Preparation and characterization of mixed SnO_2:CdO thin films as gas sensor

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Abstract

In this study, tin oxide (SnO_2) and mixed with cadmium oxide (CdO) with concentration ratio of (5, 10, 15, 20)% films were deposited by spray pyrolysis technique onto glass substrates at 300ºC temperature. The structure of the SnO_2:CdO mixed films have polycrystalline structure with (110) and (101) preferential orientations. Atomic force microscopy (AFM) show the films are displayed granular structure. It was found that the grain size increases with increasing of mixed concentration ratio. The transmittance in visible and NIR region was estimated for SnO_2:CdO mixed films. Direct optical band gap was estimated for SnO_2 and SnO_2 mixed CdO and show a decrease in the energy gap with increasing mixing ratio. From Hall measurement, it was found that all the films prepared possess n-type carriers of the charge. The maximum sensitivity of SnO_2:CdO mixed films toward NO_2 gas was achieved at (10) mixed concentration ratio of CdO at the optimal operating temperature 200°C and maximum sensitivity is equal to (101.75%) with response time (14.6 s) and recovery time (57.0 s).

Key words
SnO_2 : CdO thin films, gas sensor, electrical properties.

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تحضير وخصائص مزيج للاغشية اوكسيد الكادميوم-اوكسيد القصدير كمتحسس غازي

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الخلاصة

في هذه الدراسة، اوكسيد القصدير مزج مع اوكسيد الكادميوم وبتراكيز (5، 10، 15، 20)% لتحضير اغشية بطريقة التحلل الكيميائي على قواعد من الزجاج عند درجة حرارة 300 سليزية. التركيب للمزيج كان متعدد التبلور مع قمم (110) و(101). مجهر القوة الذرية بين ان الاغشية تظهر تركيب منتظم. واظهر ان الحجم الحبيبي يزداد مع زياده نسب تركيز الخلط. تم دراسة النفاذية للمنطقة المرئية و القريبة من تحت الحمراء للمزيج. فجوة الطاقة كانت من النوع المباشر للاغشية المحضرة وتقل بزيادة نسبة الخلط مع اوكسيد الكادميوم، من دراسة هول وجد ان جميع الاغشية حاملات شحنة من النوع السالب N. اعظم تحسس لغار اوكسيد النيتروجين كان عند النسبة 10% من اوكسيد الكادميوم وعند درجة حرارة 200 سيليزية وكانت 101.75% مع زمن استجابه 14.6 ثانيه وزمن ارجاع 57 ثانية.

Introduction

Thin films are more advantageous part for gas sensing applications due to higher surface to volume ratio and controlled surface morphology over their bulk counter [1-3].

Spray pyrolysis is a processing technique being considered in research to prepare thin and thick films, ceramic coatings, and powders. The method has been employed for the deposition of dense films, porous films, and for powder production. Spray pyrolysis has been used for several decades in the glass industry and in solar cell production.

Tin oxide (SnO_2) has a tetragonal rutile structure, n-type semiconductor with wide energy band gap (3.7 eV) [4] with high chemical stability. Their properties depend on their microstructure, the quantity of mixed impurities and the size effects of their particles [5]. Tin oxide thin films have beneficial properties, such as transparency for visible region, reflectivity for infrared region and a low electrical sheet resistance, making them suitable for a wide variety of applications such as gas sensors, electrodes in solar cells, good environmental stability infrared reflectors for glass windows, transparent electrodes in electroluminescent lamps and displays etc [6-8].

CdO is an n-type semiconductor with a rock-salt crystal structure (FCC) and possess direct band gap between (2.3eV and 2.5eV) [9]. It's have high electrical conductivity and high optical transmittance in the visible region of solar spectrum [10].

In this paper, the structural, morphological, optical, electrical properties and gas sensor of the undoped tin oxide and mixed with cadmium oxide concentration ratios (5,10,15, 20)% films with 0.1 molarity were studied.

Experimental

SnO_2 and SnO_2:CdO with cadmium oxide concentration ratio (5, 10, 15, 20)% thin films were deposited by the Spray pyrolysis technique from aqueous solutions containing tin chloride penthydrate pentahydrate and cadmium chloride as a precursor with 0.1 molarity using compressed air at pressure 1 bar as a carrier gas and a flow rate of 4 sec /min. Automated spray pyrolysis equipment is used for the synthesis of thin film in this work. The thickness of the film was 100 nm.

Glass slides cut in small pieces are used as a substrate on which films are grown, so these glass slides are cleaned using ethanol and distilled water, then these glass slides were ultrasonically cleaned. The substrates were then placed on the substrate heater to provide proper heating and to obtain a homogenous films, temperature was kept at 300^oC.

The x-ray diffraction data were recorded on a Rigaku Mini-flex X- ray diffractometer using Cu K_α radiation source (λ=1.5414 Å) at 2θ values between 20˚ and 80˚ at room temperature. The accelerating voltage of 30 KV, emission current of 20 mA and scanning rate of 0.05% were used. Surface morphology and roughness of the film was studied using AFM model (AA3000 Scanning Probe Microscope SPM, tip NSC35/AIBS from Angstrom Ad-Vance Inc). The optical properties of **(**SnO_2: CdO**)** thin films were investigated by UV–VIS spectrophotometric (UV-265 Shimadza) between 300-1100 nm wavelength range. For gas sensor the test was performed at various sensing temperatures with 6 V bias voltages for NO_2 gas.

Results and discussion

1. X-ray diffraction analysis

The results of x-ray diffraction which represent the all mixing ratio for prepared thin films on glass substrates are show in Fig. 1.

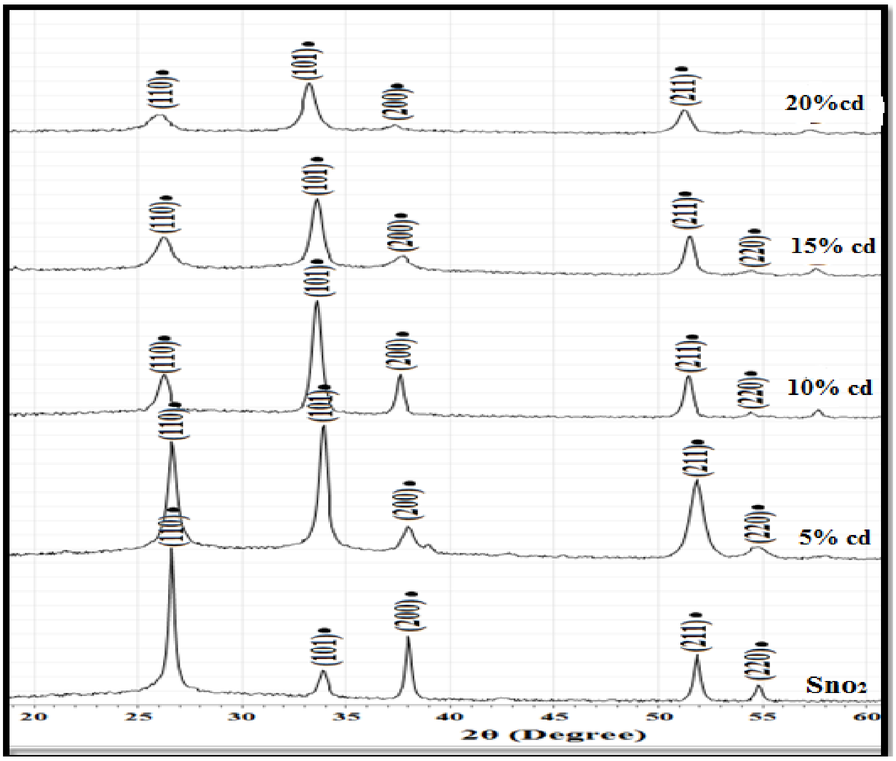


Fig.1: X-ray diffraction of SnO_2: CdO Thin Film.

The observed peaks (110), (101), (200), (211), (220), (310) and (301) in the XRD pattern are matching well with the reported ASTM card no.05-0467 data of pure SnO_2. The intensity of the major peaks (110), (101), (200) and (211) are dominated and show that SnO_2 has been successfully deposited through spray pyrolysis technique. The (110) plane is the dominant due to its stability. Growth of this plane helps in achieving high oxygen vacancy concentrations at low temperatures (near to room temperature). The intensity of the major peaks (110) is decrease with increasing the CdO concentration in the films

The results are in a good agreement with data mentioned in the literature [11, 12]. Table 1 show the grain size of (110) plane for SnO_2:CdO thin films.

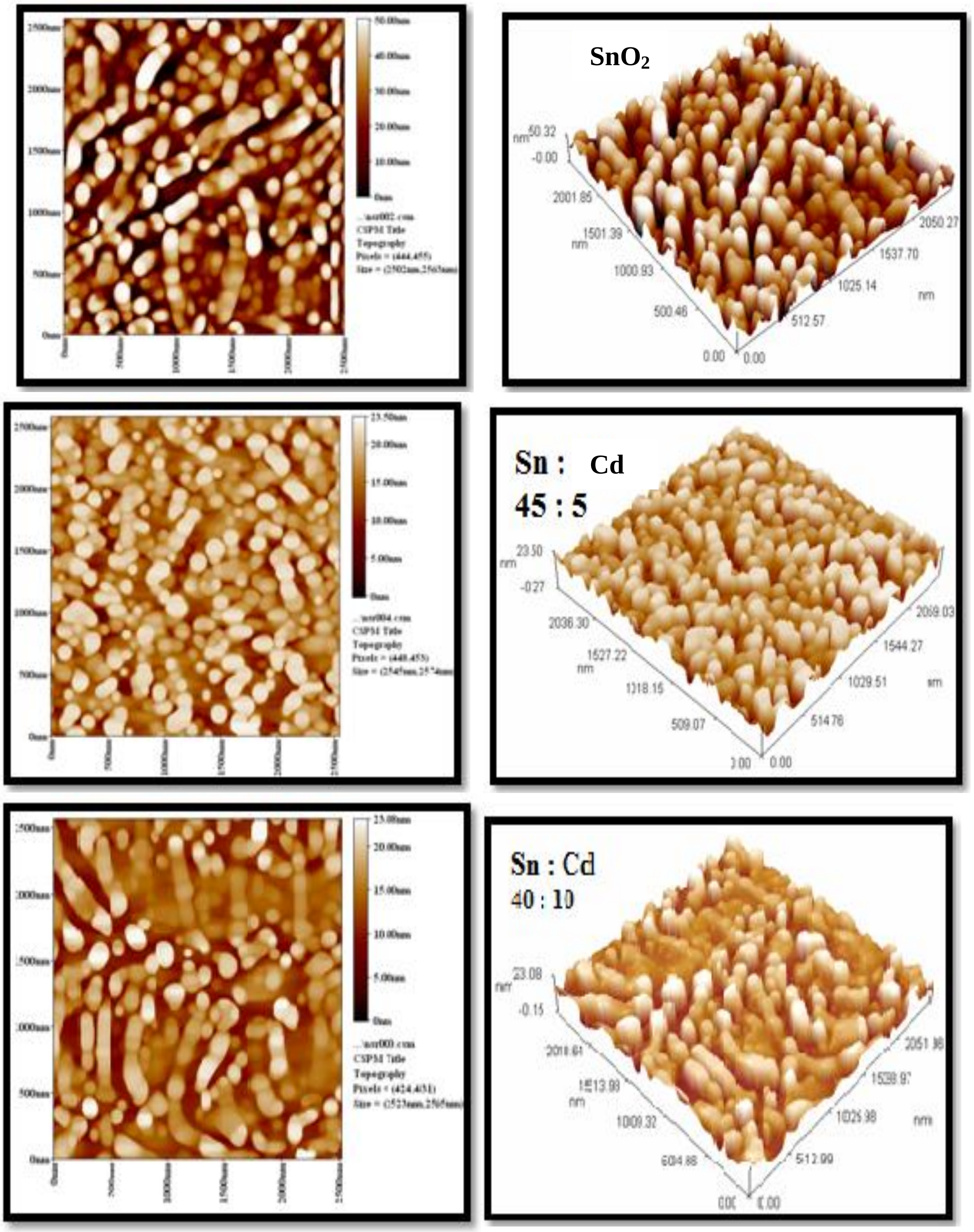
Table 1: XRD parameters for SnO_2:CdO thin films.

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	hkl	d_{hkl} Std.(Å)
pure	26.6120	0.3169	3.3469	25.8	(110)	3.3498
5%	26.6438	0.5120	3.3430	16.0	(110)	3.3498
10%	26.2284	0.5830	3.3950	14.0	(110)	3.3498
15%	26.2359	0.8654	3.3940	9.4	(110)	3.3498
20%	25.9952	0.9210	3.4249	8.9	(110)	3.3498

From Table 1 it can be observe there was a decrease in particle size (G.s) with increasing cadmium confused.

2. Atomic force microscopic

Two and three-dimensional AFM images, for un-doped SnO_2 mixed with CdO thin films for different mixed ratio (5, 10, 15, 20)ml deposited on glass substrate with dimensions of (2.5×2.5) cm^2 at 300℃ are shown in Fig. 2.



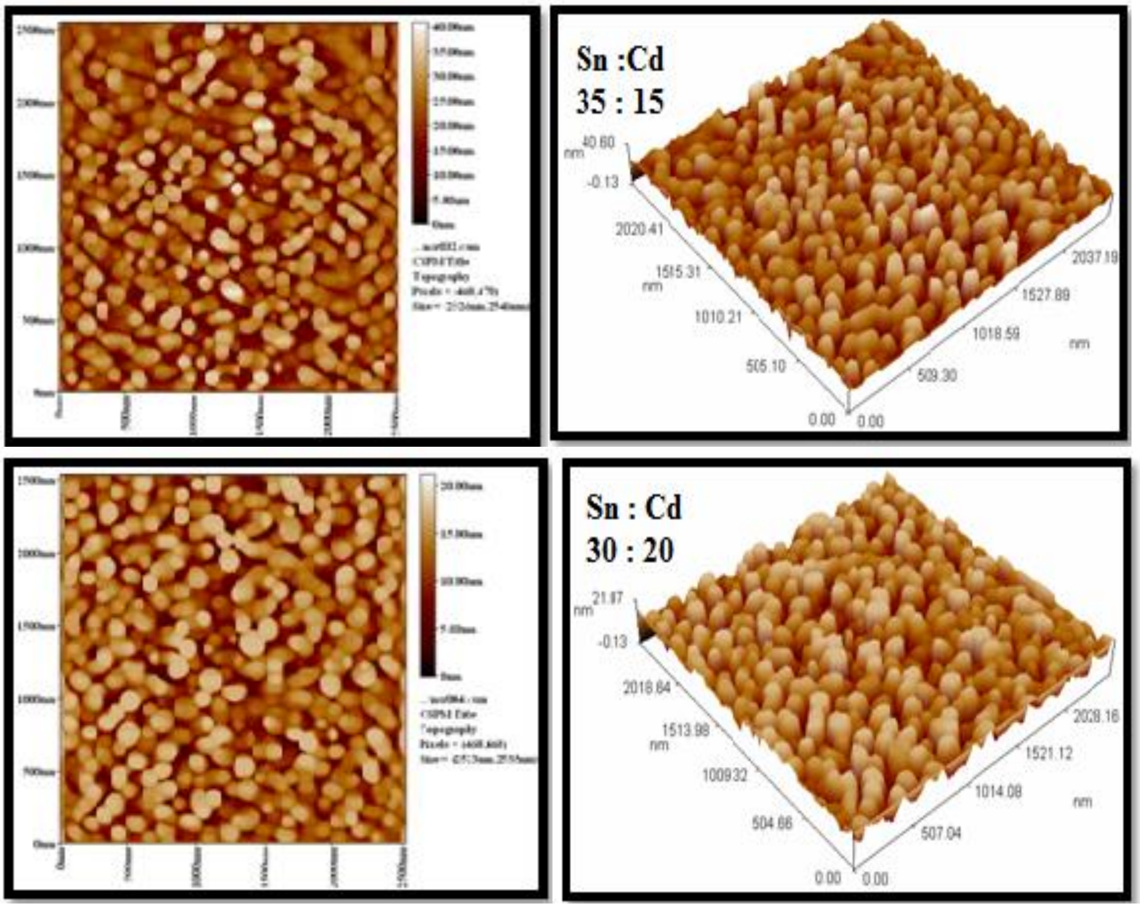


Fig. 2: AFM images for SnO_2 at different mixed with CdO.

AFM images show that the average grain size of SnO_2 was 106.25 nm. The root mean square roughness and the average roughness were found to be 12.1 nm and 14 nm, respectively. It is important to note that these obtained values are averaged and there is a statistical variation associated with them, which depends on the location of the measurements that are performed on the samples [13].

AFM images of films revealed higher surface area of granular which is good for film-gas interaction and results in higher sensitivity, where the gas sensitivity has a proportional relationship with the film roughness [14] Morphology parameters include average diameter, average roughness, and average r.m.s roughness for samples are tabulated as shown in Table 2.

Table 2: Morphology parameters of SnO_2:CdO.

addition ratio	**Average diameter (nm)**	**Average roughness (nm)**	**r.m.s roughness (nm)**
Pure	**106.25**	**12.1**	**14**
45 : 5	**94.30**	**2.94**	**3.51**
40:10	**133.11**	**2.96**	**3.51**
35:15	**88.68**	**5.42**	**6.47**
30:20	**95.97**	**2.94**	**3.57**

AFM analysis for SnO_2 film showed that there are much bigger quasi bar-shape grain formed in the film, also it has a good uniformity revealing a uniform growth of the films. This was in good agreement with [15]. The increase of roughness can be explained by the grain growth and some structure densification of the deposition processes [16].

3. Optical properties

3.1. Transmission (T)

Transmission spectrum is a significantly associated with the structure of energy levels which are in turn connected with chemical and crystalline structure of the material and therefore general characteristics of that material [17].

Fig. 3 shows the optical transmittance of SnO_2 :CdO thin films mixed with (5, 10, 15 and 20) ml of CdO films as a function of wavelength ranging from (300-1100) nm which are sprayed on glass substrate and kept at constant substrate temperature of 300°C.

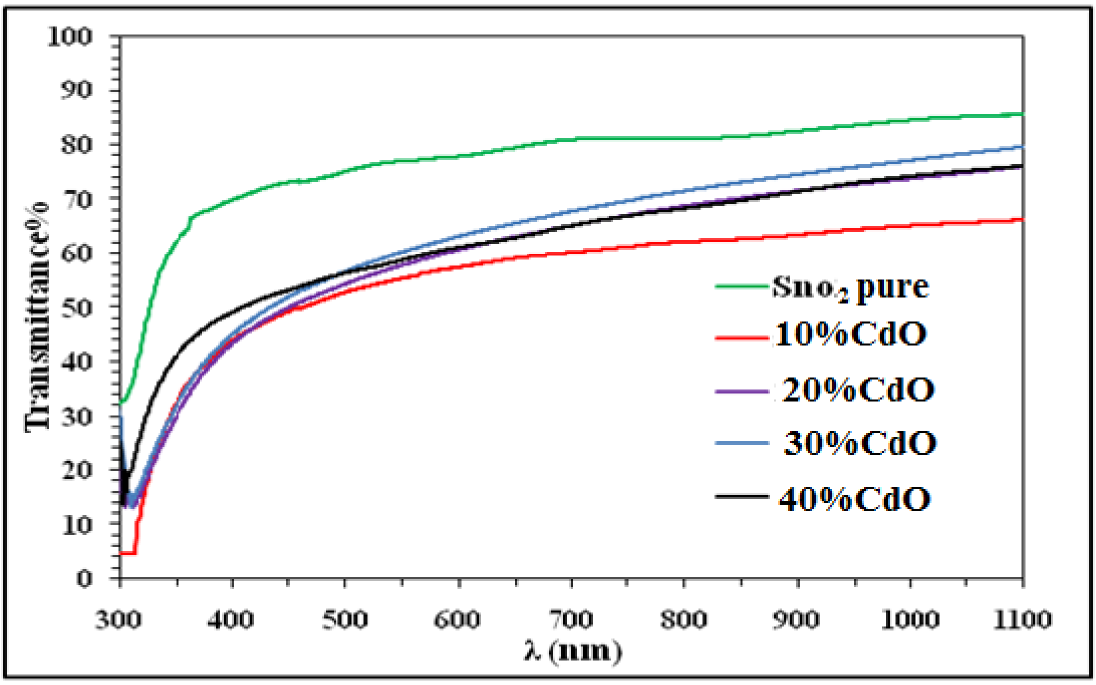


Fig. 3: Transmission as a function of the wavelength for un-doped Sno_2 and mixed with Cdo at different mixed ratio.

The transmittance was increased with the increasing in wavelength with a lower rate. A sharp decrease in the transmittance of the films at wavelength below 400 nm, is observed, This is probably due to the absorption edge in this region [18, 19]. The transmittance curve recognizes the smooth increase of transmission in the visible region and attained maximum transparency less than 75% in the NIR region which reflects nature of the film. This behavior may be due to the scattering of photons by crystal defects or probably due to the increase in the metal to oxygen ratio [20].

3.2. Optical energy gap

The study of optical energy gap (Eg^{opt}) is of great significance to determine the possibility of using the prepared thin films in the manufacture of differentiated devices, also it gives a clear idea of the optical absorption and considered a measure of the basis for selective spectrum [21]. The optical energy gap values have been determined using Tauc formula .It is found that the relation for r =1/2 yields linear dependence, which means that the optical band gap has direct allowed transition.

The variation of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ is illustrated in Fig. 4. The optical energy gap for SnO_2 films is about (3.7) eV. This obtained result is very close to other (Eg^{opt}) values which was found in literature [22].

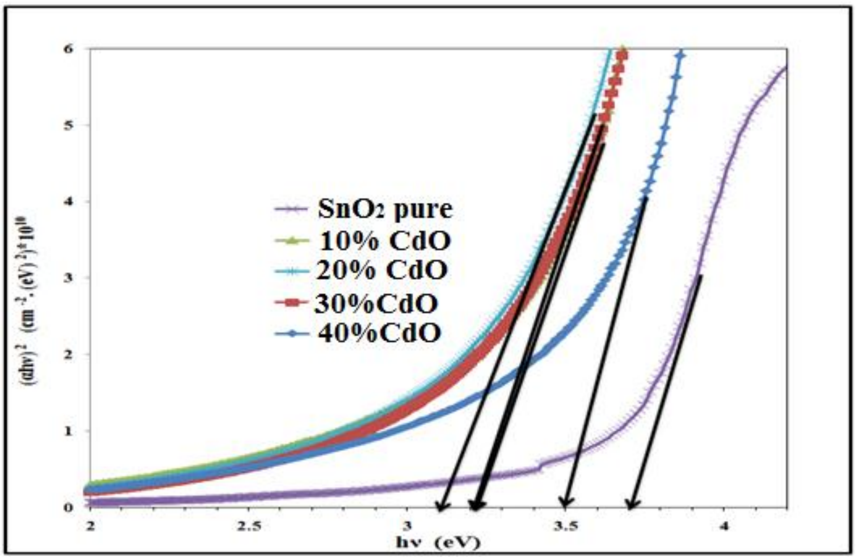


Fig. 4: Energy gap for SnO_2 mixture with CdO at different concentrations.

It can be observed that (Eg^{opt}) increases slightly above 10 mL from CdO and shifts towards IR region as the concentration in the films increases for all films, as shown in Table 3. This is because of the effect of impurity or disorder and any other defects during prepared processes of thin films, additionally it is may be due to the changing in the size effect for nanostructure which was responsible for this shift [4].

Table 3: Eg^{opt} variation with CdO at different concentrations

Sample	E_g (eV)
SnO_2	3.70
SnO_2 : CdO 45 :5	3.20
SnO_2 : CdO 40 : 10	3.10
SnO_2 : CdO 35 : 15	3.20
SnO_2 : CdO 30 : 20	3.50

3.3. Hall effect

Table 4 show the Hall measurements of pure films at temperature 300 °C for different SnO_2:CdO percentages (5, 10, 15, 20)ml which are deposited on glass substrate (conductivity σ, Hall coefficient R_H, carrier concentration n_H, and mobility μ_H).

Table 4: Hall measurements of SnO_2 thin films at different mixed ratio of CdO.

addition ratio	n_H (cm^{-3})	R_H (cm^3/c)	σ_{RT} ($\Omega^{-1}.cm^{-1}$)	μ_H ($cm^2/v.sec$)
SnO_2	$2.537x10^{11}$	$-7.325x10^{6}$	$1.64X10^{-6}$	1204
SnO_2:CdO 45: 5	$5.835x10^{15}$	-106.7	0.1014	109.7
SnO_2:CdO 40 : 10	$3.714x10^{19}$	$-1.681x10^{-7}$	17.17	1.724
SnO_2:CdO 35 : 15	$3.886x10^{17}$	-71.61	0.4346	3.112
SnO_2:CdO 30:20	$1.148x10^{16}$	-543.7	0.3215	174.8

The negative sign of Hall coefficient confirmed the n-type conductivity and the mixed process did not affect the type of the charge carriers. CdO contains defects such as interstitial cadmium atoms and oxygen vacancies. These defects can be easily ionized and the electrons induced by this process can contribute to the conduction of electricity, causing CdO to act as an n-type semiconductor.

3.4. Gas sensor

Response of sensors depends on two factors, namely: the speed of chemical reaction on the surface of the grains, and the speed of the diffusion of gas molecules to that surface. At low and higher temperatures the sensor response is restricted by the speed of chemical reactions and the speed of the diffusion of gas molecules to that surface respectively. At some intermediate temperature the speed values of two processes become equal, and at that point the sensor response reaches its maximum. According to this mechanism for every gas there is a specific temperature at which the sensor response attains its peak value [23].

Fig.5 shows the sensitivity as a function of operating temperature for SnO_2 and mixed with different concentrations of CdO. The gas sensitivity tests were performed at 25°C and increased to 100°C and 200 °C and 300 °C.

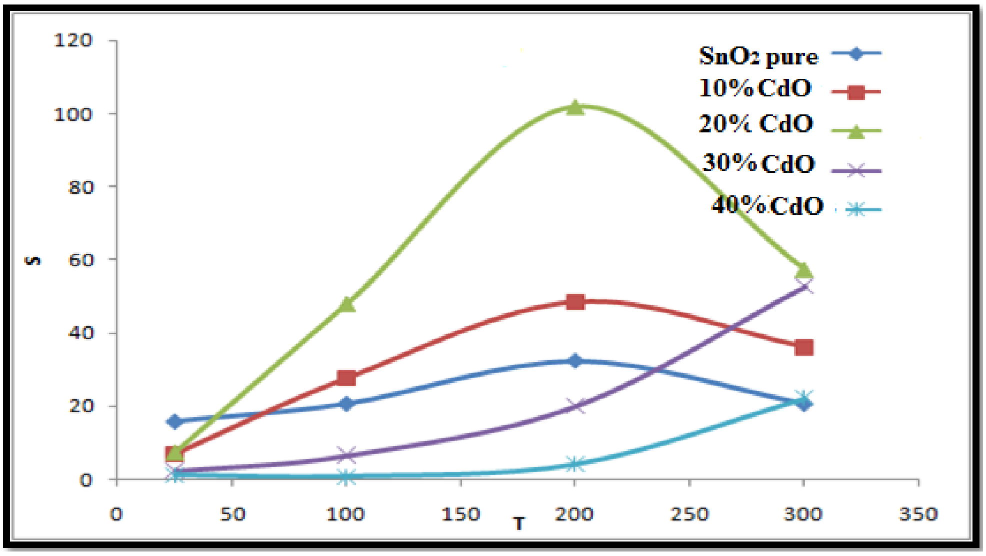


Fig. 5: Sensing characteristics of SnO_2: CdO thin film towards NO_2 gas.

The resistance and sensor sensitivity to NO_2 gas increase linearly with increasing temperature for the range R.T. to 200 ^oC. After which it began to drop with increasing temperature (except for pure and 15% CdO). The optimum operating temperature for the SnO_2 : CdO thin films NO_2 gas sensor was found to be around 200℃.

3.5. Response and recovery of the sensor

The response time of a gas sensor is defined as the time it takes the sensor to reach 90% of its maximum/minimum value of conductance upon introduction of the reducing/oxidizing gas. Similarly, the recovery time is defined as the time required recovering to within 10% of the original baseline when the flow of reducing or oxidizing gas is removed [24].

Fig. 6 and 7 show the relation between the response time and the recovery time as a function of operation temperature at different etching time for the pure SnO_2 and their compositions with (45:5, 40:10, 35:15, 30:20) for SnO_2: CdO deposited on glass with 3 % NO_2: air and bias voltage of 6V.

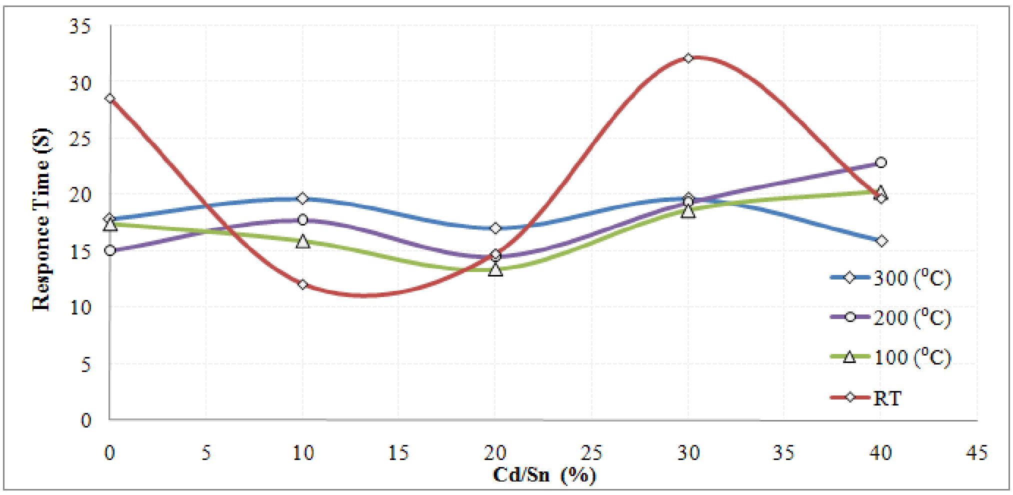


Fig. 6: The variation of response time as a function of time with different operating temperature of SnO_2 : CdO thin films towards NO_2 gas.

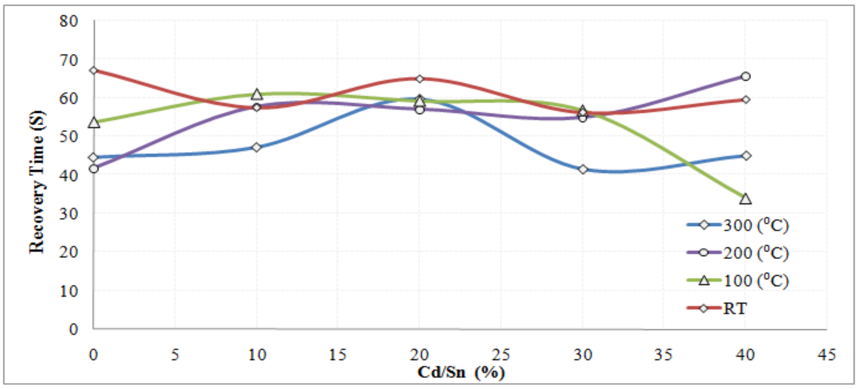


Fig. 7: The variation of recovery time as a function of time with different operating temperature of SnO_2 : CdO thin films towards NO_2 gas.

The response is quick (17.9 s) and recovery is fast (44.6s). The high oxidizing ability of adsorbed oxygen species on the surface particles and high volatility of desorbed by-products explain the quick response to NO_2 and fast recovery. This reveals that the decrease of response \recovery time with increasing of operation temperature. The figure show that the (10 min) etching time sample exhibits a fast response speed of (15.1s) and recovery time (41.7s) at 200°C operation temperature for SnO_2 film. This reveals that a (10min) etching time is the best one to achieve fast response sensor. The gradual increase in the operating temperature led to an improvement of the films responsitivity.

The values of sensitivity, response time and recovery time of un-doped SnO_2 and mixed with different ratio of CdO are shown in Table 5.

Table 5: Response time, recovery time and sensitivity of un-doped SnO_2 and mixed with different ratio of (5, 10, 15, 20)ml CdO.

Sensitivity %

sample	0	5	10	15	20
RT	15.79	6.849	7.395	2.264	1.240
100 (°C)	20.68	27.528	47.929	6.465	0.879
200 (°C)	32.42	48.345	101.754	20.000	4.185
300 (°C)	20.65	36.036	57.238	52.597	22.292

Response time (s)

RT	28.6	12.1	14.8	32.2	19.7
100 (°C)	17.5	15.9	13.4	18.6	20.3
200 (°C)	15.1	17.8	14.6	19.4	22.9
300 (°C)	17.9	19.7	17.0	19.7	15.9

Recovery time (s)

RT	67.2	57.5	65.0	56.3	59.6
100 (°C)	53.7	61.0	59.2	56.8	34.1
200 (°C)	41.7	57.7	57.0	54.9	65.7
300 (°C)	44.6	47.2	59.6	41.5	45.0

There is an increase and decrease in the sensitivity indicates the adsorption and desorption phenomenon of the gas. The higher sensitivity may return to the optimum number of inequality on the porosity, largest surface area, larger rate of oxidation and the optimum surface roughness [25]. The sensitivity as well as response time depend on operating temperature since the chemical kinetics in solid-gas reaction is governed by the dependence of temperature [26].

Conclusions

SnO_2 : CdO composition thin films were successfully deposition on glass substrates by chemical spray pyrolysis technique. X-Ray diffraction analysis showed polycrystalline structure SnO_2:CdO composition. The AFM images displayed all samples are granular structure. AFM images of films revealed higher surface area of granular which is good for film gas interaction and results in higher sensitivity, where the gas sensitivity has a proportional relationship with the film roughness. The energy gap increased with the increase of CdO percentage of the composition. SnO_2 : CdO composition thin films were n-type charge carriers. Gas sensor measurement of pure SnO_2 and mixed have high resistivity for NO_2.

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