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Influence of Laser Energy on the Structural and Optical Properties of (CdO):(CoO) Thin Films Produced by Laser-Induced Plasma (LIP)

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Abstract

In this work, The influence of laser energy on structural and optical properties of (CdO):(CoO) thin films deposited on glass slides by the pulse laser deposition technique (PLD) was studied using The laser used was Nd:YAG laser with (λ=1064 nm) and duration (9 ns) with different laser energies (200-500 mJ) for (1:1). X-ray diffraction patterns showed that all the films had a polycrystalline with cubic crystal structure. As for the topography of the films surface, it was measured using AFM, where the results showed that the grain size and the average roughness increase with increasing laser energy. The optical properties of all films were studied and the results showed that the absorption coefficient within the wavelength range (280-1100 nm) increases with increasing laser energy, It was shown that the optical power gap value for direct transitions decreased by increasing laser energy within the range (4.25-3.55) eV.

Key words

Laser Induced Plasma (LIP), (CdO):(CoO) thin films, structural properties, optical properties.

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تأثير طاقة الليزر على الخصائص التركيبية والبصرية لاغشية CdO:CoO المنتجة بالبلازما المحتثة بالليزر

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الخلاصة

في هذا العمل تم دراسة تأثير طاقة الليزر على الخواص التركيبية والبصرية للاغشية الرقيقة (CdO):(CoO) التي تم اعدادها على الشرائح الزجاجية بواسطة تقنية الترسيب بالليزر النبضي (PLD) في الفراغ بأستخدام ليزر النيديميوم ياك بطول موجي (1064 نانومتر) والفترة الزمنية 9 نانوثانية وبطاقات ليزرمختلفة (200-500) ملي جول) للتركيز (1:1). اظهرت أنماط حيود الأشعة السينية أن جميع الأغشية التي تم تحضيرها ذات تراكيب متعدد التبلور مع بنية بلورية مكعبة. أما بالنسبة لطوبوغرافيا السطح للاغشية، فقد تم قياسها بواسطة (AFM) حيث اظهرت النتائج ان الحجم الحبيبي ومعدل الخشونة يزداد مع زيادة طاقة الليزر. كما تمت دراسة الخصائص البصرية لجميع الاغشية واظهرت النتائج ان معامل الامتصاص ضمن نطاق الطول الموجي (280-1100) نانومتر يزداد مع زيادة طاقة الليزر، وتبين ان قيمة فجوة الطاقة الضوئية للانتقالات المباشرة انخفضت بزيادة طاقة الليزر ضمن المدى (4.25-3.55) الكترون فولت.

Introduction

Cadmium oxide (CdO) is an N semiconductor of interesting properties, such as low electrical conductivity [1]. It has a molecular weight of (128.4 g/mol), density (8.15 g/cm-3), as well as having a forbidden energy gap of ranging between (2.16-2.6) eV. CdO can be used in many practical applications and different technological industries as a translucent conductive material and a thin film. [2]. Cobalt oxide (CoO) is an important material that is used in different fields, such as heterogeneous catalysts. [3], energy storage [4], and in electrochemical devices, etc. Nanostructures of (CoO) have been shown to show capacitance in negative potential and may also serve as suitable positive electrodes in devices [5]. The electronic and optical characteristics of nanoparticles for (CoO) are powerfully dependent on their size and form [6]. CoO has a molecular weight of (74.933gm/mole), density (6.11 gm/cm^{-3}), and a forbidden energy gap ranging between (2.2 - 2.4) eV [7].

The deposition method by pulsed laser ablation technique is one of the best and low coast techniques for the deposition of semiconductors, metals, and their oxides under different technological conditions [8]. Pulsed laser deposition (PLD) preferably uses high-energy laser pulses with an energy density of more than 10^8 (W/cm^2) to deposit a thin layer of a single target. There are several techniques that can be used for the purpose of deposition, including chemical bath deposition (CBD), magnetron sputtering (MS), chemical vapor deposition (CVD), and pulsed laser deposition (PLD) [9-11].

This research aims to prepare (CdO:CoO) thin films using PLD method on glass substrates and study the effect of changing the energy of the laser pulse on the structural and optical properties

Experimental work

In this work, PLD was chosen for the deposition (CdO:CoO) films. Thin film growth is achieved by directing the laser onto the target (pellet), which leads to the evaporation of the material and its growth on the substrate. The laser used for the growth method of films is Nd: YAG laser with a wavelength of 1064 nm. The evaporation process depends on the laser parameters such as laser energy and pulses duration [12]. X-ray diffraction (XRD) was used to calculate the crystalline structure and grain size of the (CdO:CoO) films prepared by PLD techniques. The grain size (D) was calculated by using Scherrer's equation [13].

$$\boldsymbol{D = \frac{K.\lambda}{\beta \cos \theta}} \qquad (\mathbf{1})$$

where k is a constant taken to be 0.94, λ is the wavelength of X-ray (1.54Å), β is full width at half maximum (FWHM), and θ is Bragg's angle [14].

The optical properties were studied using a double beam UV-Vis spectrophotometer (MetertechSP8001, Taiwan). The optical band gap was estimated graphically by applying Tauc's relation for direct transition [15]:

$$\boldsymbol{\alpha h\upsilon = B(h\upsilon - E_g)^r} \qquad (\mathbf{2})$$

where α is the absorption coefficient, B is a constant that depends on the material's nature., h is Planck constant, ν is the frequency of photon, E_g is optical energy gap, and r is a constant that depends on the nature of the transition. The pulse laser deposition (PLD) technique was used, (which is located in the plasma Research Laboratory in the Physics Department at the College of Science, University of Baghdad). The experiment was conducted in a vacuum chamber under vacuum conditions (2.5×10^{-2} mbar). The (CdO:CoO) target was formed under (6 pa) pressure for a duration of (10 minutes) using a hydraulic piston (type SPECAC) to

form a disc of the target material with a (1 cm) and (0.4 cm) diameter and a thickness, respectively. In this work, glass slides were used to study the structural and morphological properties of (CdO:CoO) thin films.

Nd:YAG laser of wavelength (λ), energy (E= 200, 300, 400, 500) mJ, frequency (*f*= 6) Hz, and number of shots of 100 pulses. The incident Nd:YAG SHG Q-switching laser beam makes an angle of about 45° degrees with the target surface. The system consists of two vacuum systems; the first vacuum is called a rotating vacuum system with two stages, as well as, a pressure and temperature gauge and a vacuum chamber, as shown in the Fig.1. The crystal structure and morphology were studied by X-ray diffraction (XRD) and atomic force microscopy (AFM). The films were also examined by ultraviolet spectroscopy (UV) to determine their optical properties.

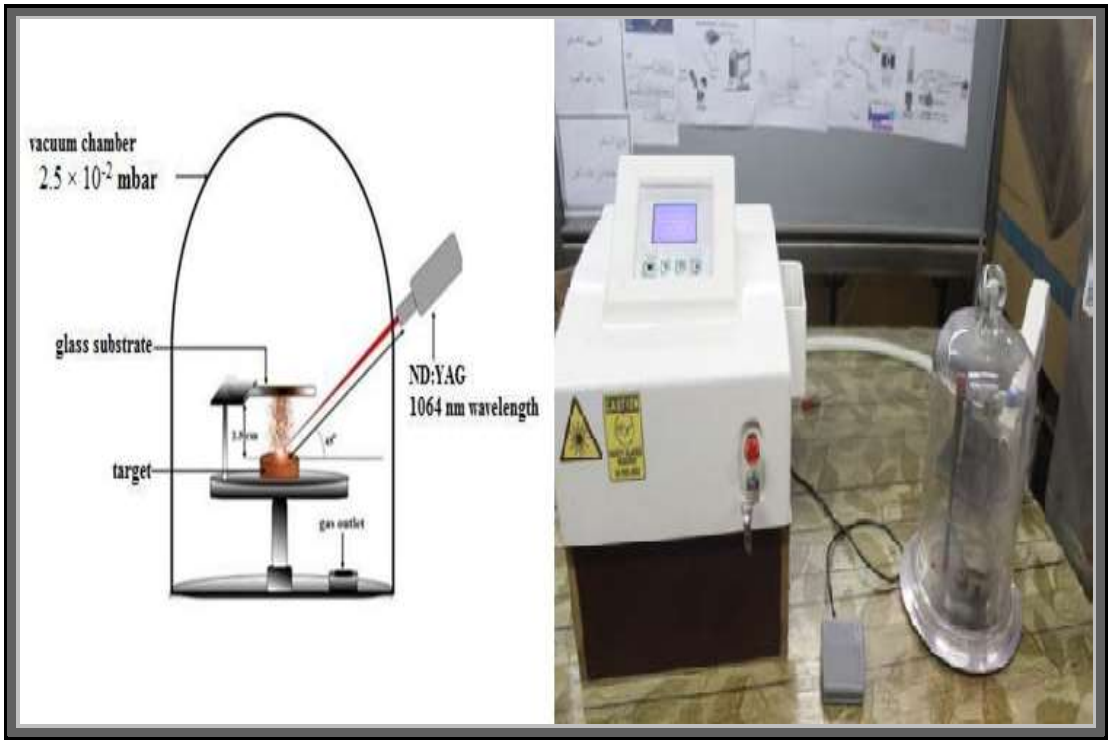

Fig. 1: Schematic diagram of pulsed laser deposition system.

Results and discussion

1- X-ray diffraction examination

X-ray diffraction technique showed that all the thin films were prepared with polycrystalline structure.

Fig.2 shows the (XRD) patterns of the (CdO):(CoO) composite films with different energies. These patterns are shown to have peaks centered at 2θ = [(33.02), (36.6), (38.8), (43.13), (55.02), (62.03), (66.09), (74.23), and (69.01)], belonging to Miller indices [(111), (200), (220), (311) and (222)]. The peaks at the angles (33.02),(38.8),(55.02),(66.09), and(69.01) belong to (CdO), but the peaks at the angles (36.6), (43.13), (62.03), and (74.23) belong to (CoO), These results agrees with data of the JCPDS Card (No:05-0640). It can be observed from the figure that the (CdO:CoO) thin film is of polycrystalline structure, It can be clearly seen that the film is preferentially orientated along (111) crystallographic directions. Experimental inter-plane spacing, and crystalline size were calculated by Scherer's equation. It was notice that increasing the energy caused a decrease in the intensity of the peaks, in

addition to shifting the angles to larger 2θ values Moreover increasing the energy led to an increase in crystallization as shown in (Table 1). This is an agreement with Zhao (2002) [16].

Figs.3-5 shows the XRD results of (CdO and CoO) powders and of the mix powder (CdO:CoO). The direction of the intensity spikes on the XRD plot at the different 2θ incidence angles can be related to the structure of the substance and the crystalline orientation [17]. It is observed from the Fig.3, and Fig.4 that both CdO and CoO deposited powders are of polycrystalline structure [18].

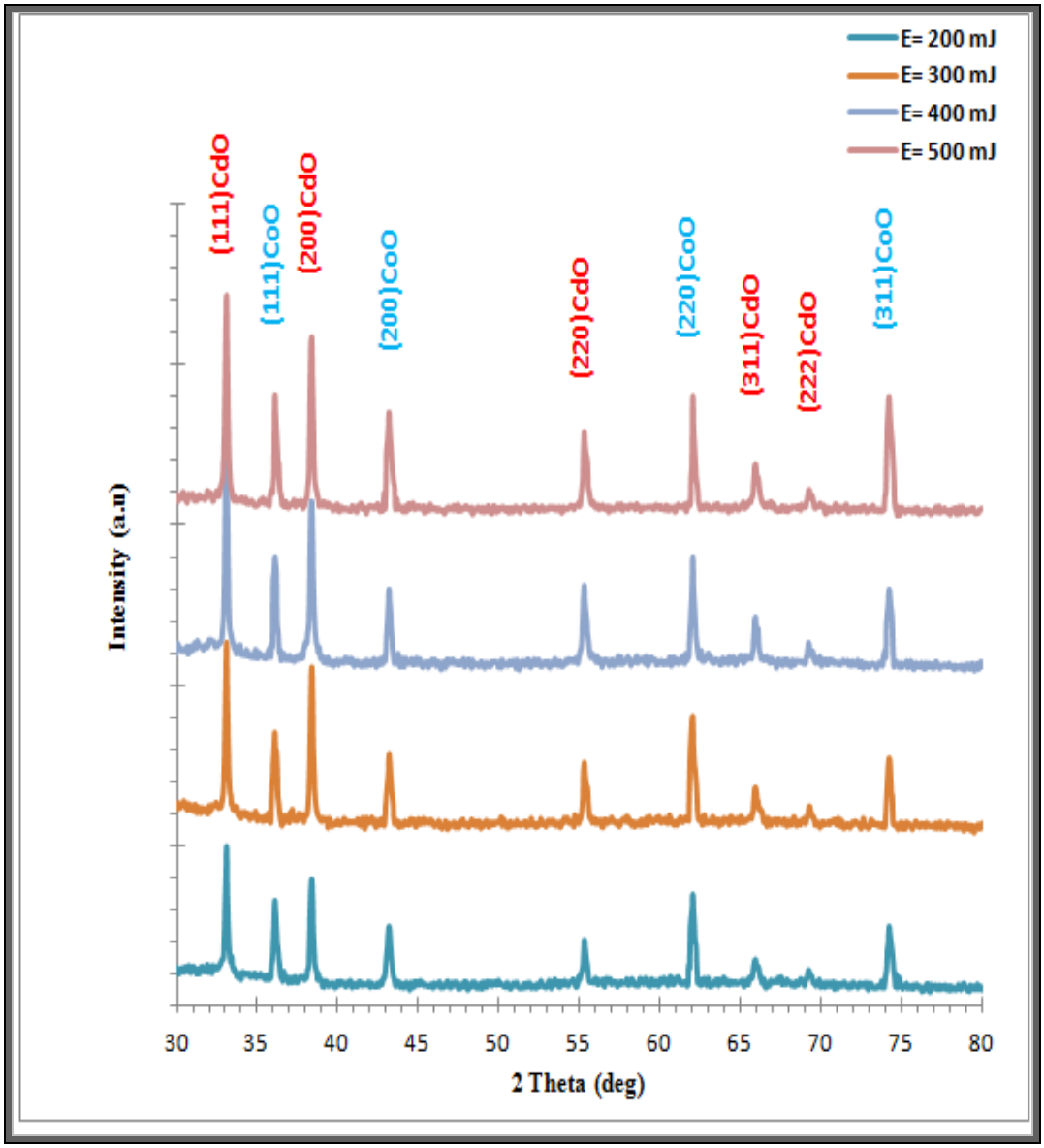

Fig. 2: XRD pattern for CdO:CoO thin films prepared with different laser energies.

Table 1: The results of X-ray examination of CdO:CoO thin films deposited with different energies.

Laser energy	material	hkl	FWHM	2θ	G.S (nm)	Avg G.S
200mJ	CdO	111	0.1968	33.0217	42.20493	35.27549
		200	0.1968	38.3223	42.83389	
		220	0.1968	55.2724	45.65251	
		311	0.3236	65.9182	29.30348	
		222	0.5904	69.3305	16.38263	
	CoO	111	0.1968	36.63	42.62119	39.29422
		200	0.2952	43.13	29.00128	
		220	0.269	62.03	34.51705	
		311	0.1953	74.13	51.03736	
300mJ	CdO	111	0.1968	33.0217	42.20493	37.35725
		200	0.1968	38.3223	42.83389	
		220	0.2952	55.2724	30.43501	
		311	0.246	65.9182	38.54718	
		222	0.2952	69.3305	32.76527	
	CoO	111	0.1968	36.63	42.62119	40.76254
		200	0.264	43.13	32.42871	
		220	0.2512	62.03	36.96292	
		311	0.1953	74.13	51.03736	
200mJ	CdO	111	0.1968	33.0217	42.20493	40.50201
		200	0.1968	38.3223	42.83389	
		220	0.246	55.2724	36.52201	
		311	0.1968	65.9182	48.18398	
		222	0.2952	69.3305	32.76527	
	CoO	111	0.1815	36.63	46.21405	41.82506
		200	0.2312	43.13	37.02932	
		220	0.2812	62.03	33.01951	
		311	0.1953	74.13	51.03736	
500mJ	CdO	111	0.1968	33.0217	42.20493	42.72997
		200	0.1968	38.3223	42.83389	
		220	0.1568	55.2724	57.29856	
		311	0.246	65.9182	38.54718	
		222	0.2952	69.3305	32.76527	
	CoO	111	0.1953	36.63	42.94854	42.6588
		200	0.2391	43.13	35.80585	
		220	0.2512	62.03	36.96292	
		311	0.1815	74.13	54.91789	

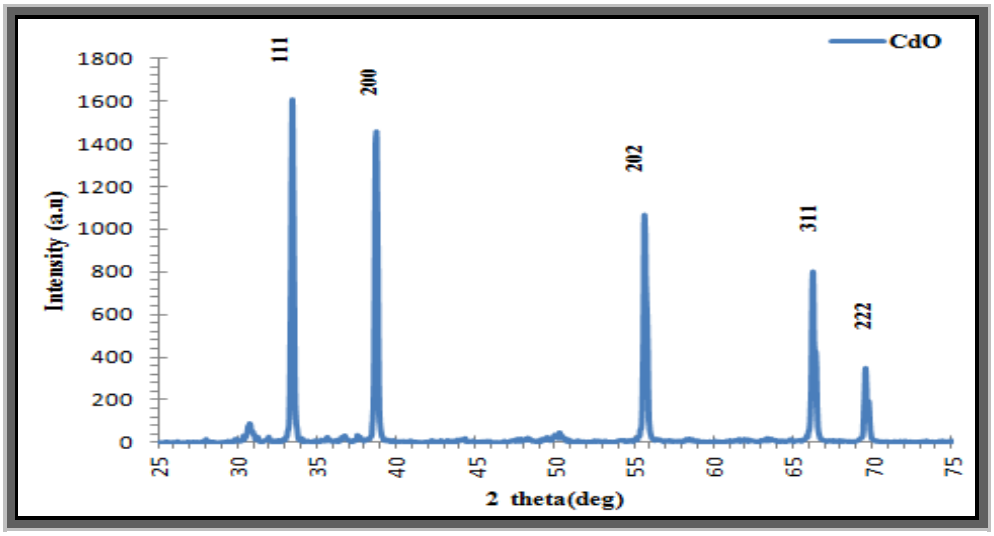

Fig. 3: Patterns of XRD for CdO powder.

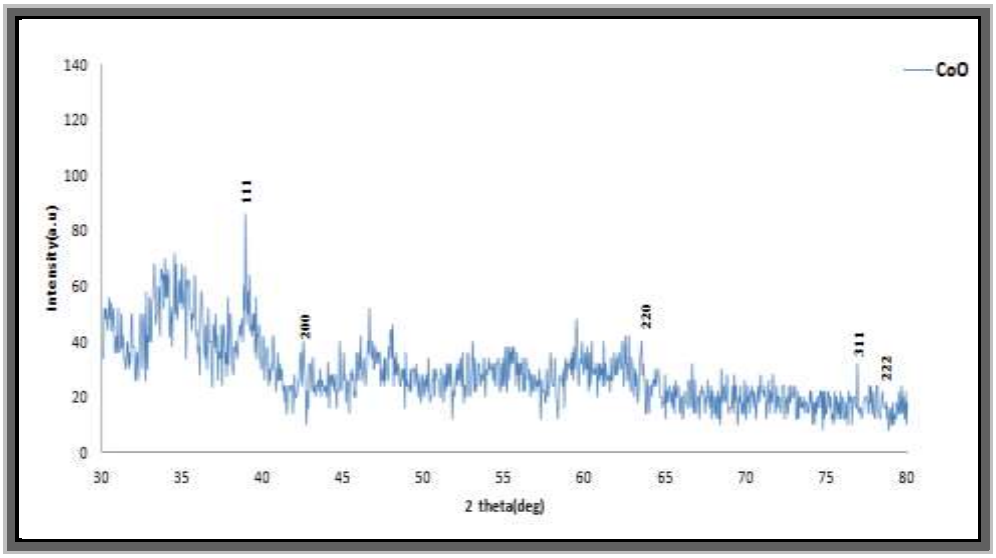

Fig. 4: Patterns of XRD for CoO powder.

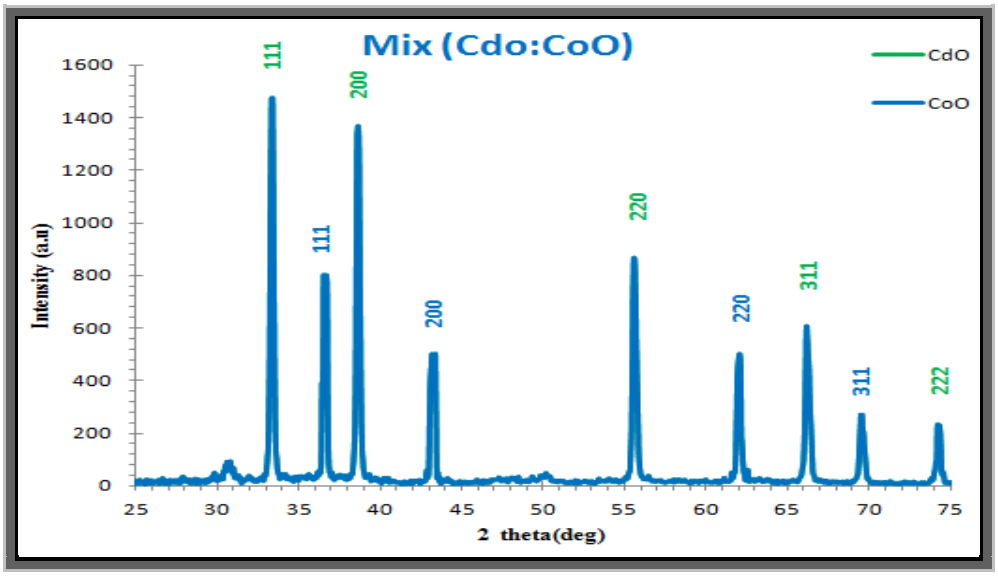

Fig. 5: Patterns of XRD for mix powder (CdO:CoO).

2- Atomic Force Microscope measurements (AFM)

The topography of the deposit surfaces was studied with an atomic force microscope. Fig.6 shows (AFM) images of CdO:CoO thin films with different energies.

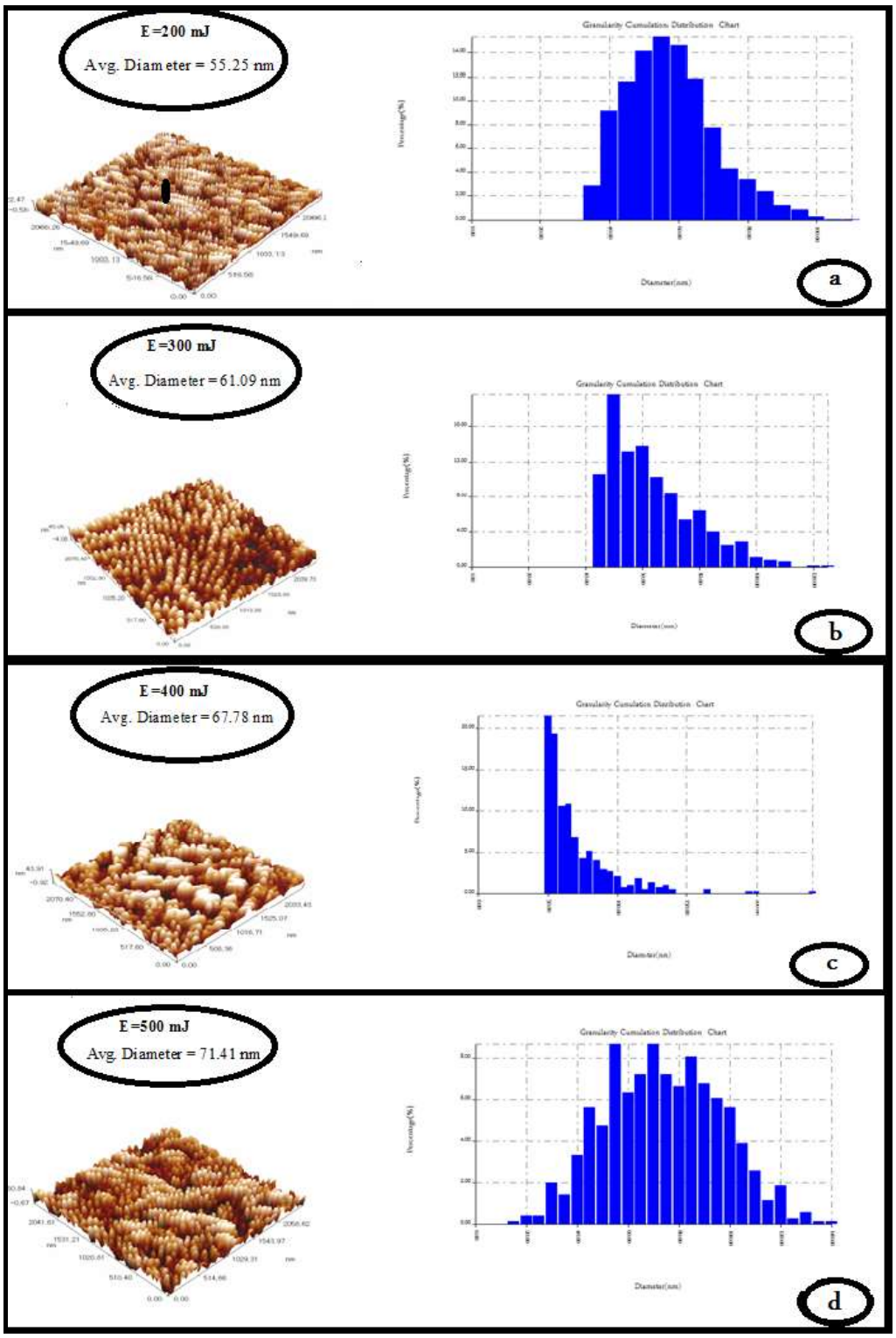

Fig.6: AFM images of CdO:CoO thin films deposited with different laser energy: (a)200mJ, (b)300mJ, (c)400mJ, and (d)500Mj.

Table 2 shows the AFM parameters (average diameter, Root mean Square and average roughness) for CdO:CoO thin films. The thin films were deposited on glass substrate by laser pulses.

Table 2: AFM parameters (Average Diameters, RMS and Average Roughness) for CdO:CoO thin films at different energy.

laser (mJ Energy)	Avg. Diameters	Root Mean Sq.(nm)	Avg. Roughness (nm)
200	55.25	6.65	5.75
300	61.09	12.50	10.7
400	67.78	12.96	11.2
500	71.41	14.64	12.7

It was noticed that the granular diameter increases as the laser power energy increases This increase is due to two reasons: the first reason is that large grains are produced because of the increase of the laser energy, and the second reason is that the increase in laser energy causes small grains to combine and hence welding process occurs, producing large grains, so roughness of the surface as well as the diameter of the grain will increases [19].

3- Optical properties measurements

1. Absorption coefficient

The absorption coefficient was calculated from Eq. (3) [20].

$$\alpha = \frac{2.303A}{t} \qquad (3)$$

where t is the thickness of sample and A is the absorption.

Fig.7 shows the variation of absorption coefficient (α) with wavelength in the range of (280-1000) nm at thickness of sample (t=200 nm) prepared at RT. It was observed that the absorption coefficient (α) increases as the laser energy of the (CdO: CoO) films increases and has high value of the absorption coefficient (α) are larger than 10^4 cm^{-1} which leads to increasing the probability of occurrence direct transition between valence band and conduction band. The absorption coefficient increases rapidly at wavelength less than cut off wavelength. The reason for the increase of the absorption coefficient with wavelength is to generate donor levels (i.e. localized states) within the forbidden energy gap and conduction band [21].

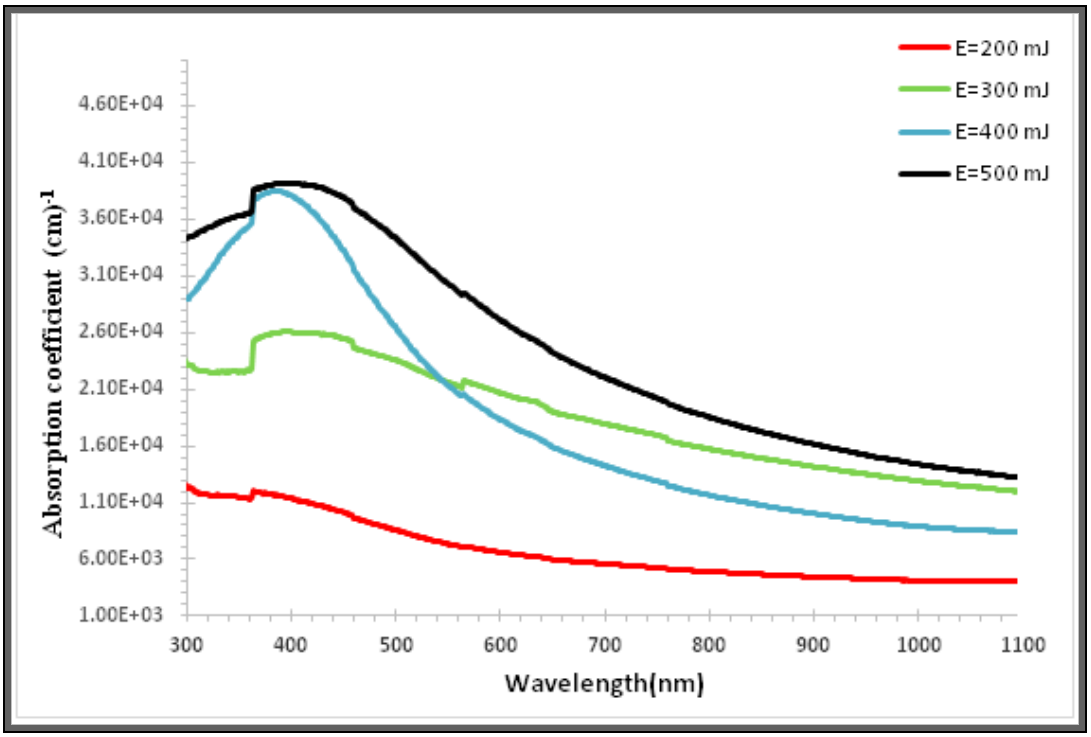

Fig.7: The variation of the absorption coefficient with wavelength of CdO:CoO films with different laser energy.

2. Calculation of the optical energy gap (Eg)

The optical energy gap of allowed direct electronic transitions for CdO:CoO thin films were calculated using Tauc equation (Eq. 2) [22] as the value of r = 1/2 by drawing between $(\alpha h\upsilon)^2$ and $(h\upsilon)$ the energy of the falling photon and by extending the straight line of the curve to intercept the photon energy axis at the point $(\alpha h\upsilon)^2=0$. The optical energy gap for the allowable direct transport of CdO:CoO films is shown in Fig.8. It is observed that the value of the energy gap decreases as the laser energy increases, resulting in the formation of localized levels near the conduction band, and so the absorption of photons is greater as the laser energy increases. (the values are shown in the Table 3). These results are found to in agreement with those of the Zheng (2011) [23].

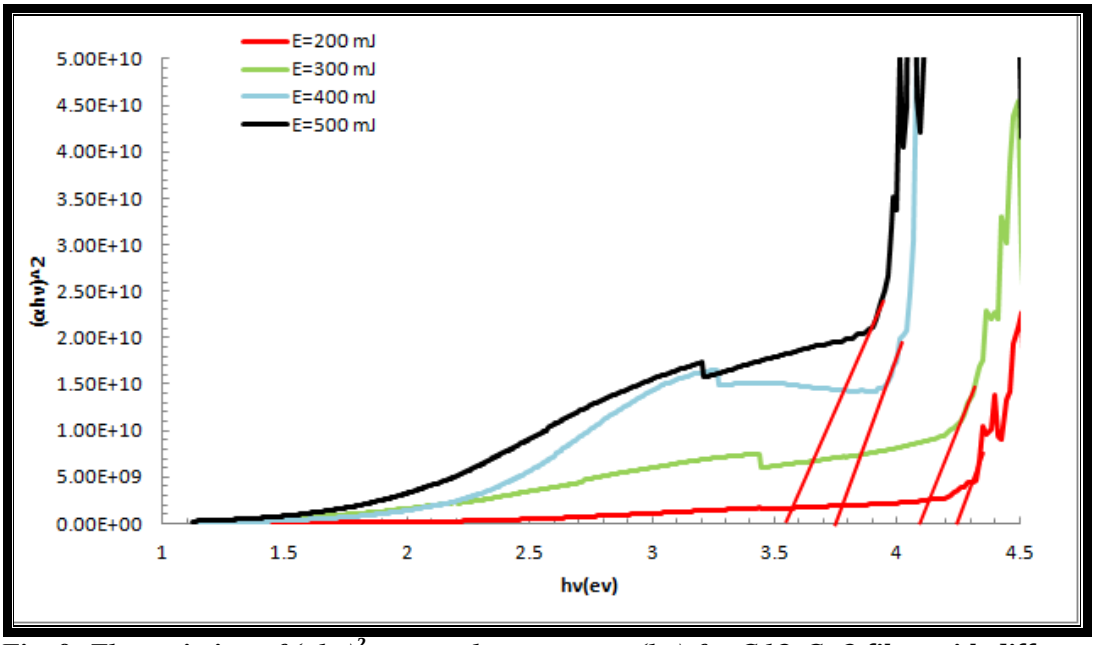

Fig. 8: The variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for CdO:CoO films with different laser energy.

Table 3: The energy gap values for CdO:CoO thin films.

Laser energy (mJ)	E_g(eV)
200	4.25
300	4.1
400	3.75
500	3.55

Conclusions

Thin films of CdO:CoO have been prepared on a glass substrate by pulsed laser deposition (PLD) technique. X-ray results showed that all thin films were polycrystalline and have a cubic structure with the dominance of direction (111). The results of AFM showed increase of the diameters average and the roughness average, in addition to the root mean square (RMS), with laser energy increase. As for the optical properties measurements, it was found that the absorption coefficient increases as the laser energy increases, whereas the energy gap, on the other hand, decreases with the laser energy increases.

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