of (400) °C, we note decreased average grain size of the (28.4-61.34) nm as in Fig.(2C). Increasing average grain size in the range (31.24-65.40) nm when the temperature increase to (450) ^{o}C, as shown in Fig.(2D), and increases more when you increase the degree to (500) ^{o}C. The (EDS) spectra of the ZnO/n-Si and dopant $Mg_{0.05}ZnO_{0.95}$/n-Si thin films at different substrate temperatures(400,450, and 500) ^{o}C by (CSP) are given in Figs.(2a,2b, 2c, and 2d). Which show that the films contain the elements (Si, N, O , Zn, and Mg) as expected, indicating formation of the Mg_xZnO_{1-x} /n-Si films.

4.3 Atomic force microscopy (AFM):

Figs.(3a, 3b, 3c, 3d, and 3e) shows the surface topography of the thin films. It shows 3-D and granularity accumulation distribution of (AFM) images for the ZnO/n-Si, and dopant$Mg_{0.05}ZnO_{0.95}$/n-Si thin films at different substrate temperatures (400,450,and 500)^{o}C, and nitrogen pressure (4.5) bar, with scanning area (2000×2000)nm^2. From figures shown can that describe the general appearance of the $Mg_{0.05}ZnO_{0.95}$ films prepared, as are deposited vertical to the surface of the substrate silicon is made up of nanorods (NRs), as shown in the pictures. It can identify the parameters that can be found through (AFM) technique are the average diameter, the total number of granules, surface thickness, roughness average, the root mean square (RMS) of the average of roughness, and the average of height. Note down the average diameter of the ZnO in increase the temperature and this leads to increased grain size and thus lead to increased roughness average as in Fig.(3b). We note average increase diameter with dopant $Mg_{0.05}ZnO_{0.95}$/n-Si, which leads to a decrease grain size, and this is due to the Mg ion radius smaller than the radius of the Zn ion, as shown in Fig.(3c). When temperatures (450, and 500)^{o}C increased grain size as in Figs.(3d, and 3e).

5. Gas sensors

One of the common disadvantages of $Mg_{0.05}ZnO_{0.95}$/n-Si gas sensors is the high temperature required for the sensor operation. For this reason, the effect of the operation temperature on the thin films sensitivity was studied with the aim of optimizing the operation temperature to the lowest possible value. The operating temperature is defined as the temperature at which the resistance of the sensor reaches a constant value[15]. Figs.(4a, and 4b) show the variation of sensitivity as a function for operation temperature in the range (25-300)^{o}C of the $Mg_{0.05}ZnO_{0.95}$/n-Si films for different substrate temperatures (400,450,and 500) ^{o}C. The sensing test was done by using (3)% NO_2: air mixed ratio and bias voltage (6Volt) were applied on the electrodes for all samples. The variation of the temperature reveals resistance of the film decreases as the temperature increases from room temperature to (200) ^{o}C showing a typical negative temperature coefficient of resistance(NTCR) due to thermal excitation of the charge carriers in semiconductor [16]. An increase in temperature leads to a decrease in electron mobility and a subsequent increase in resistance. These results are similar to researchers[16,17]. Below (200)^{o}C temperature, oxygen

adsorption at the surface is mainly in the form of O^{-2}, while above (200)°C, chemisorbed oxygen is present in the form of O^{-}, due to the conversion of O^{-} into O^{-2} oxygen adsorbs the additional electron from the $Mg_{0.05}ZnO_{0.95}$/n-Si, which is attributed to increase in the resistance of the sensor film as temperature rises further. After this detailed explanation, there are no sensitivity at high Mg-content ratios, and the optimal ratio of Mg-content was (5)%. We note that the optimum operating temperature is room temperature for the Mg-content (5)%. In addition, whenever they are low temperature sample preparation was response to NO_2 gas in a concentration of (30) ppm, with the maximum response at operation temperatures of (300, and 200) °C are of (67.82, and 90.80)%, respectively. The sensors with higher resistance yield, and higher response to the gas under test. Better of dopant Mg_xZnO_{1-x}/n-Si ratios are small Mg-concentrations for the manufacture of gas sensors. Fast response time (6.3s) occurs also, and quick recovery time is (44.1s). sensitivity better. It was observed that the optimum operating temperature is(200) °C as shown in Fig. 4b. Figs. (5a, 5b, 5c, 5d, and 5e) show the relation between the response and the recovery times with the operating temperature of the ZnO/n-Si, and dopant $Mg_{0.05}ZnO_{0.95}$/n-Si thin films for NO_2:air and bias voltage (6Volt). The response and recovery times are defined as the time need to reach (90)% of a single change. From Fig.(5a) it took (26.4s) for the ZnO/n-Si time sensor to response and (38.7s) to recover at(300)°C, when substrate temperature (400)°C. While from Fig.5b $Mg_{0.05}ZnO_{0.95}$/n-Si sensor took (6.3s) to response and (44.1s) to recover at(25) °C. As for Fig.(5c) ZnO/n-Si sensor took (22.5s) to response and (71.1s) to recover at (25) °C. In the temperature (400) °C, as shown in Fig.(5d) takes a response time (15.3s) and recovery time (42.3s), at operating temperature (200)°C. We note that the response time to the proportion of $Mg_{0.05}ZnO_{0.95}$/n-Si of (5)% (faster than the pure ZnO response time, either recovery time be more, and that the optimum operating temperature is (200) °C when the preparation temperature (400) °C. At a substrate temperature of (500) °C, we note that the highest sensitivity at room temperature and response time (28.8s), and recovery time (99.9s), as shown in Fig. (5e).

6. Conclusions

We have successfully prepared ZnO- doped MgO with different substrate temperatures by chemical spraying pyrolysis (CSP) technique, the average Crystallite sizes and Roughness was decrease with doping by MgO. This reduction in grain size might also be responsible for decreases of the optimal operating temperature to (200)°C. Enhancement sensitivity occurs at low level doping concentration (5)% due to the smaller grain size; higher is the surface to volume ratio. The pure ZnO, and MgZnO thin films sensors show a good measurable.

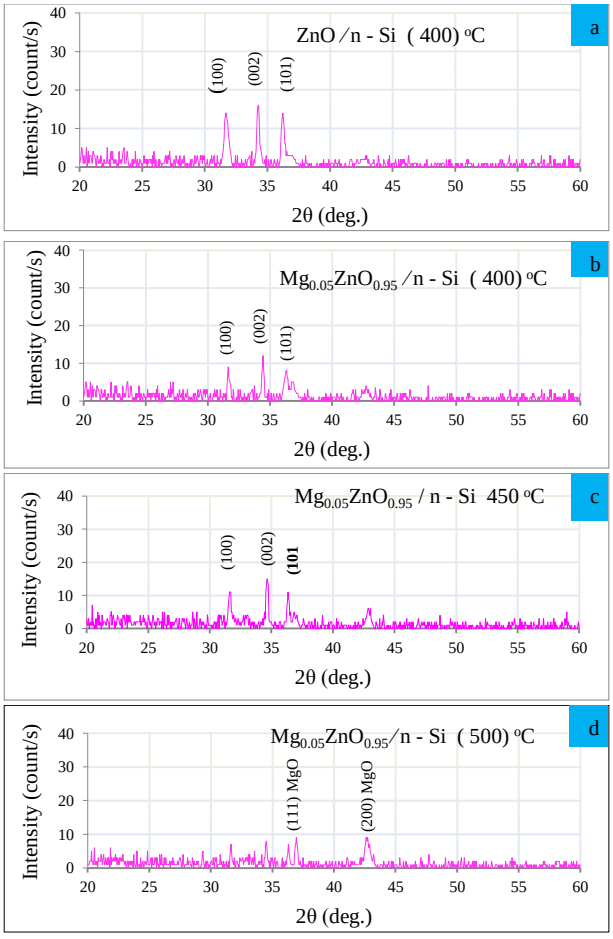

Fig.1: XRD patterns for ZnO/n-Si and doped $Mg_{0.05}ZnO_{0.95}$ /n-Si gas sensor at different temperatures (400,450, and 500) °C.

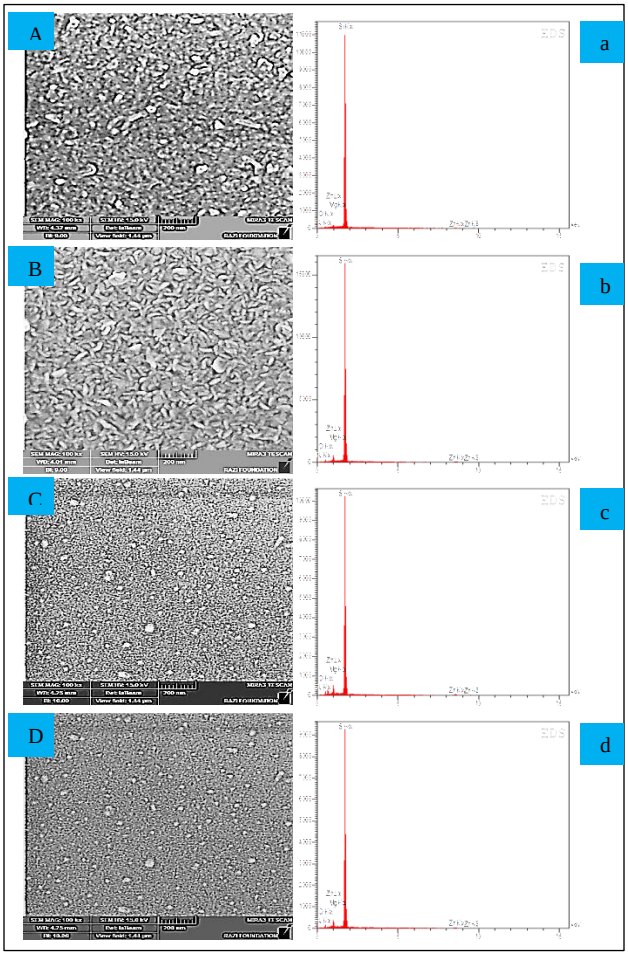

Fig.2: FESEM and EDS for ZnO/n-Si, and doped $Mg_{0.05}ZnO_{0.95}$ /n-Si gas sensor at different temperatures(400,450,and 500) °C.

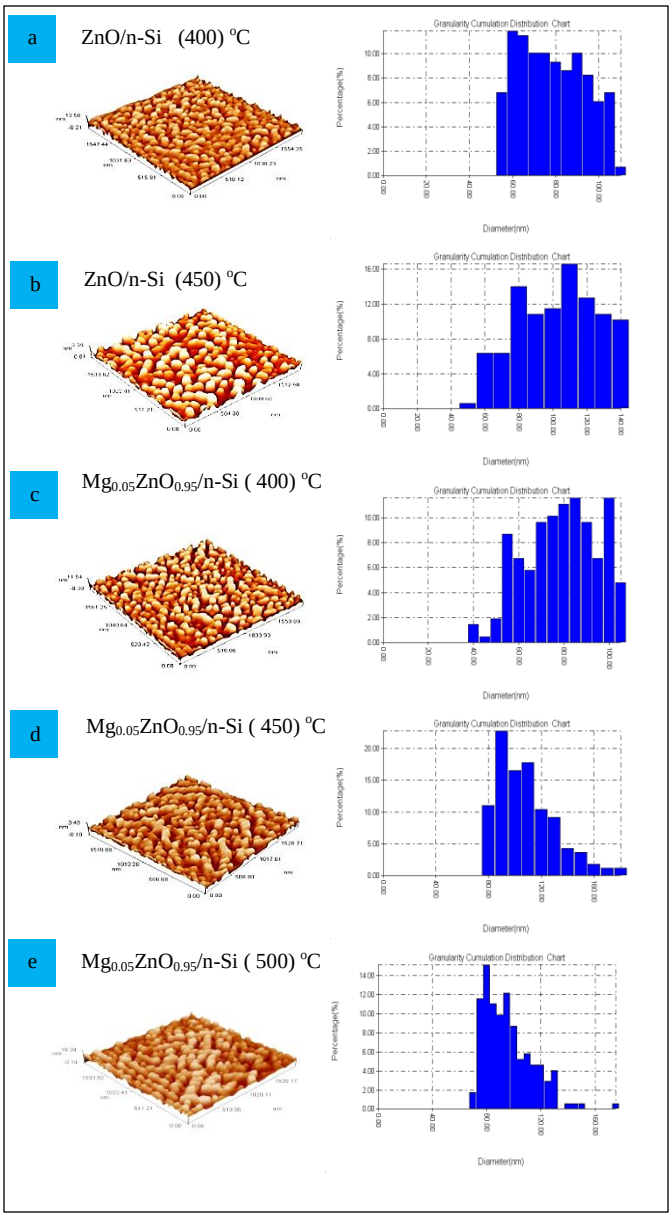

Fig.3: 3-D AFM image and granularity accumulation for ZnO/n-Si gas sensor and $Mg_{0.05}ZnO_{0.95}$ /n-Si with different temperature (400,450, and 500) °C.

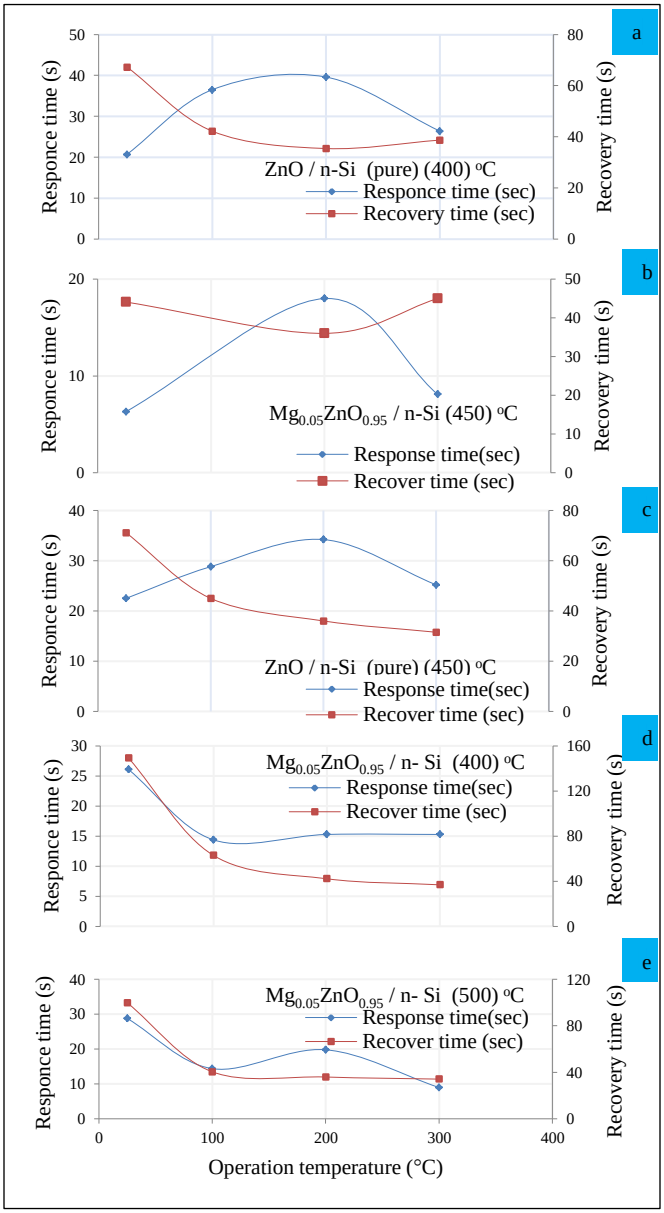

Fig.5: The variation of response time and recover time with different operating substrate temperatures for ZnO/n-Si and $Mg_{0.05}ZnO_{0.95}$/n-Si sensor at different temperatures (400,450, and 500) °C.

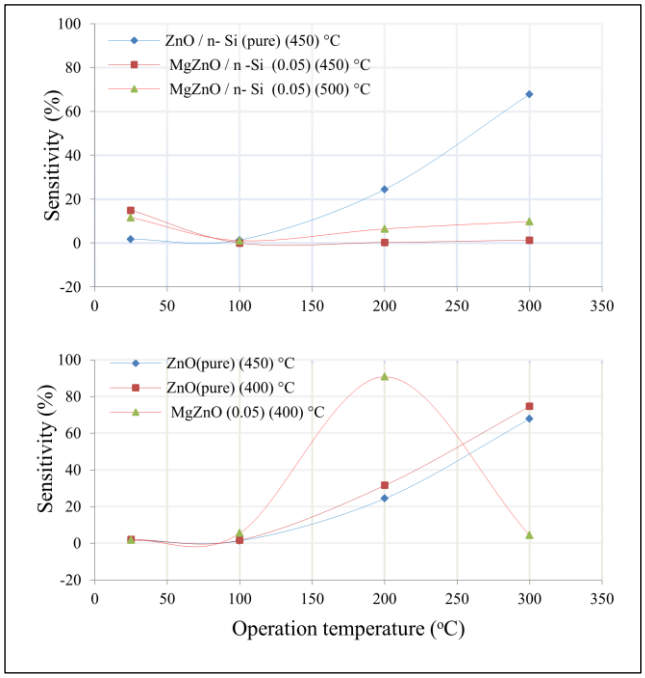

Fig.4: The variation of sensitivity with the different operating temperature of the ZnO/n-Si, and doped $Mg_{0.05}ZnO_{0.95}$/ n-Si gas sensor at different temperatures (400,450,and 500) ^{o}C.

6. References

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