

PREPARATION OF MIXED In_2O_3 – CdO THIN FILMS BY CSP TECHNIQUE FOR LIGHT SENSING

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In this work, chemical spray pyrolysis deposition (CSP) technique was used to prepare a mixed In_2O_3 - CdO thin films with different CdO content (10, 30 and 50)% volume ratio on glass substrates at 150 °C substrate temperature. The surface morphology and structural properties were measured to find the optimum conditions to improve thin films properties for using as photo detector. Current –Time, the sensitivity and response speed vary for each mixture. Samples with 10% vol. CdO content has square pulse response with average rise time nearly 1s and fall time 1s.

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1. Introduction

Indium oxide In_2O_3 is transparent conductive oxide TCO material, it can be used as an n-type semiconductor[1]. The crystalline form exist in two phases, the cubic (bixbyite type) with $a = 10.12 \text{ \AA}$ [2] and hexagonal. Both phases have a band gap of about 3 eV[3]. The hexagonal phase is produced at high temperatures and pressures or when using non-equilibrium growth methods [3] with lattice parameters $a = 5.487 \text{ \AA}$, $c = 5.7818 \text{ \AA}$ and calculated density 7.31 g/cm^3 [4], it was used in many applications such as some types of batteries [5], thin film infrared reflectors, some of gas sensors and resistive element in integrated circuits. Cadmium Oxide is an n-type semiconductor having direct band gap of 2.45eV. The crystal structure is a rock salt type. It is important to give some analysis to the electronic structure of CdO because of its specific optical and electrical properties such as, its high transparency in the visible region of the solar spectrum, as well as a high ohmic conductivity. Cadmium oxide thin films have been used for many applications such as gas sensors [6], solar cell[7], and photodiodes[8] etc. The thin films of CdO have been grown using a variety of techniques such as sputtering[9], activated reactive evaporation[10], solution growth CBD [11]. In this work, a surface morphology, structural and current –time properties of a mixed In_2O_3 - CdO thin films with different CdO contents (10, 30 and 50)% on glass substrates were studied.

2. Experimental method

A different solutions of CdO content (10, 30 and 50)% were used to prepare In_2O_3 - CdO mixtures. InCl_3 with purity 99.9% and CdCl_2 with a purity of 99.9% provided by Flukea, was used to form 0.2 M aqueous solutions. The needed weight was calculated according to the following equation:

$$w = \frac{[M] \times \text{Molecular weight of solute} \times V(ml)}{1000}$$

where M: molar concentration

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Glass slides was chosen as it smoothness and possesses high transmission of light within the visible region, these substrates were cut to 1 cm × 2.5 cm Dimensions for all measurements. The substrates were cleaned by soaking them sequentially with a detergent solution, alcohol and distilled water and put them in an ultrasonic for 15 min, then they were washed with distilled water, dried by blowing air and wiped by soft papers. Film homogeneity and crystallinity affected by the substrate temperature, so that the substrate temperature was adjusted at 150 ± 10 °C. To avoid substrate cooling, spraying was achieved in periods of about 5 s separate by 10 s wait. The solution flow rate was optimized to 1 ml/min. The distance between the substrate and spray nozzle is adjusted at 30 ± 2 cm as shown in Fig. 1. After the deposition operation has completed, the substrates remain on the heater until the temperature reaches room temperature. The prepared films are annealed in air at 400 °C for one hour to increase the crystallinity of the films [12].

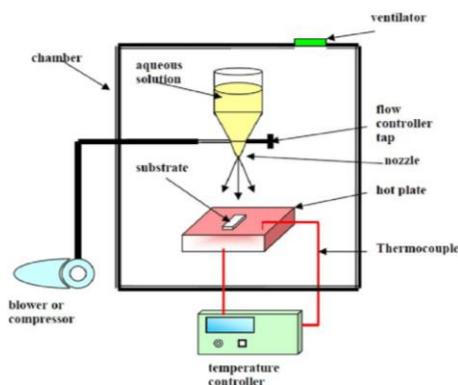


Fig. 1. Schematic of the spraying pyrolysis system (CSP).

Stainless steel foils were used to prepare mesh mask for photo sensitivity as shown in Fig. 2.

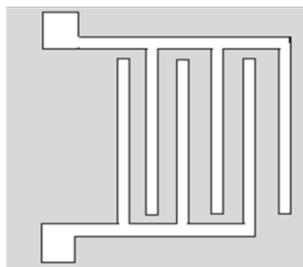


Fig. 2. Schematic of mesh mask.

3. Results and discussion

Fig. 3 shows the X-ray diffraction patterns for mixed oxide In_2O_3 -CdO thin films prepared at different CdO contents, these figures elevated that the x-ray diffraction data of thin films coincides with that of known cubic structure according to the International Centre for Diffraction. Experimental Inter-planar spacing d_{hkl} (estimated by Bragg's law), crystallite size (evaluated by Sherrer's formula) and their corresponding planes, as one can note that the crystallite size and d_{hkl} decrease 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 because of nano size of prepared materials [see Table 1] [13].

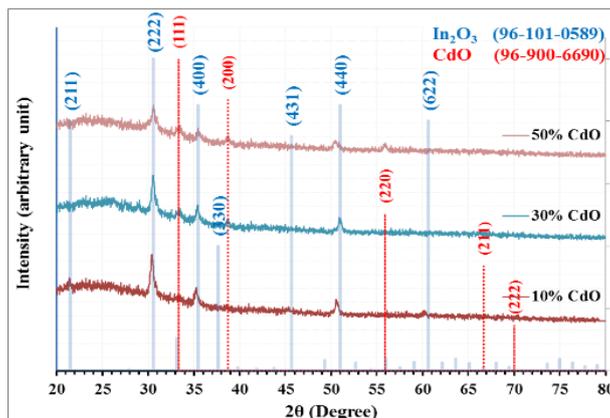


Fig. 3. X-ray diffraction patterns for In_2O_3 -CdO mixed thin films.

Table 1. Structural parameters: Inter-planar spacing, crystalline size for In_2O_3 -CdO mixed thin film with different ratio.

Sample	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	Crystallite size (nm)	hkl	d_{hkl} Std.(Å)	Phase	Card No.
10	21.3746	0.4811	4.1537	16.81	(211)	4.1315	In_2O_3	96-101-0589
	30.3780	0.4123	2.9400	19.98	(222)	2.9214	In_2O_3	96-101-0589
	35.2577	0.4811	2.5435	17.33	(400)	2.5300	In_2O_3	96-101-0589
	50.5842	0.5497	1.8030	15.99	(440)	1.7890	In_2O_3	96-101-0589
	60.2062	0.6873	1.5358	13.37	(622)	1.5256	In_2O_3	96-101-0589
30	30.5155	0.4810	2.9271	17.13	(222)	2.9214	In_2O_3	96-101-0589
	33.3333	0.5497	2.6858	15.09	(111)	2.6848	CdO	96-900-6690
	35.3952	0.5497	2.5339	15.18	(400)	2.5300	In_2O_3	96-101-0589
	38.6942	0.5497	2.3252	15.32	(200)	2.3251	CdO	96-900-6690
	50.8591	0.4810	1.7939	18.30	(440)	1.7890	In_2O_3	96-101-0589
50	30.4467	0.6185	2.9336	13.32	(222)	2.9214	In_2O_3	96-101-0589
	33.4708	0.7560	2.6751	10.98	(111)	2.6848	CdO	96-900-6690
	35.6014	0.6186	2.5197	13.49	(400)	2.5300	In_2O_3	96-101-0589
	38.6254	0.6873	2.3291	12.25	(200)	2.3251	CdO	96-900-6690
	50.5155	0.8247	1.8053	10.66	(440)	1.7890	In_2O_3	96-101-0589
	55.8763	0.4811	1.6441	18.70	(202)	1.6441	CdO	96-900-6690

Fig. 4 shows the scanning electron microscope images. The images indicate that the increase of CdO concentration (10, 30 and 50%) will produce grains which aggregate to form clusters which result a decrease in the sensitivity of the mixture to incident light and this agree with the response curves in Figs. (5, 6 and 7) [14].

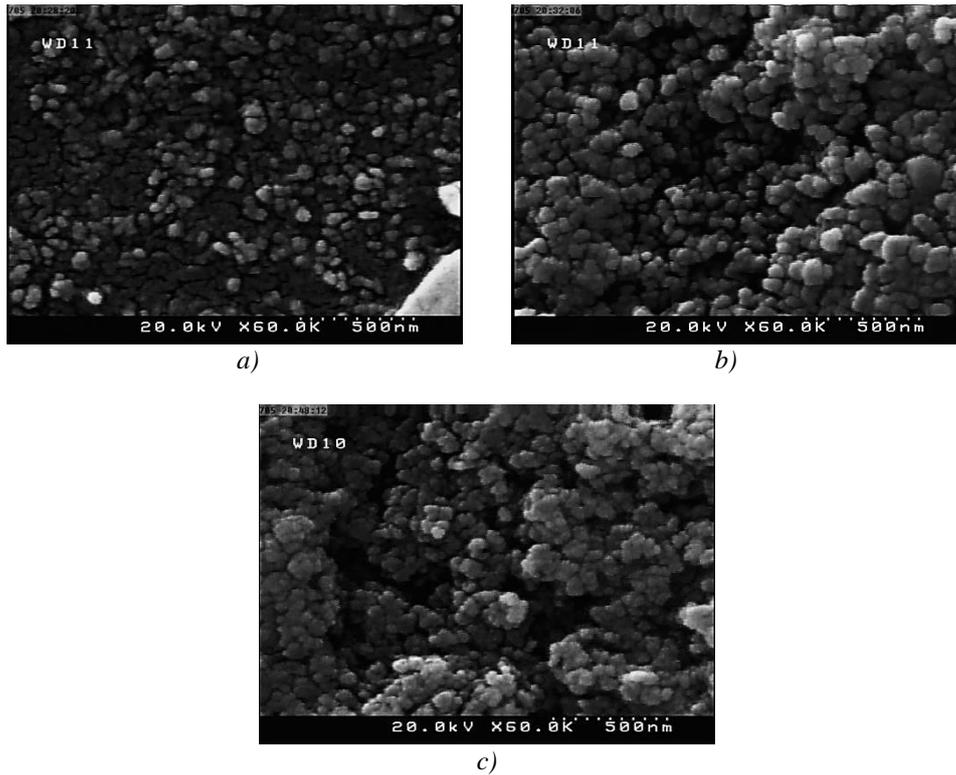


Fig. 4. SEM images for a) 10 % CdO; b) 30 % CdO; c) 50 % CdO.

A light with wavelengths (240 and 566) were used to study the sample sensitivity where 240 nm represents the working region for In_2O_3 which is sensitive for UV light and 566 nm represents the working region for CdO which is sensitive for visible light [12]. When the light turned on, conductivity increased and after the light was turned off, the current returned to its original value. This process was repeated many times for In_2O_3 -CdO mixture with different CdO ratios (10, 30 and 50)% respectively.

Due to the different crystalline structure of the samples and the difference in the locations of the localized levels of defects, the sensitivity and response speed vary for each mixture as shown in figures (5, 6 and 7). In the case of light on, the electrons in the nanoparticles were excited which resulted an increase in the conducting current but when the light source tuned off (switch off) then these nanoparticles reversibly between higher and lower states of conductivity. Only sample with 10% CdO content has square pulse response. The average rising time in this sample nearly 1s and lowering time 1s when the light was turned off [15, 16].

The sensitivity vary with CdO concentration for both wavelength (240nm and 566nm) due to the variation in the layers structure and energy level location within the gap, in addition to the aggregation and growth of the grains on the layer surface. Table (2) shows that the maximum sensitivity was found for both wavelengths at 10% CdO content which is 59% and 42% at wavelengths 240 nm and 566 nm, respectively.

Table 2. The sensitivity for a mixed In_2O_3 -CdO thin films with different CdO contents (10, 30 and 50)%.

Sample	Sensitivity (%)	
	240 nm	566nm
In_2O_3 : 10% CdO	59.573	42.149
In_2O_3 : 30% CdO	52.905	11.776
In_2O_3 : 50% CdO	51.941	11.356

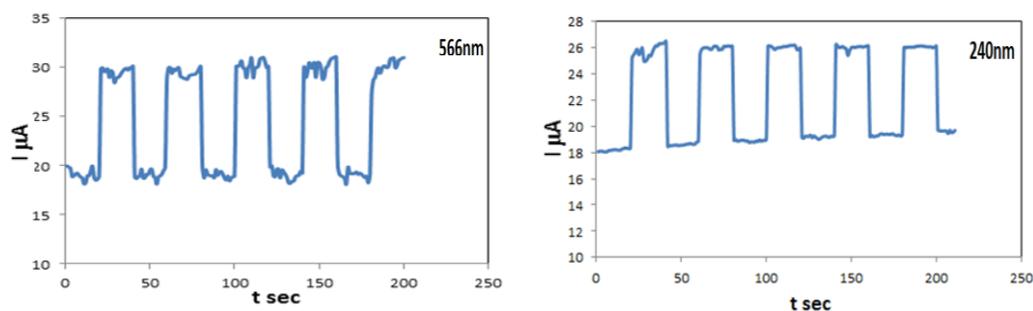


Fig. 5. Photo response with time for In_2O_3 -CdO at 10% CdO thin films.

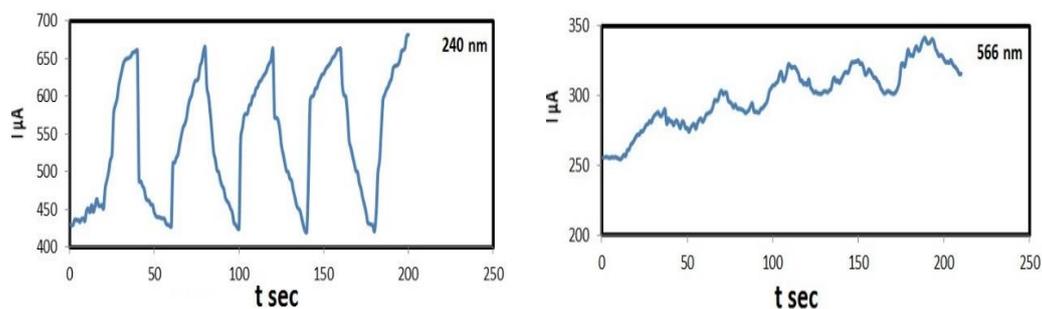


Fig. 6. Photo response with time for In_2O_3 -30 % CdO thin films.

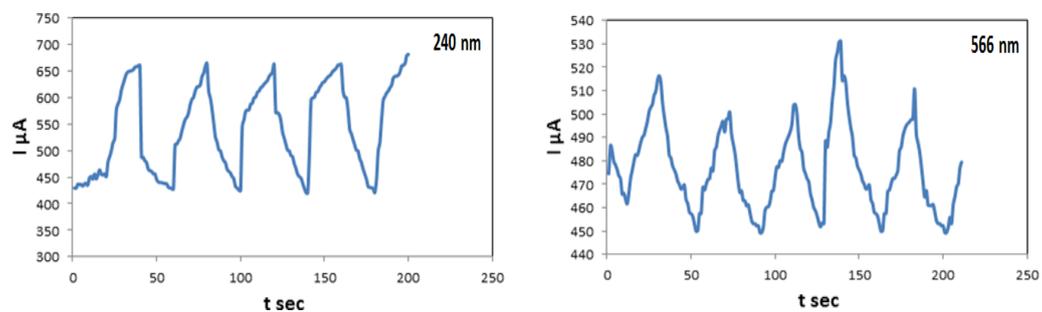


Fig. 7. Photo response with time for In_2O_3 -50% CdO thin films.

4. Conclusions

In_2O_3 -CdO thin films were prepared successfully by CSP method. It appeared possibility to control the light response of the photodetector by varying the mixed ratio. Grain size varies according to concentration ratio of CdO within mixture. Only sample with 10% CdO content has square pulse response. The sensitivity and response speed vary for each mixture due to the different crystalline structure.

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