

OPTICAL PROPERTIES OF CdSe FILMS AT DIFFERENT THICKNESS AND ANNEALING TEMPERATURES

E. M. NASIR, H. K. AL-LAMY, H. J. ABDUL-AMEER

Department of Physics, College of Science, University of Baghdad, Baghdad, Iraq

Cd_xSe_{1-x} with (x=0.5) compound have been prepared as alloys successfully. The compound prepared was used to produce films. CdSe films with different thickness (0.5, 1, 1.5, 2) μm by heating evaporation on glass under vacuum (10⁻⁵) mbar with rate of deposition equal to 1.5 × 10⁻³ μm/sec. The deposited films on glass are examined at many temperatures (373, 423 and 473)K. XRD type of all cadmium selenide films indicated which these films are hexagonal crystalline and it has direction is (002). The average grain size in this direction is about (35.847)nm; the grain size increases with increasing thicknesses. The optical test founded CdSe films has optical energy gap (E_g^{opt}), it reduce from (2.02) to (1.92) eV and from (2.02) to (1.74) eV associated with elevated temperatures of annealing (R.T – 473)K and thickness (0.5– 2) μm, respectively. The dielectric constants, optical constants refractive and extinction coefficient were investigated.

(Received July 2, 2016; Accepted October 15, 2019)

Keywords: CdSe alloys, Thermal evaporation, Structural properties, Optical properties, Annealing.

1. Introduction

During last years, there is great attention toward semiconducting materials due to have optoelectronic characters and have many applications in photoconductive and photovoltaic detectors and solid state devices. Cadmium selenide have high photosensitivity and have band gap of (1.74)eV that make it important substance used in technology^[1,2].

Cadmium selenide is promising material because its important in technology wherever, it have many electrical and optical properties, and have mechanical stability therefore it used as semiconductor^[3,4]. CdSe is an important material for many technologies including light-emitting diodes, solar cells and thin-film transistors^[5]. Also it possible used in several applications such as light amplifiers, gas sensors, photo-detectors, photo cells and lasers^[2,6]. Cadmium selenide has n-type conductivity in thin film, and that depend on cadmium and selenide vacancies, it have great role in the conduction^[3,4]. The very high transmittance of the films in the visible region, and the brilliant orange color of the films make CdSe films useful aesthetic window glaze material^[6]. Vacuum-deposited CdSe films often possess n-type conductivity due to large amount of Cd in the films due to much pressure of Se vapor under hot medium^[7]. Se vacancies are removed by annealing in Se under 400°C^[3-8].

Perna and Capozzi (1998)^[9] founded optical and structural properties of CdSe films accumulated by laser on silicon (100) and (111). It studies effect of the substrate orientation on the luminescence features and growth. Photoluminescence spectra of films are calculated (10-300) K. The Parameters which related to interaction between the electron-phonon. The temperature is depended on exciton line width^[9]. Konda *et. Al* (2007)^[10] founded the significant improvement of photocurrent in diode that formed from Cd and Se. that occur due to large improvement in electromagnetic field. The large improvement in photoluminescence and raman^[10,11]. The essential aim of this research involves investigating influence of temperature and thickness on optical and structural characterizations.

*Corresponding author: eman.itabi@gmail.com

The semiconductor optical properties are included interaction between light and electromagnetic radiation, absorption, polarization, diffraction, scattering effects and reflection. The better values of the gap are gotten by the optical absorption^[11]. Radiation absorption by semiconductors results in electronic transition between C.B and V.B. this may be divided into direct and indirect transitions^[12].

(λ) is maximum wavelength that makes the electron-hole pair as^[13]:

$$\lambda(\mu\text{m}) = \frac{hc}{E_g} = \frac{1.24}{E_g(\text{eV})} \quad (1)$$

When intensity of the light (I_0) on film of thickness (t), transmitted intensity can be given as^[14]

$$I = I_0 \exp(-\alpha t) \quad (2)$$

Where α : is coefficient absorption, t : is film thickness. The absorption edge becomes wide for an ideal, polycrystalline and amorphous semiconductor because the allowed localized levels is found in energy gap. The width of the localized levels can be calculated using Urbach Rule^[15]

$$\alpha = \alpha_0 \cdot e^{(h\nu/\Delta E)} \quad (3)$$

$h\nu$ is energy of the photon, ΔE is width of levels in the gap, α_0 is constant.

The transition is between bottom of conduction and top of valence band without alteration in the wave as:

$$\alpha(h\nu) = B (h\nu - E_g)^r \quad (4)$$

R is a constant, B is constant included bands properties.

The direct transition at $\vec{\Delta k} = 0$ is called allowed transition, if the transition occurred between the C.B bottom and V.B top, R value is become $1/2$ ^[14,15]. In indirect transition, top of the valence and minimum of the conduction differ (i.e. $\vec{\Delta k} \neq 0$)^[16]. Indirect transition requires phonons absorption to balancing the crystal momentum. The electrons cannot make a direct (perpendicular) transition from the valence band to the conduction band because of the change in their crystal momentum. Such transition may take place by a two-step process. The electron is absorbs two photon or absorbs a one photon and emits one phonon. This transition is also described by the eq. (4). The allowed indirect transition occurs from V.B top to C.B bottom, and, $r = 2$. Wherever, the transitions are occur in any point on V.B top to C.B bottom and $r = 3$ ^[15].

Optical constants involved:

1- Extinction coefficient (k), 2- Refractive index (n), 3- Real parts, 4- Imaginary parts, (n) could evaluate as equation^[16].

$$n = \left[\frac{4R}{(R-1)^2} - k^2 \right]^{1/2} - \frac{(R+1)}{(R-1)} \quad (5)$$

R : is the reflectance as^[15]:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (6)$$

The extinction coefficient has linked with wave exponential decay as^[15-17]:

$$k = \frac{\alpha \lambda}{4\pi} \quad (7)$$

λ : is incident radiation wavelength as^[16]

$$\alpha = 2.303 \frac{A}{t} \quad (8)$$

T: is sample thickness, A: is absorption. Imaginary part and real part (ϵ_r and ϵ_i) could be evaluated by^[17]:

$$\epsilon_r = n^2 - k^2 \quad (9)$$

$$\epsilon_i = 2nk \quad (10)$$

2. Experimental

The $\text{Cd}_x\text{Se}_{1-x}$ with ($x=0.5$) compound was prepared as alloy by using stoichiometric and high purity (99.999%) cadmium metal packed under argon, obtained from Certified Chemicals, UK and high purity (99.999%) selenium metal obtained from Balzers, Switzerland. The element weighted according to its atomic weight and then mixing in quartz tube evacuated at pressure of (10^{-3} mbar). The tube was sealed and heated in electrical program controller furnace of type (Nabertherm), Germany, at a rate of 120K per hour in steps up to 773K, and balanced at the temperature for (2) hours and then raised to 1173K, and also balanced at the temperature for (2) hours and then cooled at 25 C, then ampoule was broken and the prepared compound of CdSe was taken out and powdered to a fine grain powder. The powder of the compounds was used as a source of the evaporation to prepare the films. The used films are prepared by vacuum evaporation methods at 25 C with deposition rate (R_d) of about (1.5×10^{-3} $\mu\text{m}/\text{sec}$) and thickness (0.5, 1, 1.5 and 2) μm and annealing temperature (373, 423, and 473)K. CdSe structure is tested by X-ray by using a Shimadzu XRD-6000 Japan. Size of Crystallite CdSe was evaluated by Scherrer's formula:

$$D = \frac{K'\lambda}{\beta' \cos \theta} \quad (11)$$

λ is wavelength of X-ray, D is size of the crystallite, θ is Bragg's diffraction angle, K' some constant with a value of 0.9, β' is angular line width of half maximum intensity^[2]. The optical properties of CdSe films deposited on glass substrates with different thicknesses and annealing temperatures at constant substrate temperature 300K were studied in the wavelength rang (0.4-1.1) μm by using Shimadzu UV-visible recorder spectrophotometer model UV-160.

3. Results and Discussions

3.1 X-ray diffraction

It included film of cadmium selenide which make at many thicknesses (0.5, 1, 1.5, 2) μm , as Fig.(1), and 2 μm film exposure to 473K for (1) H as Fig. (2)

X-ray level peaks in all films showed the films are crystalline. Table (1) demonstrated d-values with standard (JCPDS- ICDD file No. 8-459). Results of d-values are same with values for the hexagonal compounds. It meaning the prefect directions lies along [002]. Also it similar to results of Al-Lamy *et al.*,^[17] and Nasir *et al.*,^[18]. The cadmium selenide films make by chemical deposition by Nair *et al.*,^[19].

The crystallite size (grain diameter), D, of the CdSe films are calculated by using the Scherrer's formula (11), and as Table (1). The table showed size of films increases with thickness increasing, doping and annealing that occur due to the recrystallization. Our results are same with results of Kissinger^[20], Hayashi *et al.*^[21] and Perna *et al.*^[22]. The peak of X-ray diffraction showed prefect crystallization as in^[20, 23].

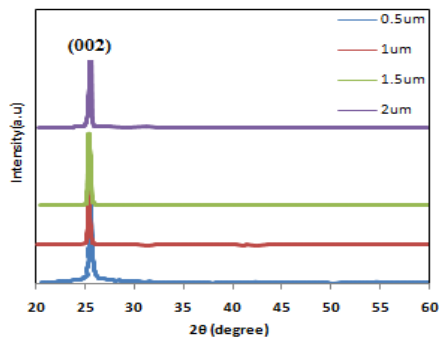


Fig.1 X-ray diffraction pattern of CdSe film having (0.5, 1, 1.5, 2) μm thickness at R.T

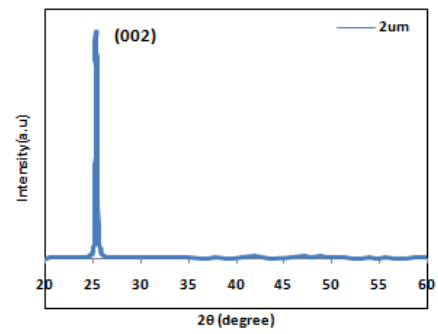


Fig.2. X-ray diffraction pattern of CdSe film having $2\mu\text{m}$ thickness annealed at 473K for one hour

Table (1): X-ray diffraction data for CdSe films.

T_a (K)	Thickness (μm)	2θ (degree)	$d_{\text{stand.}}$ (\AA)	(I/I_o) stand.	$d_{\text{exp.}}$ (\AA)	(I/I_o) exp.	(hkl)	D(nm)
R.T	0.5	25.459	3.510	70	3.4957	100	002	27.303
	1	25.386	3.510	70	3.5056	100	002	27.974
	1.5	25.434	3.510	70	3.4991	100	002	37.791
	2	25.387	3.510	70	3.5055	100	002	38.249
473	2	25.441	3.510	70	3.4981	100	002	38.967

3.2 The Optical Properties

The absorbance range of the used films in our study is tested with many temperatures and thicknesses as Fig. (3), the absorbance range changed to be long wavelengths with increasing temperature. The absorbance become low with elevated of temperature attributed to changing size of the crystal and transmittance is increased. The absorbance becomes high with thickness increasing due to thicker film.

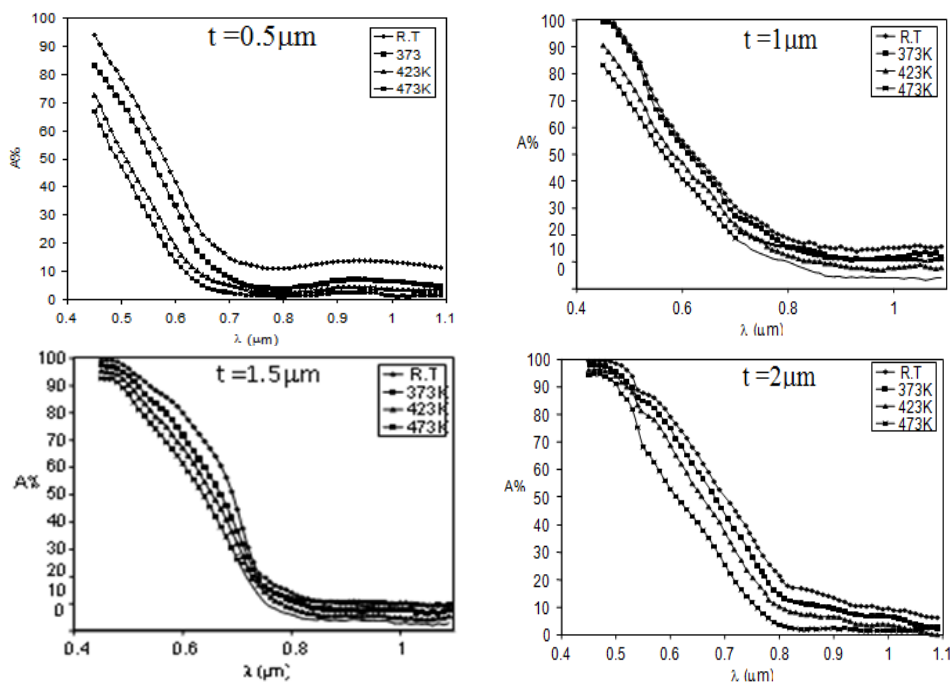


Fig.3. Absorbance spectrum as a function of wavelength for CdSe films at different thicknesses and annealing temperatures

The transmittance becomes high with increasing of the temperature. The changed of transmittance to be short wavelengths with increasing of temperature due to the crystal structure of the film by increasing the thickness as Fig. (4). The transmittance become low but not with elevating of thickness and changed to long wavelengths, that belong to creation levels at the energy band by the thickness, that same with results of Baban *et al.*^[5] and Hambrock *et al.*^[24].

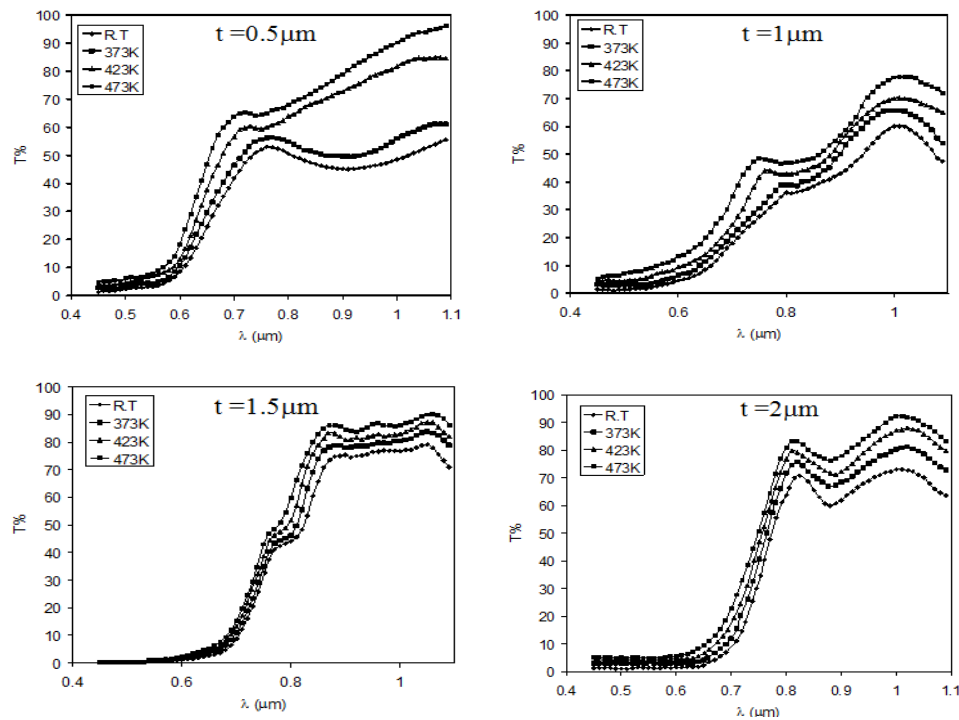


Fig. 4 Transmittance spectrum as a function of wavelength for CdSe films at different thicknesses and annealing temperatures

The absorption coefficient α was determined, wherever; the absorption coefficient versus variation is examination of the wavelength of many thicknesses and temperatures as Fig. (5). α decreased with increased T_a of the thicknesses as Table (2). That same with results of Rassam^[25]. The absorption coefficient variation as a function of films thickness is non-systematic, and that belong to the crystal structure of the films. (α) Become high with the increasing of the thickness. As well as (α) has similar to the properties of the absorbance as equation (8). The absorbance become high with increasing of the thickness of the films.

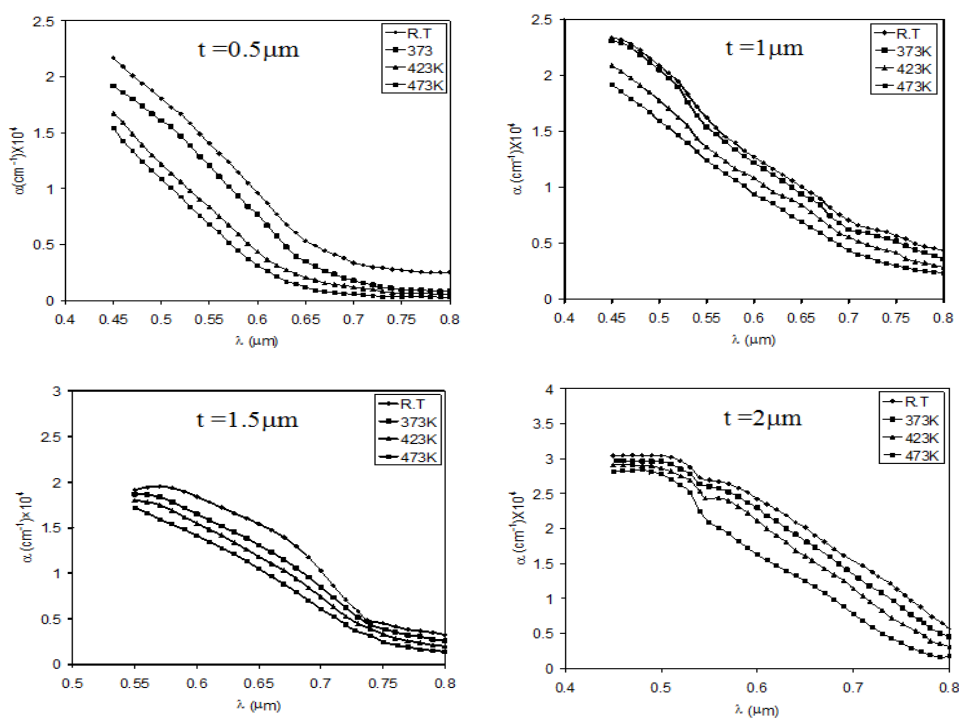


Fig. 5 Absorption coefficient as a function of wavelength for CdSe films at different thicknesses and annealing temperatures.

The optical energy gap of films is detected. A plot of $(\alpha h\nu)^2$ versus $h\nu$ films with many thicknesses and temperatures as Fig. (6). the plot is linear showed direct band gap of the films. The values of the optical energy gap are decreases with increasing of T_a due to the growth of the crystallites as shown in Table (2) and Fig. (6). The result data is same results of Ichimura^[26], Eman *et al.*^[27], and Baban *et al.*^[28]. Gap of the optical energy become low with elevating the thickness as Fig. (7), Table (2). That occur due to increasing of the density in the E_g , that results change to lower values as well as like data of Al-Fawadi^[29]. Value of E_g become low with increasing of the thickness(0.5-1) μm ; while the variation in energy gap value with thickness more than 1 μm is very slight. The refractive index of CdSe is which submitted for many temperatures and thicknesses as Fig. (8) and Table (2), that mean the refractive index become high with elevated (T_a) value for increasing of the films compactness under heating with increasing of thickness. The results are same with results of Baban *et al.*^[5]. The (n) variation are showed in figure (9). This is due to different effective thickness of the films, and to the variation in crystal structure of the films.

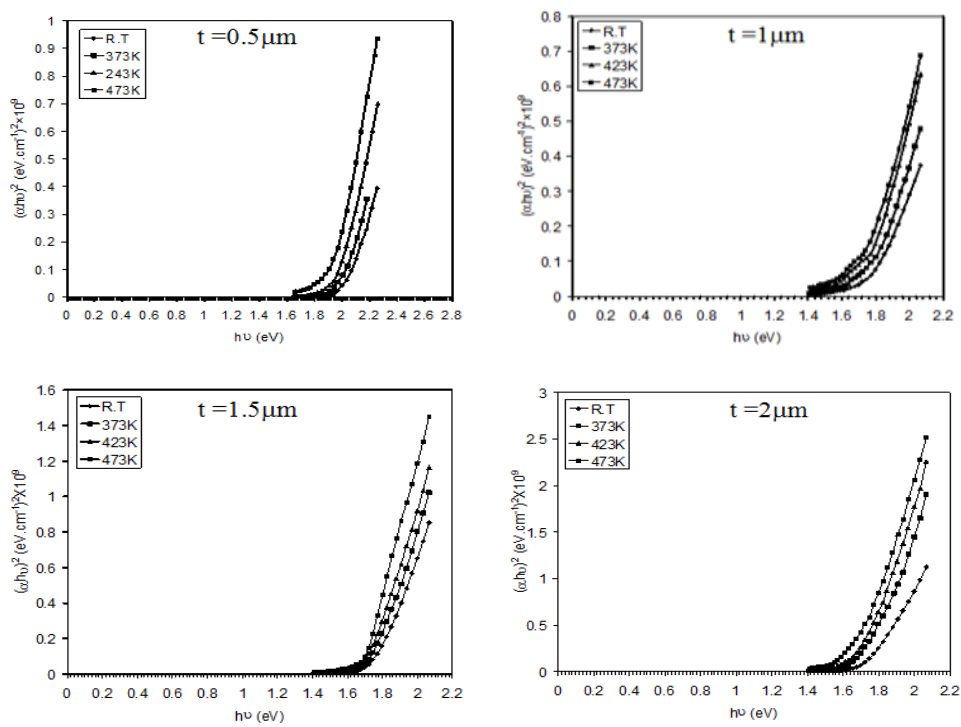


Fig. 6 $(\alpha h\nu)^2$ as a function of $h\nu$ for CdSe films at different thicknesses and annealing temperatures

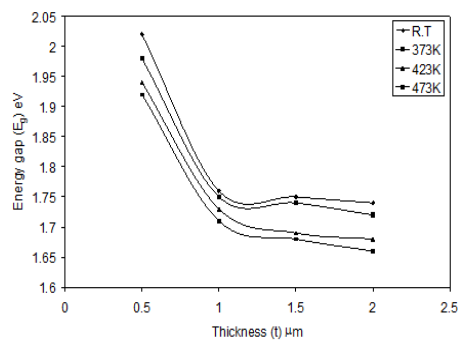


Fig. 7 Variation of energy gap of CdSe films a function of thickness at different annealing temperatures at $\lambda = 0.8 \mu\text{m}$

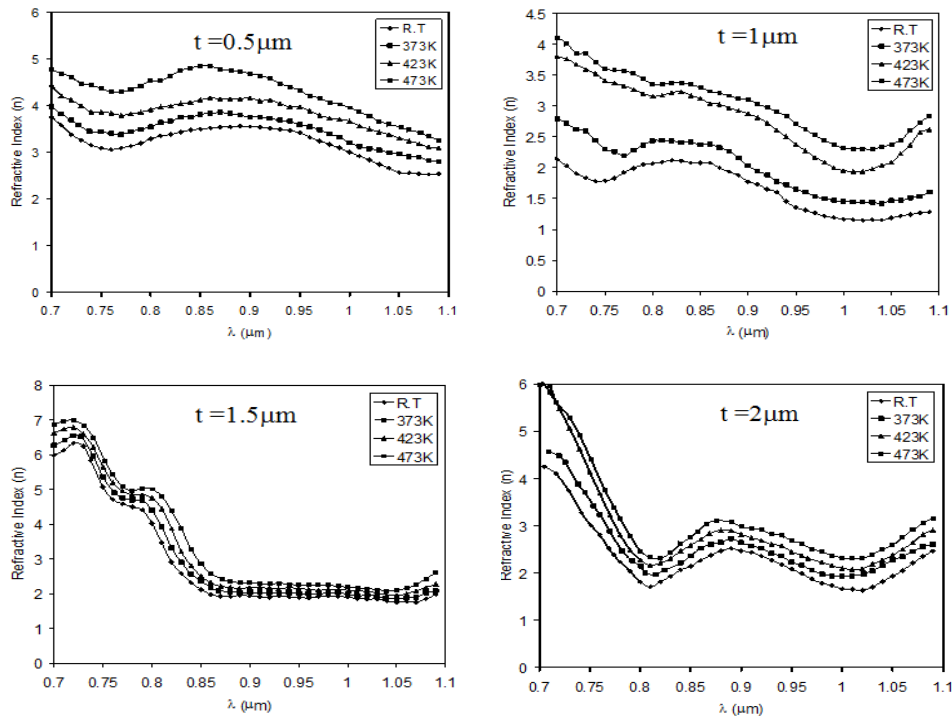


Fig. 8 Refractive index as a function of wavelength for CdSe films at different thicknesses and annealing temperatures

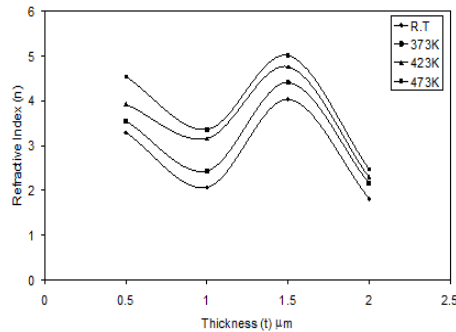


Fig. 9 Variation of refractive index as a function of thickness of CdSe films at different annealing temperature at λ = 0.8 μm

The extinction coefficient (k) decreases with increasing of annealing temperatures for all films, and decreases by increasing of thickness in the range (0.7– 1.1)μm as shown in Fig. (10) and Table (2). That belong to same reason that confirmed before because (k)properties is same to (α).

The variation of k versus films thickness is not systematic as shown in Fig. (11). fall and Rise in the extinction coefficient are for absorbance variation with increase of thickness.

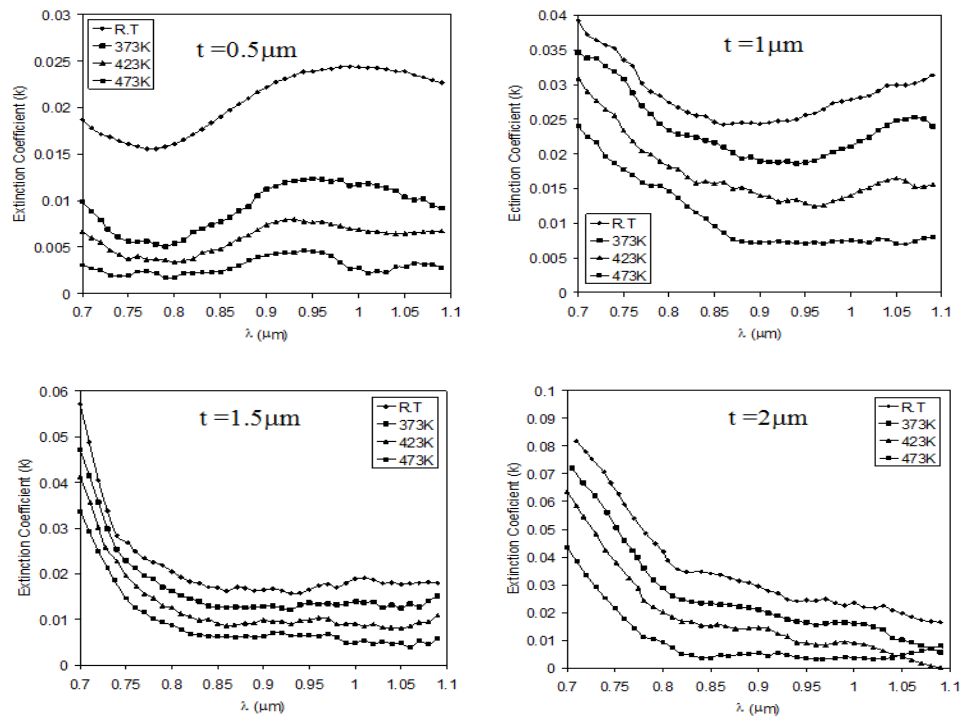


Fig. 10 Extinction coefficient as a function of wavelength for CdSe films at different thickness and annealing temperatures

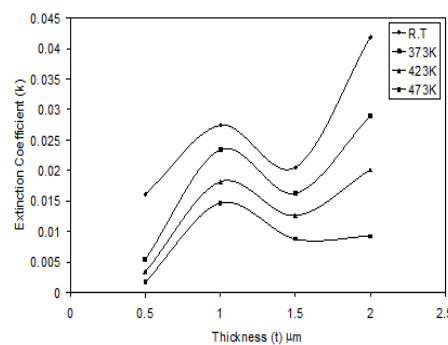


Fig. 11 Variation of extinction coefficient as a function of thickness of CdSe films at different annealing temperatures at $\lambda = 0.8\mu\text{m}$

The dielectric constant formed from imaginary part and real part according to electromagnetic frequency. The imaginary part and real part of CdSe films versus wavelength was found in $(0.7-1.1)\mu\text{m}$ as range at several thicknesses and several temperatures as Fig. (12) and (14). Imaginary part and real part variation with elevated of the radiation wavelength for the changing of absorbance and reflectance. The real part have same value with refractive index because (k^2) is small when it compared with (n^2) but imaginary part based on (k) value, that is linked with absorption. Imaginary part is radiation absorption by carriers^[29]. However real part become high with increasing of temperatures due to same reason which mentioned before, but imaginary part become low with increasing of temperatures of the annealing.

The variation of imaginary part and real part of film thickness are demonstrated in Figs. (13) and (15) wherever, it showed all the changed between imaginary part and real part values are non-systematic, that indicate to the material possess a specialized property with thickness.

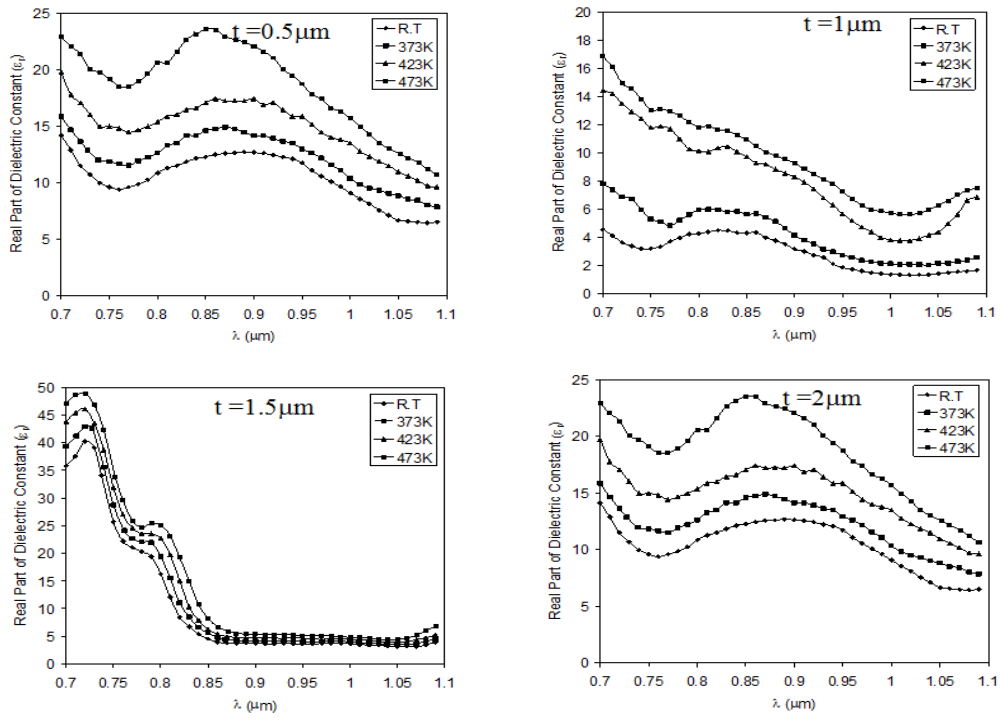


Fig. 12: Real part of dielectric constant a function of wavelength for CdSe films at different thicknesses annealing temperatures

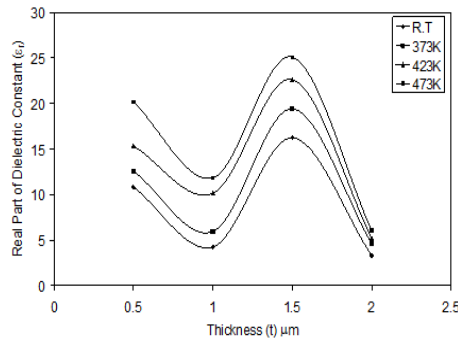


Fig. (13): Variation of real part of dielectric constant as a function of thickness For CdSe films at different annealing temperatures at $\lambda = 0.8 \mu\text{m}$

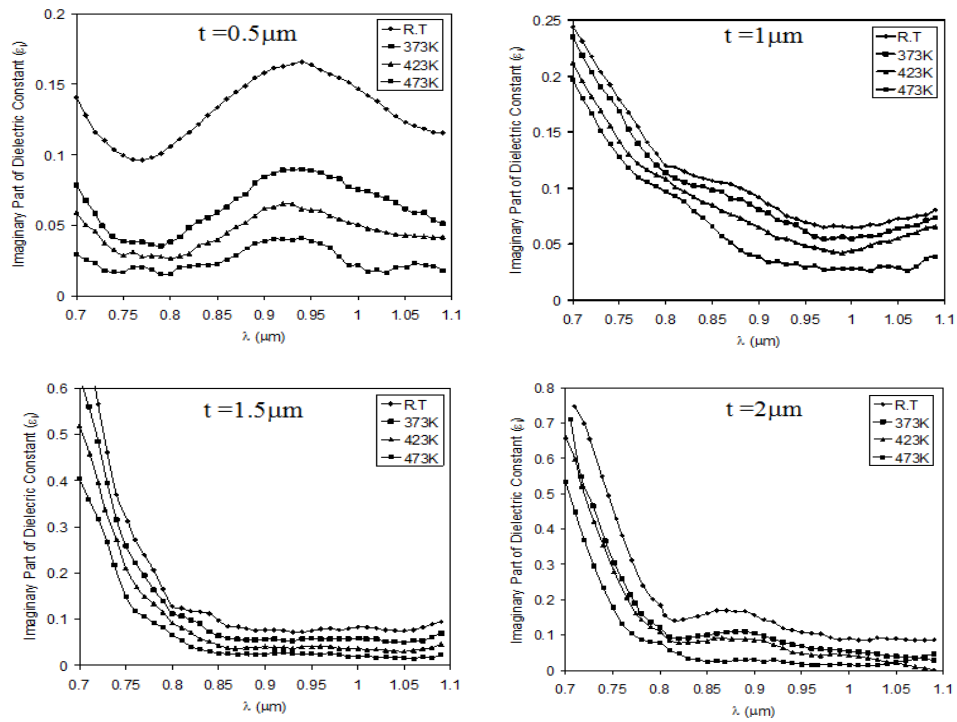


Fig. (14): Imaginary part of dielectric constant as a function of wavelength for CdSe films at different thickness and annealing temperatures

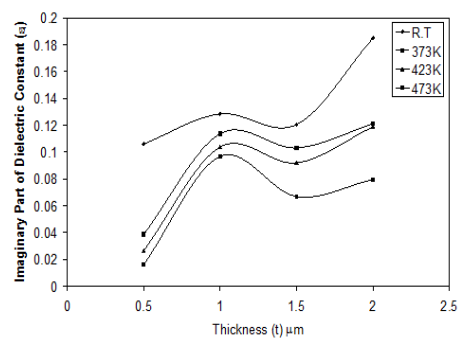


Fig. (15): Variation of imaginary part of dielectric constant as a function of thickness for CdSe films at different annealing temperatures at $\lambda = 0.8\mu\text{m}$

Table (2): Optical properties parameters of CdSe films at different thicknesses and annealing temperatures at $\lambda = 0.8\mu\text{m}$.

Thickness (μm)	T _a (K)	$\alpha \times 10^4$ (cm^{-1})	E _g (eV)	N	k	ϵ_r	ϵ_i
0.5	R.T	0.253	2.02	3.291	0.016	10.831	0.106
	373	0.085	1.98	3.549	0.005	12.596	0.038
	423	0.052	1.94	3.917	0.003	15.347	0.026
	473	0.027	1.92	4.536	0.001	20.17	0.015
1	R.T	0.430	1.76	2.066	0.027	4.269	0.128
	373	0.357	1.75	2.439	0.023	5.948	0.113
	423	0.285	1.73	3.16	0.018	10.14	0.103
	473	0.230	1.71	3.36	0.014	11.84	0.096
1.5	R.T	0.322	1.75	4.03	0.020	16.24	0.120
	373	0.255	1.74	4.406	0.016	19.417	0.103
	423	0.198	1.69	4.758	0.012	22.642	0.091
	473	0.138	1.68	5.01	0.008	25.099	0.066
2	R.T	0.567	1.74	1.816	0.041	3.297	0.185
	373	0.454	1.72	2.15	0.028	4.62	0.121
	423	0.316	1.68	2.285	0.020	5.223	0.118
	473	0.173	1.66	2.466	0.009	6.084	0.079

4. Conclusions

The analysis by XRD found films of CdSe are hexagonal crystalline and perfect direction is (002) in all experimented temperatures, vary doping and thicknesses. The grain size increases with increasing thicknesses and doping. The optical transitions in CdSe film has direct optical energy gap reduce with elevated temperatures of annealing; and reduce with elevating thickness.

References

- [1] E.M.N.Al-Fawadi, " Um-Salama Science Journal ",**3**(2), 278 (2006).
- [2] E.M.Al-Fwade, S.K.J.Al-Ani,Th.K.Al-Ani, "Iraqi Journal of Physics",**9**(16), 61, (2011).
- [3] H. H. Mohammed, S. K.J.Al-Ani, E.M. N.Al-Fwade, "Renewable Energy", **25**(4), 585 (2002).
- [4] E.M.N. Al-Fwadi, M.F.Al-Alias, F.Y.M. Al-Shaikley, "Iraqi Journal of Physics",**5**(1), 63, (2008).
- [5] C. Baban, G. I. Rusu, P. Prepelita, J.Optoelectron. Adv. M., **7**(2), 817 (2005).
- [6] D. D. O. Eya, The Pacific Journal of Science and Technology, **7**(1), May (2006).
- [7] R. M. Moore, J. T. Fischer and F. Koziol, Thin Solid Films, **26**, 363 (1975).
- [8] A. Giardini, M. Ambrico, D. Smaldone, R. Martino, G. P. Parisi, V. Capozzi, G. Perna, Applied Surface Science, **106**, 144 (1996).
- [9] G. Perna, V. Capozzi and M. Ambrico, J. Appl. Phys., **83**(6), (1998).
- [10] R. B. Konda, R. Mundle, H. Mustafa, O. Bamiduro, A. K. Pradhan, Appl. Phys. Lett., **91**, 191111, (2007).
- [11] C. Kittel, "Introduction to Solid State Physics, 8th ed., John Wiley and Sons, Inc., New York, (2005).
- [12] M. A. Green, Solar Cells, Operating Principles, Technology and System Applications", Prentice Hall, Inc., Englewood Cliffs, (1982).
- [13] J. I. Pankove, "Optical Processes in Semiconductors", Prentice – Hall, Inc., Englewoodcliffs, New Jersey (1971).
- [14] J. Millaman, "Microelectronics", Murray-Hill, Book Company Kogakusha, (1979).
- [15] J. S. Blakemore, "Solid State Physics", 2nd ed., W. B. Saunders Company, Philadelphia, (1974).

- [16] J. C. Mainfacier, J. Gasiot and J. P. Fillard, "J. Phys. E. Sci. Instrum.", **9**, (1989).
- [17] H. K. Al-Lamy, E.M.N.Al-Fawade, H. J. Abdul Ameer, "Iraqi Journal of Physics",**5(7)**, 169, (2008).
- [18] E.M.Nasir, H. Kh. Al-Lamy , H.J.Abdul-Ameer, "Proceeding of 3rd scientific conference of the College of Science, University of Baghdad 24 to 26 March."2169-2164, (2009).
- [19] M. T. S. Nair, P. K. Nair, R. A. Zingaro and E. A. Meyers, J. Appl. Phys., **74(3)**, 1879, (1993).
- [20] N. J. S. Kissinger, M. Jayachandran, K. Perumal and C. S. Raja, "Bull. Mater. Sci.", **30(6)**, 547 (2007).
- [21] T. Hayashi, R. Saeki, T. Suzuki, M. Fukaya and Y. Ema, J. Appl. Phys.,**68(11)**, 5719 (1990).
- [22] G. Perna, V. Capozzi, S. Pagliara, M. Ambrico and D. Lojaco, "Thin Solid Films",**387**, 208 (2001).
- [23] E.M.N.Al-Fawad, " Um-Salama Science Journal ",**5(4)**, 593 (2008).
- [24] J. Hambrock, A. Birkner and R.A. Fischer, J. Mater. Chem., **11**, 3197 (2001).
- [25] N.T. Rassam, "Structural, Electrical and Optical Transport Properties of Evaporated CdSe_{1-x}T_x Thin Films", Ph.D. Thesis, University of Baghdad, Collage of Education (Ibn AL-Haitham), Dept. of Physics, (2000).
- [26] M. Ichimura, N. Sato, A. Nakamura, K. Takeuchi and E. Arai, Phys. Stat. Sol., (a) **193(1)**, 132 (2002).
- [27] Eman M.N.Al-Fawadi Tariq. J. Alwan, Iqbal S. Naji, Um-Salama Science Journal ",**6(1)**, 149 (2009).
- [28] C. Baban, G.G. Rusu, I. I. Nicolaescu and G.I. Rusu, J. Phys.: Condens. Matter, **12**, 7687, (2000).
- [29] E.M.N.Al-Fawadi, " Um-Salama Science Journal ",**3(1)**, 180 (2006).