

## NANOCRYSTALLINE Ce-DOPED CdO THIN FILMS SYNTHESIS BY SPRAY PYROLYSIS METHOD FOR SOLAR CELLS APPLICATIONS

A. S. MOHAMMED<sup>a</sup>, D. K. KAFI<sup>a</sup>, A. RAMIZY<sup>b\*</sup>, O. O. ABDULHADI<sup>a</sup>,  
S. F. HASAN<sup>a</sup>

<sup>a</sup>Ministry of Education, Direction of Education in AL-Anbar

<sup>b</sup>Department of Physics, College of Science, University of Anbar, Anbar, Iraq

In this study, CdO:Ce thin films were prepared by spray pyrolysis technique on glass substrates for (3, 5 and 7%) doping concentrations of cerium with 100nm of thickness. The prepared films were characterized using X-ray diffraction (XRD), atomic force microscope (AFM), and transmittance measurements. XRD analysis exhibited a cubic crystalline structure with multi directions of pure CdO structure, and the monocline structure of Ce. The crystalline size dropped with the increasing of Ce concentration (64.4 – 44.78) nm, also the strain increased (0.034 – 0.048) rad of pure CdO and CdO:Ce7% films, respectively. The optical band gap energy ( $E_g$ ) be found at (3.96, 3.98, 4.0 and 4.02) eV for the prepared CdO: Ce films with (0, 3, 5 and 7) Vol.% of concentration.

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### 1. Introduction

Transparent metal oxide materials as cadmium oxide (CdO) are semiconductors operating in the visible electromagnetic spectrum with high electrical conductivity and optical transparency [1,2], CdO is one of the n-type semiconductor which closely of metallic conductivity [3]. Bulk CdO has a direct energy band gap ( $E_g$ ) of ~2.3 eV, crystal structure (FCC)[4] with a lattice constant of  $a = 4.6483 \text{ \AA}$  [5]. Now, CdO enters widely applications as windows for solar cells, photo devices ,flat panel display, [6] and gas sensors[3]. The physical properties (electrical, structural and optical) of CdO films depend on the synthesis conditions[6,7]. Many methods were used to prepare the CdO such as sputtering [8], chemical vapor deposition (CVD)[9], spray pyrolysis [10], thermal evaporation[11], sol-gel[12], and electrochemical[13]. The spray pyrolysis technique has some advantages as quite simple, cheap; [14]. The aim of this study is to utilized a spray pyrolysis method to prepare CdO thin films and estimated the effect of Ce doping on the, structural and optical properties.

### 2. Experimental setup

CdO thin films have been deposited by spray of a solution of 0.1 M cadmium acetate in 1:1 volume ratio of deionized water (DW) and methanol on (25 × 25)mm of glass substrates at 250°C. The cerium nitrate with 0.1 M in DW (3, 5, and 7) Vol.% was mixed with the cadmium acetate solution were used to prepare the CdO:Ce thin films. The optimized sedimentation parameters such as "spray time (10s), spray interval (30s), spray nozzle- substrate distance (35 cm), were kept constant. The pressure of the carrier gas was 4.4 MPa. For each concentration, several sets of films were prepared and their structural, optical qualities were found to be highly reproducible and stable". The crystalline structures and the surface morphologies of the prepared films were tested by utilized XRD and AFM. Optical transmittance and the absorption spectrum in the wavelength of 200–1100 nm for the samples were measured with a UV–Vis spectrophotometer.

\*Corresponding author: [asmat\\_hadithi@uoanbar.edu.iq](mailto:asmat_hadithi@uoanbar.edu.iq)

### 3. Result and discussion

#### 3.1. Structural properties

The Fig. 1 showed the CdO:Ce thin films with different Ce-doping concentrations (3, 5, and 7) vol.% XRD analysis for range between (20°-60°) in 2theta. According to (ASTM) card [15], the structure of CdO<sub>2</sub> films showed a polycrystalline. The preferential growth was along (210) direction, and the other peaks associated with (111), (200) and (220) directions.

The cerium doping with (3, 5, and 7) vol.% concentrations inhibited the growth of CdO crystals, that is may be due to of the high difference in the electronegativity values of both Cd and Ce, which leads to the predominance of the Ce growth on the CdO growth.

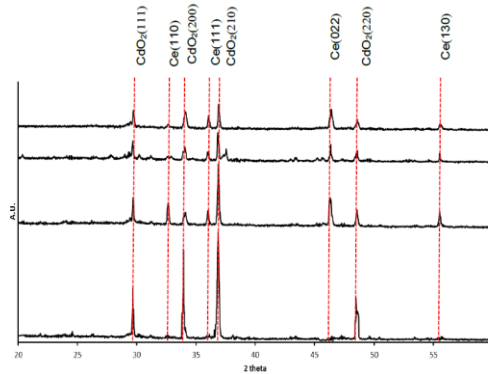


Fig.1. the XRD pattern of the CdO:Ce thin films.

The crystallite size (D) of the prepared thin films was calculated using the Scherrer's equation[16].

$$D = \frac{0.9 \lambda}{\beta \cos \theta} \quad (1)$$

where  $\beta$  is the full width at half maximum (FWHM) of a diffraction peak in radians,  $\lambda$  is the wavelength and  $\theta$  is the Bragg's angle. The average crystallite size decreased linearly with the increasing of the concentration of Ce found to between 44.78 nm and 64.4 nm as shown in Fig. 2 and Table 1.

The developed in the strain of CdO crystals was calculated using the equation[17]:

$$\xi = \frac{\beta \cos \theta}{4} \quad (2)$$

The strain of CdO crystal increased with Ce:3% and Ce:5%, while it dropped by with Ce:7% compared with the pure CdO films as shown in Fig. 2 and Table 1.

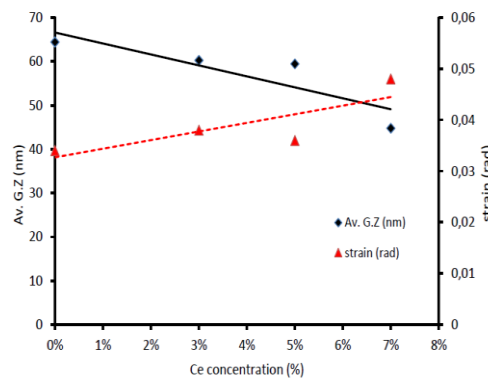


Fig. 2. the grain size as a function of the concentration of Ce.

Table.1. the variation in the crystallite size and strain as a function of concentration of Ce.

Ce concentration (%)	Av. G.Z (nm)	strain (rad)
0	64.4	0.034
3	60.23	0.038
5	59.45	0.036
7	44.78	0.048

### 3.2. Morphological characterizations

Atomic force microscopy (AFM) technique has been utilized to study the surface morphologies of the CdO and Ce doped CdO thin films which are shown in Fig. 2.

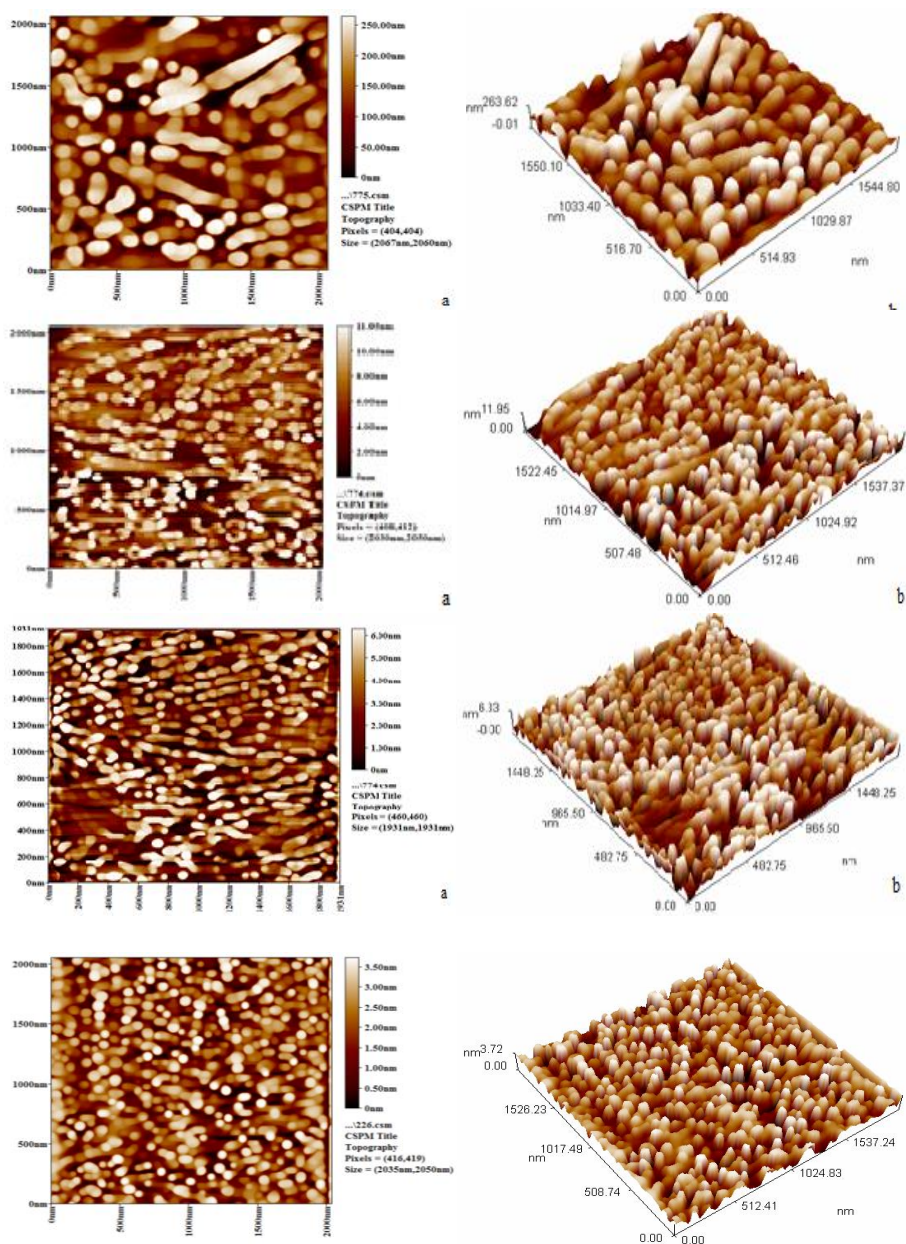


Fig. 3. The atomic force microscope 2-D and 3-D Image of prepared films.

The cerium doped films show a smooth surface compared to the CdO thin films. The grain size, roughness and Root mean square of the pure film is measured to be (109.88, 3.11 and 2.65) nm, respectively. Further, all the average size, the root mean square and the roughness of the prepared films decrease with the increasing of the doping concentration of Cerium are shown Table 2, respectively.

Table 1. The Average sizes and roughness average for pure and doped CdO films.

Doping ratio(vol.%)	Average Grain sizes from AFM (nm)	Root mean square (nm)	Roughness Average (nm)
( Pure)	109.88	3.11	2.65
3	83.03	1.8	1.58
5	73.75	1.06	0.871
7	73.52	0.915	0.778

### 3.3. Optical properties

Fig. 4 illustrated the spectrum of transmittance in the range of (200–1100 nm). The result showed that adding Ce to CdO film effect on the transmittance for all the prepared samples. However, most value of the transmittance in the visible spectral region. At 550 nm wavelength, the transmittance values be found at ( 61, 66, 73 and 71)% of pure CdO films and the doped CdO films by (3, 5, and 7) vol.% respectively.

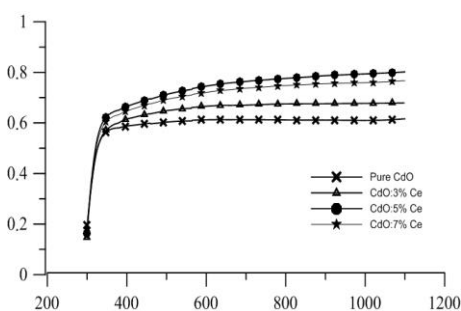


Fig. 4. Transmittances spectra of pure CdO and doped with different Ce (0,3,5,7)%.

The ability of a material to absorb light is measured by its absorption coefficient. The relation between absorption coefficient( $\alpha$ ) and wavelength ( $\lambda$ ) as shown in Fig. 5. The calculated values of absorption coefficient for all prepared films were found to be ( $\alpha > 104 / \text{cm}$ ) for visible spectra, it has been shown that absorbance decreases with increasing Ce-doping concentration in (3 and 5) vol.%.

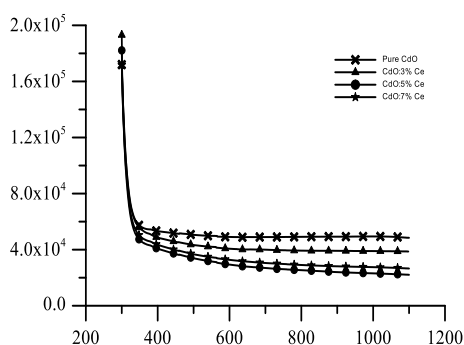


Fig. 5. Variation of absorption coefficient as a function of wavelength.

The optical energy gap of the pure and doped films was estimated from the relation[18]:

$$\alpha hv = (hv - E_g)^{1/2} \quad (3)$$

The equation has been used to find the values and types of the band gap energy of the prepared films, which had an allowed direct band gap energy. The pure CdO films showed a energy gap of 3.96 eV. The band gap value increases with increasing Ce-doping concentration in (3 and 5) vol.%, while it dropped by 7 viol. % as shown in Fig. 6 and Table 2. The increasing in the band gap is due to the decreasing in the crystalline size, that can be understood by comparing the XRD pattern in Fig. 1, that agreement with Khallaf[19], and may be by the inhibition of the crystalline structure of CdO.

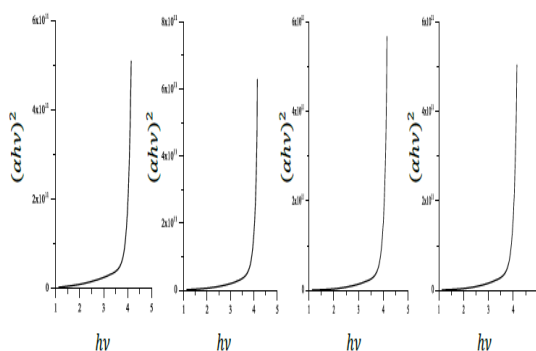


Fig. 6. Plot of  $(\alpha hv)^2$  versus  $hv$  for prepared CdO:(3, 5 and 5)vol.% Ce thin films.

Table. 2. The Average optical energy gap of pure CdO and doped films.

Doping ratio(vol.%)	Optical band energy (eV)
( Pure)	3.96
3	3.98
5	4.0
7	4.02

#### 4. Conclusions

The nanocrystalline CdO:Ce thin films were deposited on glass substrates by pyrolysis method with (3, 5 and 7) vol.%. The increasing of Ce concentration affected on both structural and optical characterization of the prepared films. The XRD patterns and AFM images showed a decreasing in the crystalline size with the increased concentration. The transmittance and the absorption coefficient also dropped with the increased concentration of Ce generally. The optical band gap energy  $E_g$  shifted to the mid-UV, that is expected to make it suitable for use in the UV detector devices.

#### References

- [1] Y. Hameş, S. E. San, Sol. Energy. **77**, 291 (2004).
- [2] B. RAY, II–VI Compounds, Elsevier.
- [3] F. P. Koffyberg, Solid State Commun. **9**, 2187 (1971).
- [4] K. Narayandass, D. Gurumurugan, J. Electron. Mater. **25**, 765 (1996).
- [5] F. A. Benko, F. P. Koffyberg, Solid State Commun. **57**, 901 (1986).

- [6] R. L. Mishra, A. K. Sharma, S. G. Prakash, *Dig. J. Nanomater. Biostructures*. **4**, 511 (2009).
- [7] K. Gurumurugan, D. Mangalaraj, S. K. K. Narayandass, *Thin Solid Films*. **251**, 7 (1994).
- [8] J. Santos-Cruz, G. Torres-Delgado, R. Castanedo-Perez, S. Jiménez-Sandoval, O. Jiménez-Sandoval, C. I. I. Zúñiga-Romero, J. Márquez Marín, O. Zelaya-Angel, *Thin Solid Films*. **493**, 83 (2005).
- [9] H. Khallaf, C. T. Chen, L. B. Chang, O. Lupan, A. Dutta, H. Heinrich, F. Haque, E. Del Barco, L. Chow, *Appl. Surf. Sci.* **258**, 6069 (2012).
- [10] C. H. Bhosale, A. V. Kambale, A. V. Kokate, K. Y. Rajpure, *Mater. Sci. Eng. B* **122**, 67 (2005).
- [11] A. Salehi, M. Gholizade, *Sensors Actuators B Chem.* **89**, 173 (2003).
- [12] L. Znaidi, G. J. A. A. Soler Illia, S. Benyahia, C. Sanchez, A. V. Kanaev, *Thin Solid Films*, 257 (2003).
- [13] O. Vigil, F. Cruz, A. Morales-Acevedo, G. Contreras-Puente, L. Vaillant, G. Santana, *Mater. Chem. Phys.* **68**, 249 (2001).
- [14] B. J. Zheng, J. S. Lian, L. Zhao, Q. Jiang, *Appl. Surf. Sci.* **256**, 2910 (2010).
- [15] ASTM data files 5-64 and 8-459, n.d.
- [16] I. M. Ibrahim, A. S. Mohammedb, A. Ramizy, *J. Ovonic Res.* **14**, 17 (2018).
- [17] A. S. Ibraheam, Y. Al-Douri, Abubaker S. Mohammed, Deo Prakash, U. Hashim, K. D. Verma, *Electrical, Int. J. Electrochem. Sci.* **10**, 9863 (2015).
- [18] Isam Ibrahim, Asmiet Ramziy, Abu Baker Sabbar Mohammed, *Rare Earth Doped NiO Nanostructure For H<sub>2</sub>S Sensor and Photodetector*, LAP LAMBERT Academic Publishing, 2018.
- [19] H. Khallaf, C.-T. Chen, L.-B. Chang, O. Lupan, A. Dutta, H. Heinrich, A. Shenouda, L. Chow, *Appl. Surf. Sci.* **257**, 9237 (2011).