Ali A. Yousif [1]
Mazin H. Hasan

[1] *Department of Physics, College of Education, Al-Mustansiriyah University, Baghdad, Iraq*

Growth of Nanostructured CdO:In Films by Pulsed Laser Deposition

In this work, indium-doped cadmium oxide (CdO:In) films were prepared by Pulsed Laser Deposition (PLD) on sapphire α- Al_2O_3 (006) substrate with thickness of about 100nm for all CdO:In films at different deposition conditions and the number of laser pulses was 100 pulses, by Nd-YAG Q-Switching second harmonic generation (SHG) pulsed laser with a wavelength of 532nm, repetition rate 10Hz and pulsed width 10ns. The effect of doping on the structure and morphology properties of the CdO:In films have been investigated by X-Ray diffraction (XRD), and Atomic Force Microscopy (AFM). The result showed that nano-crystalline and (111)-oriented CdO films were obtained at substrate temperature of 400°C, laser fluence 400mJ. The smallest grain size was obtained at 7wt.% In are 16.52nm, this indicates the superior nanocrystallinity of the films which also has observed from the SEM and AFM images. The surface morphology of the films reveals that presence of indium content in the structure did affect the surface morphology of the films significantly.

***Keywords*:** Nanostructures; Cadmium oxide; Pulsed-laser deposition; Morphology

1. Introduction

Conducting metal oxide thin films such as zinc oxide, indium oxide, cadmium oxide, etc. are widely used for various applications such as transparent electrodes, solar cells, phototransistors, liquid crystal displays, optical heaters and gas sensors [1,2]

Cadmium oxide is attracting tremendous attention due to its interesting properties like direct band gap of 2.3eV and n-type semiconductor under the nonstoichiometric condition of interstitial Cd or oxygen vacancies [3]. The crystal structure is a rock salt type, which can be regarded as the densest structure of CdO6 octahedral. Therefore, it is necessary to analyze the electronic structure of CdO in order to understand many TCOs containing Cd as a central cation. It is widely used in the application like the preparation of cadmium coated baths and manufacture of paint pigments [4].

Pulsed laser deposition (PLD) can be successfully employed to many classes of materials such as metals, semiconductors, dielectrics, ferroelectrics, electro-optic and giant magneto-resistance oxides, organic materials, polymers, magnetics, composites, etc. [5]. Phase pure and doped CdO thin films exhibit some extraordinary properties due to which they are popular in various semiconducting, optoelectronic industries, and for the fabrication of IR mirrors, thin film resistors, low emissive windows, etc. [6]. Deposition parameters in PLD process play key role in determining various properties of CdO thin films. Gupta et al. reported the effect of deposition parameters on various properties of Sn, Ti, Al and In doped CdO films prepared by PLD technique [7-10]. In this paper, CdO nanostructure was synthesized via In doped CdO films were deposited on sapphire α-Al_2O_3 (006) by pulse laser deposition technique, the structure and surface morphology properties were studied.

2. Experiment

CdO:In thin films were synthesized by pulsed laser deposition system using a second harmonic Nd:YAG laser. Thin films were grown in a vacuum chamber with background pressure of ~$1x10^{-3}$ mbar. The Nd:YAG laser was operated at the wavelength of 533 nm with the repetition rate of 10 Hz and pulse duration of 7 ns. The target to substrate distance was 3 cm.

X-ray diffraction measurement has been done and compared with the JCPDS (ASTM) cards, using Philips PW 1840 X-ray diffract meter of λ=1.54Å from Cu-Kα. The morphological features of the various films were investigated with a JEOL JSM-6360 equipped with an EDAX detector. The microstructures of the films were analyzed using atomic force microscopy (AFM, Digital Instruments Nano Scope) working in tapping mode.

The α-plane (α-Al_2O_3) single-crystal sapphire substrate (MTI Corporation) is the popular for III-V nitrides, both polished side (substrate surface is EPI polished via a spatial CMP procedure with RA<5A) with square-shaped size 10x10x0.5 mm thick were etched in H_2SO_4:H_3PO_4=3:1 followed by ultrasonic cleaning in deionized water for 15 min, and finally dried.

Film thickness measurement by optical interferometer method, this method was based on interference of light beam reflected from thin film surface and substrate bottom. He-Ne laser of wavelength 632.8 nm was used and the thickness is 100 nm determined using the formula [11]:

$$d = \frac{\Delta x}{x} \times \frac{\lambda}{2} \qquad (1)$$

where x is fringe width, Δx is the distance between two fringes and λ is wavelength of laser light

3. Results and Discussion

Figure (1) shows the XRD patterns of the prepared CdO pure and CdO:In films of different doping concentrations (1, 3, 5 and 7%). All the patterns show polycrystalline of cubic CdO structure (NaCl structure) and CdO:In films are composed of crystallites of CdO (JCPDS 05-0640) [12]. The XRD shows neither the formation of CdO and In_2O_3 nor mixed phases even at In-doping level. It can be clearly seen that all films are preferentially orientated along (111) crystallographic directions and this is in agreement with the result obtained by others on films prepared [13-15] and the preferential orientation peak for in doped films of different doping concentration became wide and less intense.

This may be attributed to the crystallinity of the CdO films being improved by increasing the doping concentration. The Al_2O_3 (006) peaks are observed for all the samples. Also, the structural parameters such as diffraction angle (2Θ), lattice spacing (d), lattice constant (a_o), full width at half maximum (FWHM), and the phases identified along (hkl) planes were evaluated from these spectra and presented in Table (1). The calculated lattice constant (a) for the dominant peak of (111) of CdO and peak of (620) for of CdO:In and the values it is in agreement with the JCPDS for all films, the grain size (G.S.) was calculated from the full width at half maximum (FWHM) (β) of the preferred orientation diffraction peak by using the Scherrer's equation [16]:

$$G.S. = \frac{0.9\lambda}{\beta COS\theta} \qquad (2)$$

where k denotes the Scherrer's constant (the shape factor of the average crystallite and can be considered 0.90), λ= 1.5406Å is the wavelength of the incident Cu Kα radiation

From the results it may be said that nanocrystalline CdO material can be grown by our locally developed pulsed laser deposition method. Smaller grain size and larger FWHM values indicate better crystallization of the materials, according to Table (1), all CdO:In films of different concentrations have better crystallinity levels as increasing in the doping concentration.

Moreover the texture coefficient Tc(hkl) is introduced to characterize the preferential crystallite orientation along the (hkl) direction defined as [17]:

$$Tc(hkl) = \frac{[(I(hkl)/I_o(hkl)]}{[Nr^{-1}\sum I(hkl)/I_o(hkl)]} \qquad (3)$$

where I(hkl), I_o(hkl) and Nr are the measured relative intensity of a diffraction peak, intensity of the standard powder diffraction peak and the number of diffraction peaks respectively

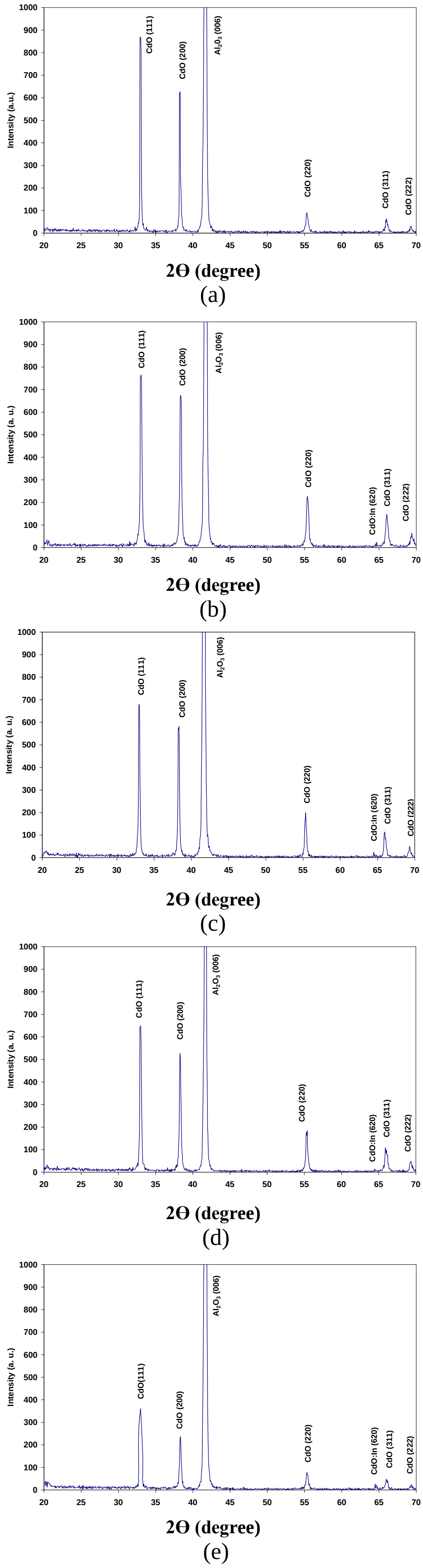

Fig. (1) The XRD patterns of the prepared CdO and CdO:In films of different doping concentrations (0, 1, 3, 5 and 7%)

If Tc(hkl)=1, for all the (hkl) planes considered, indicates a sample with randomly oriented crystallite, while values larger than one indicate the abundance of crystallite in a given (hkl) direction. Values 1>Tc(hkl)>0 indicate the lack of grains orientated in that direction. The Tc values of the preferential crystallite orientation (111) of the all films were presented in Table (2) [18]. Additionally, to have more information on the amount of defects in the films, the number of layers (N_L), the dislocation density (δ) and Number of crystalline per unit area [19].

It is well known that the AFM is one of the effective ways for the surface analysis due to its high resolution and powerful analysis software The CdO and CdO:In thin films were morphologically characterized using AFM technique. In the extreme case of thin films the surface roughness may be in the order of the film thickness and can influence all film properties such as mechanical, electrical, magnetic, gas sensor or optical properties [20].

Figure (3) shows the two and three-dimensional of the CdO and CdO:In thin films with (1, 3, 5 and 7%) In concentration deposited at room temperatures, an area of 2.5x2.5μm^2 has been used for evaluation. It can be seen that films are uniform, densely packed and pinhole free, and it shows that the morphology of these films has smaller number of grain size and are homogeneously distributed, which indicates the crystalline nature of the film. Initial visual investigations of the deposited film have shown that they are compact and have good adherence to the sapphire α-Al_2O_3 substrate. No evidence of cracking, based on AFM image (Fig. 3), the grain density reduced indicating the smaller grains agglomerate together to form larger grains of CdO and CdO:In. On the other hand, the surface roughness, root mean square (R.M.S.) and ten point heights of the films were measured using AFM technique as in Table (3). The surface roughness defined as the standard deviation of the surface height profile from the average height is the most commonly reported measurement of surface roughness. The surface roughness is unavoidable since the grains are grown with different sizes. It can be seen that the surface roughness and R.M.S. values decrease with increasing In ratio indicating as in Table (3).

4. Conclusions

The polycrystalline In-doped CdO films were confirmed to be cubic crystal structure. The XRD measurements give an indication that the crystallite size lie within the nanocrystal range of (16.52-57.9nm). From the results, it may be said that nanocrystalline CdO:In material can be grown by our developed PLD method. The morphology of the prepared films has smaller number of grain size and are homogeneously distributed and uniform, which indicates the crystalline nature of these films, and the surface roughness and R.M.S. values of these films is decreased with increasing In concentration. Also, the grain size decreases with increasing In concentration.

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Table (1) The diffraction angle (2θ), interplaner distance (d), lattice constant (a_o), FWHM, the grain size (G.S.) and the phases identified along with (hkl) planes of CdO and CdO:In films

Wt.%	Phase	2Θ Std. (deg.)	2Θ Exp. (deg.)	a_o (Å)	d_{hkl} Std. (Å)	d_{hkl} Exp. (Å)	FWHM (deg.)	G.S. (nm)	(hkl)	JCPDS
CdO	CdO- pure	33	33	4.697	2.712	2.712	0.15	57.9	(111)	05-0640
	α-Al_2O_3	41.67	41.65	-	2.165	2.165	0.094	-	(006)	46-1212
CdO:In (1%)	CdO- pure	33.05	33.0	4.691	2.712	2.708	0.25	39.64	(111)	05-0640
	CdO:In	64.77	64.7	9.099	1.438	1.439	-	-	(620)	12-0675
	α-Al_2O_3	41.67	41.7	-	2.165	2.163	0.101	-	(006)	46-1212
CdO:In (3%)	CdO- pure	33.0	33.0	4.697	2.712	2.712	0.26	33.34	(111)	05-0640
	CdO:In	64.77	64.65	9.107	1.438	1.440	-	-	(620)	12-0675
	α-Al_2O_3	41.67	41.7	-	2.165	2.163	0.102	-	(006)	46-1212
CdO:In (5%)	CdO- pure	33.0	33.0	4.697	2.712	2.712	0.30	28.77	(111)	05-0640
	CdO:In	64.77	64.7	9.101	1.438	1.439	-	-	(620)	12-0675
	α-Al_2O_3	41.67	41.65	-	2.165	2.165	0.144	-	(006)	46-1212
CdO:In (7%)	CdO- pure	32.97	33.0	4.691	2.712	2.708	0.54	16.52	(111)	05-0640
	CdO:In	64.77	64.7	9.101	1.438	1.439	0.2	34.01	(620)	12-0675
	α-Al_2O_3	41.67	41.65	-	2.165	2.165	0.147	-	(006)	46-1212

Table (2) Texture coefficient (Tc), the number of layers (N_L), the dislocation density (δ) and number of crystallines per unit area of the CdO and CdO:In films

Sample	(hkl)	Texture Coefficient T_C (h k l)	Number of Layers (N_L) (nm)	Dislocation (δ) x 10^{14} (m^2)	Number of Crystallites per unit area x 10^{12} (m^2)
CdO- pure	(111)	1.943	1.72	2.98	5.15
CdO:In (1%)	(111)	1.248	2.52	6.36	16.05
CdO:In (3%)	(111)	1.324	2.99	8.99	26.98
CdO:In (5%)	(111)	1.345	3.47	12.08	41.99
CdO:In (7%)	(111)	1.589	4.04	16.36	66.19

Table (3) AFM characteristics of CdO:In thin films grown on sapphire (α-Al_2O_3) substrate

Samples	R.M.S. [nm]	R_S [nm]	Ten point height [nm]
CdO – Pure	0.63	0.472	2.96
CdO:In 1%	0.228	0.186	0.696
CdO:In 3%	0.233	0.195	0.641
CdO:In 5%	0.238	0.196	0.621
CdO:In 7%	0.331	0.255	1.25

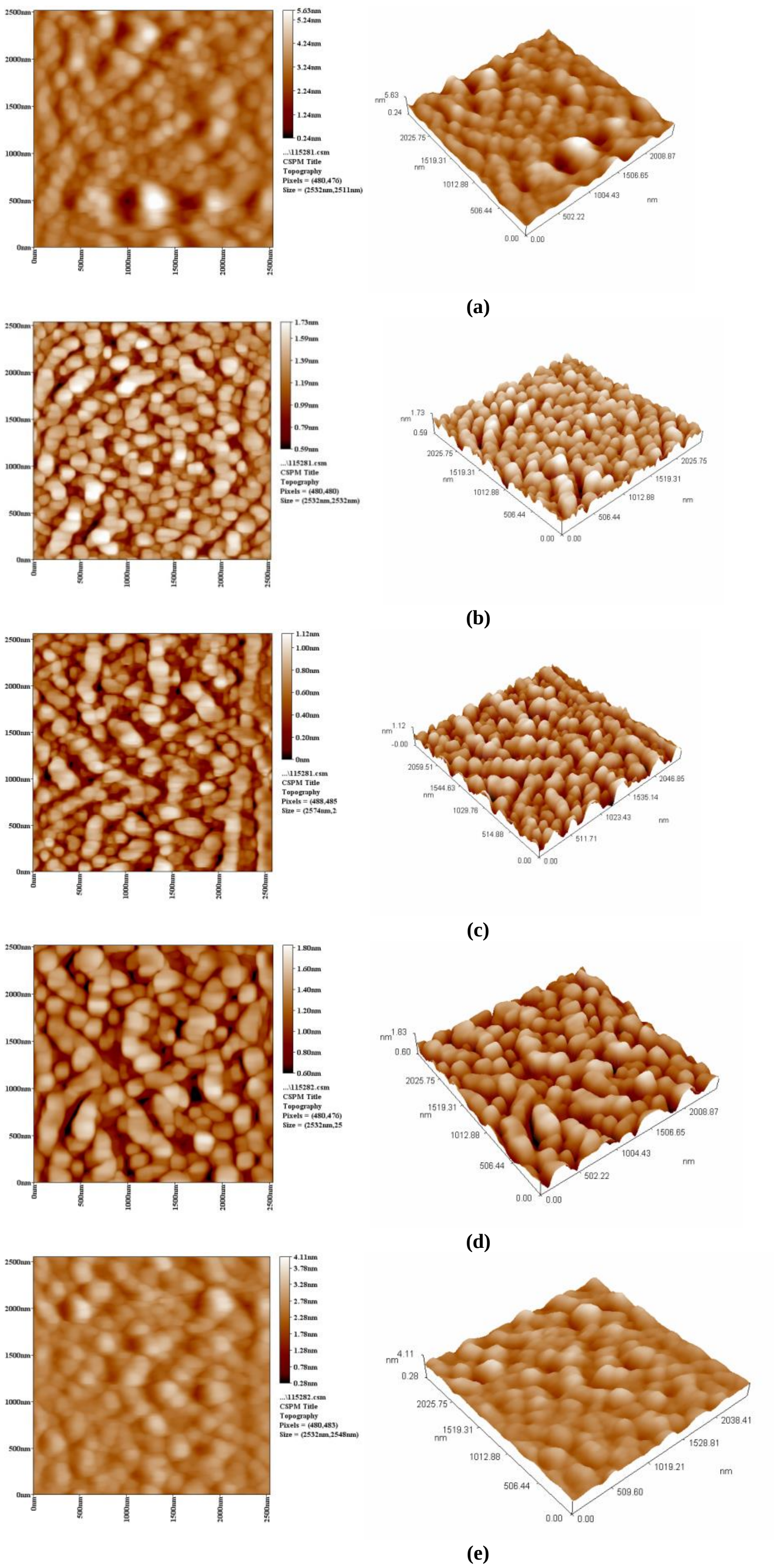

Fig. (3) 2D and 3D AFM images of pure CdO and CdO:In thin films at In concentration of 1, 3, 5 and 7%