Hydrogen sulfide gas sensing properties of In_2O_3 – CdO nanoparticles

M. K. Alyas[a], S. S. Abdulhaleem[b], I. M. Ibrahim[c*], I. M. Ali[c]
[a]*Ministry of Education, Nineveh Education, Nineveh, Iraq*
[b]*Ministry of Education, Directorate of institutional development and government coordination, Baghdad, Iraq*
[c]*Department of Physics, College of Science, University of Baghdad , Baghdad, Iraq*

Thin films of In_2O_3-CdO at various CdO contents (0.01, 0.02, 0.03, 0.04 and 0.05) were deposited on transparent substrate which is glass using chemical spray pyrolysis deposition method at substrate temperature 150 ^oC. The structural properties was studied to characterize the prepared materials by XRD analysis. Surface morphology has been illustrated using scanning electron microscopy which proved the nanosize of prepared materials. This materials have been used as gas sensor for toxic gas which is hydrogen sulfide H_2S. The sensitivity and response speed have been investigated with addition of CdO nanoparticles.

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1. Introduction

Transparent semiconductor is one of the most important compounds due to its electrical properties, which led to its use in many applications. Nanomaterials of semiconducting oxides such as cadmium oxide and indium oxide have been used in solar cells, photovoltaic devices, optical transmission devices and gas sensors[1]. Crystalline forms of Indium oxide In_2O_3 were exist in two phases, cubic and hexagonal crystalline system. Band gap of about 3 eV for both phases and N-type conductivity used in some types of batteries, some of gas sensors and as a resistive element in integrated circuits[2-7]. Cadmium Oxide CdO is among the first reported transparent n-type semiconducting oxide (TCO) and it is used extensively in solar cells, phototransistors, photodiodes, transparent electrodes and gas sensors[8]. Cadmium Oxide (CdO) films and Indium oxide In_2O_3 have been produced using different techniques such as Pulsed Laser Deposition (PLD) , Spray Pyrolysis Technique and sol–gel [9]. Due to an increase in atmospheric pollution, there is a need to fabricate sensitive devices to detect and measure different hazardous gases. Currently, standard air pollution measurements are based on expensive optical spectroscopy and gas chromatography techniques. These techniques are large, expensive and slow in terms of reaction times. Therefore, there is an urgent need to design and fabricate cheap gas sensor devices to detect diverse explosive and toxic gases[10]. In this work, In_2O_3 and CdO have been used as gas sensor against H_2S toxic gas with higher sensitivity.

2. Experimental

Before starting the deposition, the solutions according to the films components was mixed then put it on the magnetic stirrer for about 15 minutes to be sure that the mixture solutions are mixed properly and to get solution with molarity of 0.05. Prior to deposition, glass substrates were cleaned and placed on the flat plate heater surface, which it is an electrically controlled, and left them for about 10 minutes so as to allow their temperature to reach the set temperature at (150 ± 10) °C which is substrate temperature that also effects on the film homogeneity.

* Corresponding author: iftikhar.iq@gmail.com

After that, can start the deposition process within deposition time of 5 sec, then stop this process for 10 sec to avoid substrate cooling. In the spray system, the solution spray rate was maintained at 1 ml/min and compressed and purified air was used as the carrier gas with a 3 kg/cm^2 pressure where the air flow effects on the drop size of the solution so effect on film homogeneity. and The distance between the spray nozzle and the substrate was fixed at 30 cm as shown in figure(1). After the spray process is completed, then the hot plate will be shut down and the samples are left on the surface of the heater to reach the room temperature, then the substrates can be raised. The prepared films annealed in air at 400 ^{o}C for one hour to enhance the film crystallinity. The X-ray diffraction (XRD) spectra of the films were obtained to verify their crystal structure using a (Cu-Kα) radiation with $\lambda = 0.154$ nm. Scanning electron microscopy (SEM) was employed to observe the surface morphology of the films.

$InCl_3$ and $CdCl_2$ with purity of 99.9% provided from Flukea company was used to form aqueous solutions of 0.05 M. The needed weight was calculated according to the following equations:

$$w = ([M] \times M_{wt} \times V(ml))/1000$$

where M is the molarities, $M_{\mathbf{wt}}$ is the molecular weight; **V** is the volume of material.
$InCl_3$ and $CdCl_2$ were dissolved separately in 50 ml distilled water and 50 ml ethanol by magnetic stirrer with different ($CdCl_2$ solution):($InCl_3$ solution) volume ratios (0, 0.01, 0.02, 0.03, 0.04 and 0.05) to be ready for using in the spray system. After the deposition operation was completed, the substrates were left on the heater until the temperature arrived the room temperature then they were annealed as mentioned before.

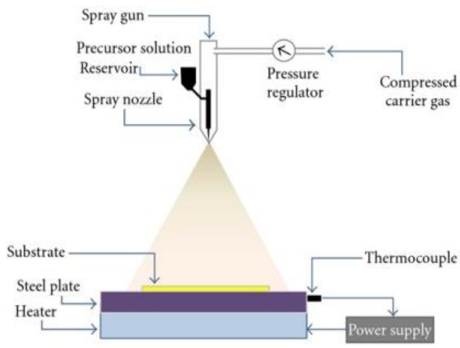

Fig. 1. Schematic of the spraying pyrolysis system.

3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns for In_2O_3-CdO thin films prepared at different CdO contents, these patterns elevated that the x-ray diffraction data of thin films coincides with that of known cubic structure according to the International Centre for Diffraction. Crystallite size calculated by Sherrer's formula D=Kλ/ßcosɵ) decreased with increasing CdO ratio and FWHM of the (222) peak became wider and the orientation poorer. Increasing of FWHM with CdO concentration suggests degradation in crystal quality [see Table (1)] where the results have been coincided with card PCPDS 96-101-0589 and 96-900-6690 for In_2O_3 and CdO respectively[12].

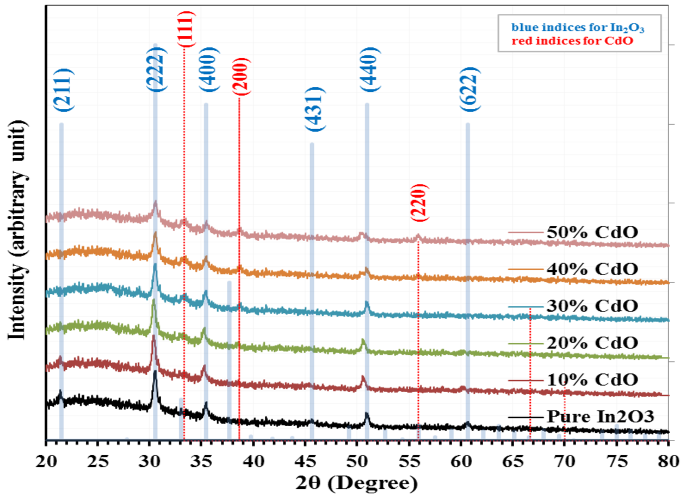

Fig. 2. XRD patterns for pure In_2O_3 and In_2O_3:CdO thin films

Scanning electron microscope images shown in Fig. 3 granular size for thin films is in the nanoscale, also grain aggregation increases with increasing concentration of CdO, the increase of CdO concentration will enhance the carrier concentration which consequently leads to an increase in the conduction current.

The gas sensitivity of pure In_2O_3 and its mixture with CdO thin films have been studied using hydrogen sulfide gas H_2S at 200^{o}C working temperature. The repeatedly pulse of sensitivity for pure In_2O_3 and its mixtures with different In_2O_3:CdO ratios (0.01, 0.02, 0.03, 0.04 and 0.05) thin films are shown in Fig. (4), one can note that the amount of sensitivity increases because of the surface nature and granular size which was demonstrated by scanning electronic images. The reaction between the gas and thin film surface may be result an increase the number of existing charge carriers near the surface due to the injection of electrons into the material. One can enhance the reaction activity and response speed by reaching working temperature because of the increase in densities and mobility of the carriers that contribute in the conducting current.

Table 1. Structural parameters for In_2O_3-CdO thin film with different CdO contents
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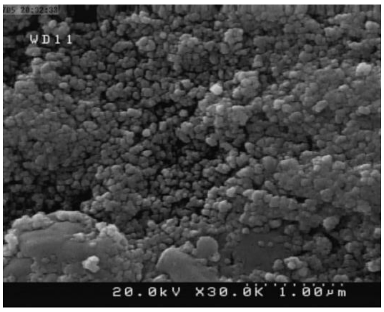
CdO Content	2θ (Deg.)	FWHM (Deg.)	D (nm)	(hkl)	Phase
0	21.3746	0.4811	16.81	(211)	In_2O_3
	30.5155	0.5499	14.98	(222)	In_2O_3
	35.4639	0.6186	13.49	(400)	In_2O_3
	45.6357	0.5498	15.68	(431)	In_2O_3
	50.8591	0.5499	16.00	(440)	In_2O_3
	60.6873	0.6186	14.89	(622)	In_2O_3
0.01	21.3746	0.4811	16.81	(211)	In_2O_3
	30.3780	0.4123	19.98	(222)	In_2O_3
	35.2577	0.4811	17.33	(400)	In_2O_3
	50.5842	0.5497	15.99	(440)	In_2O_3
	60.2062	0.6873	13.37	(622)	In_2O_3
0.02	30.3780	0.4123	19.98	(222)	In_2O_3
	33.3333	**0.6186**	**13.41**	**(111)**	**CdO**
	35.1890	0.4124	20.22	(400)	In_2O_3
	38.5567	**0.6185**	**13.61**	**(200)**	**CdO**
	50.5155	0.5497	15.99	(440)	In_2O_3
0.03	30.5155	0.4810	17.13	(222)	In_2O_3
	33.3333	**0.5497**	**15.09**	**(111)**	**CdO**
	35.3952	0.5497	15.18	(400)	In_2O_3
	38.6942	**0.5497**	**15.32**	**(200)**	**CdO**
	50.8591	0.4810	18.30	(440)	In_2O_3
0.04	30.5155	0.4811	17.12	(222)	In_2O_3
	33.4021	**0.6184**	**13.42**	**(111)**	**CdO**
	35.4639	0.5497	15.18	(400)	In_2O_3
	38.6942	**0.5499**	**15.32**	**(200)**	**CdO**
	50.8591	0.6184	14.23	(440)	In_2O_3
	55.8763	**0.6186**	**14.54**	**(202)**	**CdO**
0.05	30.4467	0.6185	13.32	(222)	In_2O_3
	33.4708	**0.7560**	**10.98**	**(111)**	**CdO**
	35.6014	0.6186	13.49	(400)	In_2O_3
	38.6254	**0.6873**	**12.25**	**(200)**	**CdO**
	50.5155	0.8247	10.66	(440)	In_2O_3
	55.8763	**0.4811**	**18.70**	**(202)**	**CdO**



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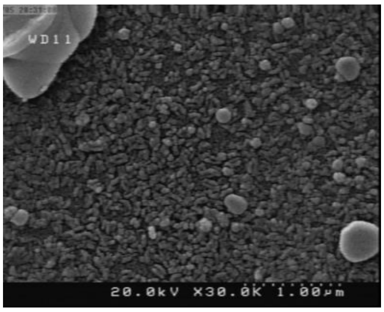

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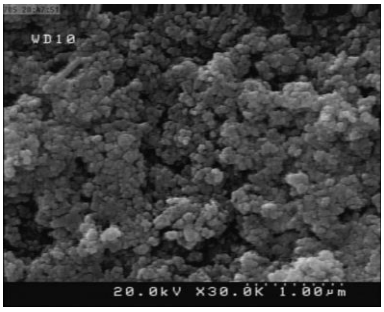

c)

Fig.(3) SEM images of In_2O_3 thin films
a) pure In_2O_3; b) 0.01 CdO addition; c) 0.05 CdO addition

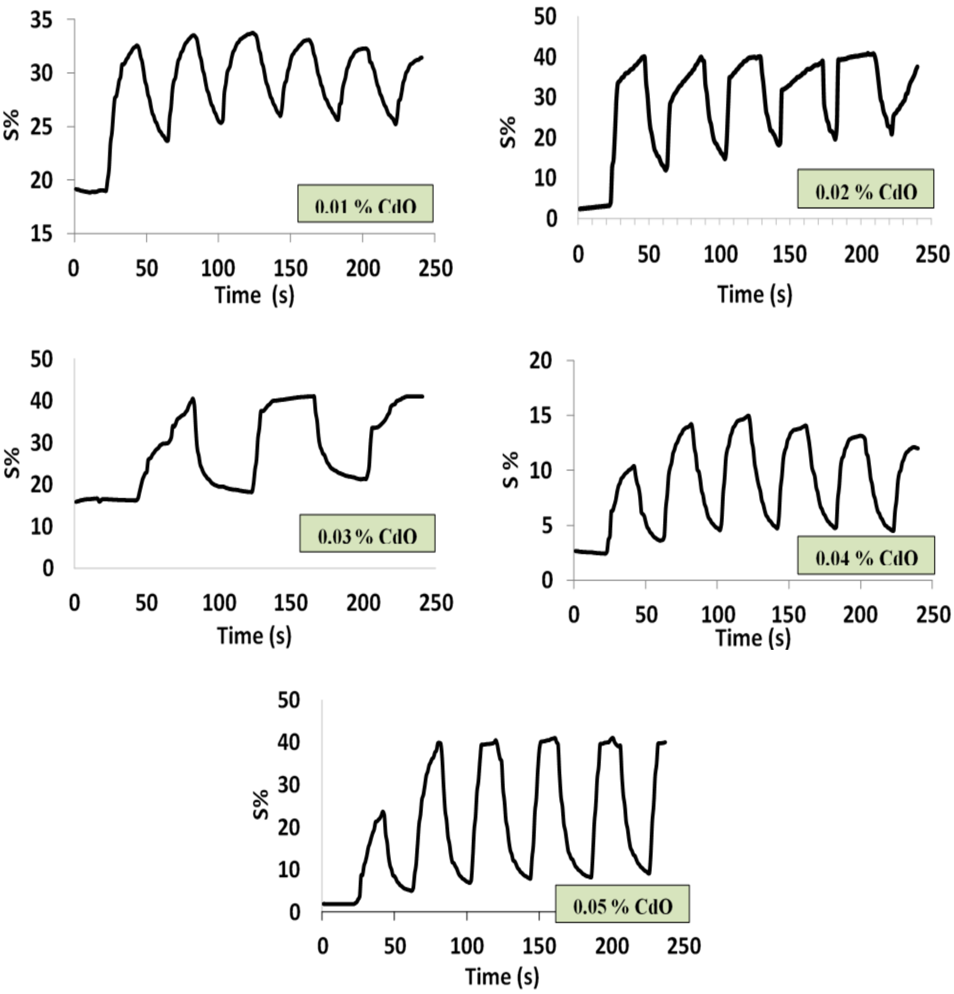

Fig. 4. Gas sensor pulse repeatidly for In_2O_3 and CdO mixture thin films at 200^oC.

Table (2) shows the sensitivity for Indium oxide thin films and its mixture with CdO which indicates that thin films prepared with 0.05 % CdO have the best sensitivity due to the degree of aggregation and the presence of high carrier density [12,13].

Table 2. The sensitivity In_2O_3 : CdO thin films against H_2S toxic gas.

CdO concentration	sensitivity %
0.01	69.4
0.02	142.6
0.03	115.3
0.04	197.9
0.05	650.9

4. Conclusion

In_2O_3:CdO thin films have been successfully prepared by chemical pyrolysis method. XRD analysis illustrates the cubic stracture for prepared material. Thin films have been prepared as nano size dimention with homogenious surface as shown in SEM images. In_2O_3:CdO thin films have neen used as gas sensing material and sensitivity for H_2S gas has been investigated.

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