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Effect of Zinc (Zn) -Doped on the Structural, Optical and Electrical Properties of $(Cdo)_{1-X}zn_x$ Films Prepared by Pulsed Laser Deposition Technique

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Abstract

Pure cadmium oxide films (CdO) and doped with zinc were prepared at different atomic ratios using a pulsed laser deposition technique using an ND-YAG laser from the targets of the pressed powder capsules. X-ray diffraction measurements showed a cubic-shaped of CdO structure. Another phase appeared, especially in high percentages of zinc, corresponding to the hexagonal structure of zinc. The degree of crystallinity, as well as the crystal size, increased with the increase of the zinc ratio for the used targets. The atomic force microscopy measurements showed that increasing the dopant percentage leads to an increase in the size of the nanoparticles, the particle size distribution was irregular and wide, in addition, to increase the surface roughness of the nanoparticles. An increase in the zinc ratio also led to a decrease in the energy gap. While the Hall effect measuring showed an increase in the concentration of charge carriers and a decrease in their mobility with increasing the doping ratio.

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Zn, CdO, Structural, Optical properties, *PLD*

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1. Introduction

Cadmium oxide (CdO) thin films are an important semiconductor for many applications [1]. One of the most important of these applications is its use as a transparent conductive oxide (TCO) due to its high transmittance to visible light in addition to its good electrical conductivity, which can be improved by changing the conditions of deposition or by mixing it with other materials [2], which can be used in many photo-electric devices [3]. There are many studies concerned with changing the properties of pure and doped cadmium oxide thin films using different deposition techniques such as thermal evaporation in vacuum [4], plasma atomization [5], pulsed laser deposition [6], spray pyrolysis [7], etc. Due to the fundamental change in the properties of nanomaterials, which depend on the shape and size of the nanoparticles, due to the increase of the effective surface area relative to the inner material, or due to the effect of quantum confinement, many researchers have been interested in studying cadmium oxide in different nanoscale shapes and with different sizes [8]. In many researches, the properties of cadmium oxide thin films have been improved by using different impurities, such as metal impurities include Sn, In and Ti etc., by using different deposition methods such as pulsed laser deposition (PLD). The properties of CdO thin films, such as electrical and optical, depend on the type and concentration of impurities used [9].

In this work, the effect of mixing ratio of cadmium oxide capsules with zinc for use in Nd:YHG laser, with different molar ratios, on the structural properties, topographic of the surface, optical properties, and electrical properties of the prepared thin films, were studied.

2. Experimental work

Pure cadmium oxide and mixed with zinc nanoparticles powders at different ratios of 0.1, 0.3 and 0.5 atomic ratio were mixed by ball mill for 20 min. The pure and mixed powders were formed into targets by pressed as pellets of 1.5 cm diameter into a mould using a hydraulic piston under 5 tons press for 10 minutes. Thin films for the different samples were prepared on glass slides inside a vacuumed chamber using Nd-YAG pulsed laser (DIAMOND-288) of fundamental wavelength, which 9 ns pulse duration and 400 mJ pulse energy. The prepared thin films were characterized by X-ray diffraction (Shimadzu XRD 6000), Atomic force microscope (AA3000 Scanning Probe Angstrom Advance Inc.), Hall Effect measurement were performed using instrument type (Ecopia HMS-3000). The thickness of thin films was measured using the reflectance probe (SR300 Angstrom Sun Technologies).

3. Results and discussions

Figure 1 shows the XRD for CdO thin films prepared by PLD technique and different Zn/Cd atm ratios. It was noticed that all film has polycrystalline structure of cubic CdO phase, of peaks positioned at deviation angles (2θ) around 33^0, 38^0, 55^0, 66^0, and 69^o corresponding to (110), (200), (220), (311), and (222) planes, respectively.

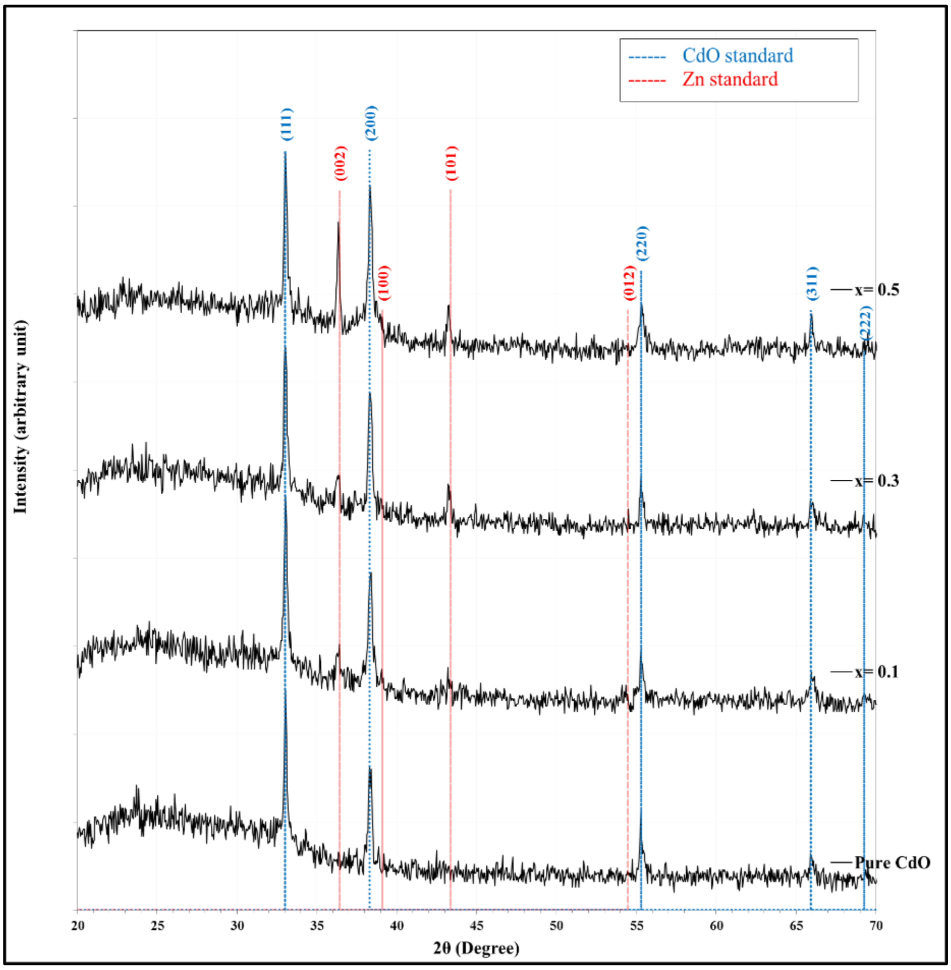

Figure 1: X-ray diffraction patterns of pure and Zn-doped CdO thin films at different ratios prepared by 400 mJ pulsed laser.

Another phase, of peaks around 36^0 and 43^0 corresponding to (002) and (101) planes for Zn hexagonal phase, respectively. The peaks width (FWHM) decreases with increasing Zn ratio indicate on increasing crystalline size. These results agree with

Usharani and Balu [7]. Table 1 displays the details of diffraction peaks contains the inter-planer distances (d_{hkl}) calculated by Bragg's equation [10], compared with the standard values, the corresponding Miller indices and crystalline size (C.S) calculated using Scherer's formula [11].

Table 1: Structural parameters pure and $(CdO)_{1-x}Zn_x$ thin film at different ratios.

Zn ratio	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	C.S(nm)	d_{hkl} Std.(Å)	Phase	hkl
Pure CdO	33.0354	0.2670	2.7094	31.0	2.7108	Cub. CdO	(111)
	38.3426	0.3103	2.3457	27.1	2.3477	Cub. CdO	(200)
	55.3197	0.3414	1.6593	26.3	1.6600	Cub. CdO	(220)
	65.9032	0.4035	1.4162	23.5	1.4157	Cub. CdO	(311)
	69.4413	0.3414	1.3524	28.3	1.3554	Cub. CdO	(222)
0.1	33.0482	0.2550	2.7083	32.5	2.7108	Cub. CdO	(111)
	36.3377	0.3290	2.4703	25.4	2.4663	Hex. Zn	(002)
	38.3845	0.2924	2.3432	28.8	2.3477	Cub. CdO	(200)
	43.2456	0.5117	2.0904	16.7	2.0856	Hex. Zn	(101)
	55.3070	0.4021	1.6597	22.3	1.6600	Cub. CdO	(220)
	66.0161	0.6579	1.4140	14.4	1.4157	Cub. CdO	(311)
	69.4152	0.6579	1.3529	14.7	1.3554	Cub. CdO	(222)
0.3	33.0482	0.2193	2.7083	37.8	2.7108	Cub. CdO	(111)
	36.3377	0.3289	2.4703	25.4	2.4663	Hex. Zn	(002)
	38.3480	0.2924	2.3453	28.8	2.3477	Cub. CdO	(200)
	43.2456	0.3290	2.0904	26.0	2.0856	Hex. Zn	(101)
	55.3070	0.4021	1.6597	22.3	1.6600	Cub. CdO	(220)
	66.0161	0.4386	1.4140	21.6	1.4157	Cub. CdO	(311)
	69.2325	0.4020	1.3560	24.0	1.3554	Cub. CdO	(222)
0.5	33.0482	0.2058	2.7083	40.3	2.7108	Cub. CdO	(111)
	36.3743	0.1828	2.4679	45.7	2.4663	Hex. Zn	(002)
	38.3480	0.2559	2.3453	32.9	2.3477	Cub. CdO	(200)
	43.2456	0.2924	2.0904	29.2	2.0856	Hex. Zn	(101)
	55.3436	0.4752	1.6587	18.9	1.6600	Cub. CdO	(220)
	66.0161	0.2558	1.4140	37.0	1.4157	Cub. CdO	(311)
	69.3421	0.4021	1.3541	24.0	1.3554	Cub. CdO	(222)

Fig. 2 shows the variation of crystalline sizes along the preferred orientation along (111) of 2θ around 33^o with the Zn molar ratio. It appears that the crystalline size increased with the Zn ratio with different values.

Figure 3 shows the atomic force microscopy images and their particle diameter distribution for CdO thin films mixed with different molar ratios of Zn. It is clear that increasing the Zn ratio cause to increase in the average diameter at the surface. It was also founded that the distribution of particle size becomes asymmetrical, irregular and wider, indicating that the particles size turns out to be varied in size. Table 2 shows that the average diameter of surface particles increases from 51.19 to 68.38 nm with increasing the Zn ratio from 0 to 50%, as well as an increase in the average roughness from 2.11 to 5.16 nm with the increase of the Zn ratio.

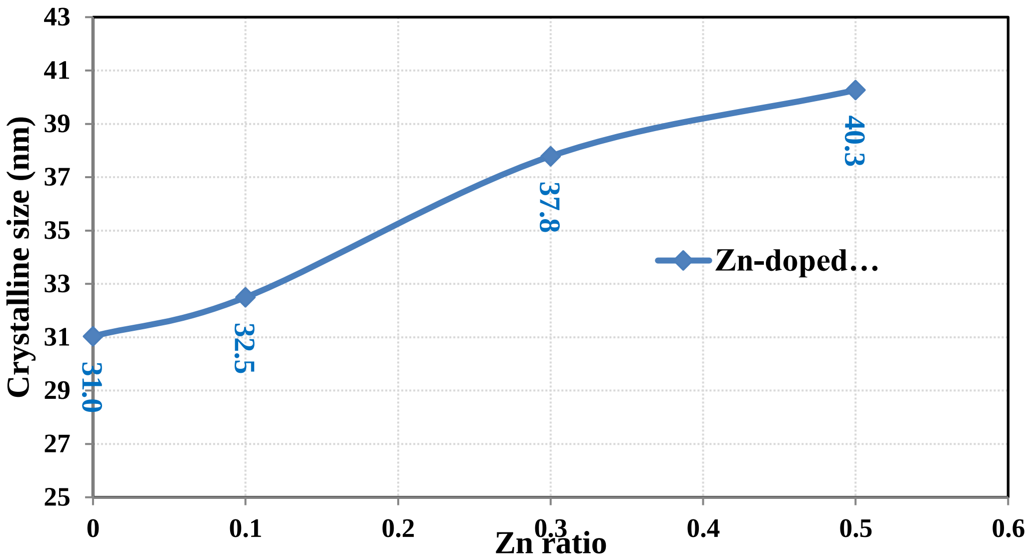

Figure 2: Variation of crystalline size for the preferred orientation with Zn ratio for (111) direction.

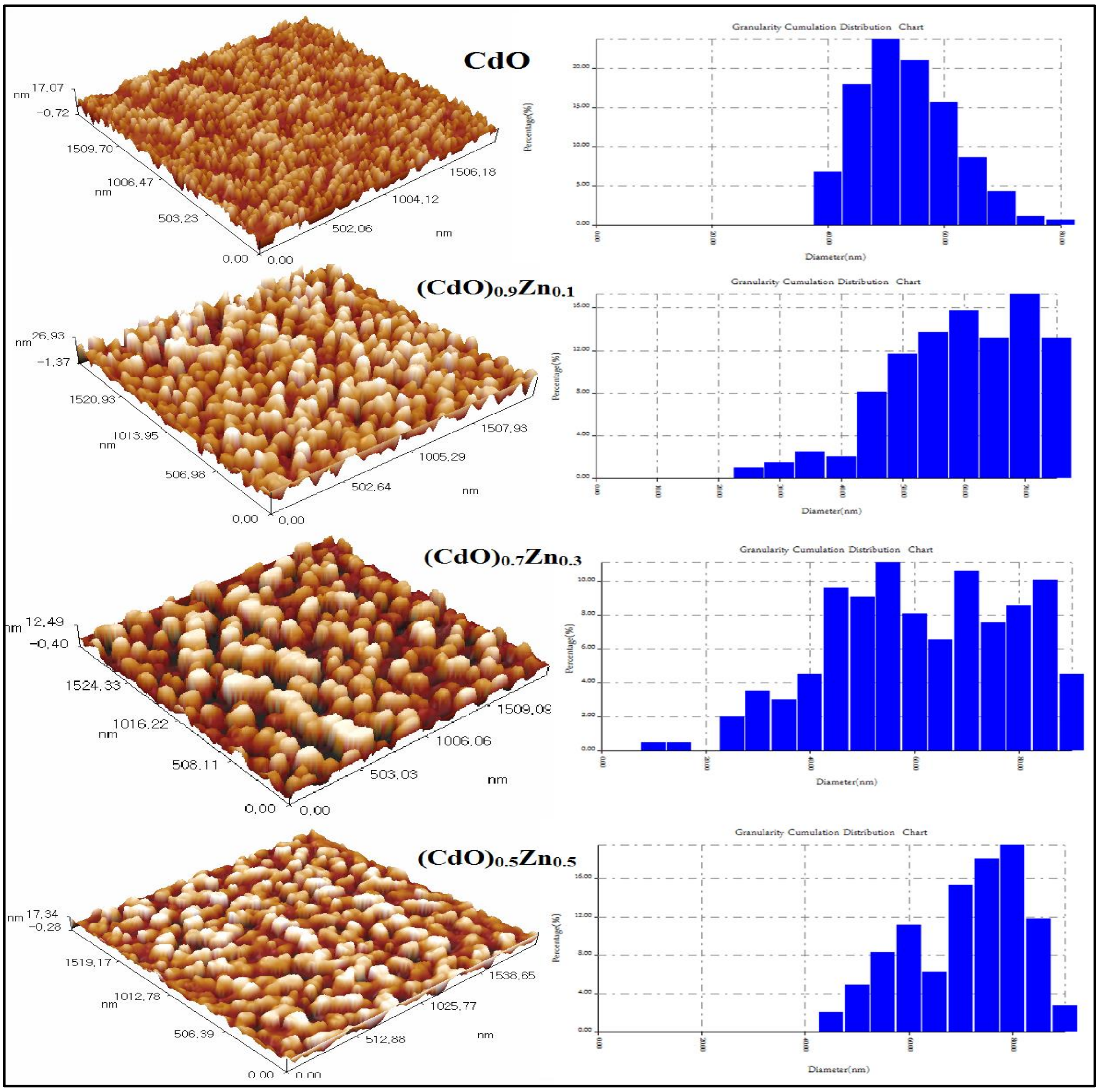

Figure 3: AFM images and their granularity accumulation distribution for pure and pure and $(CdO)_{1-x}Zn_x$ composite thin films at different ratios.

Table 2: AFM parameters for pure and $(CdO)_{1-x}Zn_x$ thin films.

Sample	Average Diameter (nm)	RMS roughness (nm)	Ave. roughness (nm)
Pure CdO	51.19	2.11	2.45
$(CdO)_{0.9}Zn_{0.1}$	56.95	3.20	3.68
$(CdO)_{0.7}Zn_{0.3}$	58.93	3.84	4.53
$(CdO)_{0.5}Zn_{0.5}$	68.38	5.16	6.21

The effect of the Zn ratio addition to the started material on the optical properties of Zn-doped CdO thin film, prepared by PLD, were examined by the UV-Visible absorbance spectroscopy. Fig. 4 shows the absorbance curves for CdO and CdO:Zn thin films prepared PLD. In general, the absorbance gradient decreases with wavelength due to the defect states near the absorption edge [12]. It was also found that the absorbance increased with decreases with the Zn ratio which act as photon traps [13].

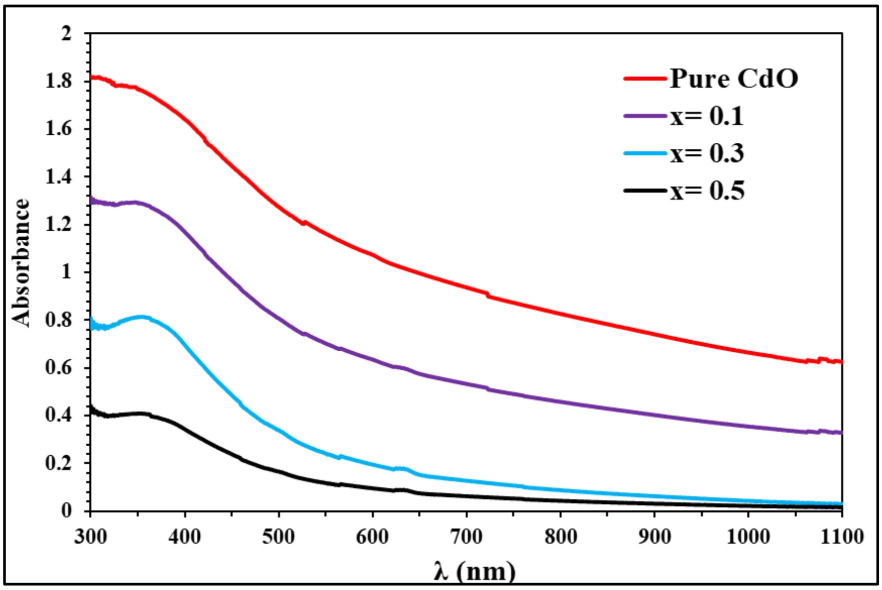

Figure 4: Variation of absorption with wavelength for $(CdO)_{1-x}Zn_x$ thin films at different ratios.

The optical energy gap for pure CdO and CdO:Zn thin films prepared by PLD on glass were determined by the *Tauc* equation [14]. The relation between $(\alpha h\upsilon)^2$ against photon energy ($h\upsilon$) were shown in Fig. 5. The interception of the tangent line with the x-axis denotes the optical energy gap (E_g^{opt}). Increasing the Zn molar ratio to 50% cause to increase the E_g^{opt} from 2.3 eV to 2.6 eV. This result agree with Yahia et al., [15]. Increase the energy gap with doping may be attributed to the Moss-Burstein effect [16]. The Moss-Burstein effect is the phenomenon in which an apparent increase in the band gap of a semiconductor due to the pushing of the absorption edge to higher energies as a result of some states close to the conduction band being filled. This effect occurs when the electron carrier concentration exceeds the density of the states, to degenerate doping. The electrons can only be excited in the conduction band above the Fermi level since all states below it is occupied. So, apparent band gap = actual band gap + Moss-Burstein displacement [17].

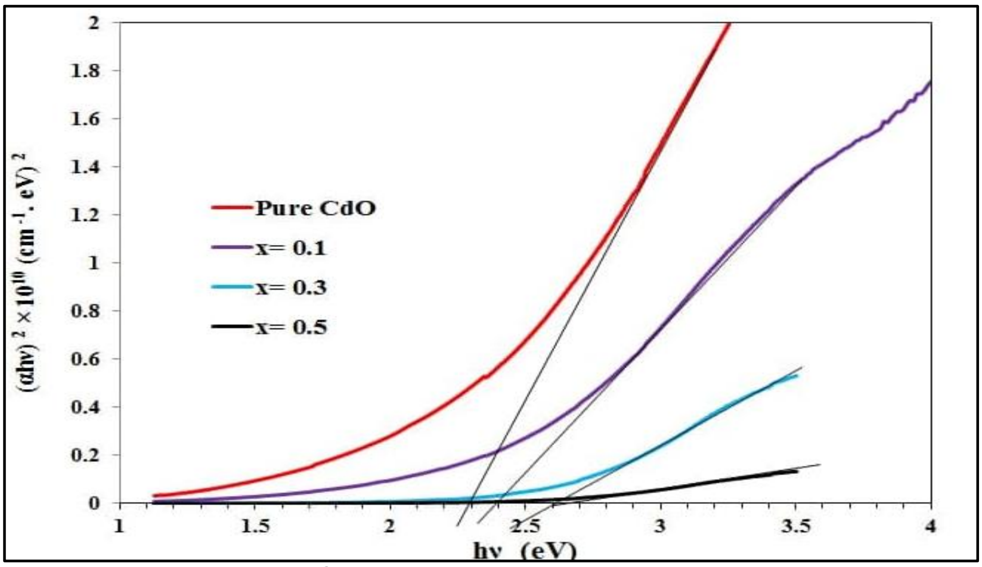

Figure 5: Variation of $(\alpha h\upsilon)^2$ versus hυ for $(CdO)_{1-x}Zn_x$ thin films at different ratios.

The study of the Hall effect of thin films gives a clear picture about of the nature of the semiconductor conduction, as it shows the type of the majority carriers of charge, their density, and their mobility. The Hall effect measurement showed that all of the prepared films were n-type. The charge carrier (N_H) and mobility (μ_H) variation with the Zn ratio were shown in Fig. 6. N_H was shown to increase with increasing zinc content from 0 to 0.3. The reason for the increasing concentration of charge carriers is due to the addition of charge carriers arising from substitutional defects within the lattice [18]. More increment in Zn ratio to 0.5 cause to reduce the concentration. Whereas the mobility decreases with the Zn ratio due to scattering arising from local impurities [19].

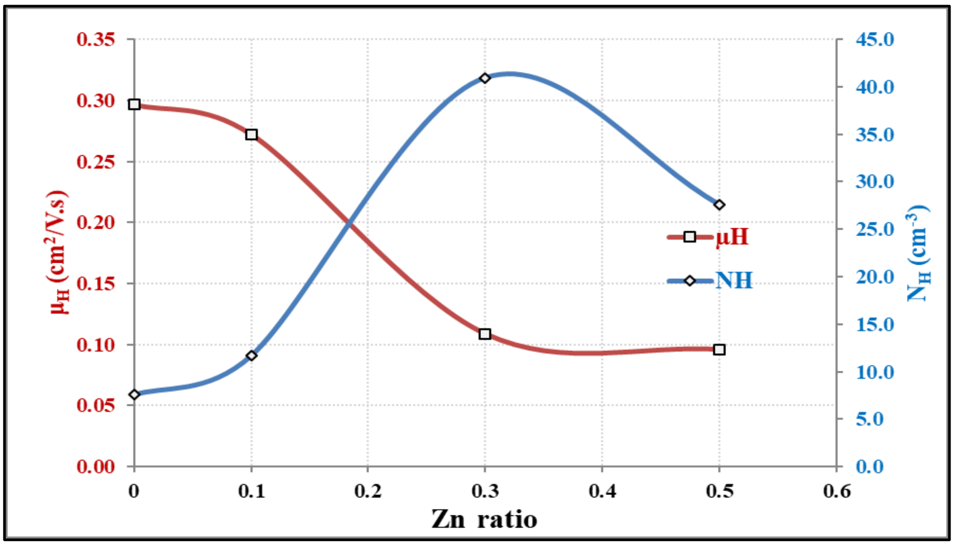

Figure 6: Variation of charge carrier concentration (N_H) and mobility (μ) with Zn ratio.

4. Conclusions

Pure CdO and CdO: Zn composite thin films at different ratios were prepared by the PLD technique from pellets of the mixed powder at different molar ratios. The X-ray diffraction illustrates polycrystalline structures corresponding to cubic CdO, and an additional Zn phase appeared for doped samples.

The crystallite size increase with increasing Zn ratio. AFM measurements show increasing average diameter and be as irregular in distribution of size and increase roughness with increasing the Zn ratio. In addition, adding Zn cause to reduce the band-gap and change both the charge carrier concentration mobility. These differences in the physical properties of the prepared thin films by altering the amount of zinc metal, in the started target, show the feasibility of simply controlling the properties of the prepared thin films.

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Conflict of interest

Authors declare that they have no conflict of interest.

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تأثير التشويب بالزنك على الخصائص التركيبية و البصرية والكهربائية لأغشية $(CdO)_{1-x}Zn_x$ المحضرة بتقنية الترسيب بالليزر النبضي

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الخلاصة

تم تحضير أغشية أكسيد الكادميوم النقي (CdO) والمشوب بالزنك بنسب ذرية مختلفة باستخدام تقنية الترسيب بالليزر النبضي باستخدام ليزر ND-YAG من أهداف عينات المسحوق المضغوط. أظهرت قياسات حيود الأشعة السينية شكلاً مكعّبًا لهيكل CdO. ظهرت مرحلة أخرى ، خاصة في النسب العالية من الزنك ، المقابلة للبنية السداسية للزنك. زادت درجة التبلور وكذلك حجم البلورة مع زيادة نسبة الزنك للأهداف المستخدمة .أظهرت القياسات المجهري للقوة الذرية أن زيادة نسبة التثبيط تؤدي إلى زيادة حجم الجسيمات النانوية ، وكان توزيع حجم الجسيمات غير منتظم وواسع ، بالإضافة إلى زيادة خشونة سطح الجسيمات النانوية. أدت زيادة نسبة الزنك أيضًا إلى انخفاض فجوة الطاقة. بينما أظهر قياس تأثير هول زيادة في تركيز ناقلات الشحنة وانخفاض في حركتها مع زيادة نسبة التشويب.