Study of Physical Properties of CdO Thin Film Prepared by Chemical Spray Pyrolysis Technique

[1]Ramiz Ahmad Al-Ansari, [2]Hiba Qays Khaleel, [3]Jinan Hussein Awadh
[4] Ghuson Hameed Mohammed and [5]Israa Razzaq Swadi

[1,2]Physics Department -College of science for Women - University of Baghdad
[3]Physics Department - College of science - Al.Nahrain University
[4,5]Physics Department - College of science -University of Baghdad

ramizov@yahoo.com

Received: 4 March 2017 **Accepted: 4 May 2017**

Abstract

In this research, cadmium oxide thin films were deposited by chemical spray pyrolysis technique on the glass substrate at 350℃ with thickness about (185) µm which calculated by interference fringe. The (XRD) measurements exhibit that the CdO films are polycrystalline with cubic crystal structure and many peaks (200), (202), (311), (222) and with preferential orientation along (111) plane. The surface morphology and roughness of the samples was studied by atomic force microscopy (AFM). The optical properties measure in the (UV –VIS), wavelength range (400-800) nm shows that the energy Gap is (2.3) eV and the optical transmittance of CdO films is about 88%. . The carrier's concentrations, Mobility Of cadmium oxide Thin film was calculated using Hall Effect measurements, Hall mobility display that cadmium oxide thin film is n-type semiconductor films. The D.C conductivity results shows that the CdO films have two values of activation energy as a result of polycrystalline structure of CdO film

Keywords: *cadmium oxide, Chemical spray pyrolysis, XRD, AFM, Hall Effect, thin films*

Study of Physical Properties of CdO Thin Film Prepared by Chemical Spray Pyrolysis Technique

Ramiz Ahmad Al-Ansari, Hiba Qays Khaleel, Jinan Hussein Awadh, Ghuson Hameed Mohammed and Israa Razzaq Swadi

دراسة بعض الخصائص الفيزيائية لغشاء اوكسيد الكادميوم المحضر بتقنية التحليل الكيميائي الحراري

[1]رامز احمد الانصاري ، [2]هبة قيس خليل، [3] جنان حسين عوض، [4]غصون حميد محمد و [5]اسراء رزاق سوادي

[1،2]قسم الفيزياء - كلية العلوم للبنات - جامعة بغداد
[3]قسم الفيزياء - كلية العلوم- جامعة النهرين
[4،5]قسم الفيزياء - كلية العلوم - جامعة بغداد

الخلاصة

في هذا البحث ، تم ترسيب اغشية اوكسيد الكادميوم (CdO) باستخدام تقنية التحليل لكيميائي الحراري على قواعد زجاجية بدرجة حرارة (350℃) وسمك (185 µm) تم حسابه باستخدام تداخل الاهداب ، حيث اظهرت الخصائص التركيبية التي شملت دراسة تحليل حيود الاشعة السينية على ان جميع الاغشية التي تم تحضيرها هي ذات تراكيب متعددة التبلورمع هيكل البلورة مكعبة والعديد من القمم(222),(311),(202),(200) حيث يكون الاتجاه السائد على امتداد المستوي (111) المقابل ل $2\theta = 10\ to\ 80$. تم دراسة الطوبوغرافية وخشونة السطح للعينات بواسطة مجهر القوه الذرية ، كما تم دراسة الخصائص البصرية بواسطة جهاز(UV-VIS) حيث لوحظ ان قيمة فجوة الطاقة هو (2.3) الكترون فولت. واظهر منحني النفاذية ان النفاذية في مدى 800–400 نانو متر. تركيز الحاملات والحركية لاوكسيد الكادميوم تم حسابه بواسطة قياس تاثير هول ، تحركية هول اظهرت ان اغشية اوكسيد الكادميوم هو شبه موصل نوع n . التوصلية الكهربائية لاغشية اوكسيد الكادميوم تبين ان غشاء CdO الرقيق يملك طاقتين تنشيط وهذا يرجع الى تركيبه المتعدد التبلور.

الكلمات المفتاحية : اوكسيد الكادميوم ،تقنية التحليل الكيمائي الحراري ،خصائص تركيبة ، خصائص بصرية، تاثير هول ، اغشية رقيقة

Introduction

CdO thin films has be vastly use as transparent conducting oxides thin films because of low resistivity and high optical transmittance [1, 2] , its optical bands gab lay between (2.2- 2.7) eV at room temperature depend on the type an method and preparations conditions [3].The combination of higher transparency in the visible range of the electromagnetic spectrum, high electrical conductivity, and high carrier concentration , these features makes CdO thin film

very useful for many application such like solar cell , phototransistor , diodes , gas sensors , heat mirror and antireflection coatings [4.5] . In the last decade, various techniques used to prepared CdO thin films such as thermal evaporation, reactive sputtering, RF magnetron sputtering, pulsed laser deposition and chemical spray pyrolysis [6]. The optoelectronic semiconductor material CdO, has been extensively studied as epitaxial and polycrystalline thin films prepared by different techniques because of its unique optoelectronic and other properties with a hope of exploring potentialities for fabrication of new scientific and technological devices. [7] .Many workers were prepared polycrystalline CdO thin films and characterized their structural, electrical and optical properties. Cadmium oxide thin films with enhanced electrical property were prepared on glass substrates at 300 °C using spray pyrolysis methods [8], X-Ray diffractions study reveal that the film exhibits cubic crystals structures. From the transmittances Spectra, it's found that CdO thins films deposited with lower precursor concentrations have high transparent. Hall measurement confirm that CdO semiconducting behaviors as n-type electrical conductivity. The result authenticated that the precursor concentrations influenced the structural, optical and electrical properties of the deposited film. The composition and optical properties of cadmium oxides thins film be studied by different methods, CdO were prepare by chemical Spray pyrolysis deposition method and study the effect of Zinc as a dopants [9]. CdO:Sn thin film deposit on glasses substrate use thermal evaporation at lower Vacuum. [10].

In this work we deposited CdO by chemical spray pyrolysis and then study some structural, optical and electrical characteristics of the prepared thin films.

Experimental details

CdO thin film was prepared by chemical spray pyrolysis method utilize a laboratory design atomizer. Cadmium acetate (Cd (CH3COO) 2·2H2O) were use a sources of Cd ions with concentration 0.1M, it is a very small crystalline grains with white color and its molecular weight 128.41 gm/mol, 1.332 gm of the acetate was dissolved in 50 ml of distiller water this solution was put on a magnetic stirrer to ensure the perfect solubility of the acetate. The result

solution was transparent and homogenous. The glass substrates after clean it was place on hot plates until itsreach350℃ . The optimize depositions parameter such as Spray times (5s), substrates Spray nozzle distances (29 cm), spray interval (55 s) and carriers gases pressures (Compressed air 10^5 NM^{-2}). the thickness of cadmium oxide films were measured by using an optical interferometer technique employing He-Ne laser (632nm) with incident angle 45° as shown in Figure (1). This method relies on the interference of the laser beam reflected from the surface of a thin layer and then substrate, the films thickness was calculated using the following formula: [11]

Thickness (t) = $\frac{L}{\Delta L} * \frac{\lambda}{2}$ ..... (1)

L = width of darkness of fringes.

ΔL = width of lightness of fringes.

λ = wave length of the laser.(632.8nm)

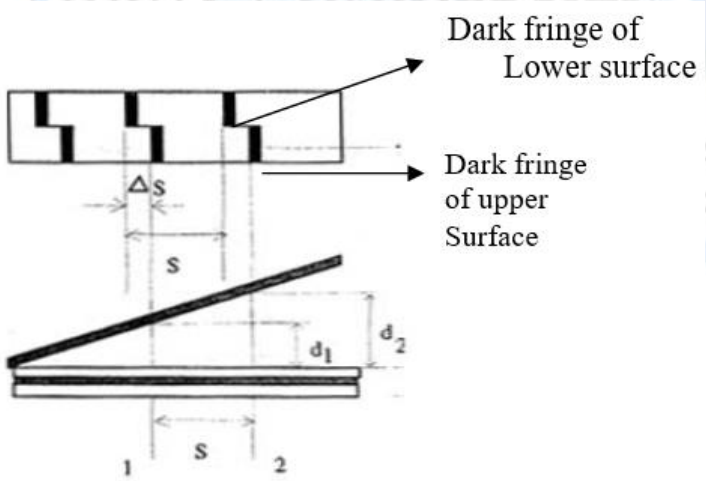

Fig. 1: Schematic of interference fringe patterns of CdO thin films

XRD measurements were recorded using Philips PW 6000, Cu Kα target and Ni as filter, λ =1:5418A by corresponding diffraction angle 2θ from 10 to 80.

The surfaces morphology of (CdO) Thin film was carried out byAtomic force microscopy AFM (A100 SGS)Angstrom Ad − Vance Inc, tip NSC35/AIBS) .

Both transmittance and absorbance of cadmiuum oxides thins film was calculated useda double–beamUV–Vis spectrometers (Shimadzu UV-1601). The electrical properties such as dc conductivity and hall measurements were study for CdO thin films. Appropriate masks was used in this measurements, these masks are put on glass substrates to deposit the aluminum using (Tungsten W) boat material by using vacuum thermal evaporation technique of type (Balzers-BAE370) under pressure (10-5 mbar) .

Result and discussions

1- X-Ray diffractions studies:

XRD patterns of CdO thin film deposit at 350Ċ are shown in (fig. 2) It can be observed from the figure polycrystalline of cubic crystal structure of the CdO thin film , it can be clearly seen that the film are preferentially orientated along (111) crystallographic directions, as well as the emergence of four diffraction peaks { (200) , (202) , (311) ,(222) } , When comparing these results with JCPDS Card (No:05-0640) it was found its agrees with the card and with the previous study despite the different preparation methods [21].

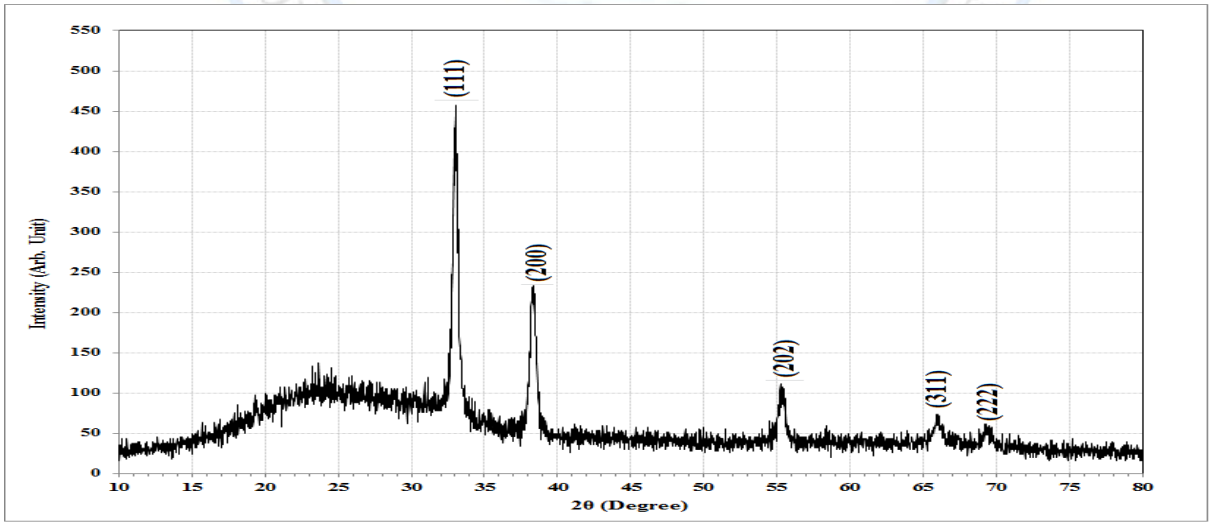

Fig 2: The X-Ray diffraction (XRD) pattern of prepared CdO thin film prepared by chemical spray method

The structural parameter like the diffractions angles (2θ) , Full widths half maximums and phase specified belong (hkl) plane are estimated from those spectra as listed in table (1)

The crystallite size of all peak was calculated using Scherrer's formula [12].

$$D=\frac{0.9\ \lambda}{\beta \cos\theta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Where λ it's the X-Ray wavelength, β must bein radians and θComplies to the positions peak the larger of G.S and smaller β value indicated better crystallizations of the material

Table (1): X-Ray diffractions parameters For (CdO) thins film

2θ (deg.)	FWHM (deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	hkl	card No.
33.0289	0.4483	2.7099	18.5	2.7108	(111)	96-900-8610
38.3326	0.4850	2.3463	17.3	2.3477	(200)	96-900-8610
55.3060	0.5200	1.6597	17.2	1.6600	(202)	96-900-8610
65.9357	0.4533	1.4156	20.9	1.4157	(311)	96-900-8610
69.2715	0.3000	1.3553	32.2	1.3554	(222)	96-900-8610

2- Atomic Force microscopy

To study the surface morphology of films materials it is important to used atomic force microscopy (AFM), it is one of the effective ways for the surface analysis due to its high resolution and powerful analysis software. as well as analysis of the AFM can calculate the thickness of film, roughness and grain size and gives an illustrative picture of the distribution of the particle size of the crystal on the surface rate . it seen from the fig (3: A, B, C) the analytical CdO thin film topographic image of the 2D, 3D, granularity normal distribution and appearance .It absorbed that the average roughness equal (11) nm, the values of Root Mean Square equal (12.9) nm its illustrate (total high surfaces and low square divide by the summation of these numbers are all unders there Square Root). The average diameter equal(97.46) nm .the CdO film exhibit a lowers surfaces Roughness with regular orient this is maybe agree with that vertical structures which is associate with these (111) CdO textures growth.

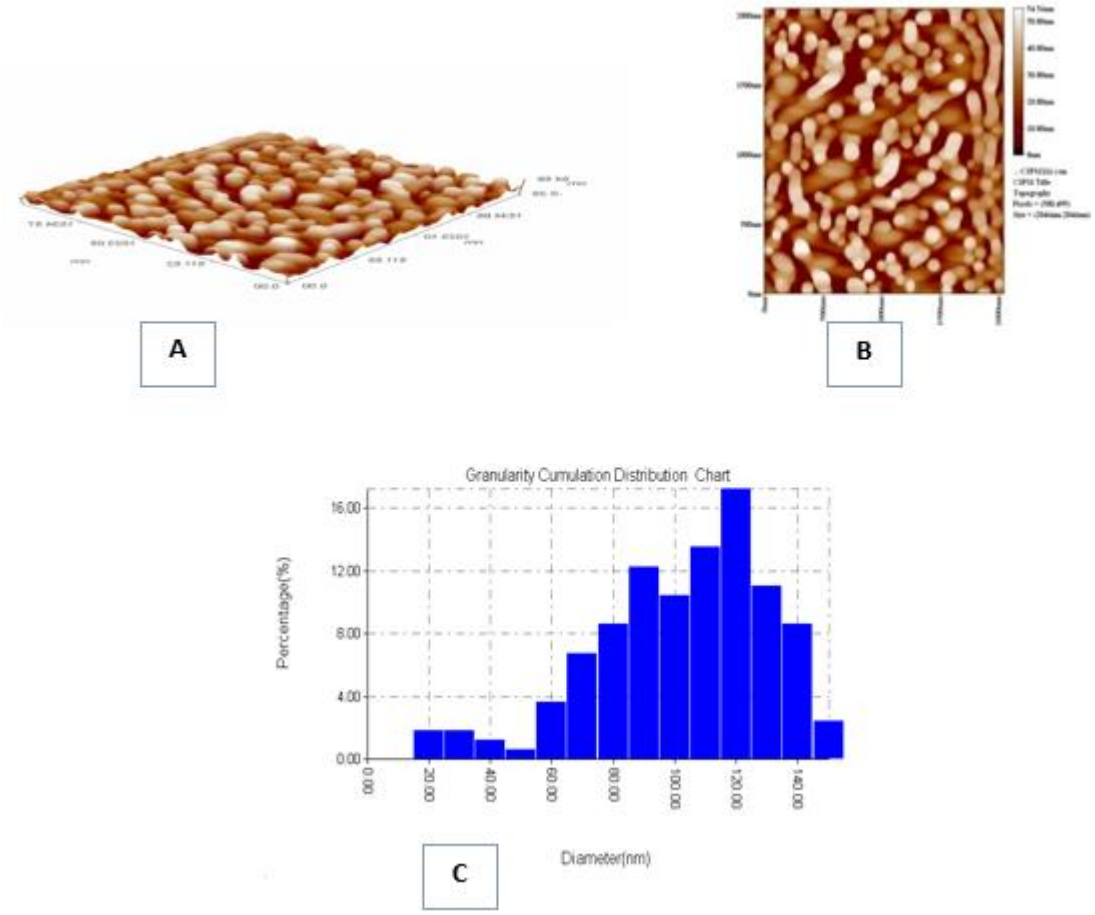

Fig (3) AFM image: A- 2D image B- 3D image C- Distribution of granular

3- Optical property

Optical characteristics of a semiconductors can be known like property these include the interactions between lights and the semiconductors, involve absorptions, diffractions, polarizations, reflections, and scattered effect [21]. Those properties were significant forever the understand of these technicality for the electrons transitions between energies band the measured of absorptions and transmissions of a S.C the optical features of semiconductors thin film were basic requirement suitable for various application on optoelectronics device. Thin films was measured by a computer-programmable, were a double beam spectrophotometer in the wavelength ranging from 200 to 2500nm in ordinary cases with the

scanning speed of the 1000nm / min.Spectra were recorded at room temperature. Transmittance and absorbance data can be used to calculate absorption coefficients of the films at different wavelengths, which have been used to calculate the band gap (E_g) by the following equation: [13]

$$\alpha\hbar v = A\,(\hbar v - E_g)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

Where A is constants, α the Absorption coefficients, $\hbar v$ the incident photon energies it can be seen that transmittance value of cadmium oxide thin film in the range (340–1040) nm, is about 88%. As show in Fig (4) also the transmittance increasing with λ as is the case of transparent conducting oxides (TCOs).

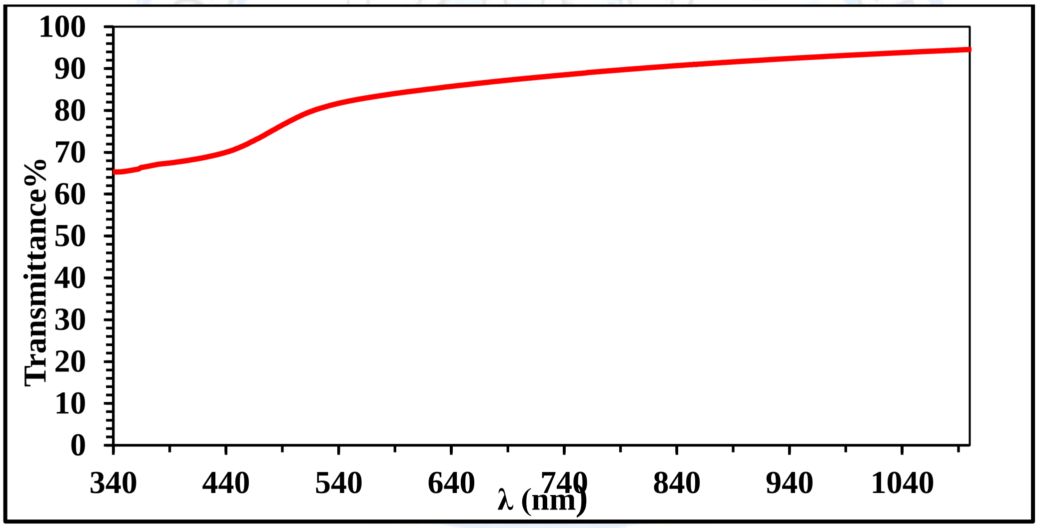

Figure (4): transmittance spectra as a functions of λ for CdO thins films prepared by chemical spray method

The optical absorption of CdO thin film seen from the Fig (5) it showed that the maximum absorption occurs at (3.5) eV. These spectra reveal that the absorption increase with the increasing of the photon energy for CdO thin film. From the value of absorption coefficient is equal ($\alpha \geq 10^4$) we can be eshmited that the transmission of CdO film is direct transmissions The optical energy gap $E_g$was predestined by presume a direct transition between valance and

conduction bands,E_g its determine by extrapolated the Straight lines portions at $\alpha = 0$ its obtaind that the value for CdO thin film is equal to 2.2 eV as show in Fig (6)

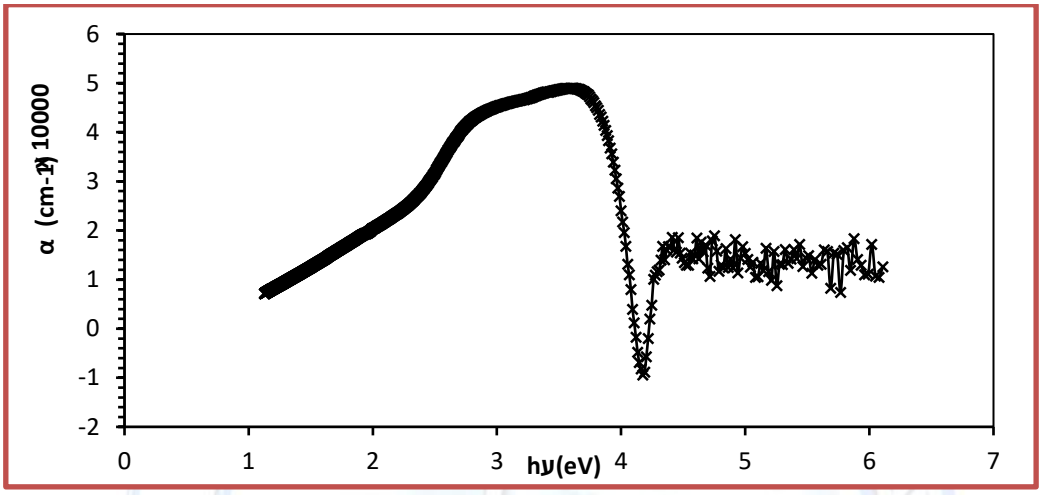

Fig (5): Absorbance coefficient for CdO thin film prepared by chemical spray method

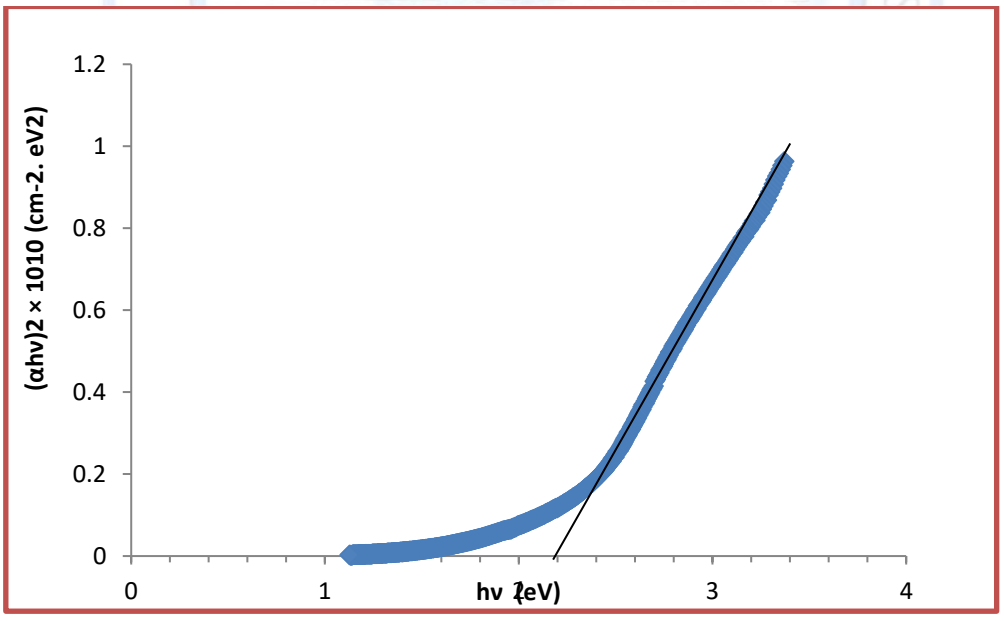

Figure (6): Optical energy gap for CdO thins films prepared by chemical spray method

The refractive index (n) is the ratio between the speeds of light in vacuum to its speed in material that doesn't absorb this light. Figure (7) shows the variation of (n) as a function of

the photon energy for CdO thin films deposited by chemical spray taqnique. It can be observed that (n) is increase with increasing of photon energy .The extinction coefficient is defined as the imaginary part of the complex index of refraction, which also associates to light absorption. Quantity that been absorbed by electrons material of the energy of incidents photons. The variation of the extinction coefficient with photon energy show that (K) increases at the range (1.5-3.5) eV of photon energy and then decreased at (4eV) with increasing of hv for CdO thin film as in Figure (8). The extinction coefficient is associated with the absorption coefficient according to the following relationship:

$k_e = \alpha \lambda / 4\pi$ ……..(4)

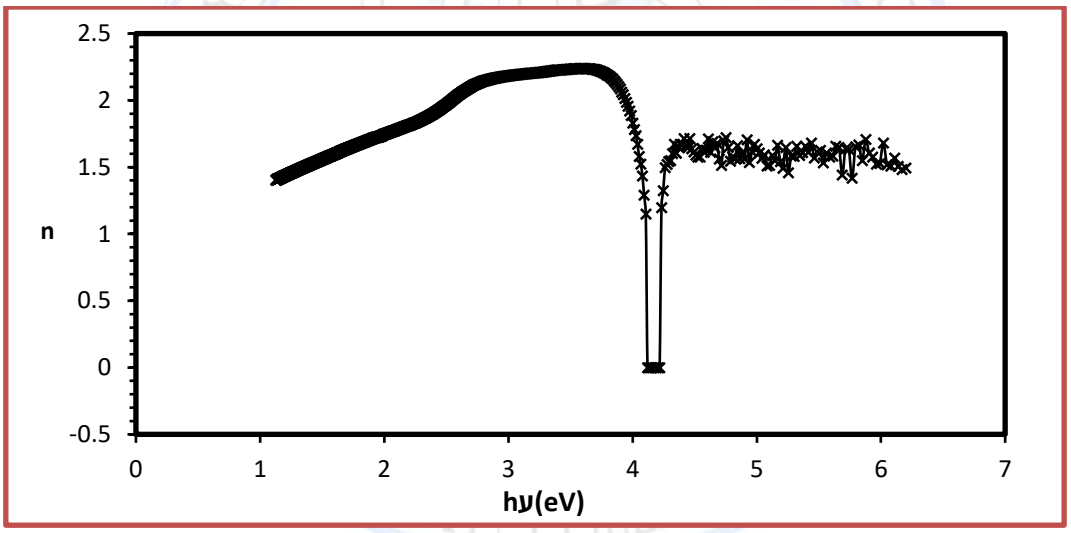

Fig (7): Refractive index as a function of wavelength of CdO thin films

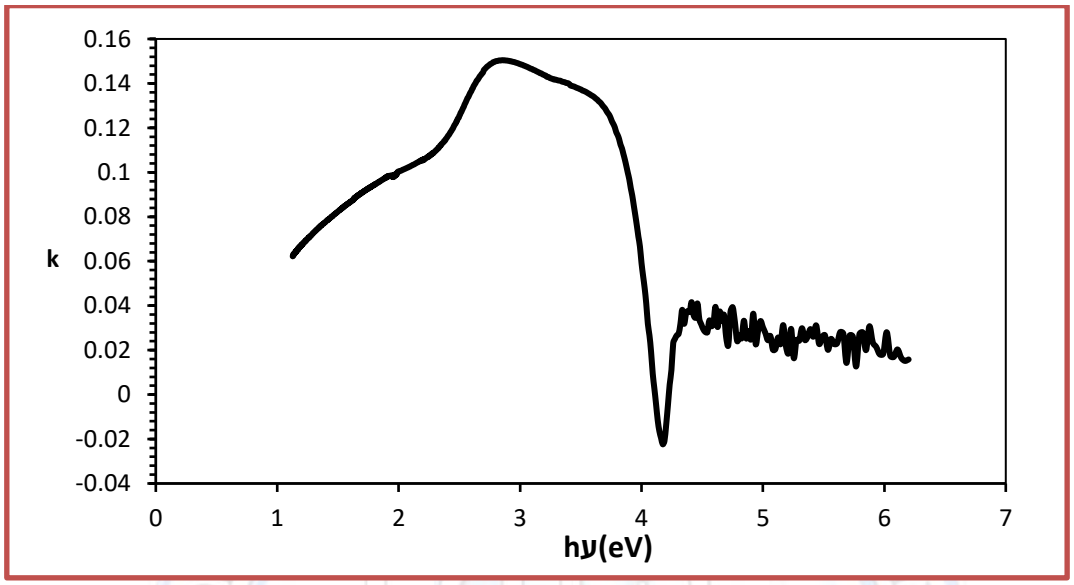

Fig (8): Extinction coefficient as a function of wavelength of CdO films

4- The electrical properties

1) DC conductivity

The electrical characteristics of the oxide semiconductors depended onto nature and quantity of impurities incorporated in the films and also the stoichiometry of the oxide. The d.C conductivity into crystalline S.C depends on existence of free electron and free positive holes. D.C measurements determined the resistivity of cadmium oxide thin films after deposit metal electrodes (Al) on the samples by using suitable masks. The electrical conductivity have been calculated as a functions of temperatures in the temperature range (20 – 200)k . The resistivity (ρ) of the film calculate used the follow formula [14]

$$\rho = \frac{R \times A}{L} \quad \ldots\ldots (5)$$

Where R isthe specimen resistances, A is the Cross- Section of films and L the distances between the electrode. The conductivity of the films were measured by the relation: [15]

$$\sigma_{D.C} = \frac{1}{\rho} \quad \ldots\ldots (6)$$

The activations energy could be calculate from the plot of lnσ versuses 1000/T accord to equations [16]

$\sigma = \sigma^{\circ} \exp\left(\frac{E_a}{K_B T}\right)$..... (7)

Whereσ° is the minimum electrical conductivity at 0K, T is the temperature, K_B is the Boltzmann's constant and Ea is the activations energies which correspond to (Eg/2) for intrinsics conductions, [17].

The activation energy was measured as show in the Fig (9) and table (2).We can notice that the films have more than one value of activation energy as a result of polycrystalline structure of CdO films, the first E_{a2} occurred in the temperature within (383-473) k and its obtained by transfers the carrier between extend state of V.B to C.B and the second one E_{a1}that occurred in the low temperature within (393-383)k ,its obtained by the transfer the carrier between localized state below C.B and above V.B.

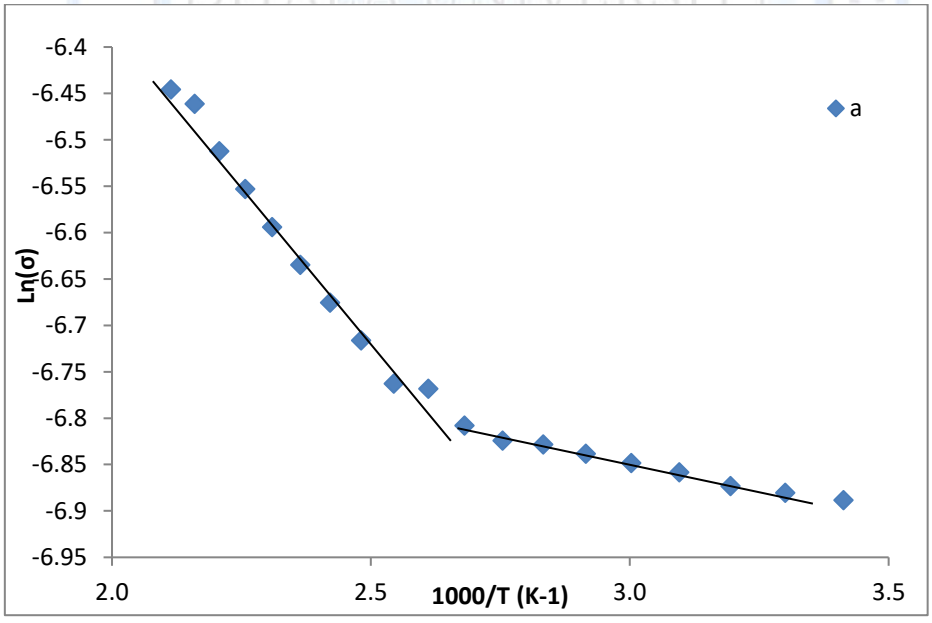

Fig (9): The variation of (lnσ) as a function of temperature for CdO thin film deposited by chemical spray taqnique

Table (2): the value of activation energy of pure CdO thin films

Sample	Ea1 (ev)	Range (k)	Ea2 (ev)	Range (K)	ΣRT ($\Omega^{-1}.cm^{-1}$)
a	0.0011	393-383	0.061	383-473	1.02×10^{-3}

2) The Hall Effect Measurements

Hall measurements is one of the rich sources of information about the initial characterization of semiconductors, electrical properties the mobility and carrier concentration can be obtained from the Hall constant in conjunction with resistivity. As the cadmium oxide is an n-type semiconductor, the carriers are electrons, which may be available from configuration that is not equal because of the presence of interstitial cadmium or oxygen vacancies these results agree with that in-published literature , table (3) below shows the resistivity (ρ) , carrier concentration, conductivity σ , (n) and mobility (μ) of CdO thin films.

Table (3): the conductivity (σ), carrier's concentration (N_e) and mobility (μ) CdO thin films

Sample	$\sigma\times10^2\,(\Omega.cm)^{-1}$	Resistivity (ρ)Ωcm $\times10^{-3}$	Carrier concentration (n) $\times\ 10^{20}/cm^3$	(μ) Mobility cm^2/Vs
CdO	1.03	2.265	-3.331	0.827

Conclusion

Cadmium oxide thin film was deposited by spray pyrolysis method at a substrate temperature of 350 ℃ . Polycrystalline nature and cubic structure of CdO films were confirmed by XRD, the major reflex along (111) direction .the thickness of the films about 180-190 mM were calculated by fringes forming and by the . AFM images showing the roughness of the film .The optical properties measure by (UV-VIS) shows the bands Gap is (2.3) eV, The average Optical transmittances of CdO film on ranged 400–800 nm, is about 88% .The carriers concentration and moblitiy of CdO thins film was calculated by hall effects measurements, Hall mobility show that the CdO is n-type S.C films. The D.C conductivity shows that the

CdO film has more than one value of activation energy as a result of polycrystalline structure of CdO films.

References

1. Mohammed Ahmed Mohammed Hassoon, stydy the opto-electronic properties of $(PbO)_{1-X}$ $(CdO)_X$ thin films deposited by Chemical Spray Pyrolysis, Ph.D Thesis, University of Babylon, College of Science (2015)
2. F. Yakuphanoglu, M. Caglar, Y. Caglar, S. Ilican, J. Alloys Comp. 506, 188 (2010).
3. O. Vigil, F. Cruz, A. Morales-Acevedo, G. Contreraspuente, L. Vaillant and G. Santana, Materials Chemistry and Physics 68, 249 (2001).
4. E. Elangovan, M.P. Singh, K. Ramamurthi, Mater. Sci. Eng. B 113 (2004) 143
5. R. Ferro and J. A. Rodriguez, Sol. Energy Mater. Sol. Cells 64, 363 (2000).
6. B. Saha, R. Thapa, and K. K. Chattopadhyay: Solid State Commun. 145 (2008) 33..
7. M.A. Yildirim, A. Ates, Sensor. Actuator. A 155 (2009) 272–277.
8. K Sankarasubramanian, R.Solaichamy , K.Sethuraman , R.Rameshbabu , and K. Ramamurthi, "Structural, Optical and Electrical Studies on CdO Thin Films Using Spray Pyrolysis Technique",Solid State Physics, Proceedings of The 57th Dae Solid State Physics Symposium 2012. AIP Conference Proceedings, 1512, p. 1036-1037 , 2013.
9. Haidar Ghazy Lazim AL-Sabehaoy, study the Structural and Optical Properties of (CdO) dopants with Zinc oxide Prepared by Chemical Spray Pyrolysis, MSc Thesis, University of Al-Mustansiriya, College of Education (2003).
10. R.S. Rusu and G.I. Rusu , " The Hall Effect In CdO:Sn Thin Films", Tomul Xlix-L, Fizica Stării Condensate, 2004.
11. Wassan Dhia Hussain, Fabrication of CdO/Si Solar Cell by DC Planar Sputtering Technique, MSc Thesis, University of Baghdad, College of Science for women (2013).
12. Hussien Hadi Kreem "preparation of cadmium oxide thin films by pulsed laser deposition and studying their properties ,pp92,2012

13. H. J. Al-Ogili, "Effect of Thickness to the Structure Properties of CdO Thin Films", Eng. and Tech. Journal, 29, 8, 2011.

14. M. Adel and K. Z. Yehya , "Influence of Substrate Temperature on Structure and Optical Properties of CdO Thin Films Prepared by Pulsed Laser Deposition" , Engineering and Technology Journal, 30 ,p. 416-425, 2012.

15. R.S. Rusu and G.I. Rusu , " The Hall Effect In CdO:Sn Thin Films", Tomul Xlix-L, Fizica Stării Condensate, 2004.

16. C. Kittel, Introduction to Solid State Physics, 8th ed ed., New York: John Wiley and Sons Inc, 2005.

17. R. S. Rusu and G. I. Rusu, "On the electrical and optical characteristics of CdO thin films" , Vol .7, (2005), p. 823 – 828.

18. I.Chambouleyron, J. M. Martínez "Optical Properties of Dielectric and Semiconductor Thin Films" Handbook of Thin Films Materials, Edited by H.S Valwa, A cadmic Press, (2001).

19. M.Mahaboob Beevi, M.Anusuya and V.Saravanan, "Characterization of CdO Thin Films Prepared By SILAR Deposition Technique", Vol. 1,(2010) ,p.151-154

20. A.R. Balu , V.S. Nagarethinam , M. Suganya and N. Arunkumar ,G. Selvan, "Effect of the solution concentration on the structural ,optical and electrical properties of SILAR deposited CdO thin films",Vol.12,(2012),p.739-749.

21. J.A.Abd,R.T.Ahmed , and N.A.Mohamed ," Australine journal of Basic and applied science effect of molar concentration on the optical and structural properties of CdO :In thin film deposited by spray pyrolysis , vol.8,no.8,pp. 166-173,2014