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Study the Electrical and Sensing Properties for Pure and Doped SnO_2 Films Prepared by Spray Pyrolysis Technique

Nahida B. Hasan*, Amani Ali Sekeb

Department of Physics, College of Science, University of Babylon, Iraq

Abstract : The electrical and sensing properties for pure and doped SnO_2 with cobalt thin films was investigate. Nano particles of SnO_2 and SnO_2:Co thin films were prepared by spray pyrolysis technique at a substrate temperature of 400^{o}C. The films deposited with 160 nm thickness. It has been measuring electrical properties such as the D.C conductivity , Hall effect and sensing properties for all thin films. The results showed that SnO_2 pure has conductivity about of [$18.842\times10^{-5}(\Omega.cm)^{-1}$] at room temperature, and this conductivity increased with increasing of Co Vol.%, also, the results showed that all films have two activation energy and this activation energy decrease with increasing of Co Vol.%. From Hall effect measurements we find that R_H value is negative that mean the carrier is (n-type) and the majority charge are electrons. From the sensing measurements, the results of pure and doped SnO_2 thin films shows good sensors characteristics for (NO_2) gas and the maximum sensitivity for doped SnO_2 sensor when exposure to NO_2 gas is 82% for 2% doping with cobalt obtained for the film at operation temperature 200^{o}C.
Keywords: Spray pyrolysis, Tin dioxide, Cobalt, electrical and sensing properties, activation energy, Hall effect, D. C. conductivity, sensitivity, response and recovery time, Thin film.

Introduction

Tin oxide (SnO_2) is an n-type semiconductor with wide band gap and unique properties such as high electrical conductivity and high transmittance in the UV-visible region. Its properties strongly depend on the deviation of stoichiometry, oxygen deficiency and the nature ofimpurity[1-3].The (SnO_2) in thin film form is found to be the most promising for gas sensing applications due to advantages such as high sensitivity, low cost, fast response and recovery speed. Tin dioxide exhibits sensitivity to various gases, and therefore catalysts are introduced to make the sensor selective[4]. SnO_2 is a special oxide material because it has a low electrical resistance with high optical transparency in the visible range. Due to these properties, apart from gas sensors, SnO_2 is being used in many other applications, such as electrode materials in solar cells, light-emitting diodes, flat-panel displays, and other optoelectronic devices where an electric contact needs to be made without obstructing photons from either entering or escaping the optical active area and in transparent electronics, such as transparent field effect transistors[5,6]. In the present work, we bring out a detailed investigation electrical and sensing properties on this film with different concentrations of cobalt prepared from spray pyrolytic decomposition of aqueous solutions of SnO_2 and Co acetates at 400 °C.

2. Experimental

To prepared tin oxide (SnO_2) doped cobalt (Co) films. Which used procures material ($CoCl_2.6H_2O$) is a solid material which has a green color and its molecular weight (257.15 gm/mole). Cobalt was added with different doping concentrations (2,4,6 and 8 Vol.%) to different concentrations of tin chloride and also dissolved in 50 ml of distilled water. The mixture was stirred by (Magnetic stirrer) at 40 ^{o}C for 30 min and then it was allowed to cool to the room temperature with continuous stirring. The deposition parameters such as spray nozzle-substrate distance (30 cm), spray time (4 s) and the spray interval (1 min) were kept constant. The electrical properties of thin films measured by Hall effect and D.C conductivity. The sensing properties of thin films measured by sensitivity and response and recovery time.

3. Results and Discussion

1-Electrical Properties

The variation of electrical conductivity as a function of temperature for pure and different doping concentrations is displayed in Table (1).Figure (1) shows the variation of Lnσ with inverted absolute temperature 1000/T.It is noticed that the films have two values of activation energy the first region is low temperature T≤ 353 K and the second region is high temperature T ≥ 353 K as a result of polycrystalline structure of SnO_2 films. It has been noticed from the figure that the D.C conductivity ($\sigma_{d.c}$) increases with increasing temperature and this is due to increase the charge carriers concentration with temperatures[7].

Table (1): D.C. conductivity parameters for pure and doped SnO_2 thin films at different concentrations of cobalt

Sample	Ea_1 (eV)	Temp.Range (K)	Ea_2 (eV)	Temp.Range (K)	$\sigma_{R.T}\times10^{-5}$ $(\Omega.cm)^{-1}$
SnO_2 pure	0.6520	(353-473)	0.1104	(293-353)	18.8418
SnO_2:2%Co	0.6410	(353-473)	0.0975	(293-353)	10.0008
SnO_2:4%Co	0.5331	(353-473)	0.0794	(293-353)	32.7826
SnO_2:6%Co	0.5153	(353-473)	0.0770	(293-353)	12.4532
SnO_2:8%Co	0.4842	(353-473)	0.0752	(293-353)	144.7136

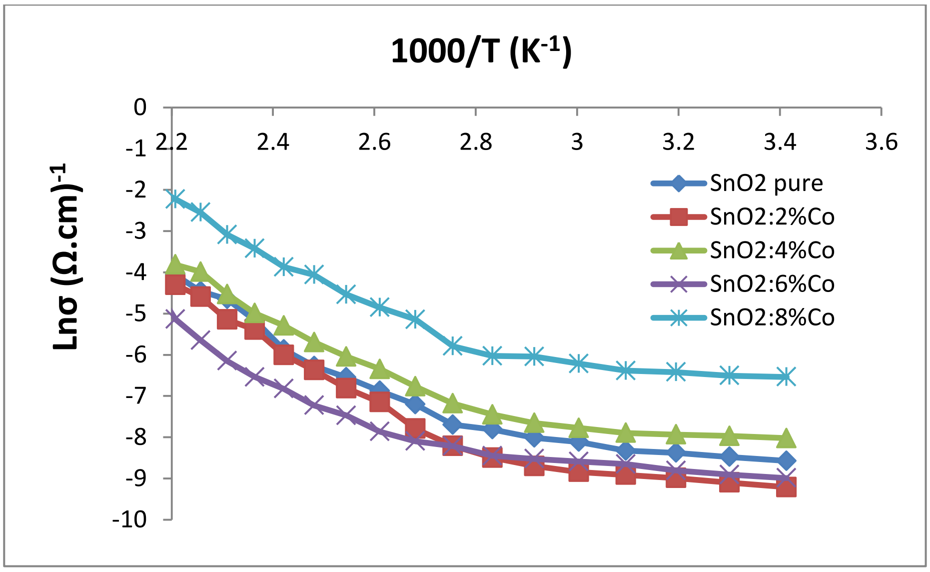

Figure (1): The relation between Ln (σ) versus reciprocal of temperature for pure and doped SnO_2thin films with different concentration of Co.

Table (2) shows the main parameters estimated from Hall effect measurements for pure and doped SnO_2thin films deposited with different concentration of Co (2,4,6 and 8Vol.%) at substrate temperature(400±10)ºC and we notice that the Hall coefficient decreases with increasing of the doping concentrations, also we can notice from the table that the carrier's concentration (n_H) increases with the increasing of concentration of Co, while Hall mobility (μ_H) decreases with the increasing of concentration of Co. From the measuring we find that the R_H value is negative that mean the films is (n-type) and the majority charge are electrons, the results are in agreement with A.R. Babar *et al*.[8,9].

Table (2): Hall effect parameters for pure and doped SnO_2 prepared thin films.

Sample	R_H (cm^3 / C)	n_H (1 / cm^3)	$\rho_{R.T}$ (Ω.cm)	μ_H (cm^2/ V.s)	Carrier type
SnO_{2pure}	-6.326E+6	-9.868E+11	5.884E+1	3.764E+1	n-type
SnO_2:2% Co	-8.201E+7	-7.612E+10	3.298E+3	2.486E+4	n-type
SnO_2:4% Co	-6.200E+6	-1.008E+12	5.310E+4	1.544E+3	n-type
SnO_2:6% Co	-1.947E+6	-3.205E+12	1.204E+5	1.046E+3	n-type
SnO_2:8% Co	-6.155E+4	-1.014E+14	1.681E+5	1.617E+1	n-type

2- Sensing Properties

Figures from (2) to (6) shows the sensitivity as a function of operating temperature in the range (25-300) °C for pure and doped SnO_2 thin films, with different concentration from cobalt (2,4,6 and 8 Vol%)which are deposited on glass substrates at an air mixing ratio, the bias voltage of 3Volt was applied on all the samples[10].It can be seen in figures that the sensitivity of all the films increases with the increasing in the operating temperature ,reaching a maximum value corresponding to an optimum operating temperature which is 200°C for all the samples. Above this temperature ,the sensitivity to NO_2 gas for all sample decreases at about 300°C.The highest sensitivity value, is 82.196% at operation temperature 200ºC at doping concentration (SnO_2:2%Co)[11].

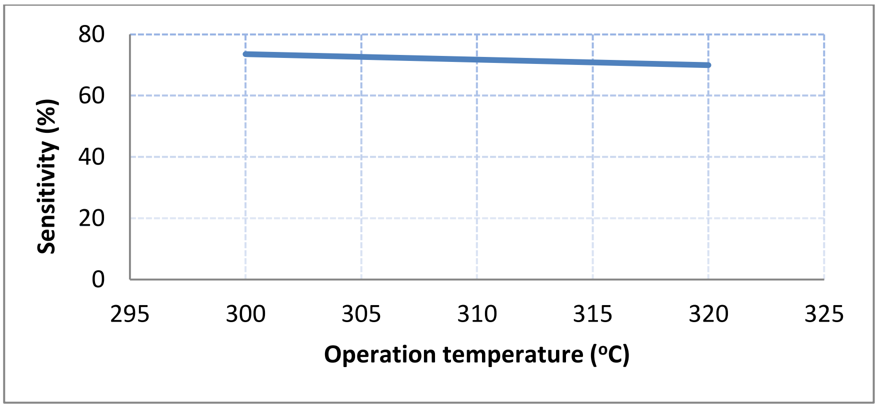

Figure (2): The variation of sensitivity with the operating temperature of pure SnO_2 thin films.

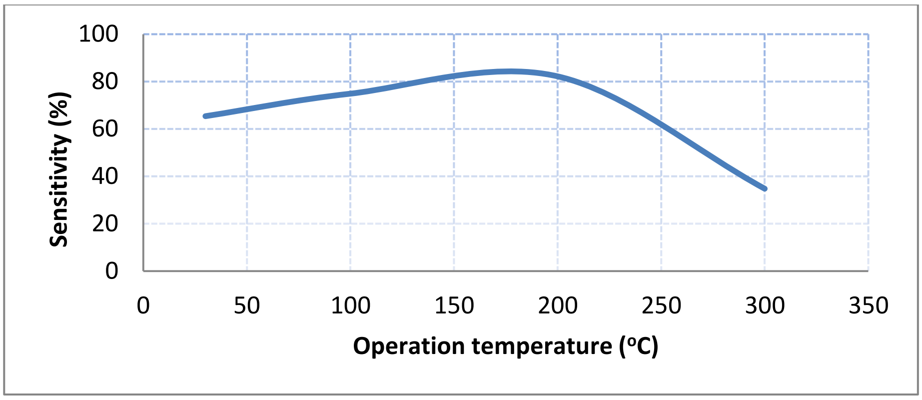

Figure (3): The variation of sensitivity with the operating temperature of SnO_2:2% Co thin films.

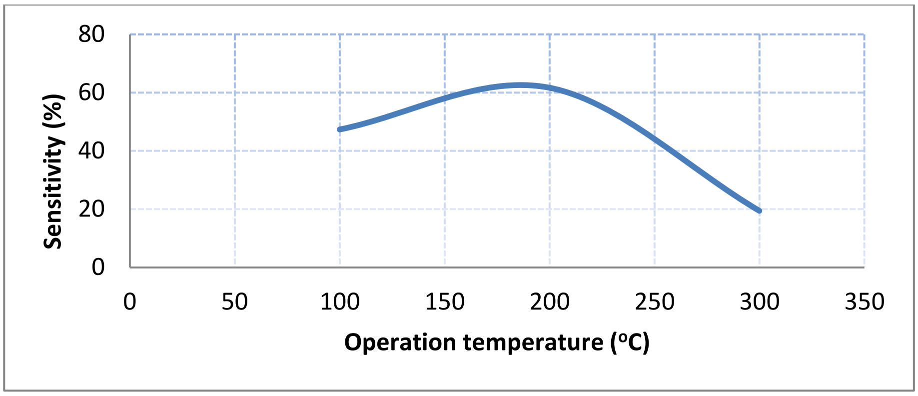

Figure (4): The variation of sensitivity with the operating temperature of SnO_2:4% Co thin films.

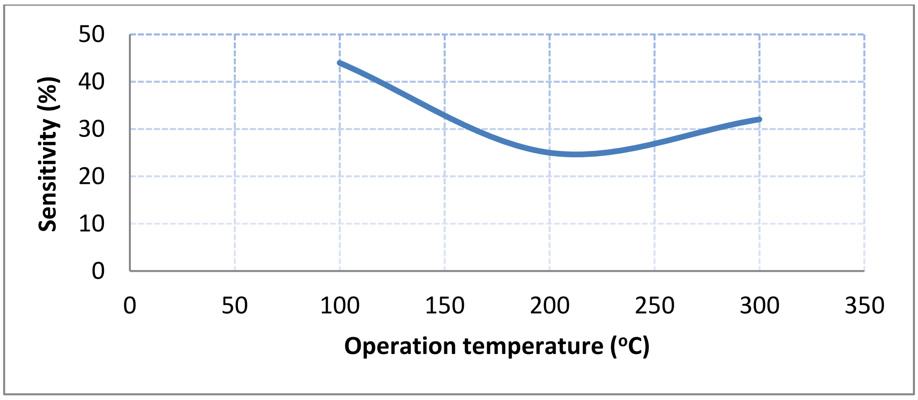

Figure (5): The variation of sensitivity with the operating temperature of SnO_2:6% Co thin films.

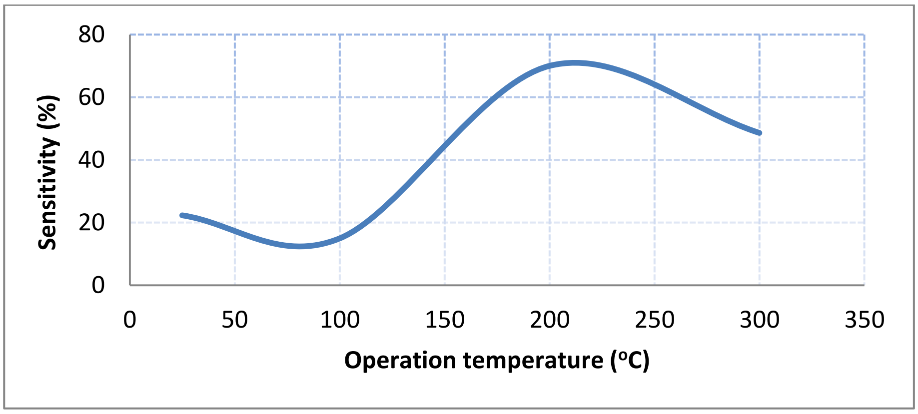

Figure (6): The variation of sensitivity with the operating temperature of SnO_2:8% Co thin films.

Figures (7) to (11) show the response and recovery time for pure $SnO_2$and doped with Co sensor when exposure to NO_2 gas. It is found to bedecreasing as the operating temperatureincreasing.It is found the responsetime decreasing as the operating temperatureincreasing.From figure (7) we can notice that the response time take the value 7.2 s for pure SnO_2 sensor and 45 s for recovery time at operation temperature 320 °C[12-14].

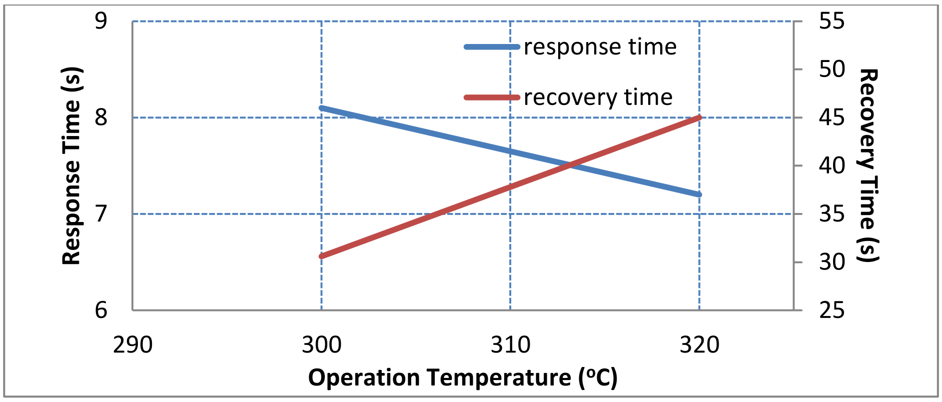

Figure (7): The variation of response and recovery time with operating temperature forpure SnO_2 sensor.

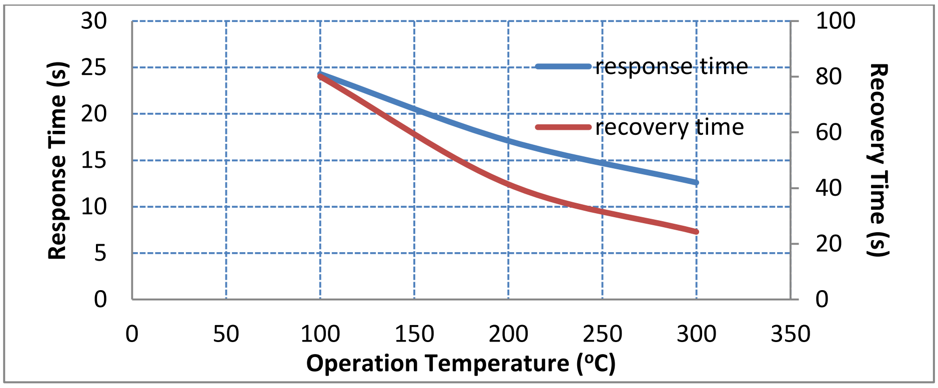

Figure (8): The variation of response and recovery time with operating temperature for SnO_2:2% Co sensor.

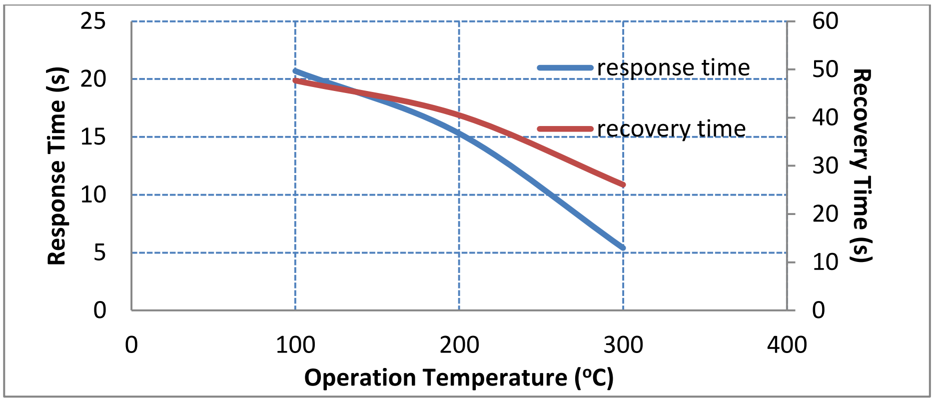

Figure (9): The variation of response and recovery time with operating temperature for SnO_2:4% Co sensor.

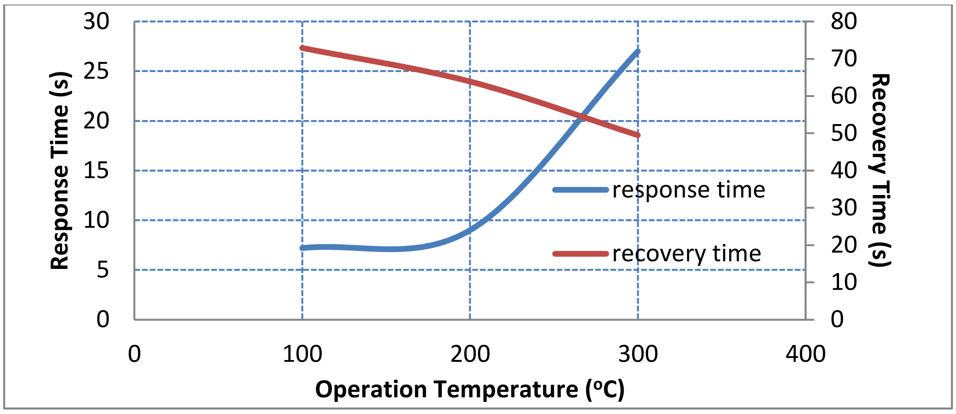

Figure (10): The variation of response and recovery time with operating temperature for SnO_2:6% Co sensor.

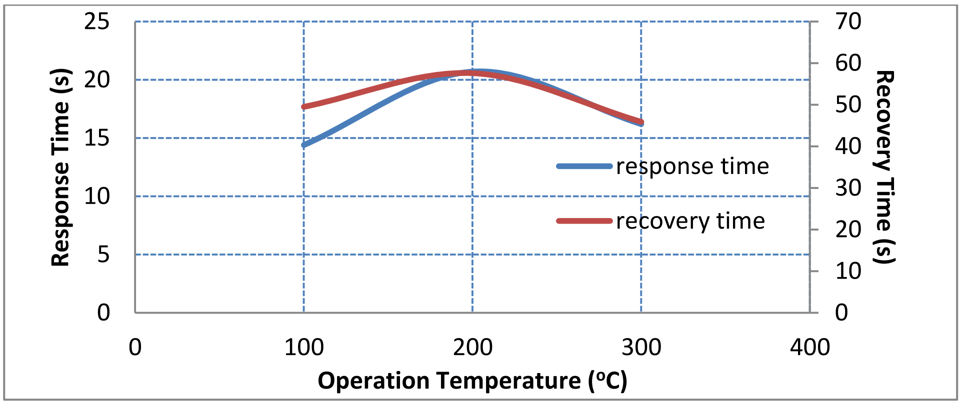

Figure (11): The variation of response and recovery time with operating temperature for SnO_2:8% Co sensor.

4. Conclusions

D.C conductivity measurements showed that increasing in conductivity with increasing of doping concentrations and there are two activation energy for all preparing samples decreases with increasing of doping. From Hall effect measurements we find that the R_H value is negative that mean the carrier is (n-type) and the majority charge are electrons. Films of pure and doped SnO_2 show good sensors characteristics for (NO_2) gas. The maximum sensitivity for pure SnO_2 sensor when exposure to NO_2 gas is 82% for 2% doping concentration obtained at operation temperature 200^{o}C.

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