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Effect of Fe-Doping on the Properties of CdO Thin Films Prepared by Pulsed Laser Deposition

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Abstract

Pure and iron-doped cadmium oxide ($(CdO)_{1-x}Fe_x$) thin films at different ratios were prepared using pulsed laser deposition technique. The X-ray diffraction showed a polycrystalline structure for all samples associated with cubic CdO structure. Another phase appeared at the highest ratio corresponding to the cubic Fe phase. Crystallinity was enhanced and crystalline size increased with increasing Fe ratio. AFM measurements showed that increase of Fe ratio led to an increase in the average particle diameter. In addition, the distribution of particle size became wide and of irregular behaviour, as well as increasing of the average roughness and the root-mean-square roughness. Increasing the Fe ratio caused the band gap to decrease from 2.3 eV to 2.1 eV. Hall effect measurements showed that the charge carrier concentration increased from 7.6 to 12.4 cm^{-3} with the increase of Fe ratio, while the mobility had the opposite behaviour, it decreased from 0.3 to 0.13 $cm^2/V.s$ as Fe content increased from 0 to 0.5 atom ratio.

Key words: Fe-doped CdO, Structural, Optical properties, PLD , Energy gap.

تأثير الحديد المطعم على خصائص الأغشية الرقيقة لأوكسيد الكادميوم المحضرة بطريقة الترسيب بالليزر النبضي

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الخلاصة

تم تحضير أغشية رقيقة من أكسيد الكادميوم النقي والمشوب بالحديد بنسب مختلفة ($(CdO)_{1-x}Fe_x$) باستخدام تقنية الترسيب بالليزر النبضي. أظهر فحص حيود الأشعة السينية بنية متعددة البلورات لجميع العينات ذو هيكل CdO المكعب. ظهر طور أخر خاصة عند أعلى نسبة تقابل طور الحديد المكعب. تم تعزيز التبلور وزيادة الحجم البلوري بزيادة نسبة الحديد. أظهرت قياسات مجهر القوى الجزيئية أن الزيادة في نسبة الحديد أدت إلى زيادة متوسط قطر الجسيمات ، بالإضافة إلى أن توزيع حجم الجسيمات أصبح عريضًا وغير منتظم، بالإضافة إلى زيادة متوسط الخشونة والجذر التربيعي لمتوسط مربع الخشونة. أدت زيادة نسبة الحديد إلى تقليل فجوة النطاق من 2.3 فولت إلى 2.1 الكترون–فولت. أظهر قياس تأثير هول أن تركيز حاملات الشحنة يزداد مع زيادة نسبة الحديد من 7.6 إلى 12.4 cm^{-3}، بينما كان للتحركية سلوك معاكس ، حيث انخفض من 0.3 إلى 0.13 $cm^2/V.s$ عندما ازداد محتوى الحديد من 0 إلى 0.5 نسبة ذرية.

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1. Introduction

Cadmium Oxide (CdO) is n-type semiconductor due to oxygen vacancies [1]. It can be used as a transparent conductive oxide (TCO) due to its high conductivity at appropriate deposition conditions [2].It can be used in solar cells and other optoelectronic devices [3].

There is a variety of CdO thin-films, which are prepared by various techniques and can be classified as vapor phase and liquid phase techniques. Vapor phase techniques involves thermal evaporation [4], sputtering [5], pulsed laser deposition [6], etc. While, solution phase techniques includes chemical bath deposition [7], SILAR method, spray pyrolysis [8], sol-gel [9], etc. These techniques were used to prepare pure and doped-CdO thin film.

There are a great effort about the fundamental properties of nano- structures semiconductor in the last few decades [10]. The most effect of nano size is the quantum confinement effect which has two major effect. The first is the band gap of semiconductor material increases with decreasing size and the second consequence is that discrete energy levels arise within the band gap at the edges of conduction and valence bands [11].

The properties of the CdO thin films have been improved by doping with different dopants such as Sn, In, Ti, and Al. CdO thin films properties, such as energy gap surface morphology, charge carrier concentration and mobility, are highly dependent on the dopant type and its concentration [12] [13][14]

In this work, the effect of mixing ratio of CdO target with Fe, at different atomic ratios, on the structural, surface morphology, optical properties, and Hall effect parameters for the prepared thin films prepared by pulsed laser deposition techinique on glass substrates was studied.

2. Experimental Details

Pure CdO powder was mixed with different molar ratios (x= 0.1, 0.3 and 0.5) of iron powder by ball mill for 15 min. The targets were prepared by pressing 2 g of the prepared mixed powder samples as a pellet of 1.5 cm diameter into a stainless steel mould using a hydraulic piston under pressure of 6 tons for 10 minutes. Thin films were deposited on glass substrates which were previously cleaned with water and detergent then with distilled water in an ultrasonic unit for 15 minutes followed by pure alcohol and finally dried with an air blower. The deposition inside a vacuumed glass chamber using Nd-Yag pulsed laser (DIAMOND-288) of 1064 nm wavelength, 10 ns pulse duration and 300 mJ pulse energy. The structural properties of thin films were examined using XRD system (Shimadzu XRD 6000) within the range of (2θ =20-70 degree) with a speed of 5.00 (degree /min). Atomic force microscope (AFM) (type AA3000 Scanning Probe Angstrom Advance Inc.) was used to examine the thin films surface morphology. Hall Effect measurements were performed using instrument type (Ecopia HMS-3000). The thickness of thin films was measured wuth a reflectance probe (SR300 Angstrom Sun Technologies).

3. Results and discussions

Fig. 1 shows the X-ray diffraction patterns of cadmium oxide thin films deposited on glass substrate by 300 mJ pulsed laser and annealed at 573^{o} K. It is observed that all films have polycrystalline structure of peaks located at diffraction angles of 2θ= 33.0354^{0}, 38.3426^{0}, 55.3197^{0}, 65.9032^{0}, and 69.4413^{0} associated with (110), (200), (220), (311), and (222), respectively. The position of the peaks changed with increasing Fe content due to the variation of lattice strain caused by lattice defects. The peaks intensities increased with increasing Fe ratio indicating an enhancement of the crystallinity, where Fe atoms act as crystalline catalysis [15]. The peaks width (FWHM) decreased with increasing Fe ratio indicating an increase of crystalline size. These results are found to be in a good agreement with the results of Zn dopant [8]. At the highest ratio of Fe doping, additional peaks appeared at 44.6741^{0} for (110), and another peak at 65.9652^{0} for (200), corresponding to the cubic Fe

phase. Table 1 shows the XRD diffraction peaks details compared with the standard inter-atomic planer distances (d_{hkl}) from International Journal of diffraction data, and the corresponding Miller indices and crystalline size. The d_{hkl} values were calculated using Bragg's law, while the crystalline size was calculated using Scherrer's formula [16].

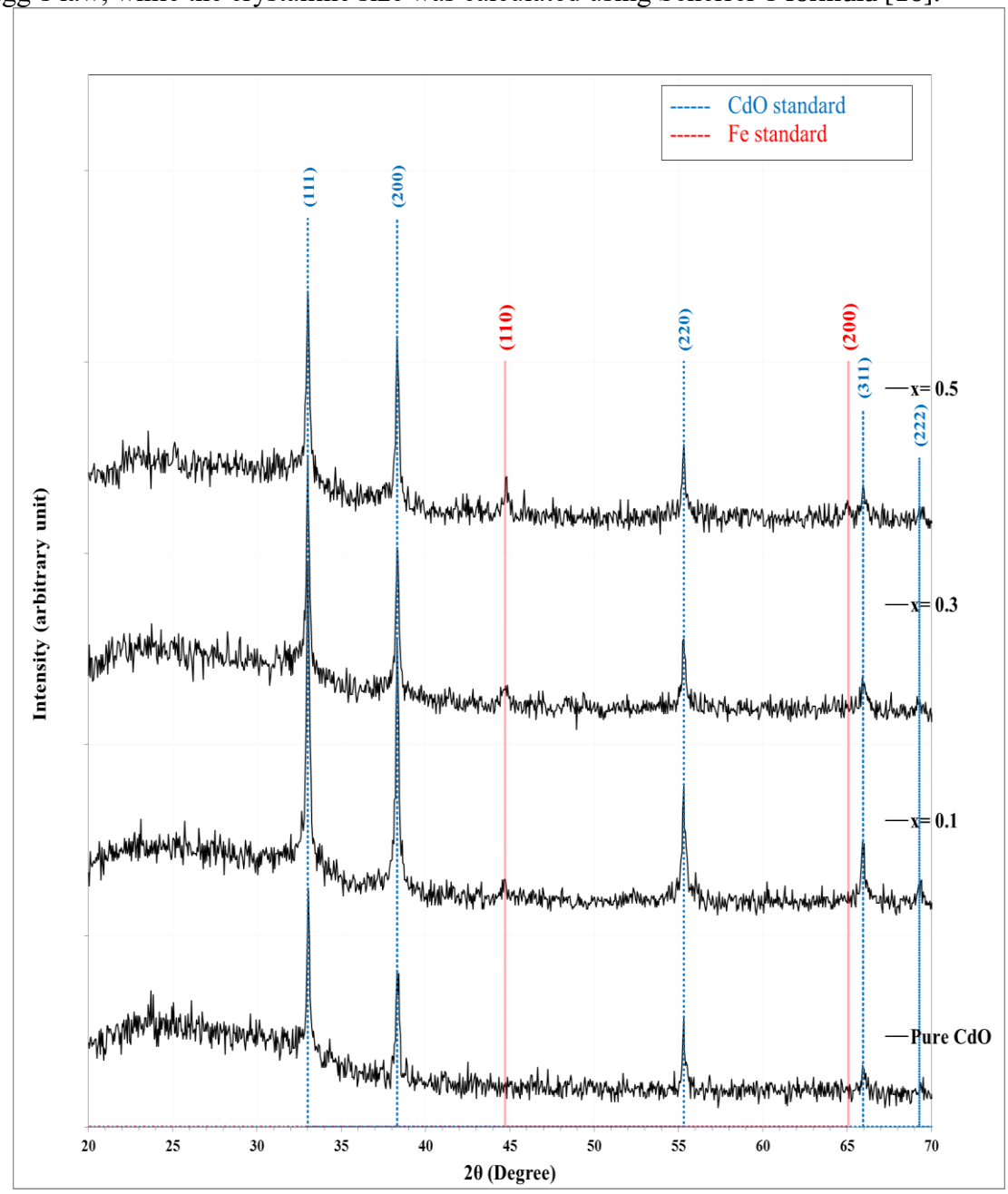

Figure 1- X-ray diffraction patterns of pure and Fe-doped CdO thin films at different doping ratios prepared by 300 mJ pulsed laser.

Table 1-Structural parameters pure and Fe-doped CdO thin film at different doping ratios

Fe ratio	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	C.S (nm)	d_{hkl} Std.(Å)	Phase	hkl	card No.
Pure CdO	33.0354	0.2670	2.7094	31.0	2.7108	Cub. CdO	(111)	96-900-8610
	38.3426	0.3103	2.3457	27.1	2.3477	Cub. CdO	(200)	96-900-8610
	55.3197	0.3414	1.6593	26.3	1.6600	Cub. CdO	(220)	96-900-8610
	65.9032	0.4035	1.4162	23.5	1.4157	Cub. CdO	(311)	96-900-8610
	69.4413	0.3414	1.3524	28.3	1.3554	Cub. CdO	(222)	96-900-8610
0.1	33.0043	0.2483	2.7118	33.4	2.7108	Cub. CdO	(111)	96-900-8610
	38.3116	0.2483	2.3475	33.9	2.3477	Cub. CdO	(200)	96-900-8610
	44.6741	0.3725	2.0268	23.1	2.0253	Cub. Fe	(110)	96-900-8537
	55.2886	0.3104	1.6602	28.9	1.6600	Cub. CdO	(220)	96-900-8610
	65.9652	0.2793	1.4150	33.9	1.4157	Cub. CdO	(311)	96-900-8610
	69.3482	0.3725	1.3540	25.9	1.3554	Cub. CdO	(222)	96-900-8610
0.3	33.0043	0.1961	2.7118	42.3	2.7108	Cub. CdO	(111)	96-900-8610
	38.3426	0.2483	2.3457	33.9	2.3477	Cub. CdO	(200)	96-900-8610
	44.6431	0.4966	2.0282	17.3	2.0253	Cub. Fe	(110)	96-900-8537
	55.3197	0.2483	1.6593	36.1	1.6600	Cub. CdO	(220)	96-900-8610
	65.9342	0.4345	1.4156	21.8	1.4157	Cub. CdO	(311)	96-900-8610
	69.2241	0.4035	1.3561	23.9	1.3554	Cub. CdO	(222)	96-900-8610
0.5	33.0043	0.1883	2.7118	44.0	2.7108	Cub. CdO	(111)	96-900-8610
	38.3116	0.2483	2.3475	33.9	2.3477	Cub. CdO	(200)	96-900-8610
	44.7672	0.2793	2.0228	30.8	2.0253	Cub. Fe	(110)	96-900-8537
	55.3197	0.1862	1.6593	48.2	1.6600	Cub. CdO	(220)	96-900-8610
	65.0031	0.4035	1.4336	23.3	1.4157	Cub. CdO	(311)	96-900-8610
	65.9652	0.4345	1.4150	21.8	1.4321	Cub. Fe	(200)	96-900-8537
	69.3482	0.4035	1.3540	23.9	1.3554	Cub. CdO	(222)	96-900-8610

The relationship between the crystalline size along the preferred orientation of (111) with the doping ratio is shown in Figure 2. It is clear that the crystalline size increased with the increase of the doping ratio but with different ratios till reaching nearly constancy at the high ratio.

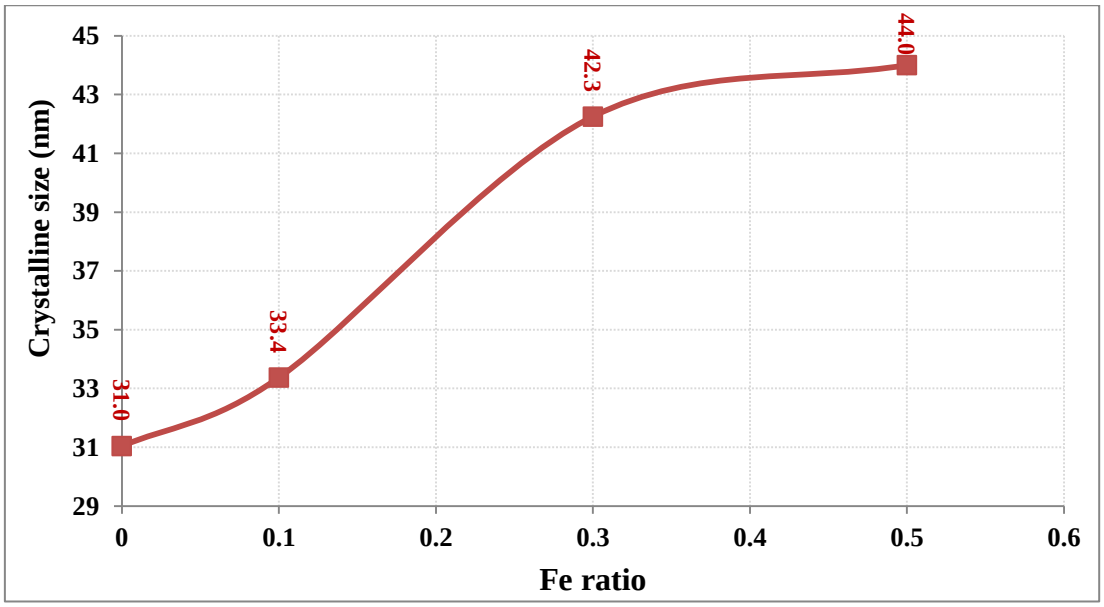

Figure 2- Variation of crystalline size for the preferred orientation with different Fe ratios

Figure-3 shows three-dimensional images of atomic force microscopy and their granularity cumulating distribution for pure and Fe doped CdO thin films. The increase in the Fe content led to an increase in the average diameter of the particles, in addition, the particle size distribution became wide and of irregular behavior meaning that the particles became varied in size from small to large. Table 2 shows that the average particle size increases from 51.19 nm, in the pure sample, to 70.58 nm with increasing Fe ratio up to 50%.In addition, there was an increase in the average roughness and the root mean square roughness of the surface with the increase of the Fe doping ratio.

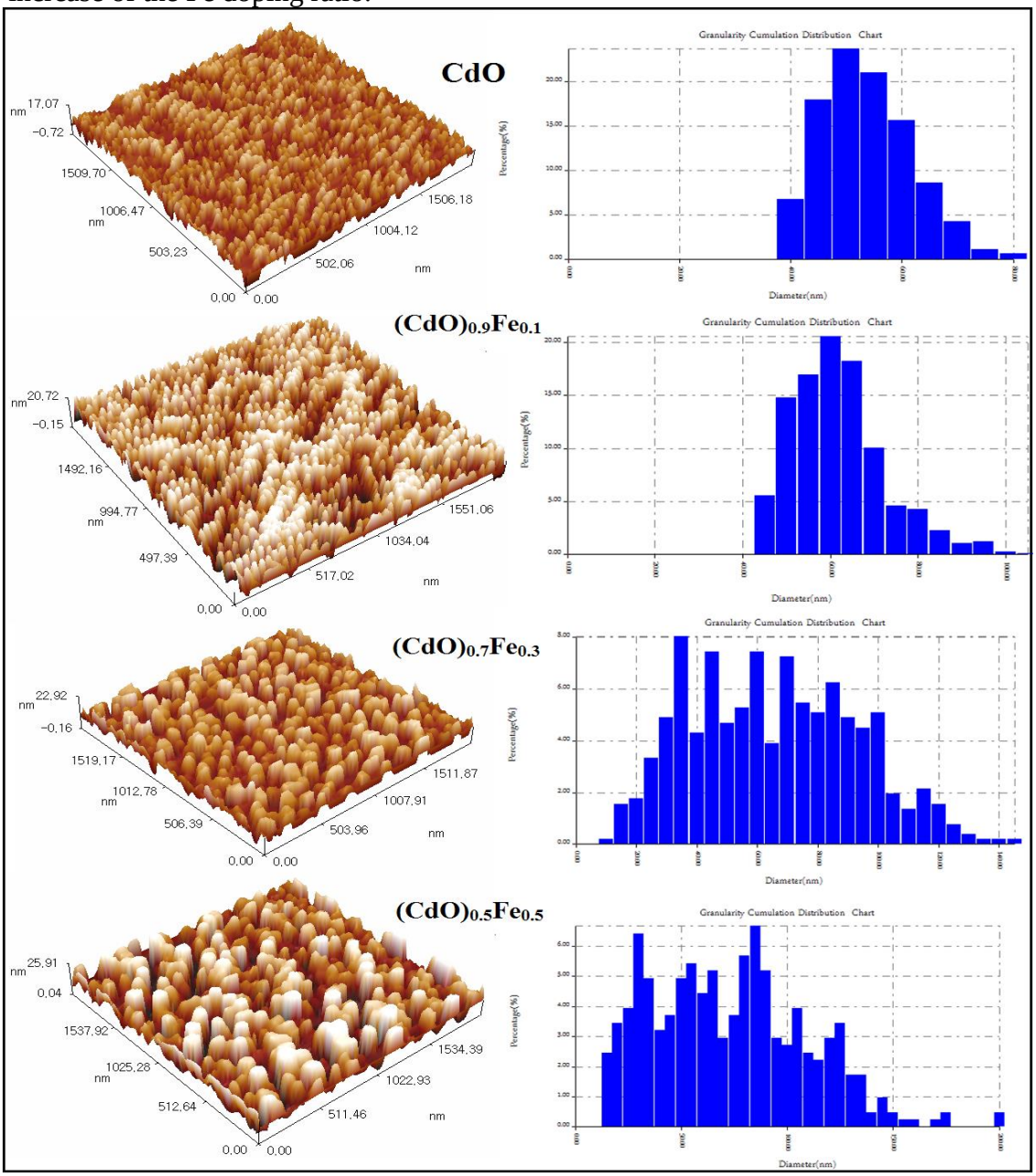

Figure 3-AFM images for pure and Fe-doped CdO thin films at different doping ratios prepared by 300 mJ pulsed laser.

Table 2-AFM parameters (Average Diameter, RMS roughness and Average roughness) for pure and doped CdO thin films prepared using 300 mJ laser energy

Sample	Average Diameter (nm)	RMS roughness (nm)	Ave. roughness (nm)
Pure CdO	51.19	2.11	2.45
$(CdO)_{0.9}Fe_{0.1}$	59.37	3.8	4.37
$(CdO)_{0.7}Fe_{0.3}$	63.04	4.66	5.49
$(CdO)_{0.5}Fe_{0.5}$	70.58	6.47	7.47

The UV-Visible near IR spectroscopy was used to study the effect the dopant ratio of Fe on the optical properties of CdO thin film prepared by pulsed laser deposition which was carried out in the wavelength range 300–1100 nm. Fig. 4 shows the absorbance curves for pure and Fe-doped CdO thin films prepared using 300 mJ laser energies. In general, the absorbance decreases with increasing the wavelength of gradient absorption edge for all prepared samples, due to the defect states near the absorption edge [17]. On the other hand, absorbance increased with increasing the Fe ratio.

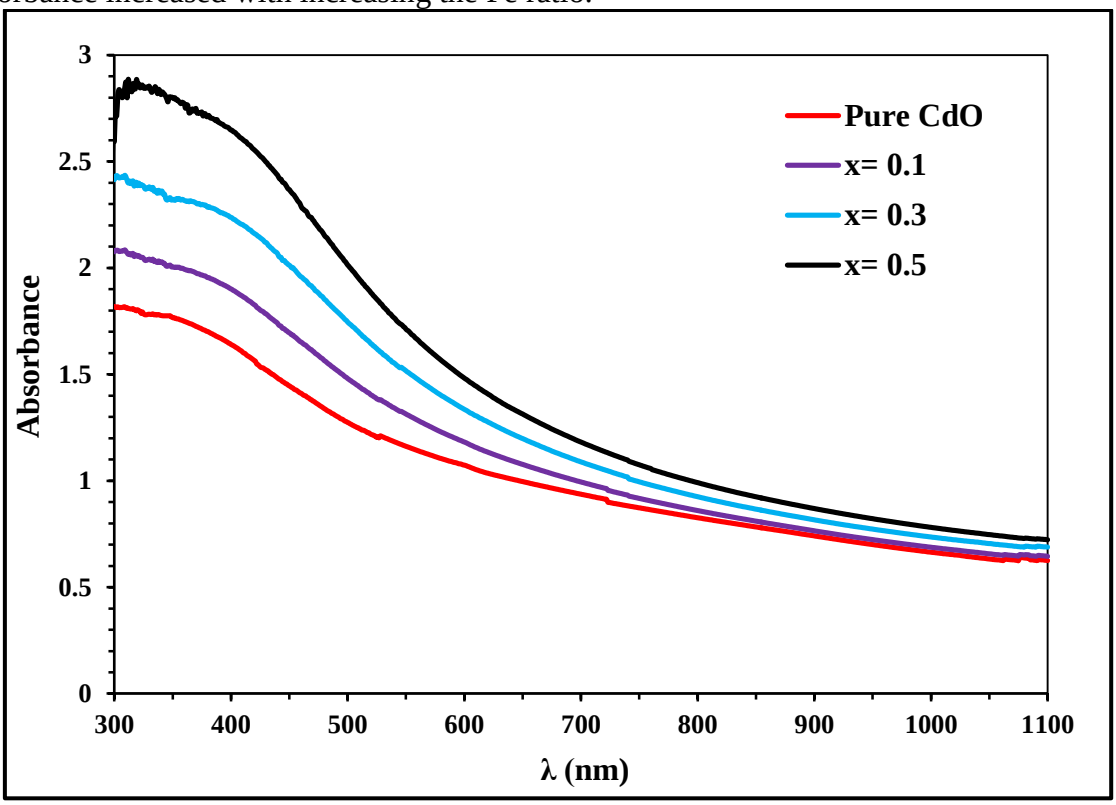

Figure 4-Variation of absorption with wavelength for Fe- doped CdO thin films at different ratios

The optical energy gap for pure and Fe-doped CdO thin films deposited by 300 mJ laser energy on glass slides were determined using Tauc relation [15]. The relations of $(\alpha h\upsilon)^2$ against photon energy ($h\upsilon$) and the optimum linear curves part are shown in Fig. 5. The interception of the tangent line of the linear part with the $h\upsilon$-axis represents the energy gap. Increasing the Fe ratio from 0 to 0.5 caused the reduction of the band gap from 2.3 eV to 2.1 eV due to the increase of the particle size. The properties of nano-size particles are affected by the quantum confinement which causes the increase of the energy gap [18].

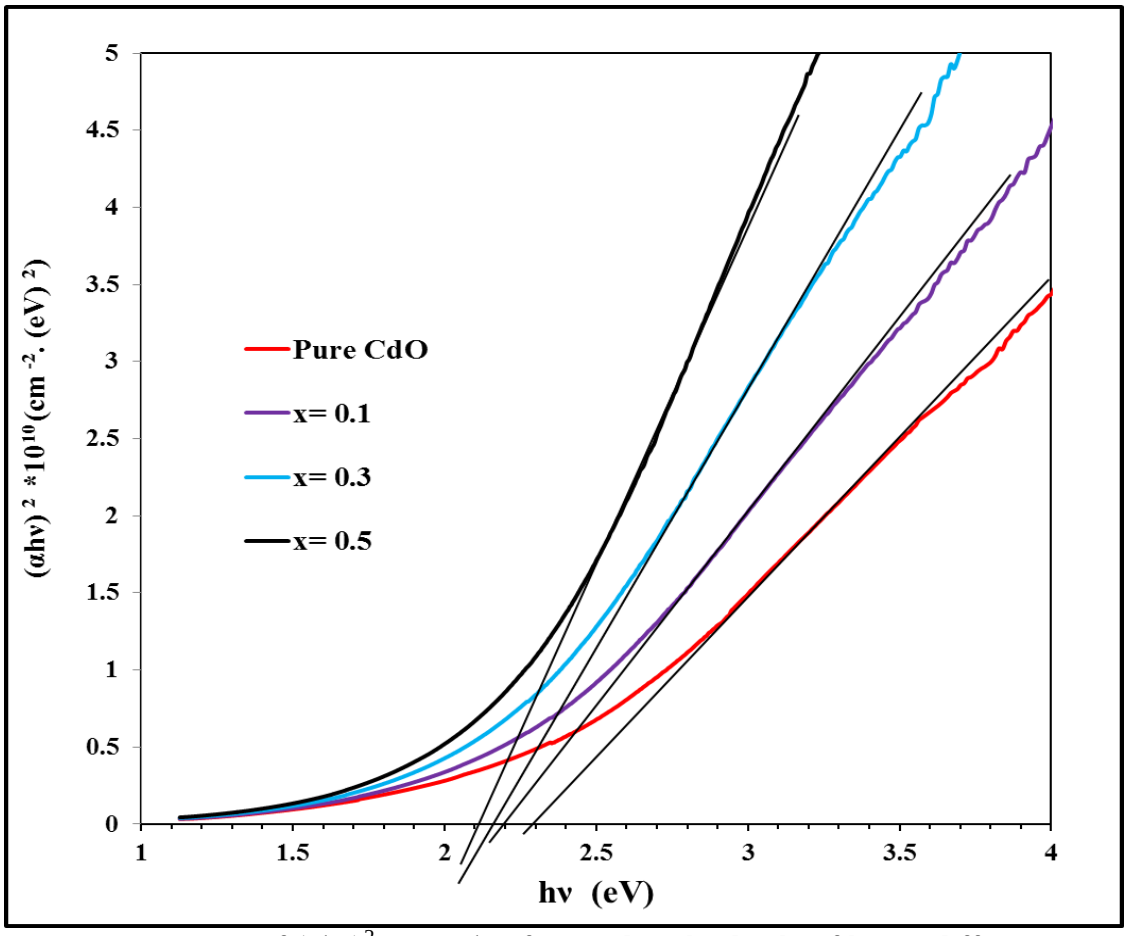

Figure 5-Variation of $(\alpha h\upsilon)^2$ versus $h\upsilon$ for Fe- doped CdO thin films at different ratios.

Hall effect measurements provide numerous data concerning semiconducting type, charge carrier density, and mobility. According to this measurements, all films were n-type. Using of Hall coefficient and sample conductivity, the charge carrier (n_H) and mobility (μ_H) were calculated. Fig. 6 shows the variation of charge carrier concentration (N_H) and mobility (μ) with Fe ratio. It is noted that N_H increases with increasing the Fe ratio from 0 to 0.3 and it was nearly stable at 0.5 doping ratio. Increasing the carriers concentration due to substitution doping which occupy lattice sites of Cd atoms resulted in extra free carrier within the lattice [19], while the mobility μ_H has opposite behavior due to scattering at ionized defects as the doping level is increased, causing the reduction of mobility [20].

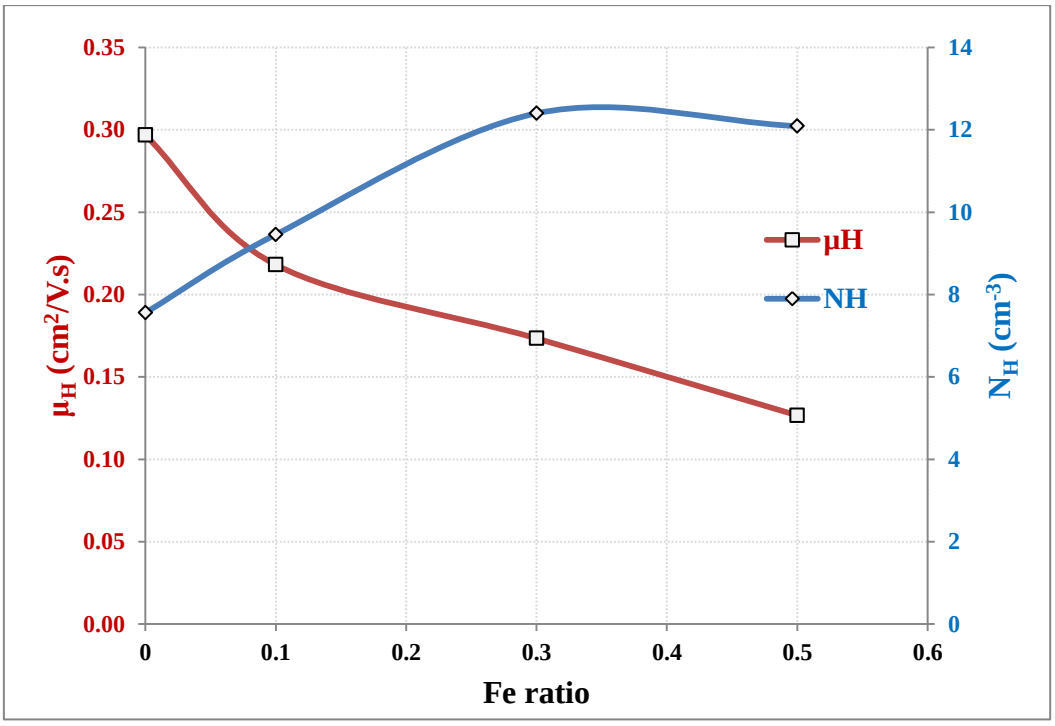

Figure 6-Variation of charge carrier concentration (N_H) and mobility (μ) with Fe ratio.

Conclusions

Pure and Fe–doped CdO thin films at different ratios were prepared by one-step pulsed laser deposition from pellet of mixed powder at the desired ratios. The X-ray diffraction shows high crystallinity structure matched with the cubic CdO and minor phase of cubic Fe. The crystallinity was enhanced with increasing Fe ratio. AFM measurements showed that the increase in the Fe ratio led to irregularity in particle distribution, increase of average diameter and roughness. Also, further increase of Fe caused reduction of the bandgap, increase of the charge carrier concentration and reduction of mobility. Where the bandgap varies from 2.3 to 2.1 eV, the charge carrier concentration increased from 7.6 to 12.4 cm^{-3}, and the mobility decreased from 0.3 to 0.13 $cm^2/V.s$ with increasing the Fe content from 0 to 0.5 atom ratio.The fundamental changes in the physical properties of the prepared films by changing the proportion of iron metal in the target components indicates the possibility of controlling the final properties of the product.

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