INTERNATIONAL JOURNAL OF SCIENCE AND NATURE

www.scienceandnature.org

In_2O_3:SnO_2 THIN FILM GAS SENSOR FOR DETECTION OF NO_2 AT DIFFERENT OPERATION TEMPERATURES

Bushra A. Hasan & Rusul M.Abdallah
University of Baghdad, College of Science, Department of Physics

ABSTRACT
Indium tin oxide ITO compound at different ratio In_2O_3: SnO_2 were prepared by putting indium oxide and tin oxide SnO_2 in an evacuated sealed quartz tube under vacuum pressure (10^{-3}Torr) in an oven at 1273 K for eight hours. Thin films of pure and Indium tin oxide ITO of different doping ratio (1,3,5,7 and 9) % wt have been prepared on glass and silicon wafer (111) type n substrates at room temperature by Pulsed laser deposition. The structure of Indium tin oxide ITO alloy and thin film of various doping ratio are identified using X-ray diffraction while the morphology were examined using atomic force microscopy. The diffraction patterns of the alloys and the prepared thin films reveals polycrystalline structures with dominate peak belonged to ITO. The EDX spectrum confirms the presence of In, Sn and O elements in prepared films .The sensing properties have been done at different temperature (R.T, 373, 473, and 573K). The gas sensing measurements to NO_2 gas that In_2O_3: SnO_2 prepared on n- Si showed good sensitivity. Maximum sensitivity (800) obtained for In_2O_3 :SnO_2 prepared on n- Si at operating temperature 573K and doping ratio 5% .

KEYWORDS: Thin Films of In_2O_3:SnO_2, XRD, AFM, PLD, EDX, Thin films gas sensors.

INTRODUCTION

In_2O_3:SnO_2 (indium tin oxide ITO) is well-known transparent conducting oxide (TCO) with low electrical resistivity. ITO is transparent but bulk form can change color highly degenerate heavily doped n-type wide gap semiconductor (band gap ~3.7eV)[1]. As a result of high conductivities ITO, exhibit metal like behavior, and also high reflectivity in the near infrared region[2-3]. The current application of ITO films affirms the providence of obtaining the lowest possible electrical resistivity with the optimized highest transparency in the visible range. It is found that the electrical and optical properties of ITO thin films are critically depend on the preparing process also by adjusting the deposition conditions the transparency and conductivity of highly degenerate and wide band gap oxide semiconductor films can be changed. The key issue to obtain the best performance of gas sensor is the ability to deposited high conductive and transparent ITO films. The high conductivity value of ITO film is resulted from the high absorption of the incident light or high opacity. Therefore, an optimized performance is sought for an effective application to gas sensor fabrication. Tin dioxide doped Indium oxide is the most used n-type semiconductor in gas sensing devices because of its capabilities to detect inflammable gases like CH_4, H_2, C_2H_5OH, CO and so on [4]. Besides, Indium Tin oxide (In_2O_3:SnO_2) nano composites that exhibited superior thermal stability against grain growth have been reported [5]. The size and the morphology of oxide composites are difficult to control, which have the most influence on their physical and chemical properties There are many preparation techniques to prepare high quality ITO films such as pulsed laser deposition[6], sol-gel [7], RF and DC sputtering [8-9]. In the present work, ITO films were deposited by PLD on glass substrate and The morphology, structural and Energy Dispersive X-ray Spectroscopy (EDX) analysis of ITO films were examined and the sensing properties of un-doped In_2O_3 and doped with different concentrations (1,3,5,7 and 9)% of SnO_2 films deposited on n-type silicon wafer (111) are investigated as a function of operating temperature and time to find the temperature dependence of the sensitivity for oxidizing gas (NO_2) .

Experimental Part

The alloy of In_2O_3:SnO_2 were prepared by quenching technique. Takes appropriate amount the of high purity (99.99) Indium oxide powder and doping with different percentages of tin oxide 99.9% (are weighed using an electronic balance with the least count of (10^{-4}gm) and put in a quartz ampoule (length ~ 25 cm and internal diameter ~ 8 mm) are heated to 1000°C and let at this temperature for 8 hours. The temperature of the furnace was raised at a rate of 10°C/min. During heating the ampoules are constantly agitated .This is done to obtain homogeneous alloys. Si wafer was cut in small pieces(1x1)cm^2.Cleaning glass slides and Si wafer substrates were performed by subjected the used substrates to several steps to remove any contamination such as dust ,oily material ,grease and some oxides using soap solution , then the glass slides and Si were placed in a clean beaker containing distilled water and with ethanol solution then the glass slides and Si were dried by blowing air. Thin films were deposited using pulsed lased deposition technique under vacuum of (10^{-3} Torr). Thin films were obtained by focusing Nd:YAG (Huafei Tongda Technology_Diamond-288 pattern EPLS) Q-switching laser beam which coming from a window is incident on the target surface making an angle of 45° with it. The characteristics of the laser tool were (1) Laser

model: Q-switched Nd: YAG Laser Second Harmonic Generatio (SHG). Laser wavelength: (1064 /532) nm.(2)Pulse energy: (100-1000) mJ. (3) Pulse width: 10ns.(4)Repetition frequency: (1,2,3,4,5,6) Hz .(5)Cooling method: inner circulation water cooling and (6)Applied voltage: 220V.The substrate is placed in front of the target with its surface parallel to that of the target. Sufficient gap is kept between the target and the substrate so that the substrate holder does not obstruct the incident laser beam .X-ray diffraction (XRD) was used to check the structures of the prepared alloys and thin films. In the present work x-ray diffractrometer type (Miniflex II), with Cu-K_α x-ray tube (λ = 1.54056 Å) is used. The morphology is obtained using atomic force microscopy AFM. EDX analysis for elemental composition of In_2O_3: SnO_2. In this work, the gas responsibility tests performed at different operation temperature beginning from (room temperature, 373, 473 and 573) ºC. The time taken for the sensor to attain 90 % of the maximum increase in resistance on exposure to the target gas is the response time. The time taken for the sensor to get back 90 % of original resistance is the recovery time . The test was performed at various sensing temperatures with 6 V bias voltage.

The sensitivity factor (S %) at different operating temperatures is calculated using equation

$$S = \left|\frac{R_a - R_g}{R_a}\right| = \frac{\Delta R}{R_a} \text{ (for oxidizing gases)}$$

RESULTS & DISCUSSION

Structural Properties

Figure .1 shows X– ray diffraction of the alloys of pure and doped indium oxide with different doping ratio, it is evident that the prepared alloys have polycrystalline the main diffraction planes (222) and other planes (321), (400), (440), and (622) corresponded to ITO structure . The pattern declared another peaks corresponded to SnO_2. The grain size of the predominant plane increases from 22.9nm to 48.1 nm as SnO_2 added to In_2O_3. The grain size get to reduced with continues addition of SnO_2 up 5% then the size of crystal get to increase and reach steady value (45.1nm) at 9% concentration of SnO_2 . The diffraction pattern of the prepared thin films displayed in figure 2. It is evident the films have polycrystalline structures with a cubic bixbyite structure (In_2O_3). The preferred plane for crystal growth located at (2θ =30.4^o) related to the plane (222) and other planes related to the ITO system likes (400)(440)and (622). The degree of crystallinity decreased with increase of doping ratio evident from increment of crystal size from 21 to 27 nm as doping ration increases from 1 to 3% but then the degree of crystalinily worse hence the crystal size decreases and reach steady value 21 nm.

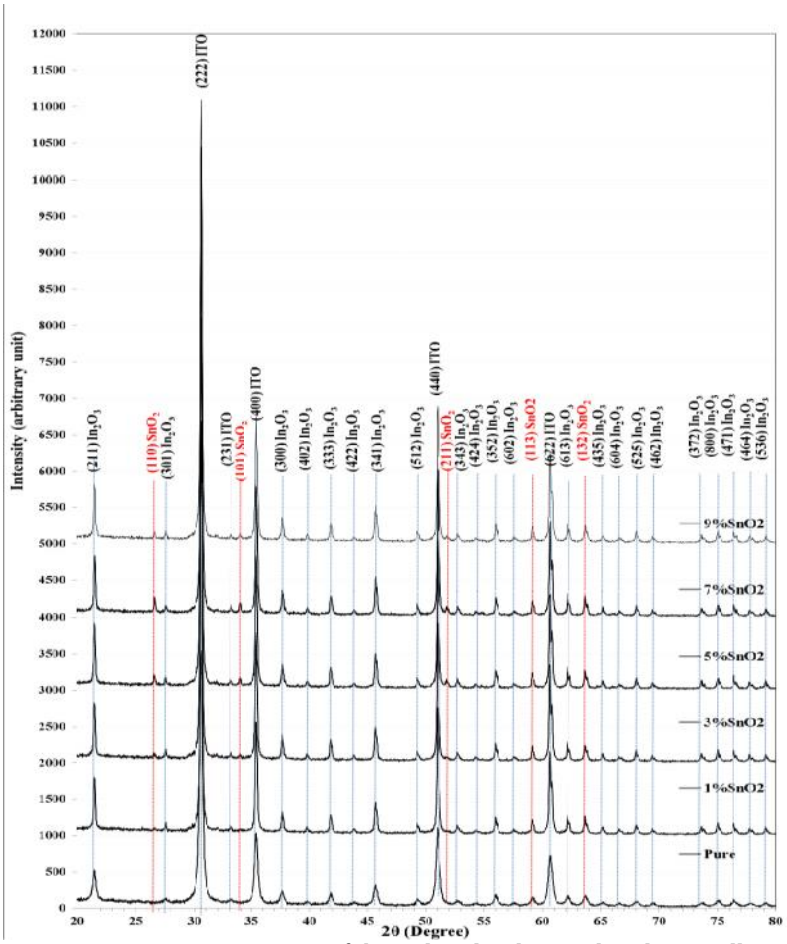


FIGURE 1: XRD patterns of the undoped and SnO_2-doped In_2O_3 alloys

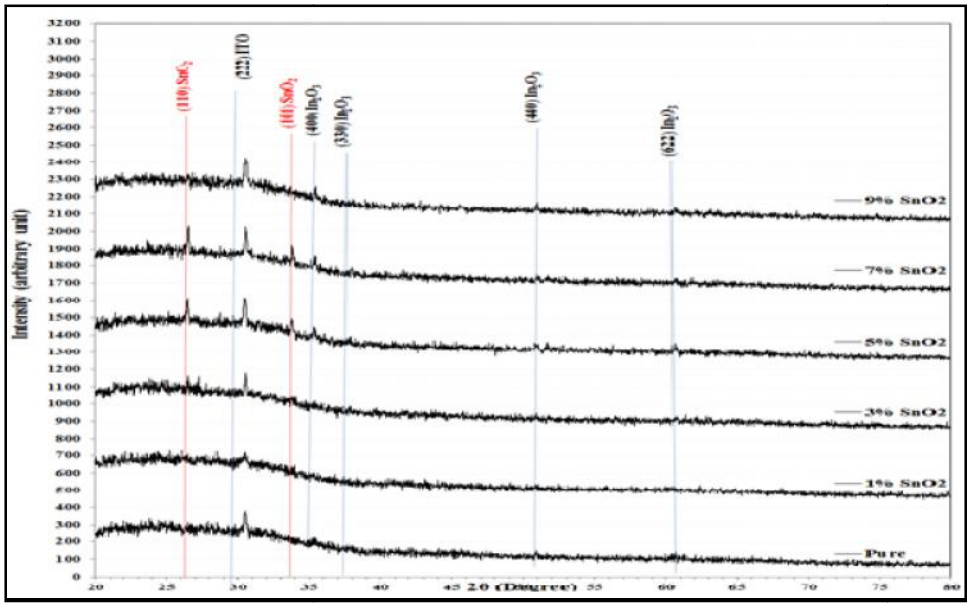


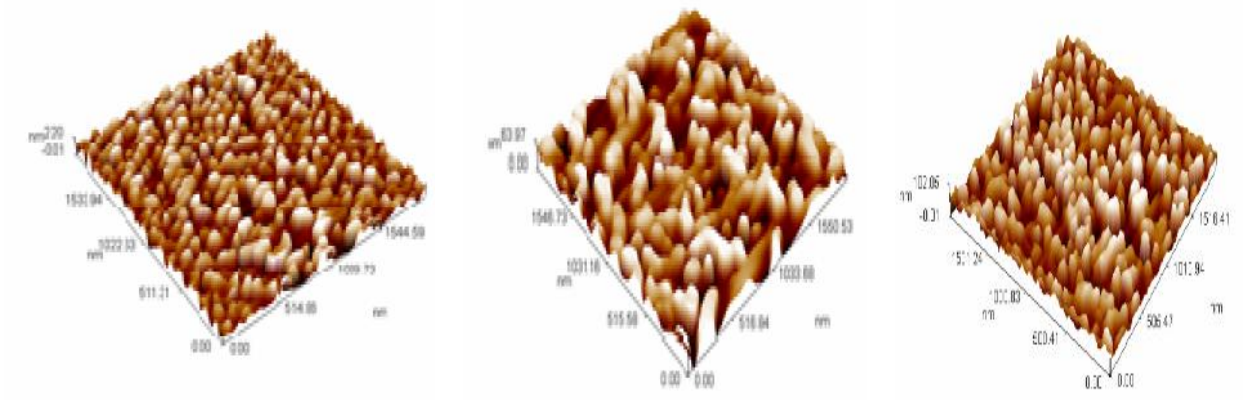
FIGURE 2: X-ray diffraction patterns of deposited In_2O_3 undoped and doped by SnO_2 with different ratio (1, 3, 5, 7,and 9) %.

Atomic Force Microscopy Analysis (AFM)

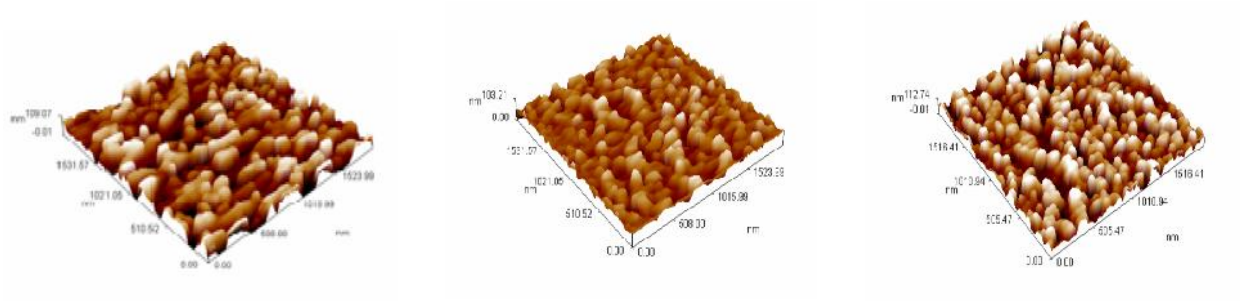
The surface morphologies of In_2O_3:SnO_2 thin films were investigated by Atomic Force Microscopy (AFM). Figure.3 shows their surface morphologies analyzed by AFM. The measured grain size and RMS roughness and peak –peak value are given in Table (1) .This Table illustrates an increment in average diameter as tin oxide added to the host material i.e. 1% then go down, although the variation of average diameter was non regular with doping ratio .The roughness of the films shows increment by increasing doping however it show reduction at 7%, while maximum values of roughness and peak –peak value are obtained at doping ratio 9% of tin oxide.

TABLE 1: AFM parameters for pure and doped In_2O_3 at different SnO_2 ratios deposited at room temperature

% SnO_2	Average diameter (nm)	Average roughness (nm)	Peak-peak (nm)
0	52.48	0.458	2.21
1	100.22	14.6	62.9
3	79.12	22	102
5	87.57	24.3	109
7	105.59	11.5	103
9	90.95	26.8	112



pure 1% SnO_2 3% SnO_2

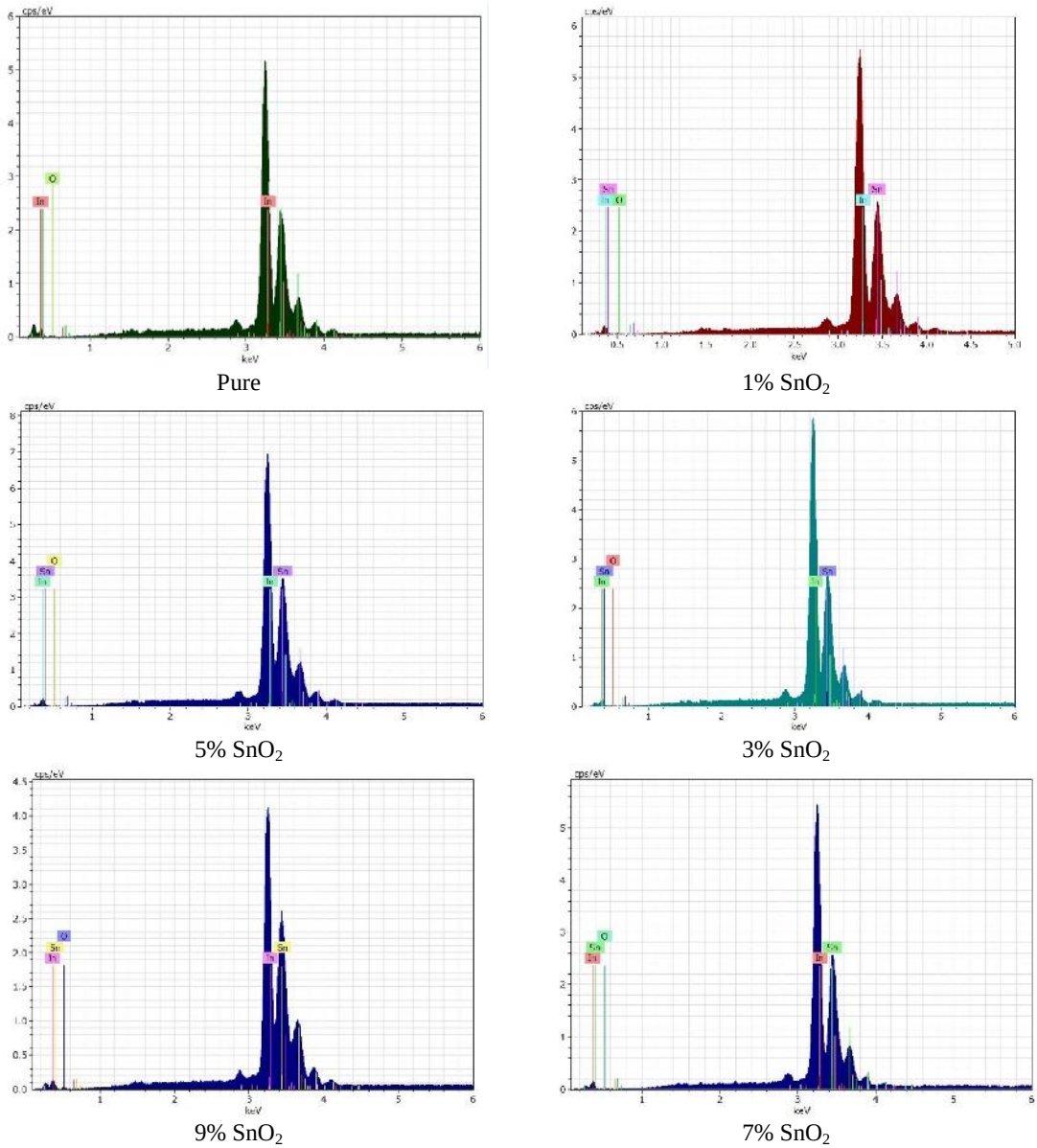


5% SnO_2 7% SnO_2 9% SnO_2

FIGURE.3 AFM images for of pure In_2O_3 thin film and In2O3 doped with SnO2 with different doping ratio

Energy Dispersive X-ray Spectroscopy (EDX) Analysis

EDX analysis for elemental composition of pure In_2O_3 thin film and In_2O_3 doped with different doping ratio of SnO_2 (1, 3, 5, 7 and 9%) wt. , as shown in figure (4). The high concentration of Indium, tin and oxygen shows that they are the main components.



Pure 1% SnO_2

5% SnO_2 3% SnO_2

9% SnO_2 7% SnO_2

FIGURE 4: EDX analysis of pure In_2O_3 thin film and In_2O_3 doped with different doping ratio of SnO2 (1, 3, 5, 7, and 9%) wt.

Gas Sensors Measurements:
Thin films sample are examined for gas sensing using NO_2 at different operation temperature beginning from (room temperature, 373, 473 and 573)ºC . Figures .5 -10 show the variation of resistance as a function of time with on/ off gas valve.

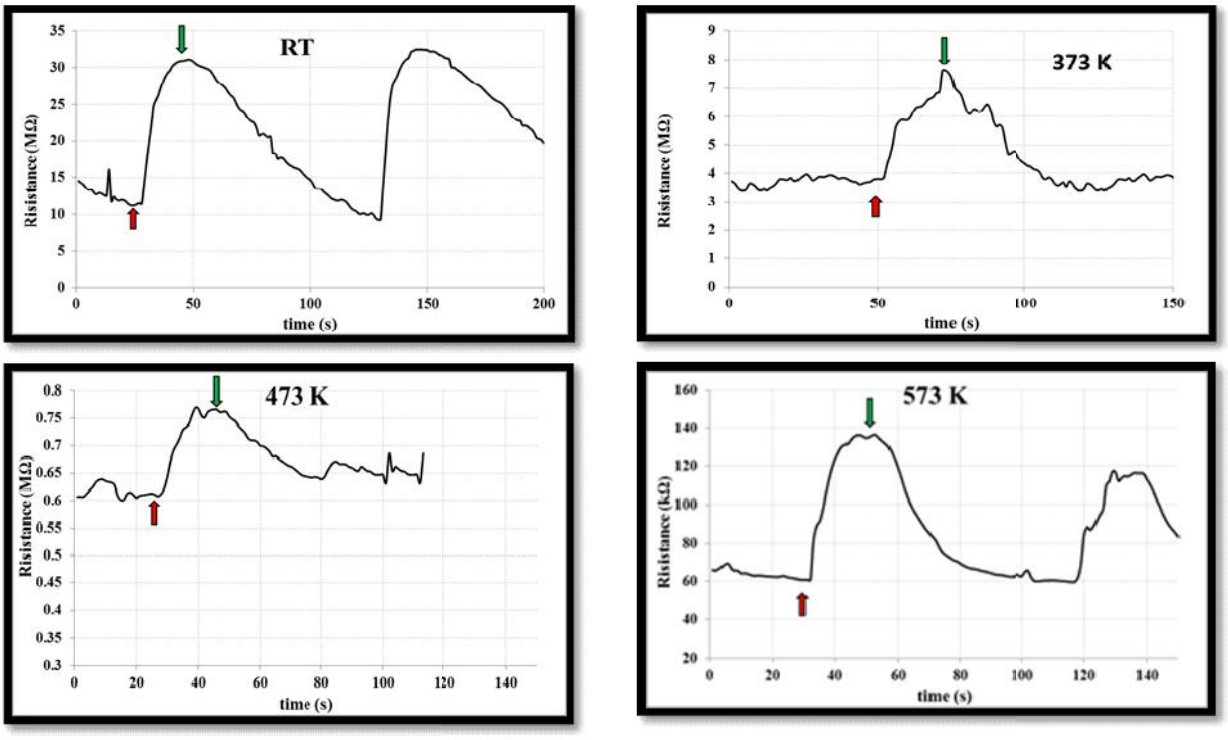


FIGURE 5: Variation of resistance as a function to the time for pure In_2O_3 deposited on n- Si at different temperatures

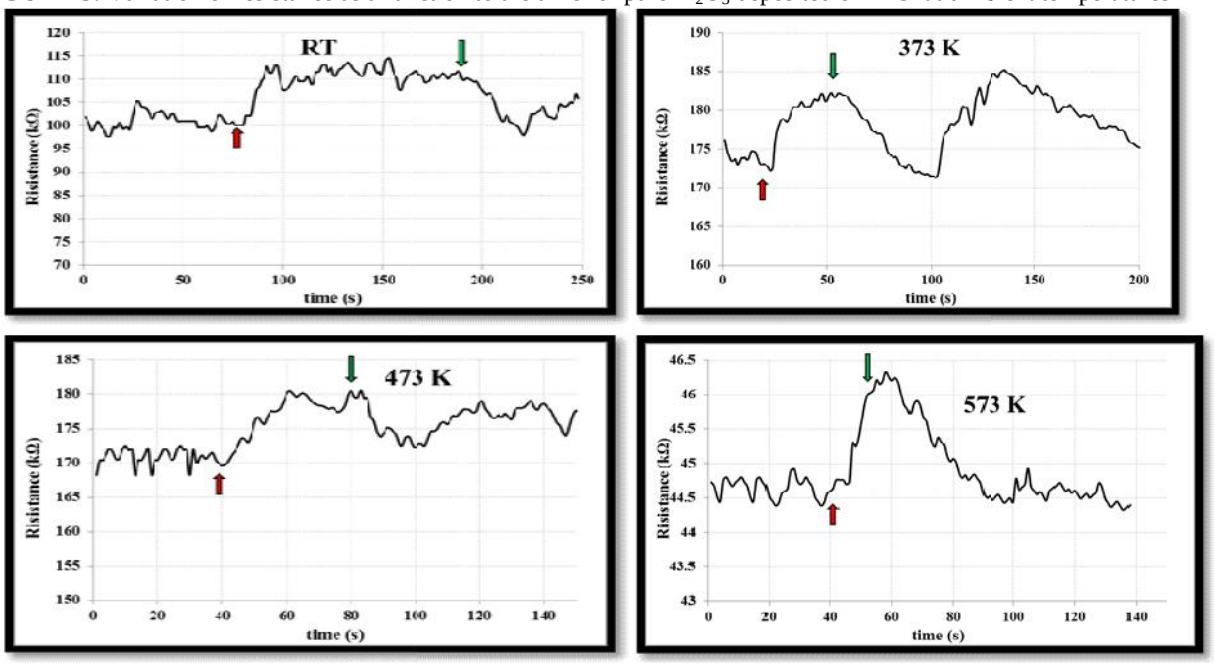


FIGURE 6: Variation of resistance as a function to the time for In_2O_3films deposited on n- Si doped with 1 wt %. SnO_2 ratio at different temperatures

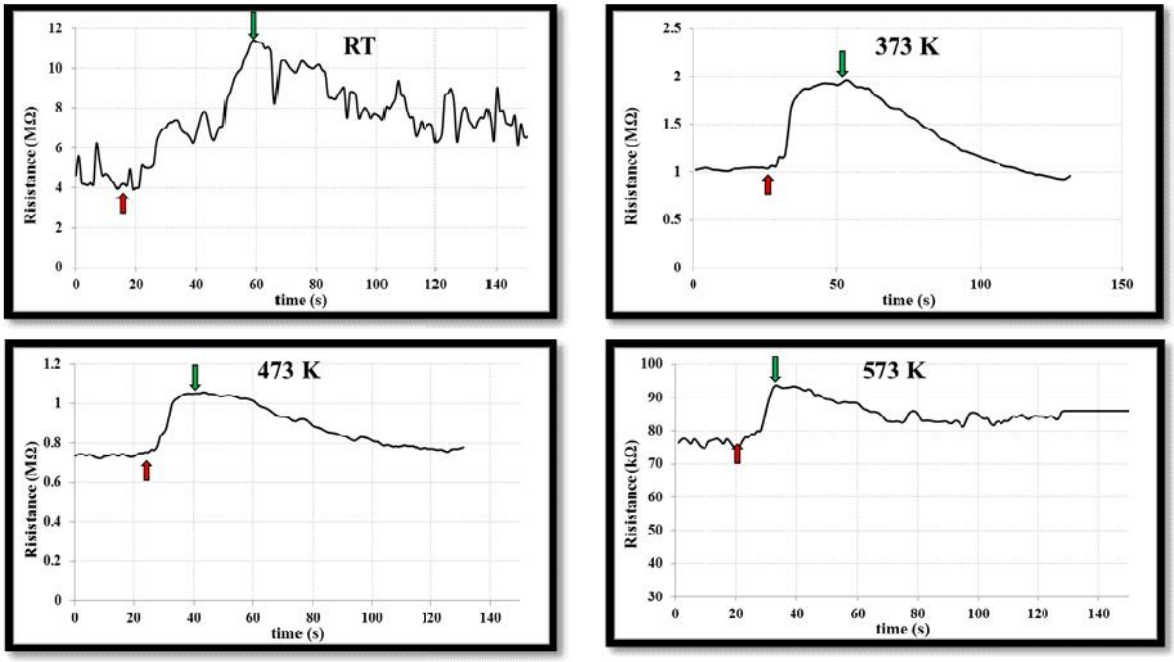


FIGURE 7: Variation of resistance as a function to the time for In_2O_3 films deposited on n- Si doped with 3 wt %. SnO_2 ratio at different temperatures

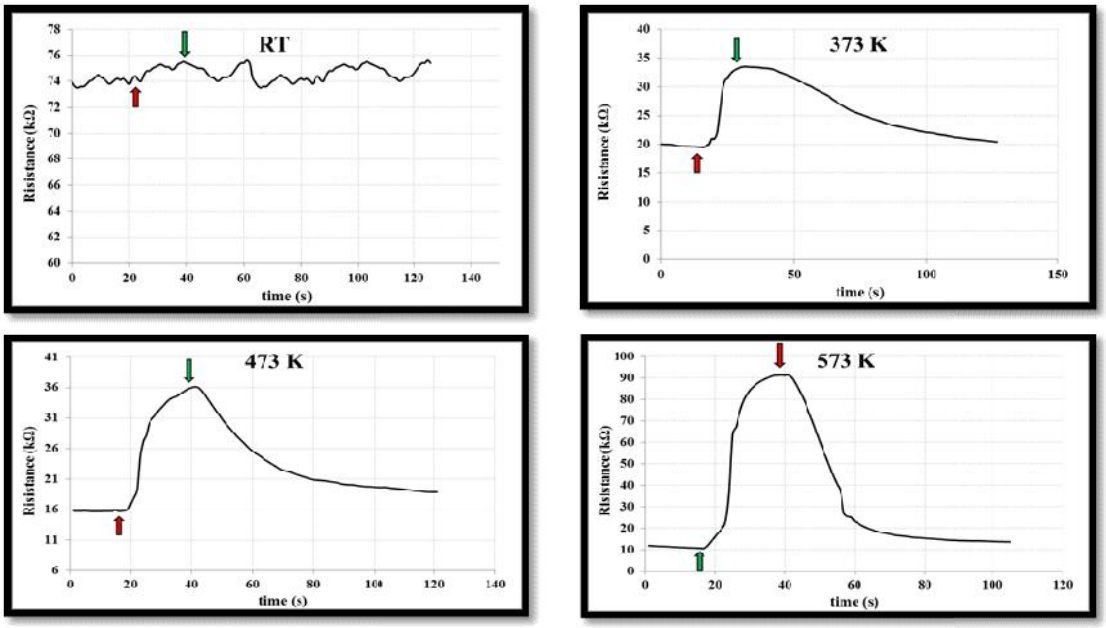


FIGURE 8: shows the variation of resistance as a function to the time for In_2O_3 films deposited on n- Si doped with 5 wt %. SnO_2 ratio at different temperatures

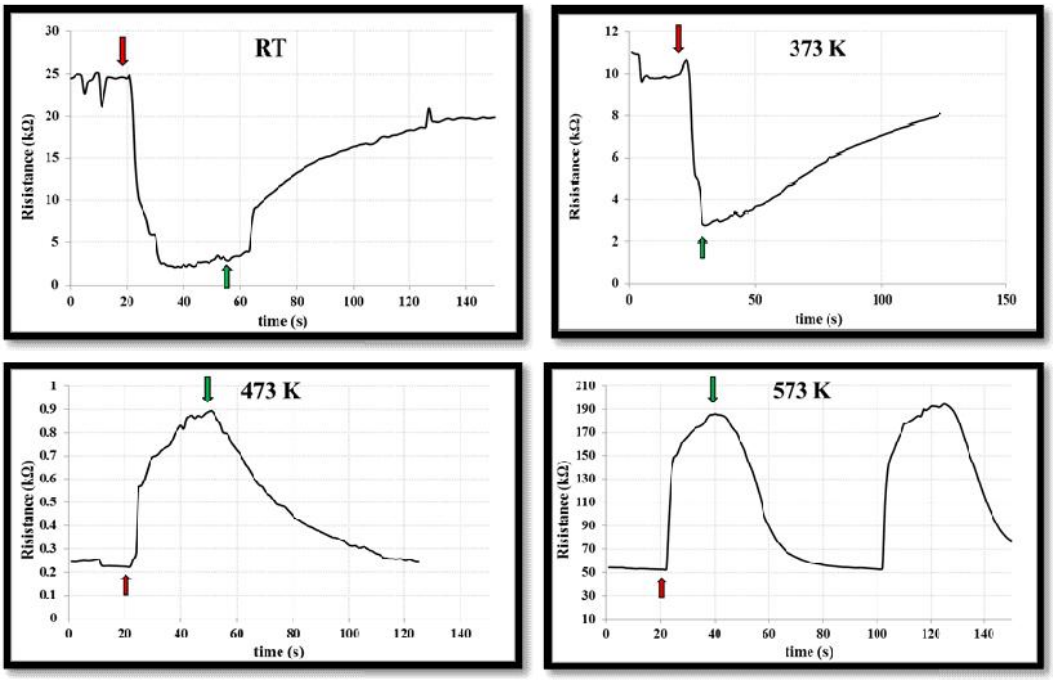


FIGURE 9: shows the variation of resistance as a function to the time for In_2O_3 films deposited on n- Si doped with 7 wt %. SnO_2 ratio at different temperatures

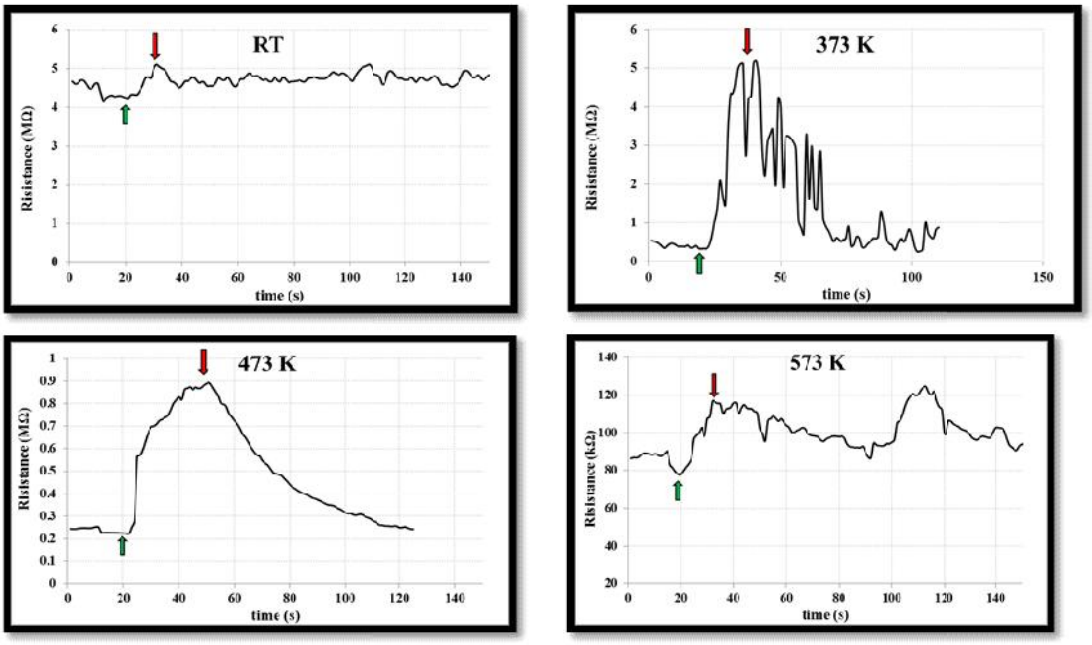


FIGURE 10: Variation of resistance as a function to the time for In_2O_3 films deposited on n- Si doped with 9 wt %. SnO_2 ratio at different temperatures

It is evident from the plots for all samples (except doping ratio 7%), the resistance of the sampl increases *i.e.* the conductance decreases upon exposure to NO_2. The conductance or surface conductivity markedly depends on the density of donors (oxygen vacancies) and acceptors (chemisorbed oxygen), the density of these species is changed as a result of the interactions take place intermediately. The reason for this behavior can be attributed to the following: NO_2 gas undergoes an ionic reaction with the surface adsorption oxygen, where the electron on the oxygen, is extracted from the semiconductor and causes the conductivity of the In_2O_3 or ITO materials to decrease, thus causing the resistance to increase .On the other hand the variation of resistance as function of time for gas sensor samples with 7% concentration of tin oxide at law temperature (R.T and 373K) get to change in reverse manner *i.e.* the resistance decreases with exposure to NO_2 vapor .This related to the transformation of ITO sample to p-type semiconductors .

Effect of Operation Temperature on the Sensing Properties

Table (2) shows the sensitivity as a function of operating temperature for pure In_2O_3 and doped with different concentrations of SnO_2, which are deposited on n-type silicon substrates.

Results show that the sensitivity of the gas sensors thin films with low doping concentrations (0,1 &3%) decreases with increasing of the operating temperature, while the sensitivity of gas sensors thin films with high doping concentration (5,7 and 9)% , showed an increasing in sensitivity with increase of the operating temperature, however the sensitivity get to reduce at high operating temperatures . Maximum sensitivity vale was obtained for In_2O_3 thin films doped with the ratio 5% SnO_2 at temperature of (573 K) which called optimal temperature. At the optimal temperature, the activation energy may be enough to complete the chemical reaction. The increase and decrease in the sensitivity indicates the adsorption and desorption phenomenon of the gas.

Response and Recovery Times

Table (3) shows the relation between the response time and the recovery time with different Tin Oxide doping ratios at different operating temperature of the un-doped and doped In_2O_3 thin films. From the table can be observed that the response and the recovery time change in non systematic sequence with operating temperatures and doping ratio In general the response get to decreases with both operating temperature and doping ratio. While the recovery time changes in reverse manner *i.e*. it increases with both operating temperature and doping ratio especially for high doing ratio and operating temperature.

TABLE 2: Sensitivity as a function of operating temperature for un-doped and doped In_2O_3 with different concentrations of SnO_2 for NO_2 gas deposited on n-Si.

Operating Temp.(K)	SnO_2 Doping ratio					
	0%	1%	3%	5%	7%	9%
R.T	181.82	13.00	175.00	2.03	88.00	19.05
373	87.5	5.81	90	65	70	700
473	26.7	5.9	50.0	125.0	309.1	309.1
573	125	3.82	21.1	800	43.75	43.75

TABLE 3: Response and recovery time of un-doped and doped In_2O_3 with different ratios of SnO_2 deposited on n-Si for NO_2 gas

%SnO_2	Response time (s) Operating Temperature(K)				Recovery time (s) Operating Temperature(K)			
	R.T	373	473	573	R.T	373	473	573
0	25	25	20	20	75	37	28	45
1	30	30	18	14	30	40	20	40
3	30	20	20	15	50	60	60	45
5	20	10	20	20	20	70	80	35
7	25	10	28	16	70	60	70	60
9	10	20	28	16	10	60	70	60

CONCLUSION

1. The prepared In_2O_3:SnO_2 alloys and thin films have polycrystalline structure with a cubic structure with a preferential orientation along (222) direction.
2. The average diameter and average roughness change in reverse manner with the increase of in tin oxide concentration. Maximum diameter and average roughness obtained are 105.59 and 26.8 nm respectively.
3. Maximum sensitivity obtained from In_2O_3:SnO_2/n-Si thin films gas sensor (800) for tin oxide concentration 5% at 573.
4. Minimum response and recovery time obtains from In_2O_3:SnO_2/n-Si thin films gas sensor were 10 at R.T.
5. Increase of operating temperature enhanced the sensitivity of the prepared In_2O_3:SnO_2 thin films

REFERENCES

[1]. Ambrosini, A., Duarte, A., Poeppelmeier, K.R., Lane, M., Kannewurf, C.R., Mason, T.O. (2000) J. Solid State Chem. 153, 41.

[2]. Brewer, S.H., Franzen, S. J. Phys. Chem. B 106 (2002) 12986

[3]. Mryasov, O.N., Freeman, A.J., Phys. Rev. B (2001) 6423, Art. No.233111.

[4]. Mandayo, G.G., Castano, E., Gracia, F.J., Cirera, A., Cornet, A., Morante, J.R. (2003) Strategies to enhance the carbon monoxide sensitivity of tin oxide thin film, Sensorsand Actuators B, 95: 90-96.

[5]. McCue, J.T., Ying, J.Y. (2007) SnO2–In_2O_3 nano composites assemiconductorgas sensors for CO and NOx detection, Chem. Mater., 19: 1009-1015.

[6]. Choi, J.B., Kim, J.H., Jeon, K.A., Lee, S.Y. (2003) Mat.science and Eng. B102 (2003) 376-379.

[7]. Stoica, T.F., Teodorescu, V.S., Blanchin, M.G., Gortner, M., M. Losurdo, M. Zaharescu Mater. Sci. Eng. B101 (2003) 222.

[8]. L. Kerkache, A. Layadi, A. Mosser, journal of Alloys and Compounds 485(2009) 46-50

[9]. M. Nisha, M.K. Jayaraj, Appl.Surf.Sci 255(2008)1790-1795.