



Investigation on the structural, optical and topographical behavior of Cadmium oxide polycrystalline thin films using electrochemical depositing method at different times

Ahmed N. Abd^{1,*}, Mohammed O. Dawood¹, Majid H. Hassoni², Ali A. Hussein³

¹Physics Department, Science Faculty, University of Al-Mustansiriyah, Baghdad, Iraq

²Physics Department, Education Faculty, University of Al-Mustansiriyah, Baghdad, Iraq

³Chemical Department, Faculty of Science, University of Al-Mustansiriyah, Baghdad, Iraq

*E-mail address: ahmed_naji_abd@yahoo.com

ABSTRACT

The optical and structure properties of Cadmium oxide (CdO) thin film prepared by electrochemical deposition method at different times (15, 30 and 60) min were investigated in this paper. Results of optical Transmission, absorption, reflection spectra, optical conductance, refractive index, extinction coefficient, real and imaginary dielectric constants studies are reported. The optical transmittance of the CdO thin film which formed at room temperature was 20% at wavelength ≈ 350 nm then increases to 60% at wavelength ≈ 1100 nm for thin film of CdO. The band-gap was also calculated from the equation relating absorption coefficient with the wavelength. The energy band gap changes from 2.3eV (Bulk CdO) to 2.45eV (CdO thin film). The plotted graphs show the optical characteristics of the film which varied with the wavelength and the photon energy. The optical conductance and band-gap indicated that the film is transmitting within the visible range. The dielectric constant and optical conductance of the film initially decreases slowly with increase in photon energy. The extinction coefficient and refractive index of the films also evaluated, which affected with the change in transmittance. The structure of synthesised CdO thin film was analyzed by X-ray diffraction XRD which revealed that the CdO thin film are polycrystalline and have several peaks of cubic face structure. The crystallite size, dislocation density, microstrain and number of dislocations of the thin film were calculated and listed.

Keywords: Cadmium oxide; thin film; optical characteristics of film; electrochemical depositing method

1. INTRODUCTION

Cadmium oxide (CdO) is transparent conducting oxides (TCOs) materials that possess both high electrical conductivity and high optical transparency (>80%) in the visible light region of the electromagnetic spectrum [1]. CdO is a n-type semiconductor with nearly metallic conductivity [2]. It has a direct energy band gap (E_g) of ~2.3 eV and two indirect transitions at lower energies [3].

It has extensive of applications as solar cells, windows, flat panel display, photo transistors etc. It was experimentally confirmed that structural, electrical and optical properties are very sensitive to the film structure and deposition conditions [4,5]. Such transparent conductors are being used comprehensive in thin film solar cells [6] and optoelectronic devices [7].

CdO films can be synthesized by many techniques such as sputtering [8], chemical vapor deposition (CVD) [9], spray pyrolysis [10], thermal evaporation [11] sol gel [12], and electrochemical [13]. The electrochemical deposition presents a simple, cost, and quick method for the synthesis of CdO nanostructure.

2. EXPERIMENTAL WORK

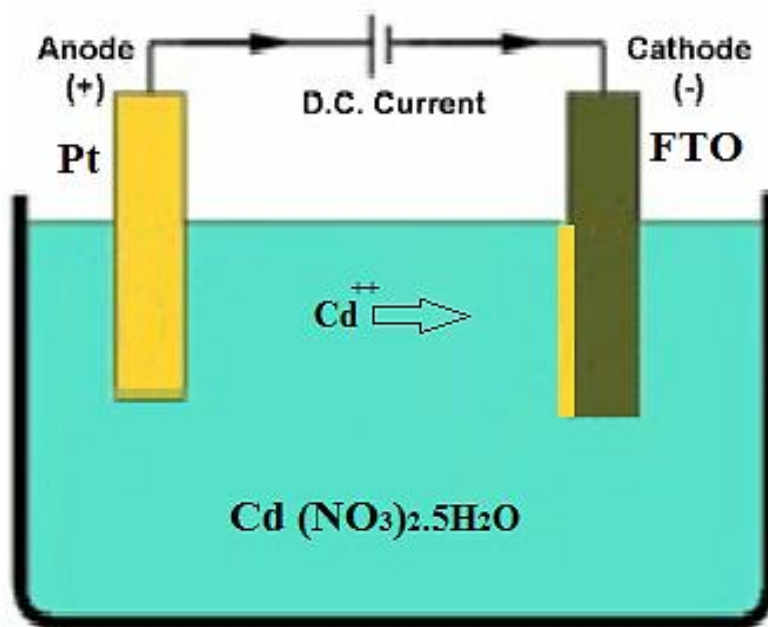


Fig. 1. Schematic diagram of electrochemical deposition system.

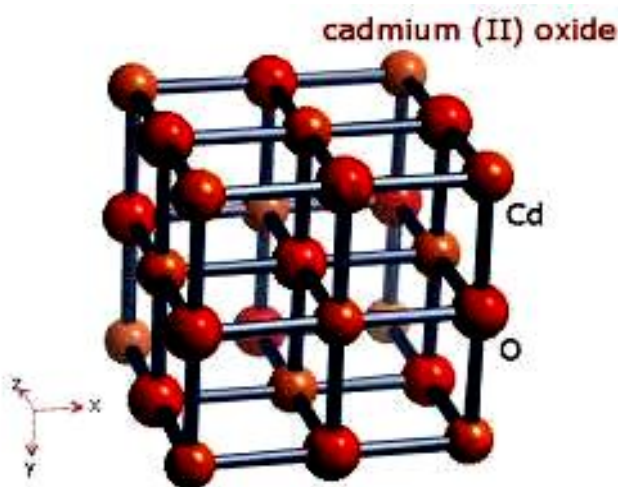
Teflon container homemade and cylindrical shape, length 9.5 cm, internal radius: 2.5 cm, external radius: 3.6 cm, distance between electrodes: 3 cm, Anode material: Pt foil, Cathode material: Fluorine Tin Oxide (FTO) glass. The deposition of the films was carried out in cell containing 1 mM $\text{Cd}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ with the a temperature ranging from 35 °C. The electrolyte pH used in this deposition was fixed at 7.5. Deposition of the films was carried out cathodically by using a power supply (Farnell type) with a standard two electrode system. FTO (TEC8) glasses of approximately 2 cm² area and resistance 8Ω/square from Dye Sol.

FTO is used here as transparent conductor. In all experimentally we fixed the voltage at -0.5 volt and the time deposition is 15 min. The electrolyte precursors $\text{Cd}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ was used in all n figure 1 deposition as shown i. After finally deposition the thin films annealing in air ambient at 300 °C to obtaining oxidation and best adhesion.

3. RESULTANTS AND DISSECTION

The XRD pattern for films deposited at Fluorine Tin Oxide (FTO) glass at different oxidation time (15,30 and 60) min showed that they are polycrystalline. The XRD patterns for CdO films are presented in Figure 2.

Several peaks of cubic face-centered CdO corresponding to (111), (200), (220), (311) and (222) planes with $a = 4.6953 \text{ \AA}$ can be seen in the figure and have been compared with standard X-ray diffraction data file (JCPDS file No. 75-0594) [15]. In the present investigation, the films exhibit a preferential orientation along the (200) diffraction plane which were grown CdO thin films on (FTO) glass substrate by the electrode deposition technique as 15 min, they show another peaks corresponding to (111) and (210) planes indicated to CdO_2 . Also, the XRD pattern for films deposited at 30 min indicatives for Fluorine Tin Oxide (FTO) glass at Fluorine Tin Oxide (FTO) glass and (200),(211),(210) and (311) planes for CdO_2 as shown in Figure 2. The XRD pattern for films deposited at 60 min showed all the peaks for Sn and SnO_2 and there is no trace of Cd oxide. The results shows that the 15 min oxidation time is the best (Scheme 1).



Scheme 1. Structure of cadmium(II) oxide.

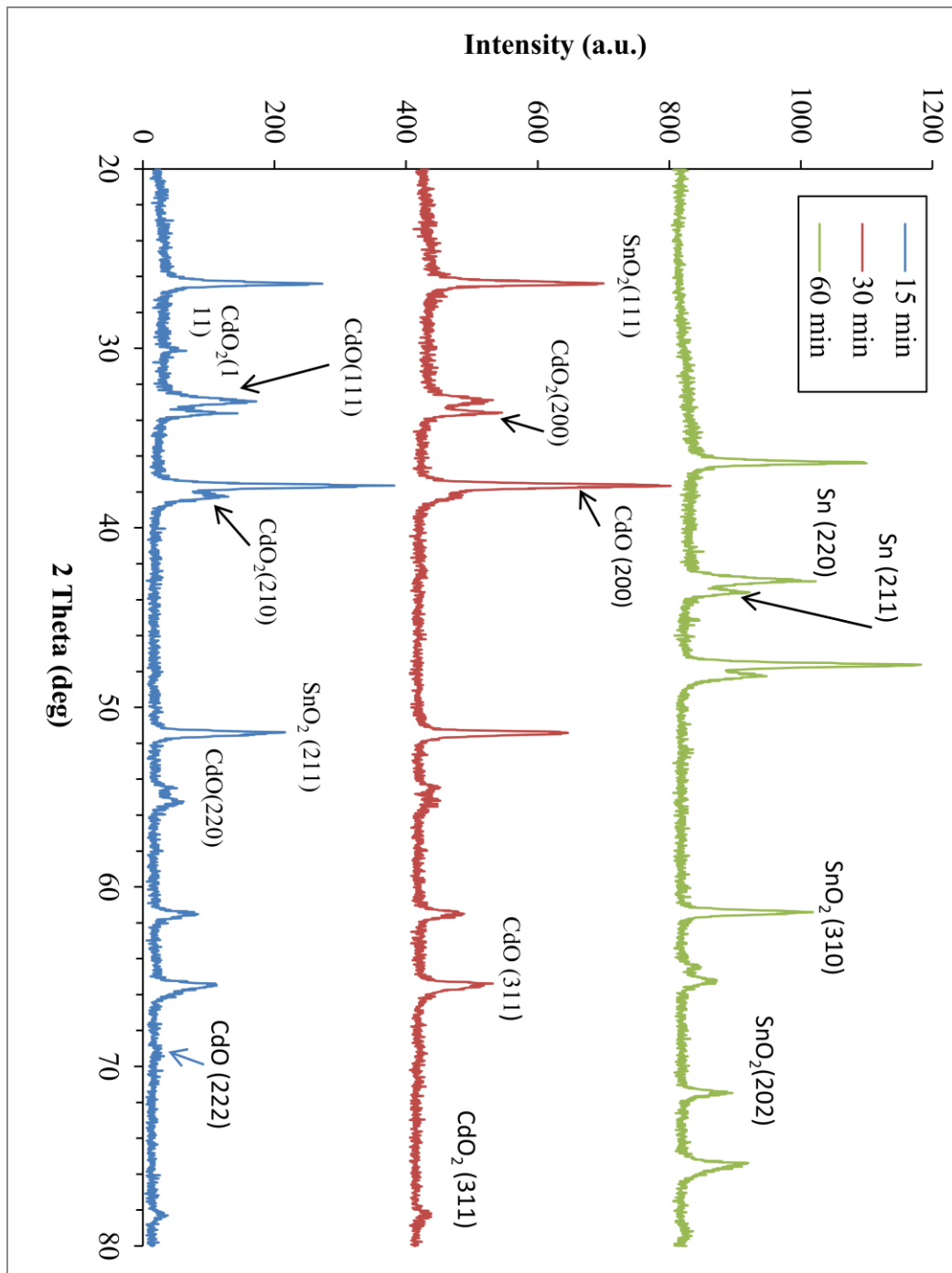


Fig. 2. XRD for CdO thin film at different oxidation time.

The information on the grain size (D), dislocations density (σ), microstrain (η) and density of dislocations of the deposited film has been obtained using Scherer's formula have been listed as shown in Table 1. In general, the grain size (D) variation between 24 nm and 76 nm was observed for the particle deposited at 5 min oxidation time.

Table 1. X-Ray characterization for CdO thin film at 15min deposition time.

2 Theta (deg)	(hkl) planes	β (deg)	D (nm)	$\sigma \times 10^{14}$ (1/m²)	$\eta \times 10^{-4}$ (lines⁻²·m⁻⁴)	$N \times 10^{19}$ lines·m⁻²
26.42	SnO ₂ (110)	0.12	32.99	2.19	5.13	9.80
30.09	CdO ₂ (111)	0.25	32.73	9.33	10.58	86.09
32.92	CdO (111)	0.40	20.60	23.55	16.81	345.25
33.62	CdO (210)	0.28	20.64	23.46	16.78	343.37
37.67	CdO (200) CdO ₂ (210)	0.25	33.40	8.95	10.37	80.99
51.42	SnO ₂ (211)	0.24	36.12	7.66	9.59	64.07
55.25	CdO (220)	0.36	24.93	16.80	14.20	208.13
65.94	CdO (311)	0.24	39.31	6.47	8.81	49.70
69.44	CdO (222)	0.13	76.44	1.71	4.53	6.75

The Transmittance spectrum is taken by Cary 100 Conc plus UV-Vis Spectrophotometer 350 nm to 1100 nm. The UV-Vis spectra is very important because it provides the details related with the optical band. The optical transmittance of the CdO thin film at 15 min deposit time was around 20% at wavelength 400 nm then increases sharply to 60% at wavelength 1100 nm as shown in Figure 2. Also it is observed that the optical transmittance spectra shift towards shorter wavelength as particle size decreases. We that causes increase in optical energy band gap but the optical transmittance of the CdO thin films at (30 and 60) min deposit time was around 38% and 17% at wavelength 400 nm respectively.

The absorbance spectrum shown at Figure 4 a sharp decrease in absorption at wavelength near to the absorption edge (510 nm) of the threshold wavelength for CdO thin film deposited at 5 min, the energy corresponding to this determines the band gap of the semiconductor material. The inset of Figure 3 shows the CdO thin film absorption coefficient α of around $4 \times 10^4 \text{ cm}^{-1}$ near to the absorption edge (510 nm).

Figure 5 shows that graph between $(\alpha h\nu)^2$ versus photon energy ($h\nu$) gives the value of direct band gap. The extrapolation of the straight line to $(\alpha h\nu)^2 = 0$, gives the value of band gap. From the UV-spectra shows the absorbance decreases with increasing wavelength and the energy gap increase from 2.3 eV to 2.45 eV from bulk to the thin film.

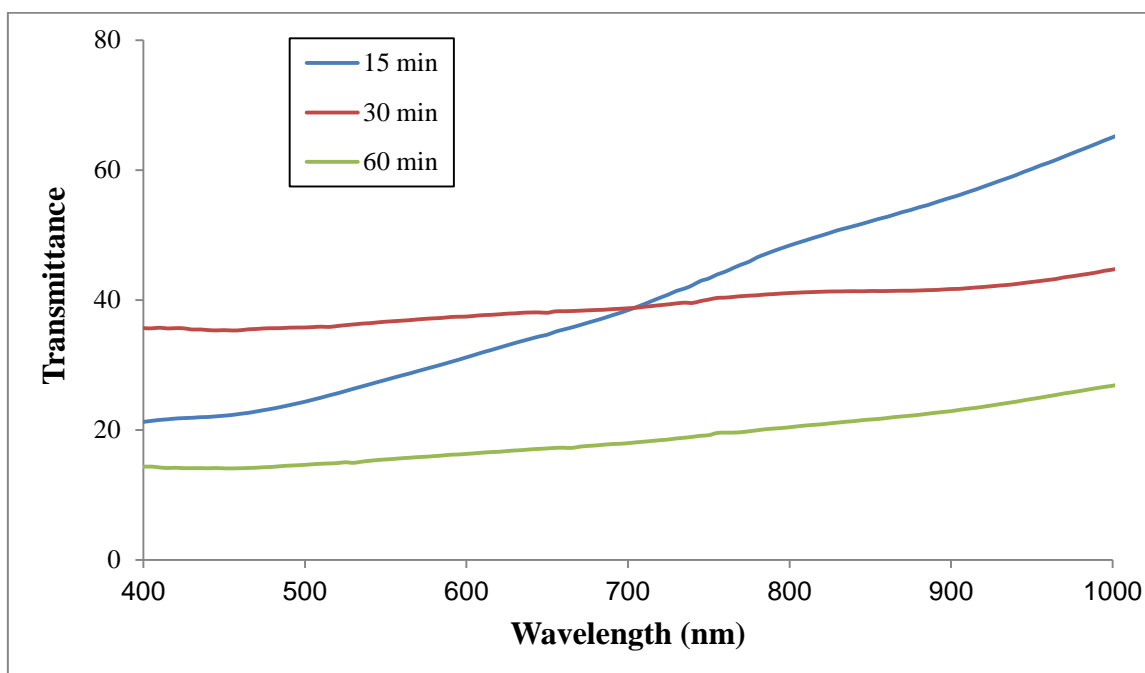


Fig. 3. Transmittance Spectra of CdO thin film at different oxidation time.

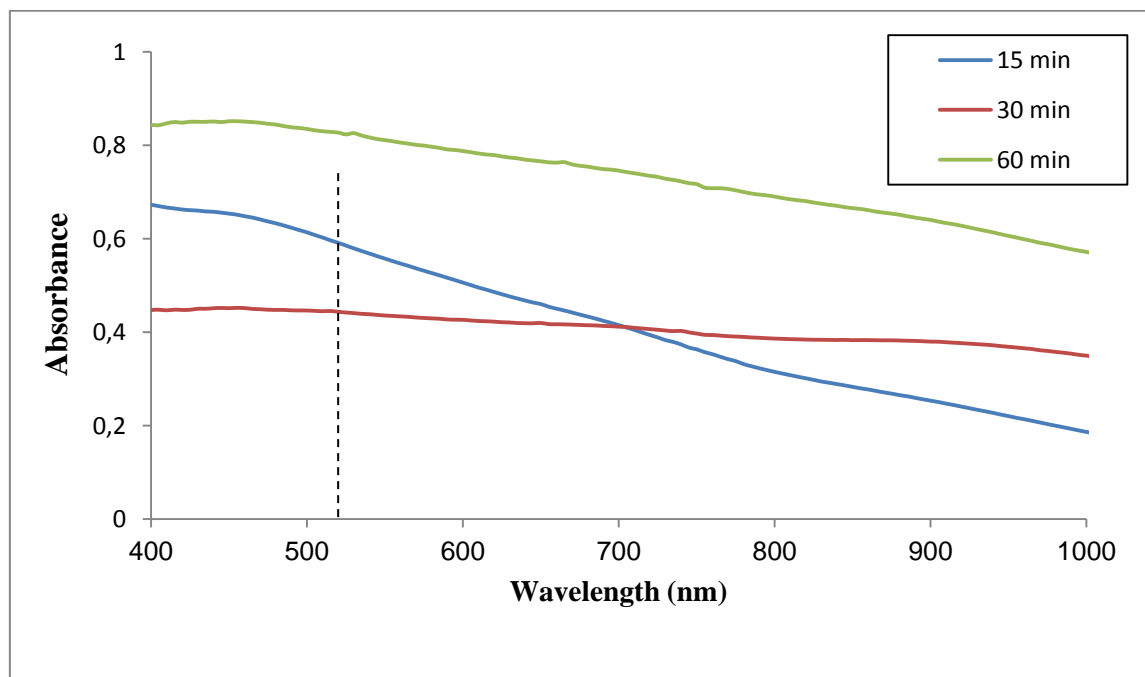


Fig. 4. Absorption Spectra of CdO thin film at different oxidation time.

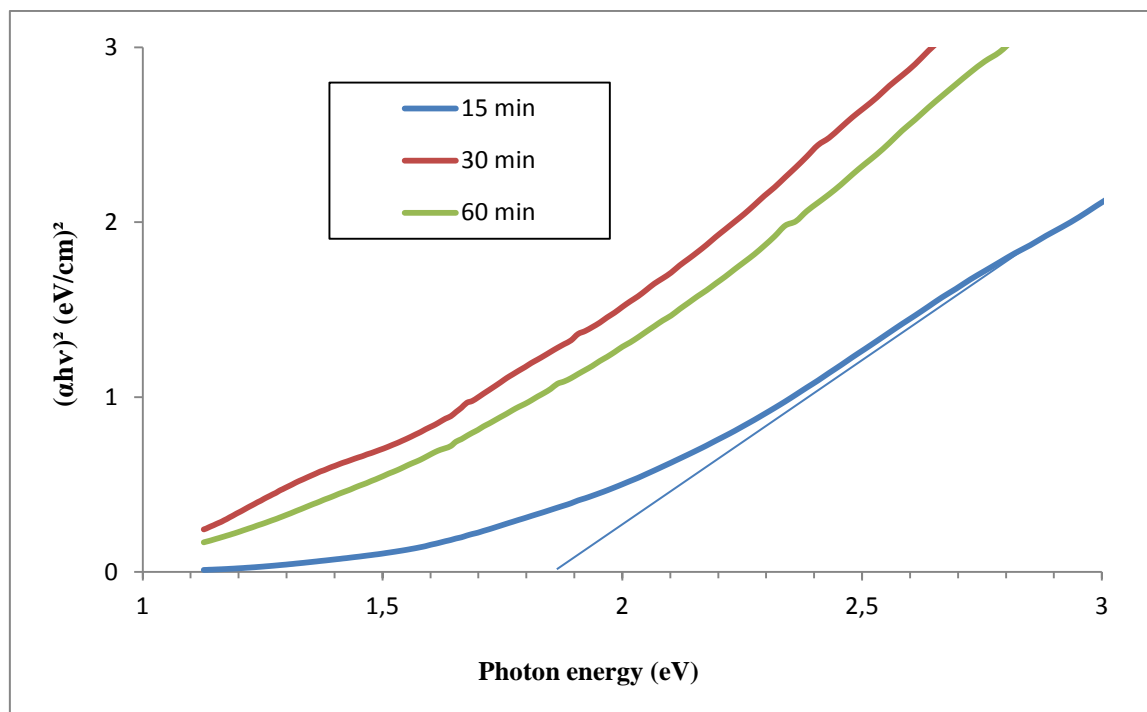


Fig. 5(a). $(\alpha h\nu)^2$ versus photon energy gap of CdO thin film.

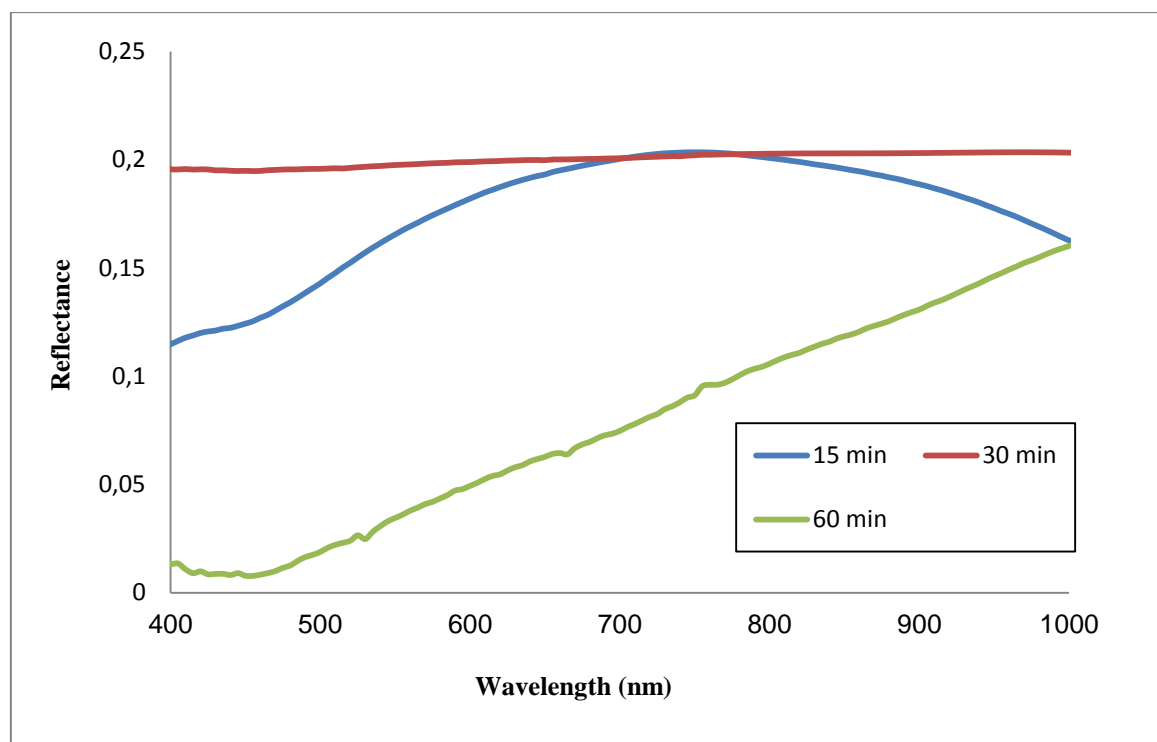


Fig. 5(b). Reflection and reflective index spectra of CdO thin film a function of wavelength.

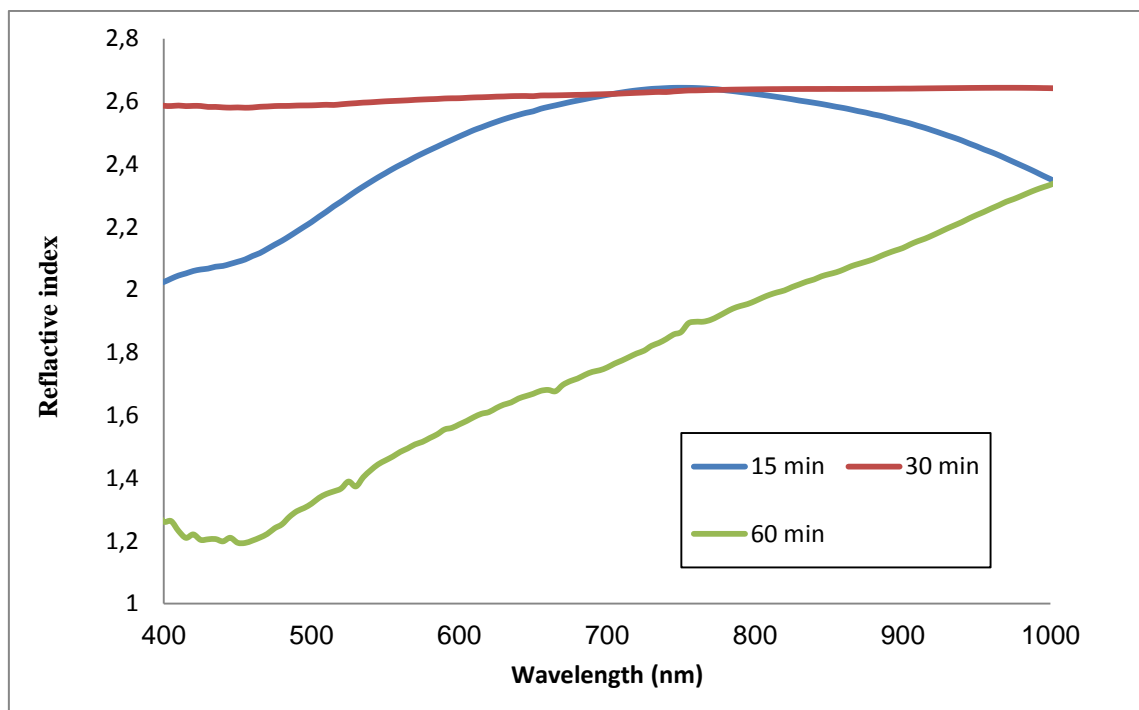


Fig. 5(c). Reflection and reflective index spectra of CdO thin film a function of wavelength.

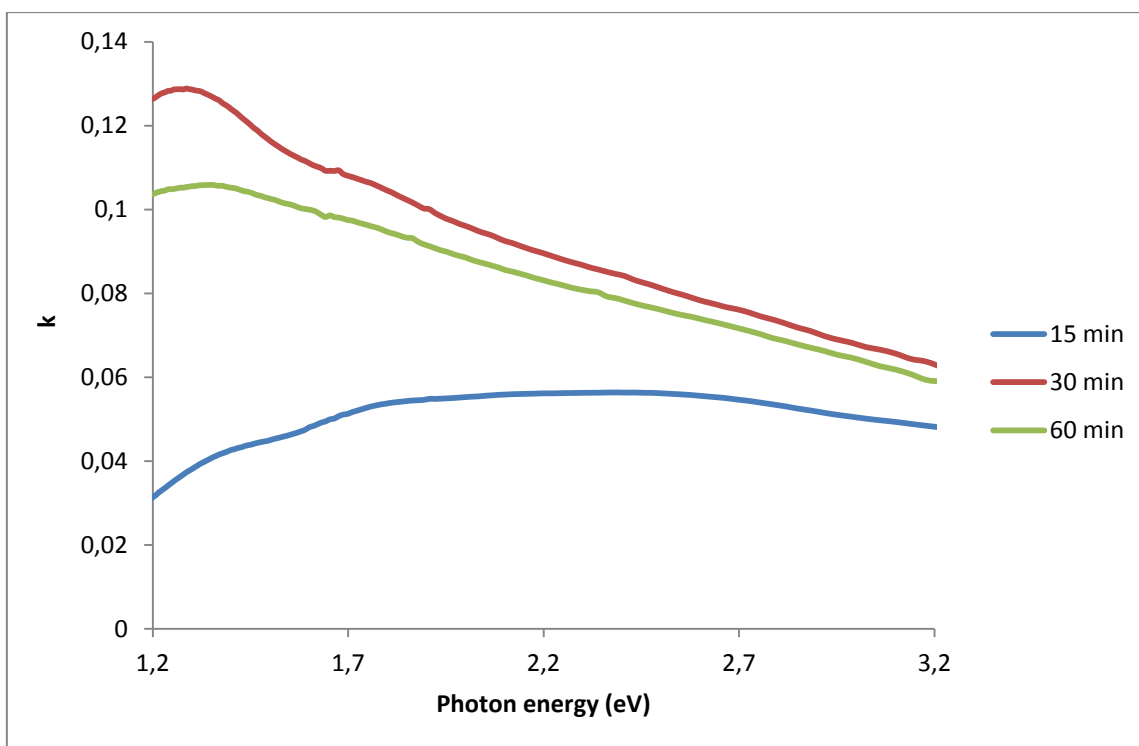


Fig. 6. Extinction coefficient versus photon energy of CdO thin film.

Figure 6 shows the plot between photon energy versus extinction coefficient (k). The extinction coefficient decrease from 1.5 eV to 2.3 eV then increase with the the absorption edge 510 nm (≈ 2.45 eV) indicated increases with photon energy from 2.3 eV to 2.7 eV.

The reflectance of CdO thin film increases from 0.1 to 0.2 when the wavelength increases from 350 nm to greater than 500 nm as shown in figure 5 and the refractive index (n) has been calculated by formula [14]:

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \quad (1)$$

The dielectric constant and absorption coefficient are related and can be obtained theoretically with the relation given by the following: [Ugwu, 2006; Okujagu, 1992; Parachiniet et al., 1980; Chalkwski, 1980; Born et al., 1970; and Jenkins et al., 1976].

$$\epsilon_r = n^2 - k^2 \quad (2)$$

$$\epsilon_i = 2nk \quad (3)$$

where ϵ_r is the real part of the dielectric constant and ϵ_i is the imaginary part of the dielectric constant.

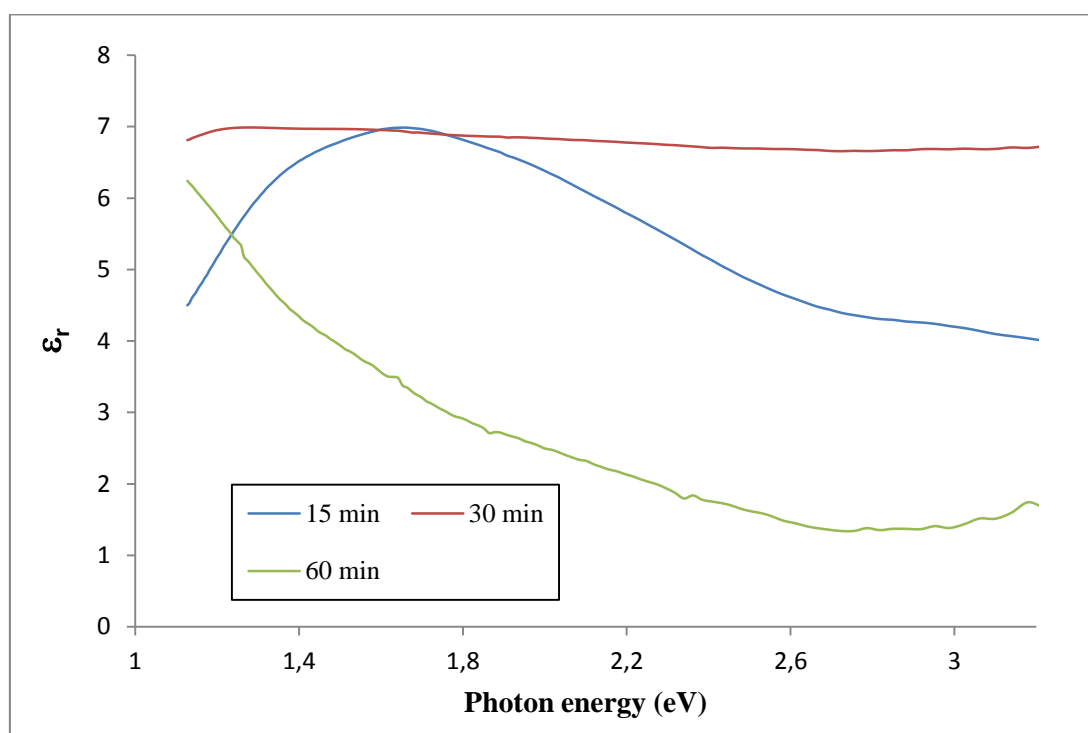


Fig. 7(a). Plot between photon energy with a: real part of the dielectric constant and b: the imaginary part of the dielectric constant.

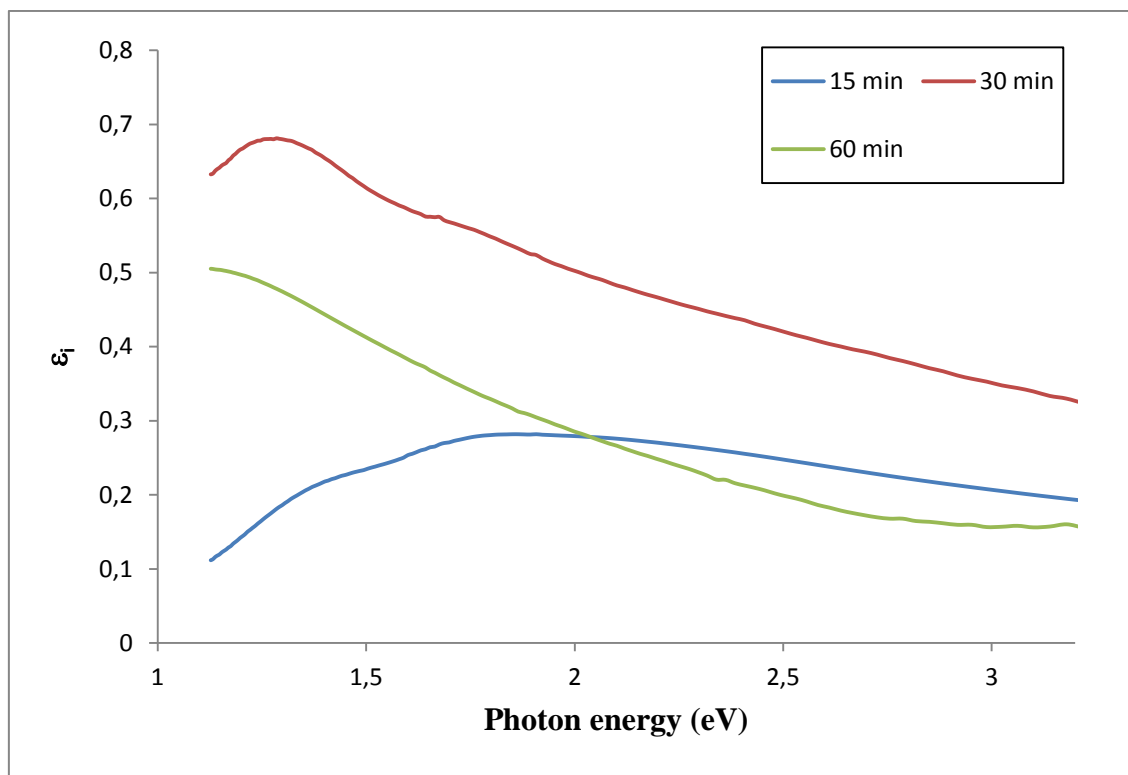


Fig. 7(b). Plot between photon energy with a: real part of the dielectric constant and b: the imaginary part of the dielectric constant.

The real part as shown in Figure 7(a) almost decreases slowly with increasing photon energy. Also the figure indicate the absorption edge is the point which decreases the real part of the dielectric constant .the imaginary part of dielectric represents the absorption associated of radiation by free carriers and imaginary part is always positive and represented loss factor or energy absorbed. Also the Figure 7(b) relieve that the imaginary part of CdO thin film decreases with increases the photon energy.

The imaginary part of dielectric constant is related to the optical conductivity (σ) which calculated from the following relation:

$$\sigma = \alpha n c \epsilon_0 = \frac{\alpha n c}{4\pi} \quad (4)$$

where: c is the velocity of the radation in the space , n is the refractive index and α is the absorption coefficient.

Figure 8 shows the relation of optical conductivity with the incident photon energy. The increased optical conductivity at high photon energy is due to high absorbance of CdO film in that region. The optical conductance and band gap indicated that the film is transmittance within the visible range.

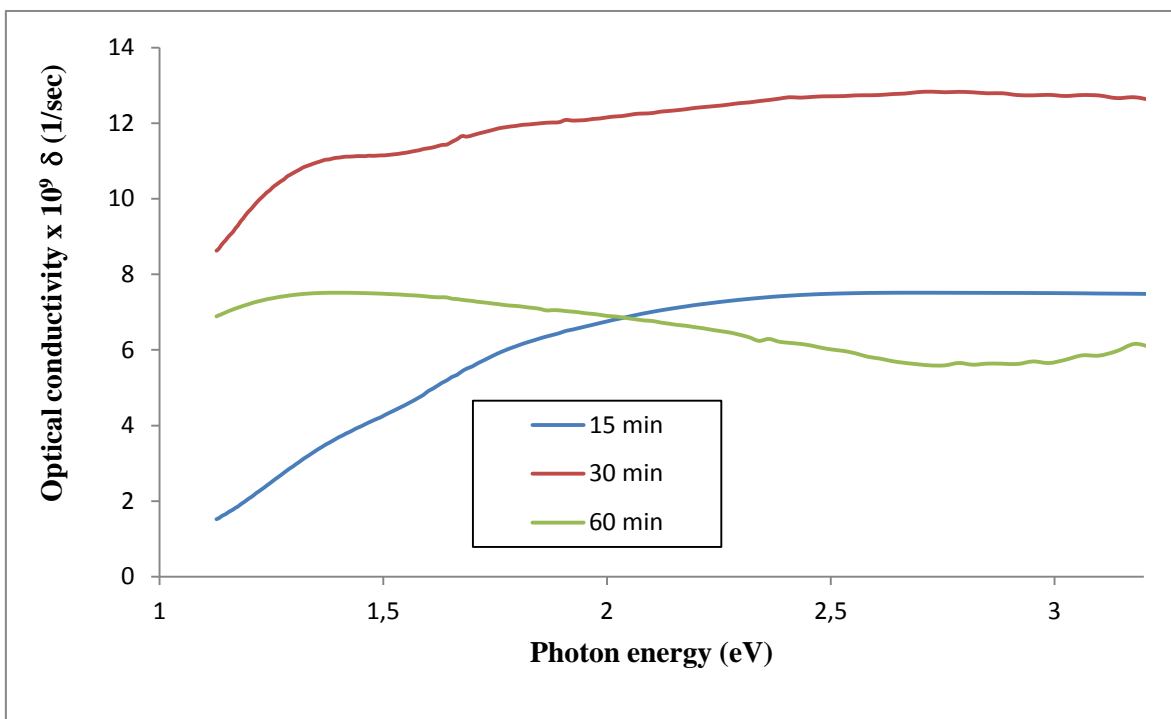
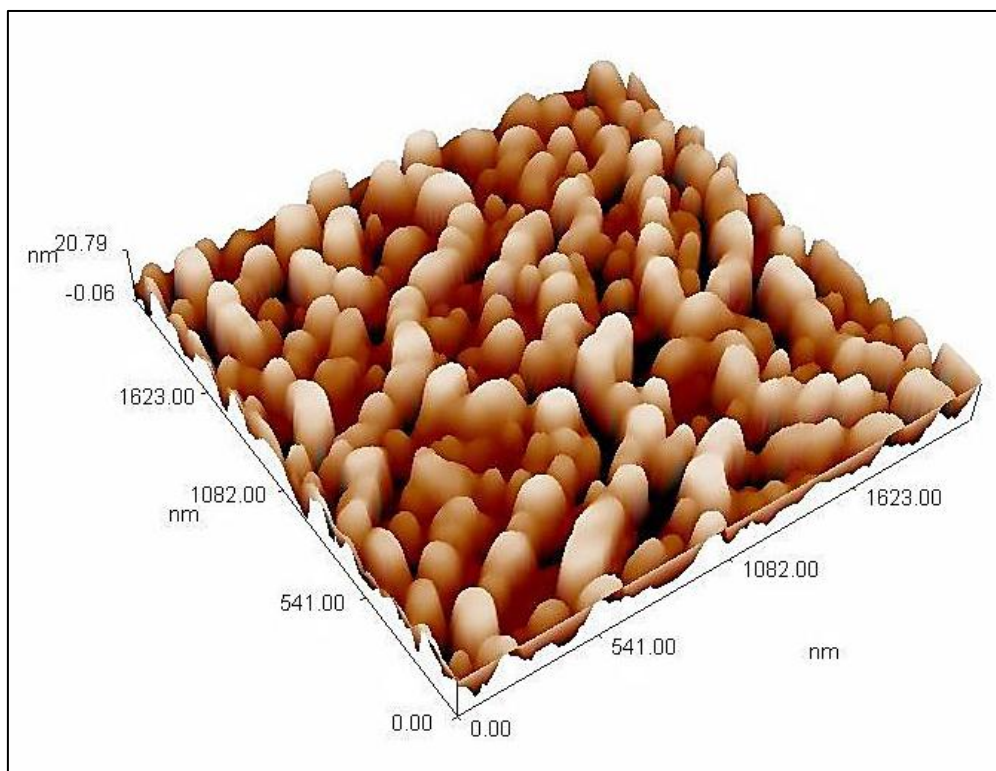
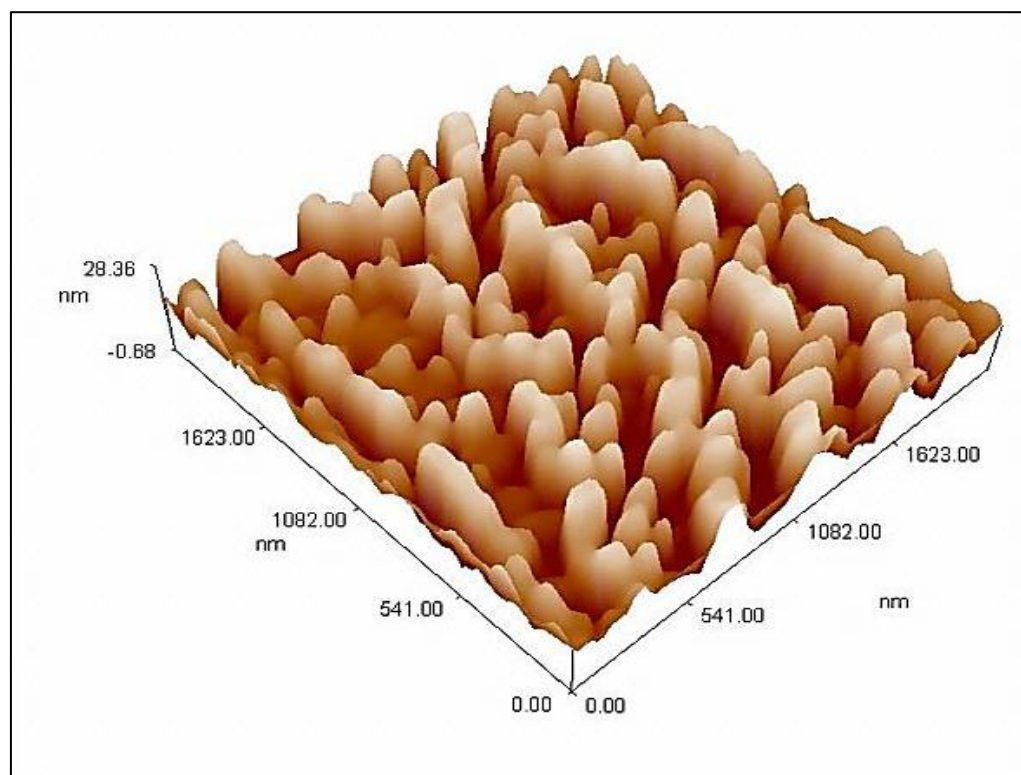
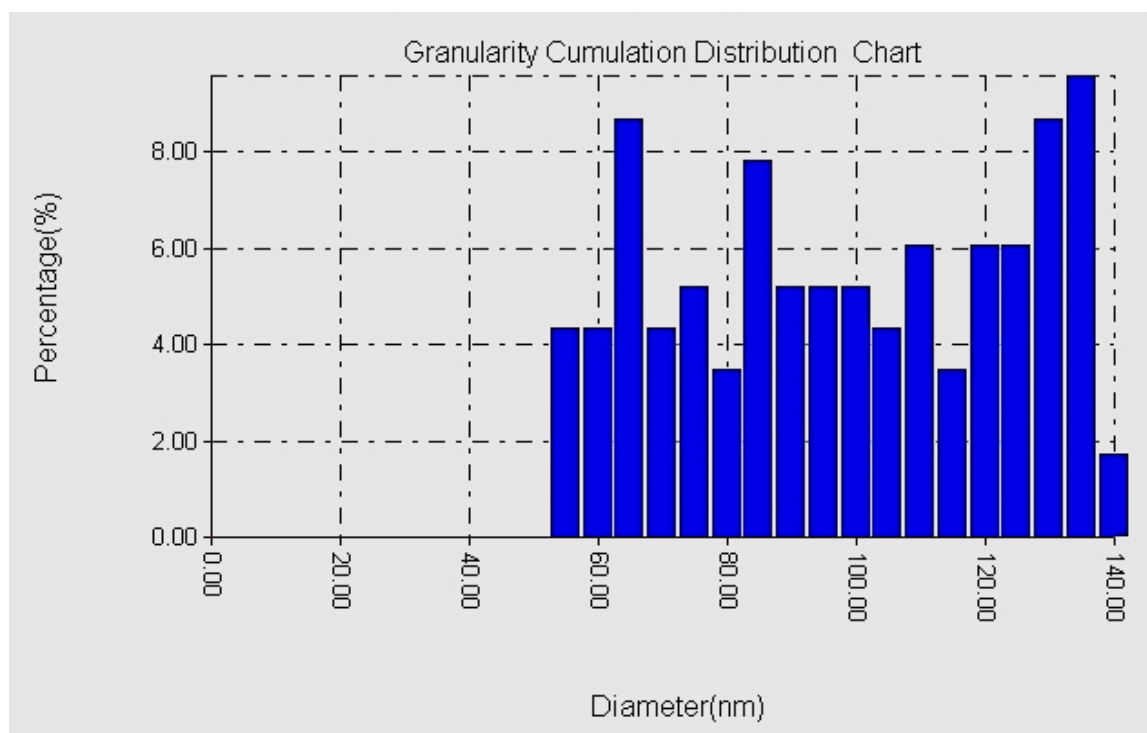
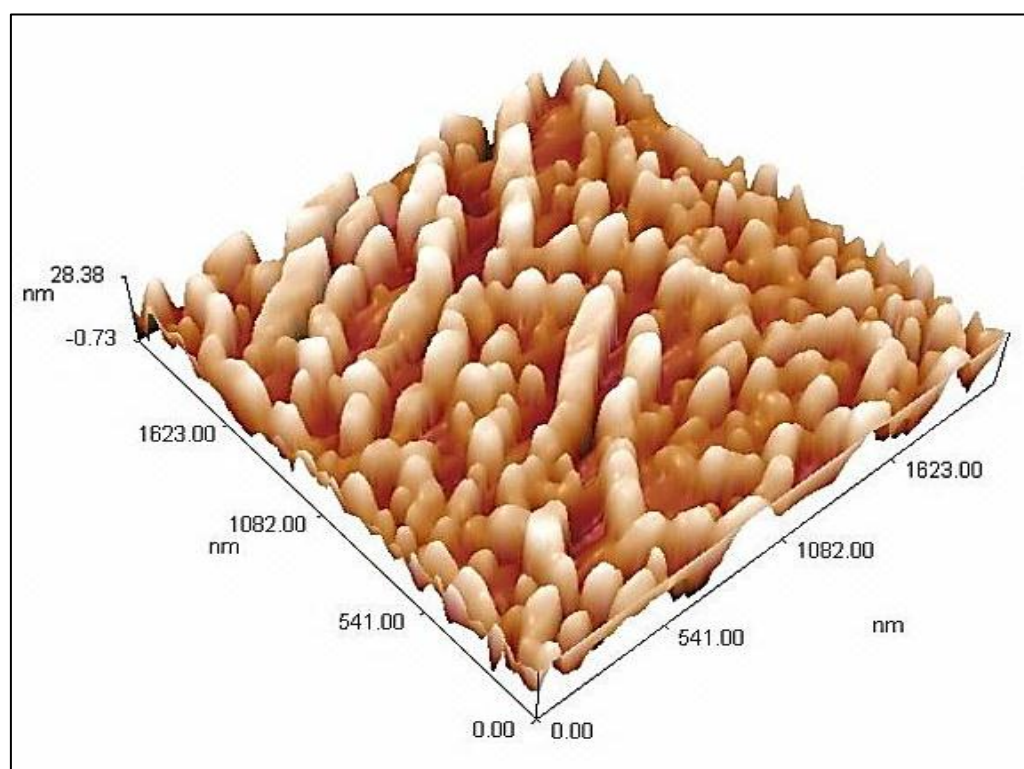
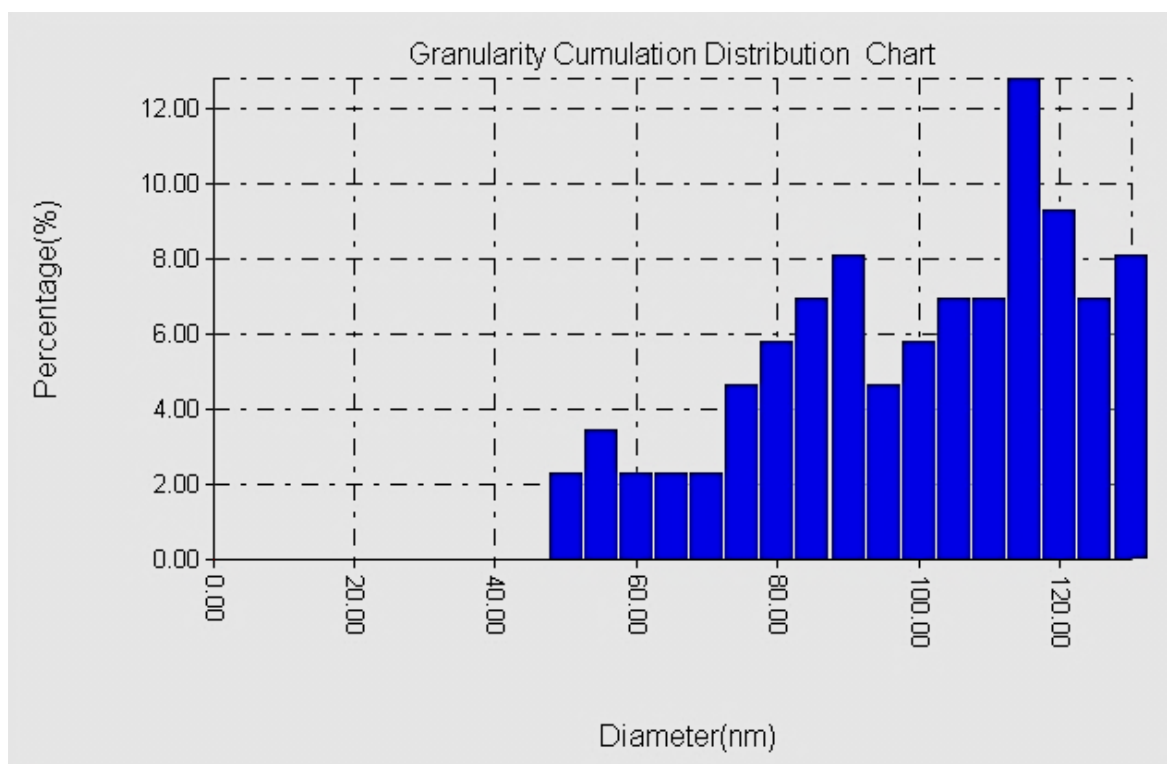


Fig. 8. Optical Conductivity of CdO thin film.







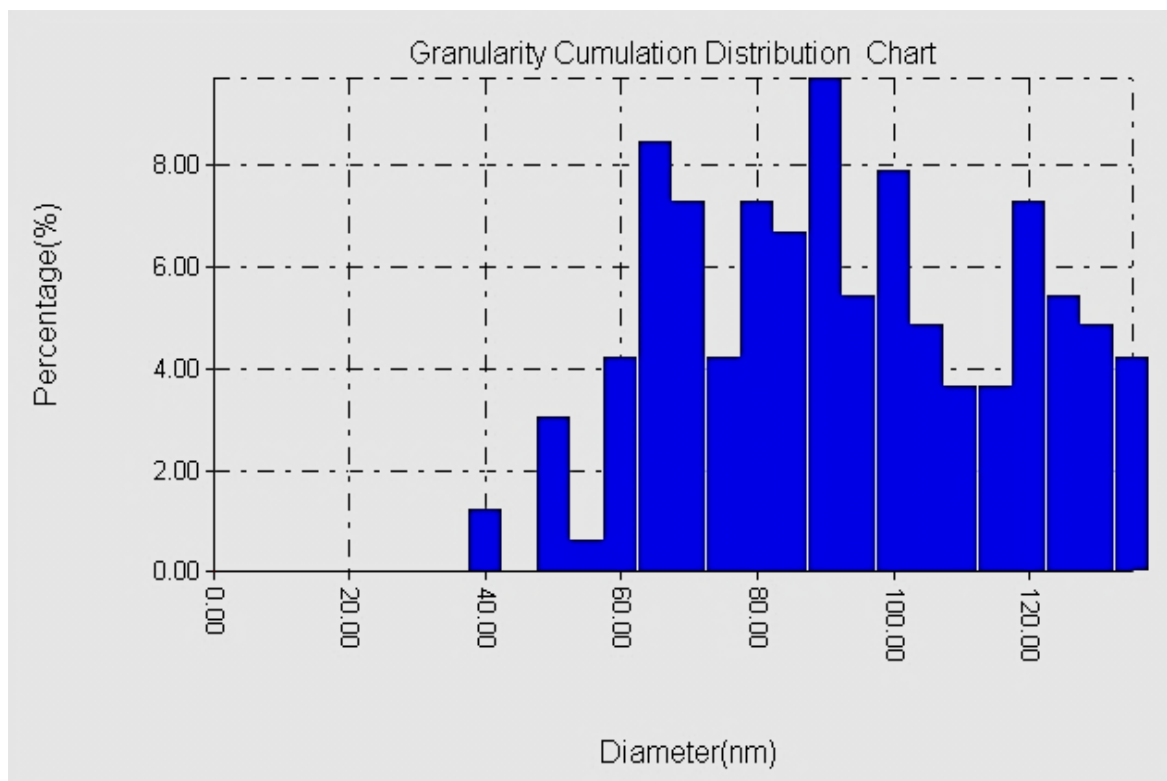


Fig. 9. 3D AFM images of CdO thin films surface and Granularity accumulation distribution chart prepared at different deposition times.

Table 2. The Average diameter, roughness average and Root mean square of CdO thin films surface and Granularity accumulation distribution chart prepared at different deposition times.

Deposition time (min)	Average Grain size (nm)	Roughness average (nm)	RMS (nm)
15	96.30	4.96	5.74
30	96.91	5.54	6.42
60	90.92	5.66	6.63

AFM was used to characterize the 3D and charts distribution of the CdO thin films at different deposition times, as shown in Fig. 9. The mean surface roughness was measured to be around 5 nm. Therefore, the low degree of roughness of the CdO thin film reduces light reflection, but increases light absorption in the visible region of the solar spectrum in solar cells.

4. CONCLUSION

This work has clearly presented how CdO thin film was grown by electrochemical deposition method (simple, cost, and quick method for the synthesis of CdO nanostructure). The behavior of the film as illustrated in the figures shows that the film is a visible transmitting thin film with a good crystallize.

References

- [1] Y. Hames and S. E. San, "CdO/Cu₂O solar cells by chemical deposition". *Solar Energy*, 77 (2004) 291-294.
- [2] F. P. Koffyberg, "Diffusion of donors in semiconducting CdO". *Solid State Commun.*, 9 (1971) 2187-2189.
- [3] F. A. Benko and F. P. Koffyberg, "Quantum efficiency and optical transitions of CdO photoanodes", *Solid State Commun.*, 57 (1986) 901 - 903.
- [4] R.L. Mishra, A.K. Sharma, S.G. Prakash, "Gas sensitivity and characterization of cadmium oxide semiconducting thin film deposited by spray pyrolysis technique," *Digest Journal of Nanomaterials and Biostructures*, 4 (2009) 511-518.
- [5] K. Gurumurugan, D. Mangalraj and S.K. Narayanandas, "Correlations between the optical and electrical properties of CdO thin films deposited by spray pyrolysis," *Thin Solid Films*, 251 (1994) 7-9.
- [6] O. Gomezdaza, A. Arias-Carbajal, Readigos, J. Campos, M. T. S. Nair, P. K. Nair, "Substrate spacing and thin - film yield in chemical bath deposition of semiconductor thin films," *Semicond. Sci. Technol.* 15(11) (2000) 1022-1029.
- [7] D.C. Renolds, D. C. Look, B. Jogai, "Optically pumped ultraviolet lasing from ZnO," *Solid State Comm.* 99 (1996) 873-875.
- [8] L. I. Popova, S. K. Andreev, V. K. Gurorguev, E. B. Manolov, "Resistance changes of SnO₂ thin films suitable for microelectronic gas sensors," *Proceedings of the 20th international IEEE Conference on Microelectronics*, 2 (1995) 581-583.
- [9] K.B. Sundaram, G. K. Bhagara, "Chemical vapor deposition of tin oxide films and their electrical properties," *J. Phys. D: Appl. Phys.* 14 (1981) 333-338.
- [10] C. H. Bhosale, A. V. Kambale, A. V. Kokate and K. Y. Rajpure, "Structural, optical and electrical properties of chemically sprayed CdO thin films". *Mater. Science Eng. B*, 122 (2005) 67-71.
- [11] A. Salehi, M. Gholizade, "Gas-sensing properties of indium-doped SnO₂ thin films with variations in indium concentration," *Sensors and Actuators B: Chemical*, 89 (2003) 173-179.
- [12] L. Znaidi, G. J. A. A. Soler Illia, S. Beyahia, C. Sanchez and A.V. Kanaev, "Oriented ZnO thin films synthesis by sol-gel process for laser application," *Thin Solid Films*, 428 (2003) 257-262.

- [13] M. Santamaria, P. Bocchetta, F. D. Quarto, "Room temperature electrodeposition of photoactive Cd(OH)₂ nanowires," *Electrochem. Commun.* 11(2009) 580-584.
- [14] JCPDS "powder diffraction file" No. 96-101-1052".
- [15] Ruby Das and Suman Pandey, Comparison of Optical Properties of Bulk and Nano Crystalline Thin Films of CdS Using Different Precursors, *International Journal of Material Science*, 1 (2011) 35-40.

(Received 14 January 2016; accepted 28 January 2016)