Study Influence of Substrate Temperature on Optical Properties of CdS Thin Films Prepared by Chemical Spray pyrolysis

Karrar Mahdi Saleh
Ashur Secondary School ,Directorate of Education Baghdad Rusafa first, Baghdad, Iraq
Amaramar123h@gmail.com

Article history: Received in:18 October 2018, Accepted in:13 December2018, Publish January, 2019

Abstract

This study aims to prepare Cadmium Sulphide (CdS) thin films using thermal Chemical Spray Pyrolysis (CSP) on glass of different temperatures substrate from cadmium nitrate solution. Constant thickness was (430 ± 20 nm) and the effect of substrate temperature on the optical properties of prepared thin films. Optical properties have been studied from transmittance and absorbance spectral within wavelengths range (360 - 900 nm). The results show that all the prepared films have a direct electron transitions and optical energy gap between (2.31-2.44 eV). They also show that the transmittance and optical energy gap of films prepared from nitrate solution increase with increasing of substrate temperature, then transmittance start downward with the continued increase in temperature (400, 450) ^{o}C.

Keywords: Optical properties, Chemical Spray Pyrolysis (CSP), Cadmium Sulphide (CdS), substrate temperature.

1. Introduction

The study of thin film materials is of interest to researchers as they are the main elements of the continuous technological advances in the fields of electron, optical and magnetic devices [1]. The term thin films used to describe a layer or several layers of solid atoms that are deposited on a solid substrate so that the thickness of the thin films is less than (1μm). Thin films have a large surface area compared to their size and therefore exhibit different characteristics than those of bulk materials. In addition, the possibility of changing their optical and electrical characteristics depend on the methods of preparation and conditions, such as changing the type of additive or change the temperature of the substrate and type such as glass, quartz, silicon or aluminum and others [2].Thin-film technology is one of the most important technologies that has contributed to the development and study of semiconductors, which have recently gained considerable interest in nanotechnology researchers and have given a clear idea of many of the physical and chemical properties of these substances whose properties are difficult to obtain naturally [3].

The importance of semi-conductor materials in the scientific and industrial fields has been emphasized for its unique physical characteristics. It has been used in many applications for example: transistor, integrated circuits, diodes used as emitters, light emitting diodes, solar cells, photovoltaic filters, reagents and magnetic memory devices [4,5]. Optical properties are very important in studying the behavior of semiconducting materials, by means of which the appropriate practical application can be learned. Visual behavior is closely related to crystalline structure of matter and the composition of energy levels. The optical characteristics

https://doi.org/10.30526/32.1.1982 Vol. 32 (1) 2019

of (CdS) thin films prepared at different substrate temperatures, including transmittance and absorption measurements for all thin films within the range of wavelengths (360 – 900) nm and at temperatures of (250, 300, 350, 400, 450) ºC and (430 ± 20nm). Reflectivity and many optical constants were calculated by means of the Transmittance and absorptive spectra of these thin films, Optical Energy gap, Extinction Coefficient, refractive index, dielectric constant real and imaginary partially.

2. Materials and methods

2.1. Preparation of Solution

Cadmium supplied thin films are introduced in a chemical degradation manner:

1. The water solution of the cadmium hydrothermal nitrate (Cd $(NO_3)_2.4H_2O$) was a quick soluble white substance in water of molecular weight (308.47g / mol) and purity (99.999 %) which was a source of cadmium ions (Cd^{+2}) 0.1M) by dissolving a certain weight of cadmium nitrate using a magnetic mixer in a certain volume of distilled water according to the following relationship [6]:

$$M = \frac{Wt}{Mwt} \times \frac{1000}{V} \tag{1}$$

Where: M is Molecular concentration**, $\mathbf{W_t}$** is The weight required to melt, **V** is Volume of distilled water, $\mathbf{M_{wt}}$ is Molecular weight of matter

2. The thiourea solution (CH_4N_2S), a white soluble powder (76.11g / mol) with purity (99%) and 0.1 mg, is a source of sulfur ions (S^{-2}).

2.2. Thin film deposition

CdS thin films are placed on the heated glass substrate at different temperatures (250, 300, 350, 400, 450) with a spray of the solution of the cadmium nitrate and the thiourea solution by spray on the hot glass substrate, limiting the reaction by the heat. Cadmium supplied is deposited on the surface of the substrate according to the chemical reaction that follows:

$$Cd\,(NO_3)_2 + CH_4N_2S \longrightarrow CdS + 2NH_4 + NO_3 + CO2$$

2.3. Factors Influencing Thin Films Properties

2.3.1. Substrate Temperature

Samples are prepared of (CdS) with a temperature degree (623k), They formed highly corrosive thin films with good homogeneity, free from aggregations and defects.

2.3.2. Solution Type

The solution has an important role in the homogeneity and adhesion thin films and degree of crystallization where the solution of cadmium nitrate was used to prepare (CdS) thin films, as well as the iron nitrate solution to prepare the doping thin films (CdS: Fe^{+3}).

2.3.3. Substrate Position

Place the substrata on the center of the electric heater plate to obtain homogeneity in the films and the spray device is vertical on the substrata.

https://doi.org/10.30526/32.1.1982 Vol. 32 (1) 2019

2.3.4. Vertical Distance

We obtained the best result at a height of (29 ± 1) cm. Increasing this distance leads to the volatilization of the solution spray away from the substrata surface. Reducing this distance leads to the concentration of the solution spray in one spot and thus the substrata is not homogeneous.

2.3.5. Spray Rate

The spray rate is calculated by the flow of the solution from the solution per minute. The best spraying rate in this experiment is (6 ml / s).

2.3.6. Average Spray Time

In this study, the solution was sprayed (8s) followed by a (2) min stop (2min) and repeated several times until the required thickness are reached.

2.3.7. Air Pressure

Air pressure was installed in the glass chamber of the spray device when all thin films are prepared up to (10^5 N / m^2) for homogeneous membranes.

3. Results and discussion

For optical properties and electronic transitions, a spectrometer (UV-1700-1650, UV-Visible Recording Spectrophotometer), supplied by Japan's Shimadzu Absorption Absorption (A) and Transmittance (T), was used for all prepared thin films and for wavelengths (380 - 900 nm) and at room temperature.

3.1. Transmittance (T)

The change in Transmittance with the wavelength of the thin films (CdS) and at different substrate temperatures, as illustrated in **Figure1**. The results showed that the Transmittance increases with the increase of the wavelength of all thin films and increases with the increase of the temperature of the substrate to (350)℃ and then begins with decreasing and continuing to increase the temperature of the substrate. This change is due to two reasons, the change of reflectivity due to the change of surface roughness and absorption due to the change of energy gap.

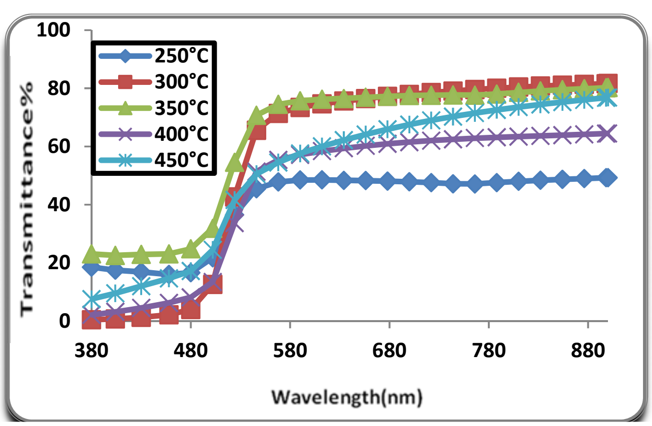

Figure 1. Transmittance relationship as function of the wavelength of thin films prepared at a different substrate temperature.

3.2. Absorbance (A)

The absorption is decreases with increasing wavelength of all thin films. This illustrated from **Figure 2**. The reason for this is that the energy of photons falling at high wavelengths (where low energies) are insufficient for electronic transitions (350℃) and then increase with increasing the substrate temperature and this may be due to a change in the value of the optical energy gap.

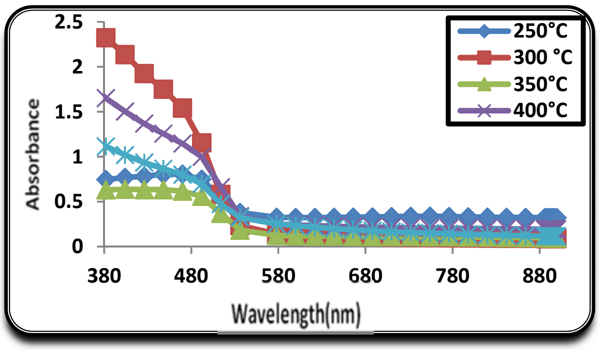

Figure 2. Absorption relationship as a function of the wavelength of the thin films Prepared at a different substrate temperature.

3.3. Reflectance (R)

The reflectivity of the surfaces of pure cadmium sulfide from the absorption (A) and the Transmittance (T) spectra of these thin films were calculated according to the following relationship [7]:

$$R + A + T = 1 \tag{2}$$

We observe from **Figure 3.** that the reflectivity decreases with the increase in wavelength and also observe that the reflectivity decreases with the increase of the substrate temperature up to (350℃) and then begins to increase with increasing temperature. This is due to the change of roughness of the surface with increasing temperature where it is known that the roughness is inversely proportional to the particle size.

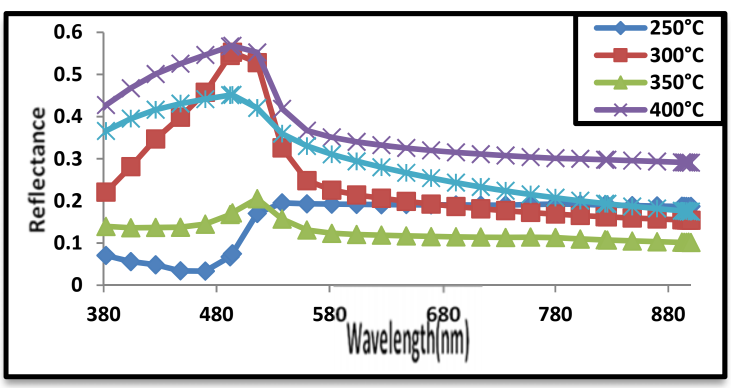

Figure 3. Relativity relationship as a function of the wavelength of the thin films Prepared at different substrate temperatures.

3.4. Absorption Coefficient (α)

It is known that the amount of energy reflected, absorbed and permeable depends on the surface and nature of the thin films material and the wavelength of the falling photonic beam [8]. The absorption coefficient was calculated using the following formula [9]:

$$\alpha = 2.303 \frac{A}{t} \quad (3)$$

The change in the absorption factor as a function of the wavelength of the (CdS) thin films and the different substrate temperatures, as illustrated in **Figure 4**. Note that all thin films have a high absorption factor ($\alpha > 104$ Cm^{-1}). This is likely to result in direct electronic transitions [10].

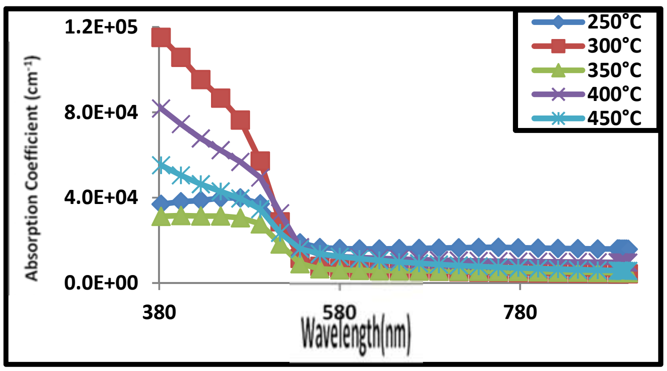

Figure 4. The absorption coefficient relationship as a function of the wavelength for thin films prepared at different substrate temperatures.

3.5. Optical Energy Gap (Eg)

The optical Energy gap is defined as the energy needed to excite the electrons from the top of the valence beam to the bottom of the conduction beam. [11] It is called the forbidden or prohibited because the period of time the electron has energy in this region is very short. [12] The most important optical constants that rely on the physics of semiconductors to manufacture many electronic devices such as solar cells, reagents, optical diodes and others [13]. The optical Energy gap was calculated using the following equation [14]:

$$\alpha hv = B(hv - Egopt)r \quad (4)$$

Where:

B: The proportionality constant depends on the nature of the material.

r: The transition order is visual and depends on the nature of the electronic transmission.

By drawing the graphic relationship between $(\alpha h\upsilon)^2$ and $(h\upsilon)$, as in **Figure 5.** the optical Energy gap was calculated when $[(\alpha h\upsilon)^{2} = 0]$ from the junction area of the tangent with the $(h\upsilon)$ axis. Thus, the intersection point represents the energy gap. **Figure 6.** shows an increase in the energy gap with increasing the temperature of the substrate. This can be explained by the fact that increasing the temperature improves the crystalline state of the grid, thus increasing the optical Energy gap.

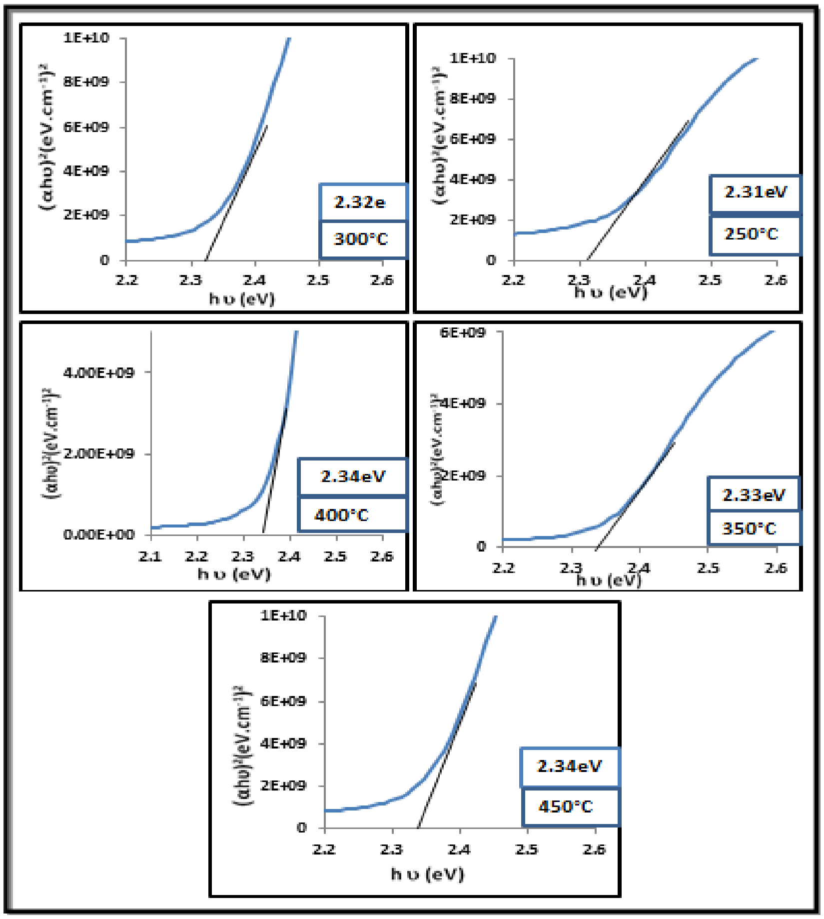

Figure 5. Relationship $(\alpha h\upsilon)^2$ with photon energy of thin films prepared at different substrate temperatures

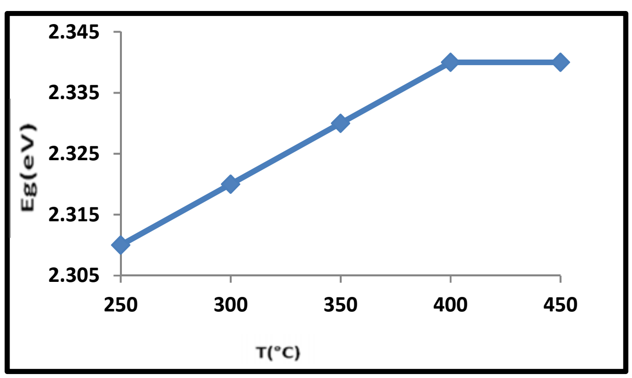

Figure 6. Optical Energy gap values for prepared thin films with different substrate temperatures

3.6. Extinction Coefficient (k_o)

The Extinction Coefficient was calculated according to the following formula [15]:

$$ko = \frac{\alpha\lambda}{4\pi} \quad (5)$$

Figure 7. shows the change in the Extinction Coefficient as a function of the wavelength of the thin films (CdS) for the different substrate temperatures. It can be noted that the coefficient of inertia decreases by increasing the wavelength, and a sharp decrease at wavelength (λ > 500 nm). This is due to the decrease in absorption at high wavelengths, when the falling photon energy is less than the energy gap value. The results show a decrease and a slight increase continuously the increase in the Substrate temperature in the values of the Extinction Coefficient, and the reason for this change to the local levels formed within the energy gap, which led to a change in the absorption coefficient and then change the Extinction Coefficient.

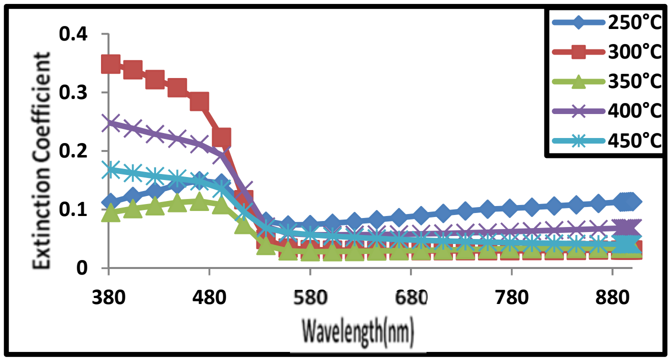

Figure 7. Extinction coefficient relationship as a function of the wavelength of thin films prepared at different substrate temperatures.

3.7. Refractive Index ($n_\circ$)

According to the refractive index using the following relationship [16]:

$$n_\circ = \frac{c}{v} \tag{6}$$

Where: C is the speed of light in the vacuum. **v**: The speed of light in the material.

Note from **Figure 8.** that the refractive index increases with wavelength increase when (λ < 500 nm). Then starts to decrease when (λ > 500nm) and that the refractive index changes as the base temperature increases. And that the highest value of the refractive index curve corresponds to the energy gap, indicating that direct electronic transmissions occur at that range of energy.

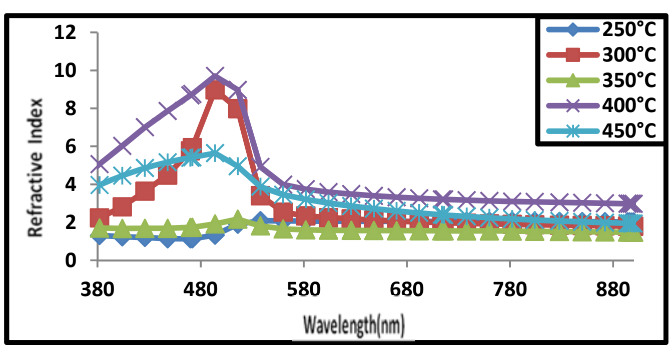

Figure 8. Refractive index relationship as a function of the wavelength of thin films prepared at different substrate temperatures.

3.8. Die

The interaction between light and center charges occurs because of the energy absorption process in the material. This reaction results in polarization of the medium charge. This polarization is usually described by the complex Dielectric Constant of the medium (ε*) [17]. According to the Dielectric Constant with its real (ε_r) and imaginary (ε_i) of the two equations:

$$\varepsilon r = no2 - ko2 \quad (7)$$

$$\varepsilon i = 2nk0 \quad (8)$$

It can be seen that the values of (ε_r) and (ε_i) increase with wavelength increase up to (λ ≈ 500 nm) and then start with decreases and for all Thin films. In addition, the values of the Dielectric Constant in its parts change with increasing the base temperature and that the values of the real part are greater than the imaginary part values, (see **Figures 9. and 10.**) respectively, since the real part represents the polarization scale of the membrane. The imaginary part represents the amount of energy dissipated by the movement of polarized aggregates and in the form of heat.

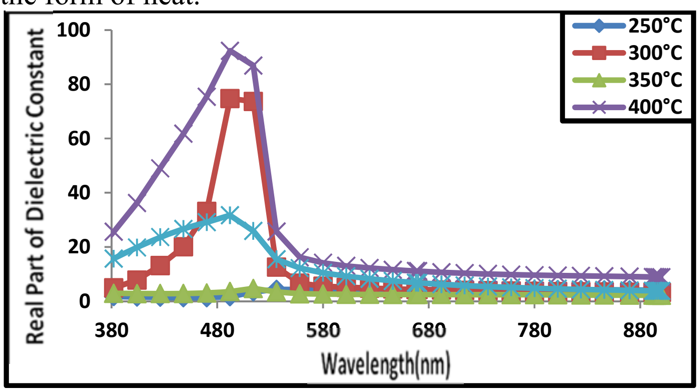

Figure 9. Relation of the real part of the Dielectric Constant as a function of the wavelength of the thin films prepared at different substrate temperatures.

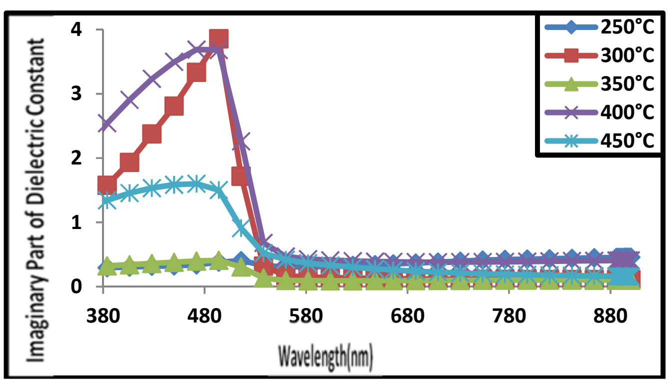

Figure 10. Relation of the imaginary part of the Dielectric Constant as a function of the wavelength of the thin films Prepared at different substrate temperatures.

4. Conclusions

CdS thin films permeability higher than 70% for thin films prepared (400 ± 10 nm) and at different substrate temperatures (300, 350) ºC while substrate temperatures (250, 400, 450) ºC were lower within the range of wavelengths (1100 - 100) nm, all thin films have a high absorption factor (α > 104 Cm^{-1}). This is likely to cause direct electron transitions within wavelengths (380-880) nm, owning all CdS thin films in the current search optical Energy gap for direct transmission allowed. By increasing the substrate temperature thin films to (250,300,350,400 ºC), the value is increased of the optical Energy gap from 2.31 to 2.34 eV and that the substrate temperature increase to 450 ºC did not change the value of the optical Energy gap 2.34eV. The increase in the value of the substrate temperature prepared thin films (250,300,350,400,450) ºC led to a change in the values of the coefficient of inertia, refractive index and constant insulation in the real and imaginary parts within wavelengths (380-880) nm.

References

1. Wasa, K.; Kitabatake, M.; Adachi, H. *Thin Film Materials Technology*. William Andrew, **2004**.
2. Eckertova, L. *Physics of Thin Films*. Plenum press, New York and London, **1977**.
3. Radi,P; Brito-Madurro,A; Madurro, J; Dantas, N. Characterization and Properties of CdO Nanocrystals Incorporated in Polyacrylamide. *Brazilian Journal of Physics***. 2006**. *36, 2*, 412-414.
4. Greve, D. *Semiconductor Devices and Technology*. **2012**.
5. Singh, J. *Electronic and Optoelectronic Properties of Semiconductor StructuresCambridge University Pres,* London, **2003**.
6. Usharani, K.; Balu, A.; Shanmugavel, G.; Suganya, M; Nagarethinam, V. Transparent Conducting CdO Thin Films Fabricated by Low Cost Simplified Spray Technique Using Perfume Atomizer. *International Journal of Scientific Research and Reviews (IJSRR)*. **2013***, 2, 3*, 53-68.
7. Gusev,A. I.; Rempel,S. V.; X-ray diffraction study of the nanostructure. Resulting from decomposition of $(ZrC)_{1-x}$ $(NbC)_x$ solid solutions. *Inorganic Materials*. **2003**, *39*, *1*, 43- 46.
8. Ilican,S.; Caglar, Y.; Caglar, M.; Yakuphanoglu, F.; Structural, optical and electrical properties of F-doped ZnO nanorod semiconductor thin films deposited by sol-gel process. *Applied Surface Science*. **2008**, *255*, *5*, 2353-2359.
9. Mott, N. F.; *Davis Electronic Processes in Non-Crystalline Materials*, 2nd ed, Clarendon Press, Oxford. **1979**.
10. Dhanam,M.; Prabhu, R. R.; Manoj, P. K. Investigations on chemical bath deposited cadmium selenide thin films. *Materials Chemistry and Phys*. **2008**, *10*, *2-3*, 289-296.
11. Ugwn, E. I.; Onah, D.U. Optical characteristics of chemical bath deposited CdS thin film charactistics within UV visible and NIR radiation. *The Pacific J. of Science and Technology***. 2007**, *8*, *1*, 155-161.
12. Acosta,D. R.; Magana, C. R.; Martines, A. I.; Maldonado, A. Structural evolution and opticl characterization of indium doped cadmium sulphide thin films obtained by spray pyrolysis for different substrate temperatures. *Solar Energy Mater. Solar Cells,* Elsevier. **2004**, *82*, *1-2*, 11-20.
13. Bilgin, V.; Kose, S.; Atay, F.; Akyuz, I. The effect of substrate temperature on the structural and some of physical properties of ultrasonically sprayed CdS thin films. *Mater. Chem. Phys*. **2005**, *94*, *1*, 103-108.
14. Dresselhaus, M. S; *Optical Properties of Solids*, Part II.**1998**.

15. Boukhachem, A.; Ouni, B.; Bouzidi, A.; Amlouk, A; Boubaker, K.; Bouhafs, M.; Amlouk,M. Quantum effects of indium ytterbium doping on ZnO-like nano-condensed matter in terms of urbach-martienssen and Wemple - didomenico single-oscillator models parameters. *ISRN Condensed Matter Phys.* **2012**, 1-10.
16. Khdayer, I. H. Fabrication and studying the photoconducting characteristics of in sb junction with silicon as A single crystal semiconductor. Ph. D. Thesis. Baghdad University. **2005**.
17. Liu, F.; Lai, Y.; Liu, J.; Wang, B.; Kuang, S.; Zhang, Z.; Liu, J. ; Liu, Y. Characterization of chemical bath deposited CdS thin films at different deposition temperature. *J. of Alloys and Compounds.* **2010**, *493, 1-2*, 305-308.