Effect of doping and sintering temperature on the optical characterization of CdS films prepared by screen printing technique

A.O. Ali[1], M. S. Moqbel[2] and K. M. Habib[3]

[1]Department of Physics College of Education-Zingbar University of Aden

[2]Department of Physics College of Education-Daleh University of Aden

[3]Department of Physics College of Education-Saber University of Aden

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Abstract

Two sets of CdS films, doped and undoped films by screen printing technique, were prepared and investigated by UV-Visible spectrophotometer. The undoped as-printed films showed high transmittance (90%) and lower reflectance (10%), while the films sintered at 400°C and 600°C showed less transmittance (60%) and little increase in reflectance (20%), the band gap energy of these films have decreased from 2.44 eV to 2.35 eV with an increase in the sintering temperature. The Doped films showed (70%) transmittance and reflectance of (20%) and increase in the band gap energy up to 3.45 eV. These results nominates the CdS films to be used as n-type window layer in solar cells. Other optical constants like refractive index (n), extinction coefficient value (K) and dielectric values have been calculated.

Key words: CdS films, optical properties, screen printing

Introduction

Cadmium sulfide (CdS) is one of the most technologically important materials, the optical properties of CdS have been studied intensively in the last four decades. Screen printing can be defined briefly, by translating a layer of a material in a desired pattern to the surface of a substrate; through several technical steps, and with definite equipments. In screen printing, you can control the smallest quantities of the dopant (the activator material) in the quantity you like, and by ball milling you can ensure the distribution of the activator and flux materials in all the sample.

Screen printing and sintering is more widely used, non vacuum deposition technique[1]. Besides of its lower cost equipment and cheapest techniques and lower cost productions, [1,2,3,6,7,12].

Sharma et al(2004),[12] prepared 15 μm screen printed CdS films having high absorption coefficient $10^4 cm^{-1}$ when sintered at the optimum sintering parameters; which is 500°C for 10 minutes in air, with the sintering flux; which is $CdCl_2$, so it is suitable for window material in heterojunction solar cell.

Experimental

The commercially available CdS powder was brought from India from Sigma Aldrich with a high purity of 99.999% and the melting point of 999°C.

Microscope slide glasses with dimensions 75 X 25 cm^2 were used to print CdS films on them and alumina substrates were used for those films which will be subjected to higher sintering temperatures.

The substrates were cleaned carefully to remove any impurities and fats by immersing the substrates in HCl for about 24 hours, then they were washed by double distilled acetone, after that they were cleaned by distilled water and were left to dry. Finally, the substrates were weighed by the sensitive balance before printing the CdS paste on them.

The process of formation of the CdS paste and the process of screen printing had been arranged according to the following steps:

1- Different quantities of CdS powder as (starting material) had been weighed by using a high sensitive four digits digital balance and $CdCl_2$ was added as sinter flux by 10% of CdS powder weight. Some samples were doped with $CuCl_2$ as activator which was added to samples in the ratio about 0.5% and 0.8% of CdS powder weight and the other samples were left without doping.

2- Mixed powders of the above mentioned compounds were crashed to fine powders and were dried in the drying oven to ensure good diffusion of sinter flux and activator in the CdS.

3- Propylene glycol (PG), as an organic binder, was added to the powders with the ratio of inorganic part (CdS: CdCl2: CuCl2) to the organic part (PG) and was kept in the proportion 3:1 to form the pastes of CdS samples.

4- The pastes were then, printed on the substrates by applying an equal and strong pressure on the rubber squeegee that was passed over the paste and the CdS paste was printed on glass and alumina substrates which were put under the wooden frame with a snap-off distance.

Finally, in order to get good adherent films to the substrates, the printed pastes were dried in the drying oven.

The sintering process of CdS films was carried out with the help of Jecons Scientific Limited Digital furnace. The furnace is operating from ambient temperature to 1400^{o}C and is provided with the internal digital sensor circuit to keep the temperatures in the chamber of the furnace at definite constant values. The CdS films were put inside the furnace and the sintering periods and sintering temperatures were counted for each CdS film.

To study the optical properties of the screen printed CdS films was carried out by using two UV spectrophotometers instruments: SHIMADZU–UV 3101PC (Japan) (UV-Visible scanning spectrophotometer) its wavelength ranges from 190-3000nm and the scanning speed of 0.2 nm/sec. The instrument is designed to measure four films at once. The other instrument is used to measure Absorbance (A) and Transmittance (T) spectra: SPECORD 205 UV-Visible (Analytik Jena-Germany) spectrophotometer the wavelengths range of the instrument is from 200-1000nm and its scanning speed 5 nm/s.

The CdS films measured were divided into two groups:

1-The first group included screen printed CdS films which were sintered at different sintering temperatures and printed on alumina substrates.

2-The second group included screen printed CdS films which were doped at different doping ratios (0.5% and 0.8%). These CdS films were screen printed on 25X75 mm glass slides.

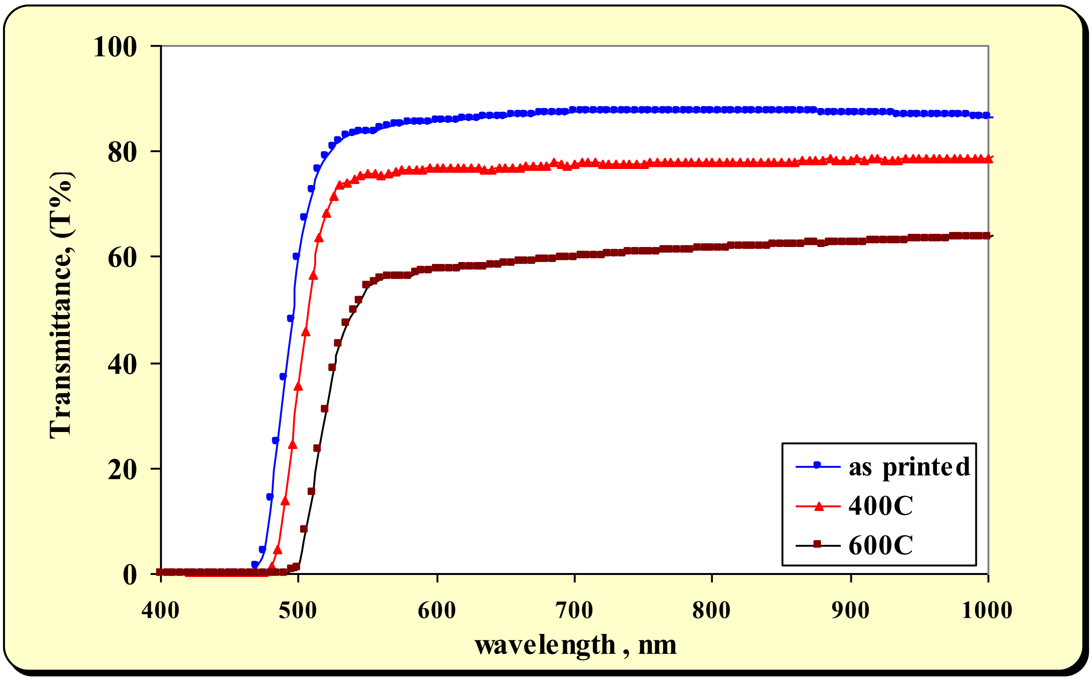
Transmittance (T) and Reflectance (R) of the films were expressed in percentage values (T%) and (R%) and were measured against wavelengths in the range (200-1000) nm. The data were presented in graphical charts and numerical values, and the optical constants of the films were calculated and tabulated.

Results and Discussion

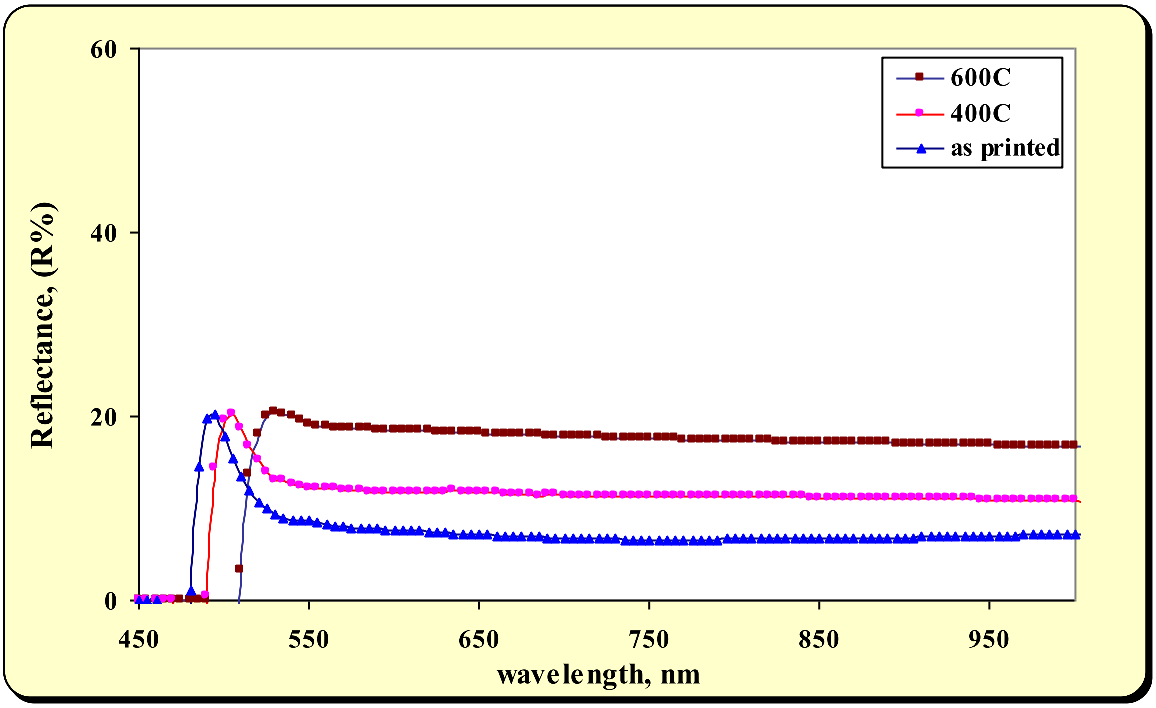
(1) Effect of sintering temperature on optical transmittance (T), reflectance (R) and energy gap (E_g) of undoped screen printed CdS films:

The optical transmittance, reflectance and energy gap of CdS film as printed and those which sintered at 400^{o}C and at 600^{o}C were studied in the range from (200 -1000 nm), the results are shown in Figs.[1],[2],[3], and [4]. Generally, a sharp increase in the spectra at ~510 nm (~ 2.4 eV) is in agreement with the reported band edge of CdS, but higher values of transmittance and lower values of reflectance were observed in the transmission and reflection spectra for as-printed CdS film. Lower transmittance and higher reflectance with a shift in the absorption edge towards the higher wavelengths were observed as a consequence of increase in sintering temperature because sintering at high temperatures enhances the growth of grains and improves the crystalline structure of the polycrystalline CdS films[9] hence scattering of the light waves occurred which encourages reflectance and discourages transmittance. The values of transmittance reached about 90% for the as printed CdS film, but it decreased to less than 60% for the CdS film which was sintered at 600^{o}C and the reflectance increased from about 10% for as-printed CdS film to about 20% for the CdS film which was sintered at 600^{o}C.

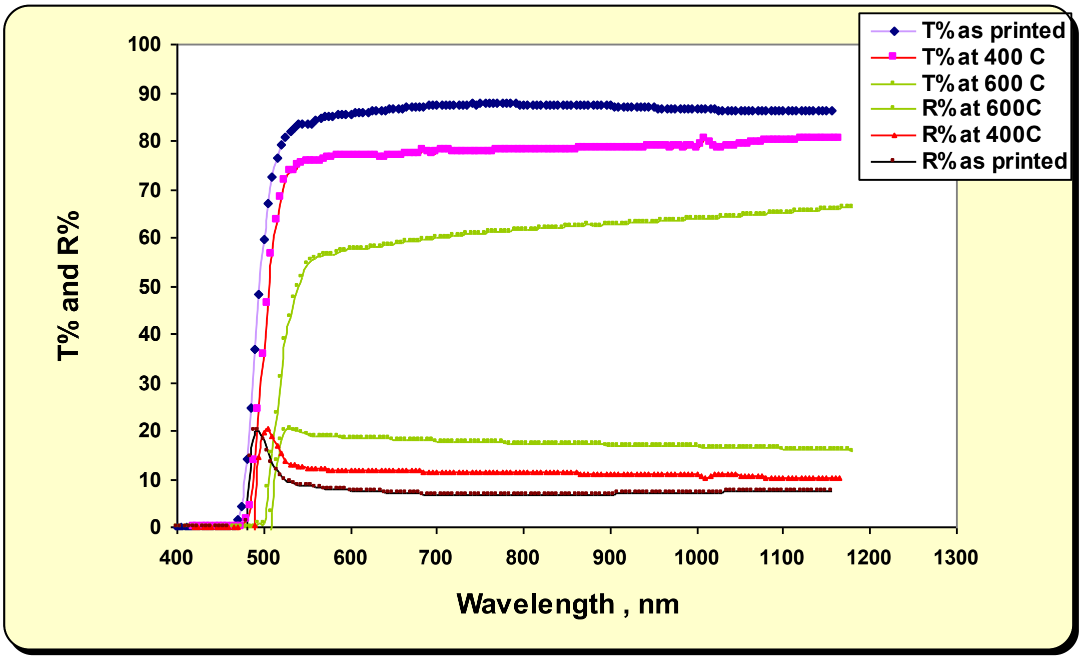
Although this dependence of the values of transmittance and reflectance on the sintering temperature is apparent, the CdS films generally presented high transparency to visible light waves which nominates them strongly to be used as windows layer in the solar cells. The results are in good agreement with results reported previously [5, 8, 9, 10, 15].



Figure[1]: Transmittance(T%) versus Wavelength of undoped screen printed films to study the effect of sintering temperatures



Figure[2]: Reflectance(R%) versus Wavelength of undoped screen printed films to study the effect of sintering temperatures



Figure[3]:Transmittance(T%) and Reflectance(R%) versus Wavelength of undoped screen printed CdS films at different sintering temperatures

The optical band gap (Eg) is calculated by extrapolating the linear region of the plots $(\alpha h\nu)^2$ vs. (hv) on the energy axis by using Tauc's and Bardeen relations for direct allowed transitions formula (1):

$$\alpha = \frac{A_o \, (h\upsilon - E_g)^{1/2}}{h\upsilon} \qquad [1]$$

where α is absorption coefficient, A_o is constant quantity and hv is photon energy.

Figure [4] shows a band gap energy of screen printed CdS films which were sintered at different temperatures. The band gap energy decreased with the increase in sintering temperature from 2.43eV for as-printed film to 2.35 eV for the CdS film which was sintered at 600°C, and standard E_g value of CdS, which is 2.42 eV, was observed for the film which was sintered at 400°C. The decrease in the band gap with the increase in sintering temperature referred to the influence of different factors such as growth of grains, change in structural parameters at high sintering temperatures and decrease in lattice strain. Another additional factor was the evaporation of sulfur at temperatures higher than melting point of sulfur. The sulfur vacancies will promote forming of oxidation phases in the structure of the film such as CdO which lower energy gap of the CdS films.

Filling the voids in the film has a significant effect in creating denser films and consequently lowering energy gap. These results are consistent with previous studies [4].

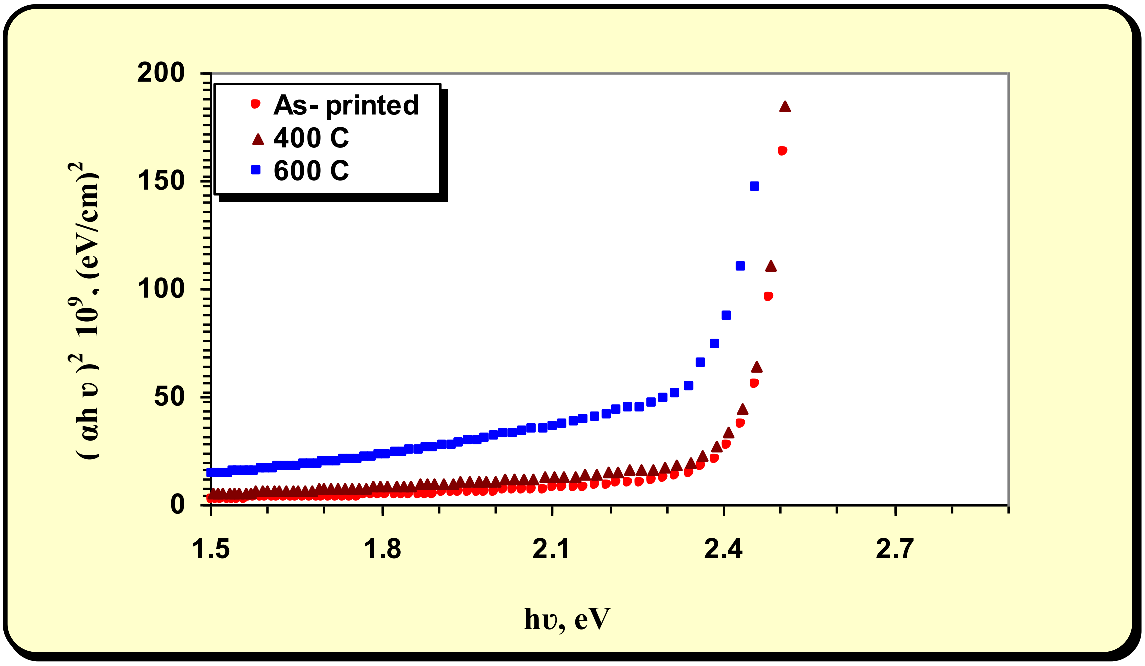
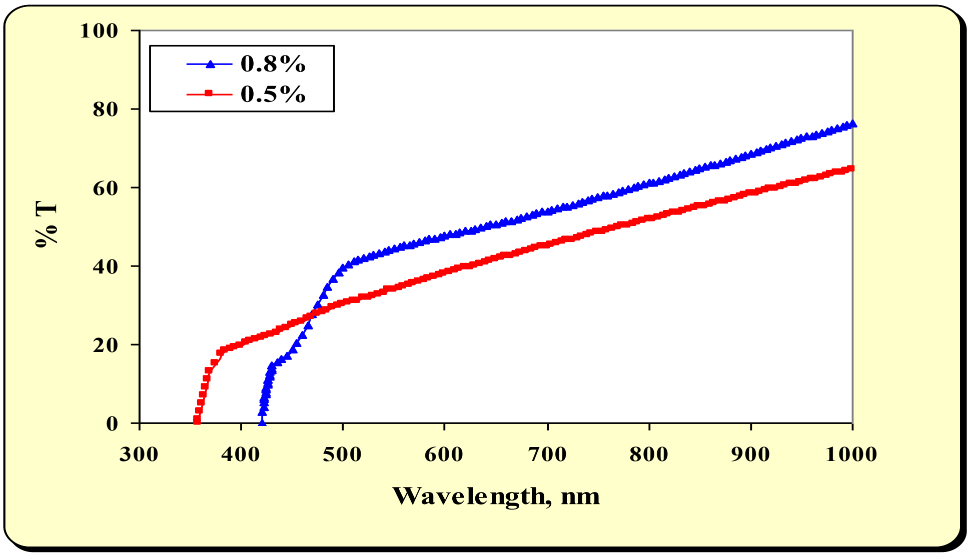


Figure [4]: Energy gap(E_g) of as-printed CdS film and sintered at different sintering temperatures

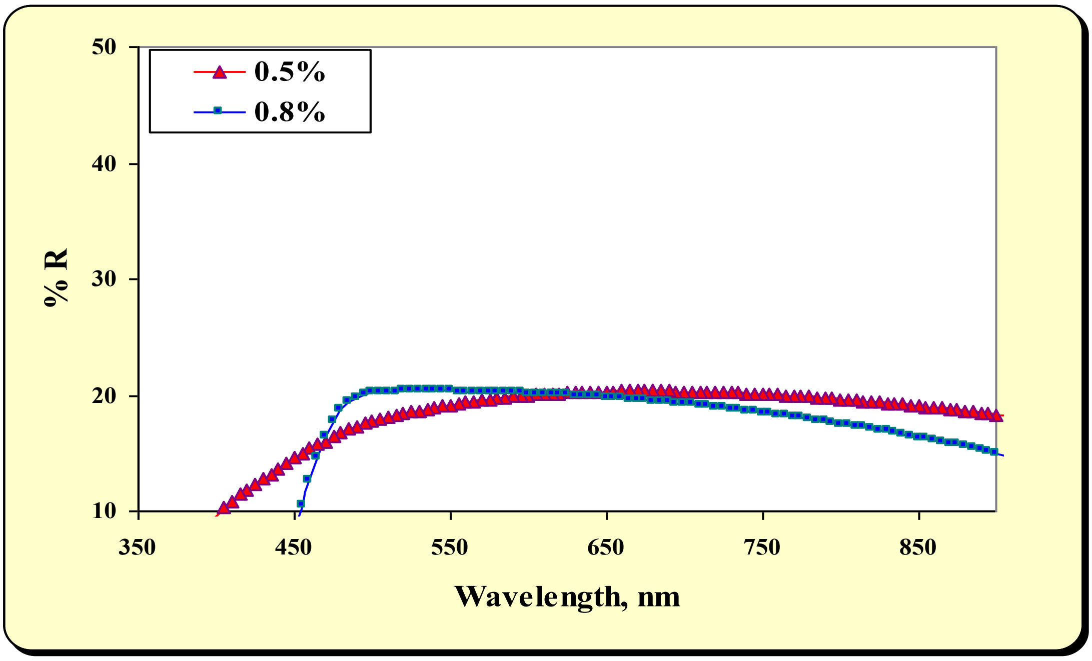
(2) Effect of doping on optical transmittance (T), reflectance (R) and energy gap (E_g) of screen printed CdS films:

To study the effect of doping on the optical transmittance, reflectance and optical energy gap, screen printed CdS films were prepared and doped with $CuCl_2$ the weight ratios of $CuCl_2$, to CdS in the samples were 0.5% and 0.8%.

Fig. [5] shows the relation between transmittance and wavelength of the doped screen printed CdS films. The films exhibit optical transmittance more than 70% in visible light waves above the absorption edge and the absorption edge shifted towards the shorter wavelength for the films doped with lower $CuCl_2$ concentration. This shift towards the shorter wavelength indicates the increase of optical band gap. For further increase in doping concentration, there is again a shift of absorption edge towards the higher wavelengths which indicated the decreasing trend in the optical band gap.



Figure[5]: Transmittance(T%) of doped screen printed CdS films Vs. wavelength



Figure[6]: Reflectance(%R) of doped screen printed CdS films Vs. wavelength

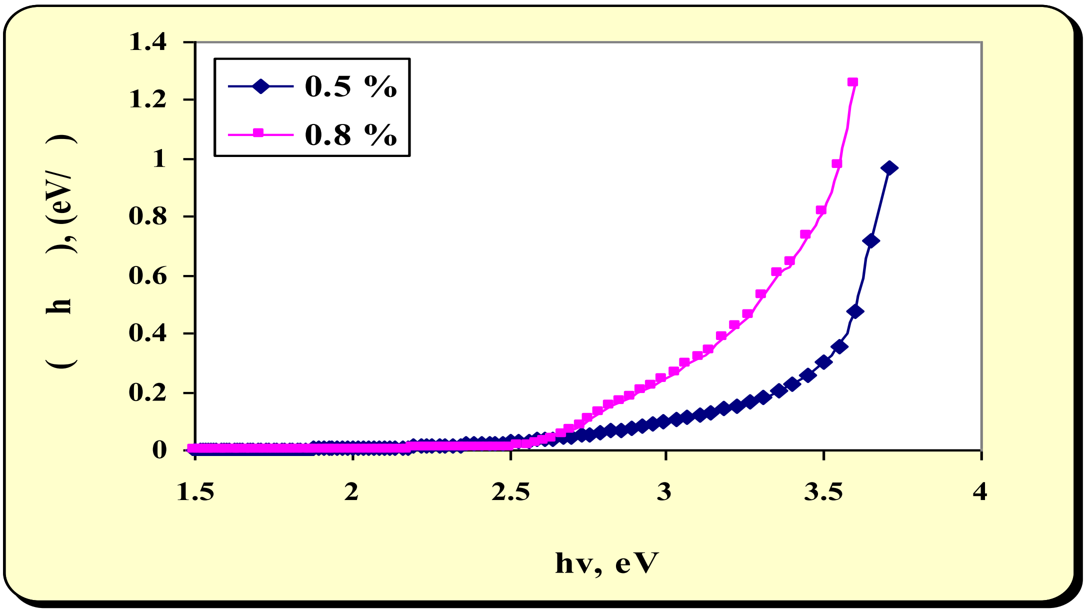


Figure [7]: Variation of the energy gap of screen printed CdS films at different doping concentrations

Figure [6] indicates that reflectance of the CdS films increased with lower $CuCl_2$ concentration which indicated that doping promotes the scattering of light waves especially the longer wavelength of the visible region.

In Figure[7], we can easily observe the effect of doping in increasing the value of band gap energy of the CdS films. So, we can conclude that doping will donate CdS a wide gap energy which is a characteristic of definite semiconductors, such as ZnS and CuS, consequently makes CdS based solar cells more efficient than the other solar cells.

(3) Effect of sintering temperatures on the Optical Constants of Undoped Screen Printed CdS Films:

Optical constants and coefficients, such as the refraction index (n), extinction coefficient (k), and complex dielectric constants, were plotted with respect to the wavelengths for undoped screen printed CdS films sintered at different sintering temperatures. The computations of these optical constants were performed by the help of suitable formulae. For refractive index (n) can be evaluated from the reflectance (R) readings as follows:

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

And for The extinction coefficient (k) can be evaluated at each wavelength (λ) according to the following relation:

$$k = \frac{\alpha \lambda}{4 \pi} \qquad [3]$$

Figure [8] shows refractive index (n) as a function of wavelength of the screen printed CdS film which was sintered at different sintering temperatures. It was observed that refractive index (n) increased with the increase in sintering temperature. The refraction index (n) was (2.39) for as printed CdS film, then it increased to (2.54) when the film sintered to 600°C which indicated that the film had better crystallinity, larger grain size and diminishing vacancies between grains which, in turn, causes increase in optical reflectance of the film. Refraction index (n) for as-printed film decreased due to lower grain sizes, presence of vacancies between grains and presence of water and binder molecules inside the film which promote the lower values of refraction index (n). These results are in good agreement with previous studies[11,18].

Figure[9] shows the relation between extinction coefficient (k) and wavelength of the screen printed CdS film which was sintered at different sintering temperatures and which showed the values of the extinction coefficient was in the order of (10^{-2}), and such low values of (k) in visible and near infra red spectra was a qualitative indication of homogeneity of the surface of polycrystalline film but, when the film was sintered to 600°C, high values of extinction coefficient (k) was observed, which can be explained as a result of the scattering of light and high reflectance at high temperature. As-printed film is full of voids and it has not good crystalline structure hence, lower value of extinction coefficient (k). The same results also reported in previous studies [13, 16, 20].

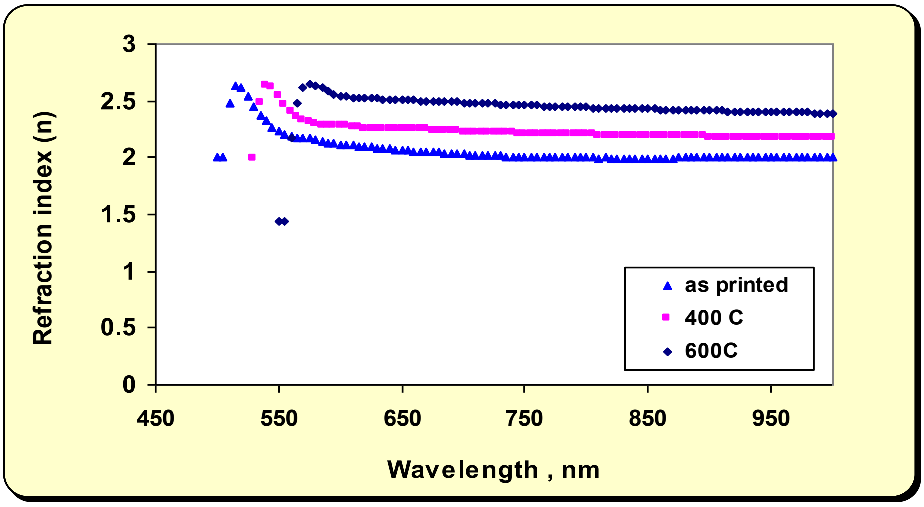


Figure [8]: Refraction index (n) of the CdS screen printed films at different sintering temperatures

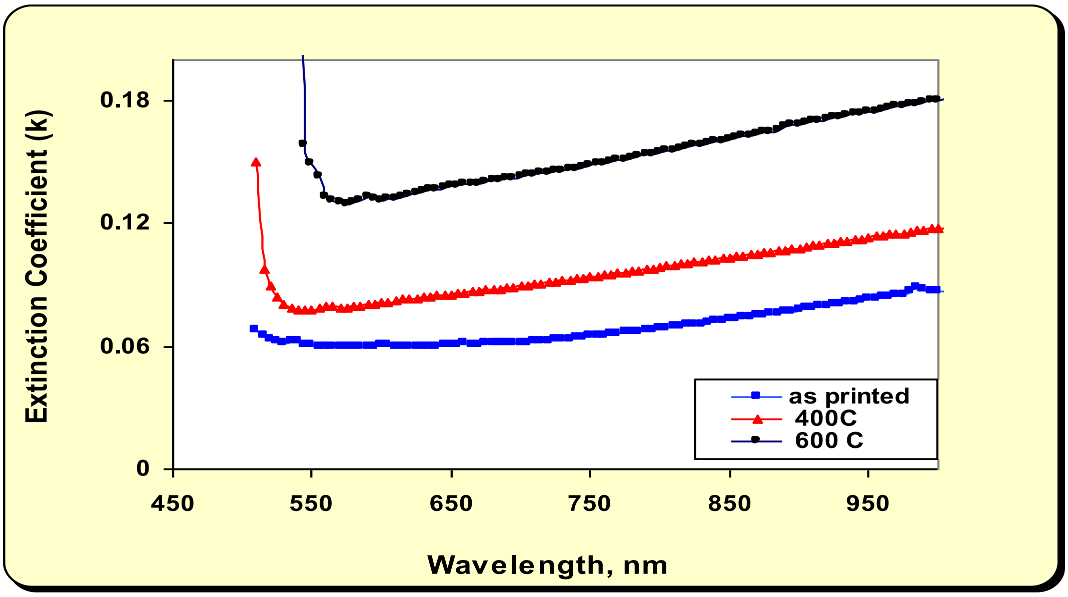


Figure [9]: Extinction coefficient (k) of the CdS screen printed films at different sintering temperatures

The complex dielectric constant consists of two parts; they are real part(ε_r), and imaginary part (ε_i) and the relations which determine their values are given as follows:

$$\varepsilon_c = \varepsilon_r^2 + \varepsilon_i^2 = (n + ik)^2 \qquad [4]$$

$$\varepsilon_r = n^2 - k^2 \qquad [5]$$

$$\varepsilon_i = 2nk \qquad [6]$$

Figures [10] and [11] indicate the real and imaginary parts of the dielectric constant as a function of wavelength of screen printed CdS film which was sintered at different sintering temperatures. The values of these constants increase with the increase in sintering temperatures in the same behavior of refraction index (n) and of extinction coefficient (k). So, they can be explained in the same manner which was used to explain Figures [8] and [9]. These results are in a good agreement with results reported previously [13, 16, 20].

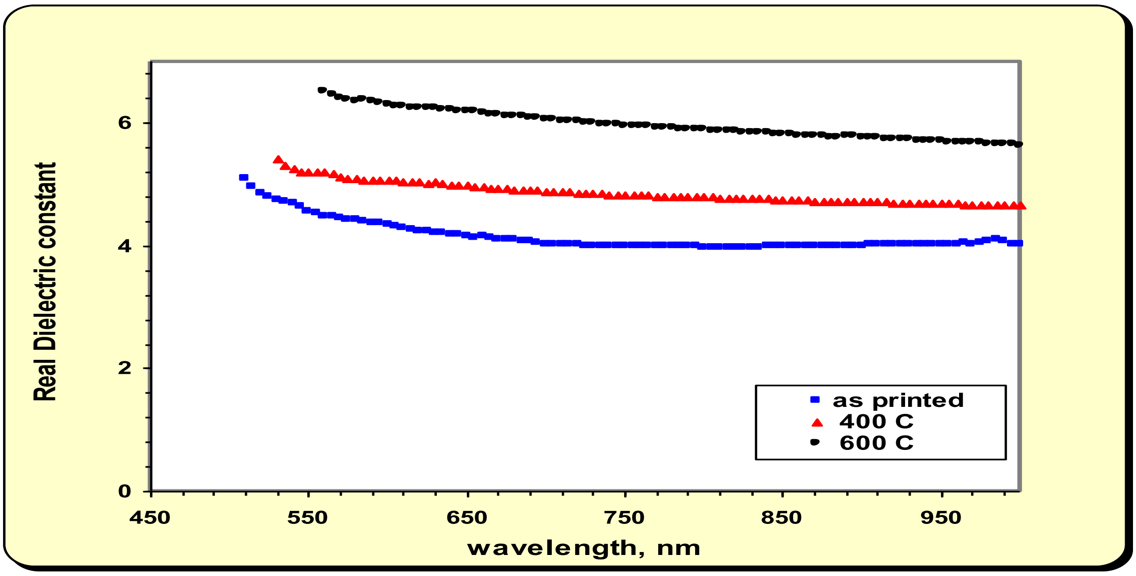


Figure [10]: Real dielectric constant of screen printed CdS film annealed at different temperatures

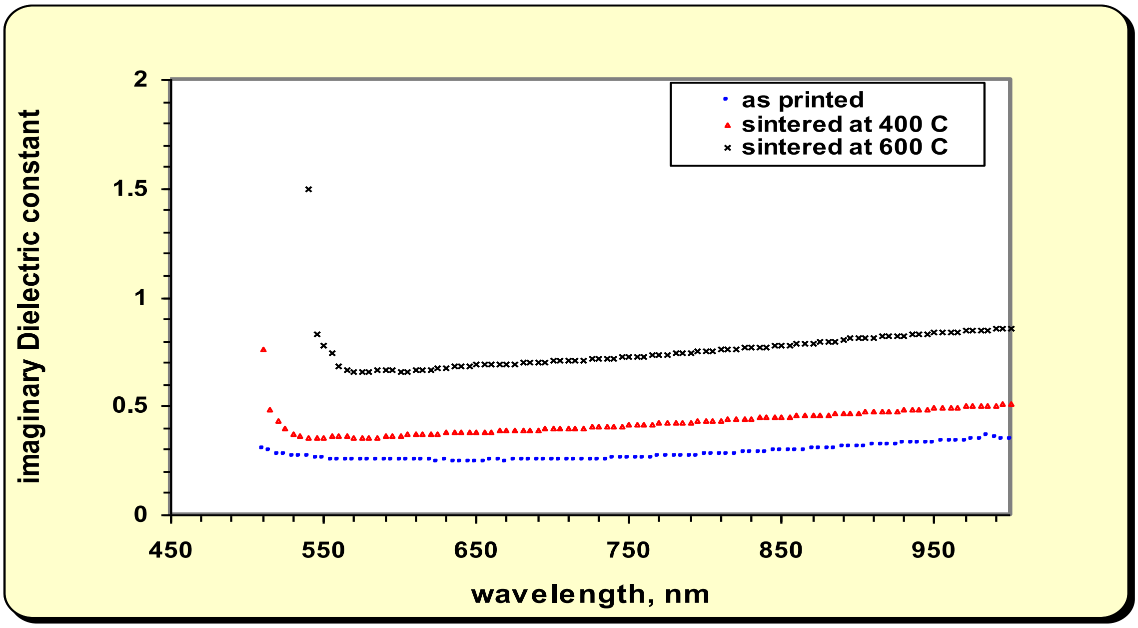


Figure [11]: Imaginary dielectric constant of screen printed CdS film at different sintering temperatures

(4) Effect of doping on the optical constants of screen printed CdS films:

Figures[12] and [13] show refractive index (n) and extinction coefficient (k) as a function of wavelength of the screen printed CdS films at different $CuCl_2$ concentrations. It is observed that refractive index (n) increases with lower $CuCl_2$ concentrations. Its value is (2.37) for films with higher doping ratio i.e., 0.8% increases to (2.64) for films with lower doping ratio i.e., 0.5% which indicated the presence of larger grain size that causes scattering of light waves and, in turn, leads to the observed increase in optical reflectance, but higher dopant concentrations indicates lower grain sizes and presence of vacancies between grains causing the lower values of refraction index (n).

On the other hand, it is observed that the value of extinction coefficient k was in the order of (10^{-3}), as shown in Table[1], which confirm the non homogeneity of the surface of the film due to the addition of $CuCl_2$. The extinction coefficient k increases with the increase in $CuCl_2$ concentrations and a sharp fall of the extinction coefficient k is also observed for the highly doped film in the shorter wavelengths. These results are in good agreement with previous study [18].

Figures [14] and [15] show the real and imaginary dielectric constants of the doped screen printed CdS films against the wavelength. The shapes of their curves resemble the shapes of the curves of the refraction index n and extinction coefficient k of the doped screen printed CdS film respectively, although despite the differences in their values. So, they can be discussed in the same way given to Figures[12] and [13].

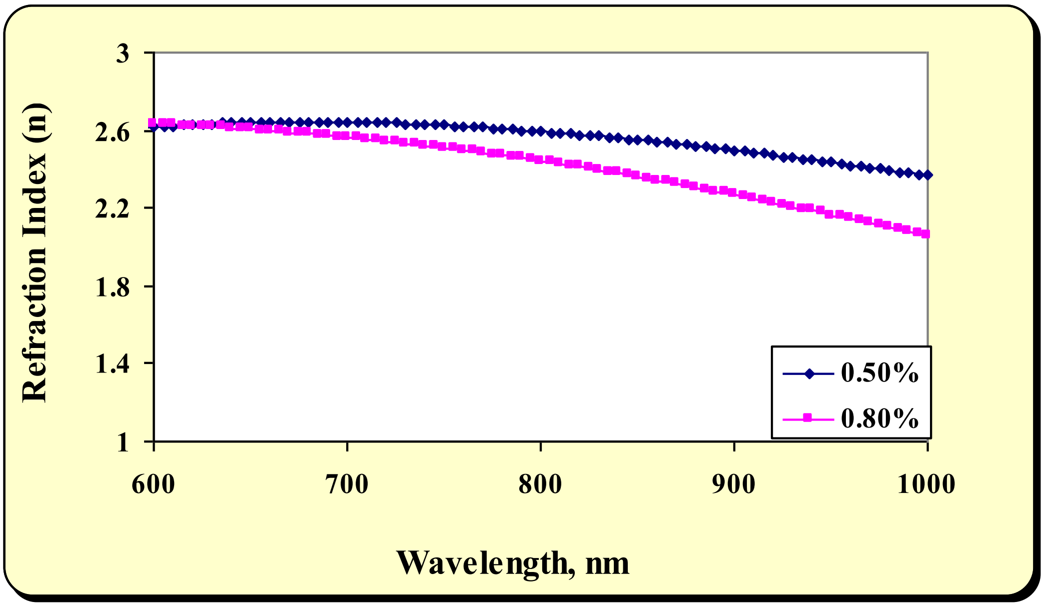


Figure [12]: Refraction index (n) of the doped screen printed CdS films at different $CuCl_2$ doping ratios

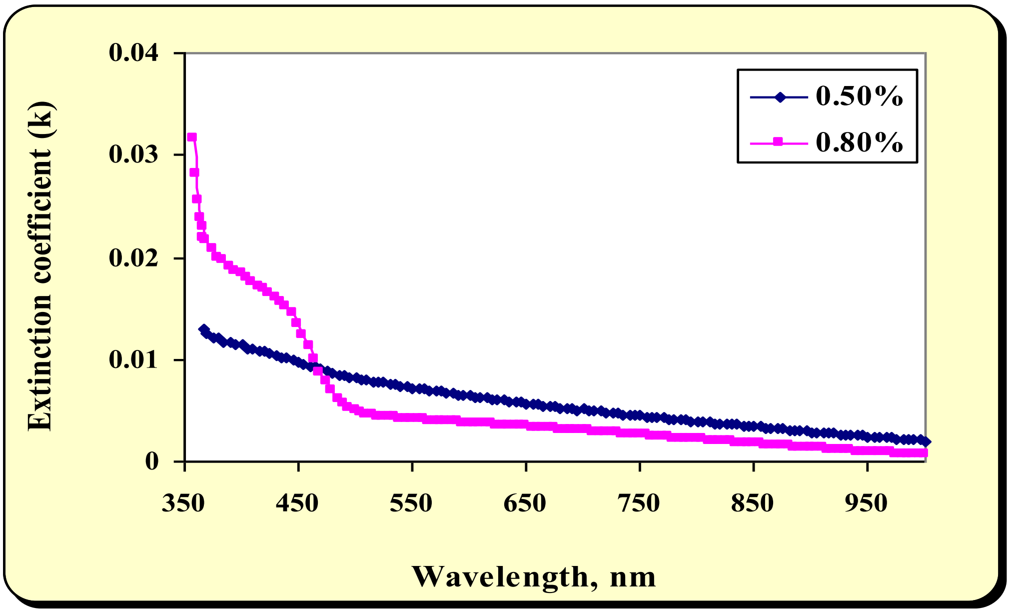


Figure [13]: Extinction coefficient (k) of the doped screen printed CdS films at different $CuCl_2$ doping ratios

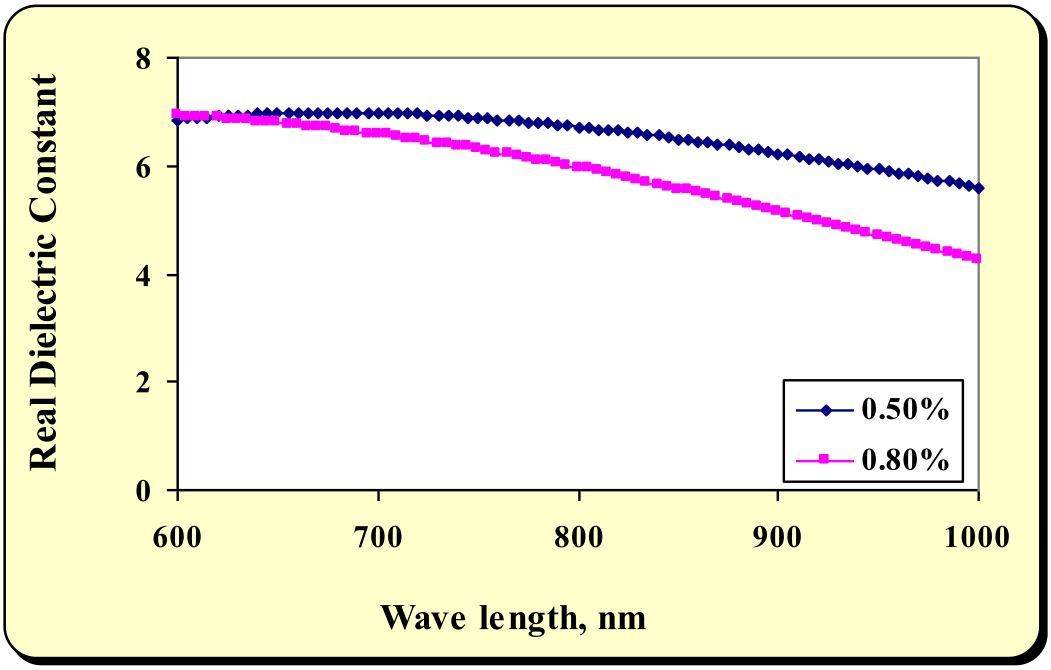


Figure [14]: Real Dielectric constant (ε_r) of the doped screen printed CdS films at different $CuCl_2$ doping ratios

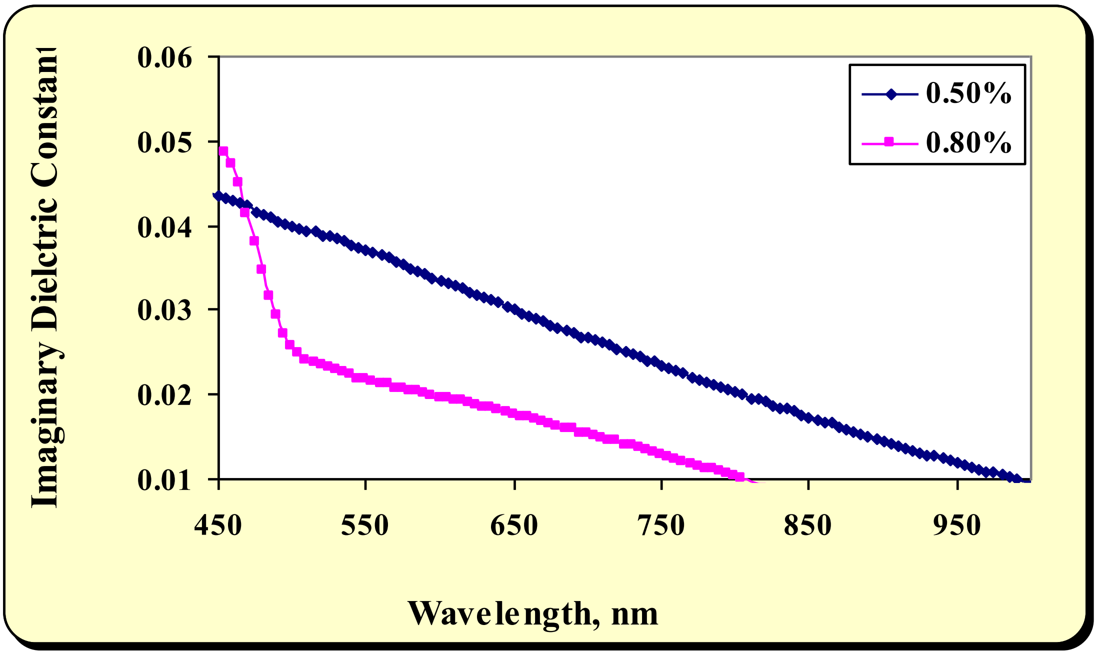


Figure [15]: Imaginary Dielectric constant (ε_i) of the doped screen printed CdS films at different $CuCl_2$ doping ratios

Table [1] calculated values of optical constants of the doped and undoped screen printed CdS films

Table (1)

Case of screen printed film	Wavelength	Transmittance T%	Reflectance R%	Refraction Index n	Extinction Coeffic. k	Real Dielectric constant Er	Imaginary Dielectric constant Ei	Energy Gap E_g
As-printed	**600**	**85.40**	**7.73**	**2.228**	**0.0599**	**4.42**	**0.136**	**2.43**
	700	**86.10**	**7.41**	**2.120**	**0.0601**	**4.22**	**0.141**	
	800	**87.67**	**6.62**	**1.999**	**0.0671**	**3.99**	**0.159**	
	1000	**86.61**	**7.15**	**2.004**	**0.0867**	**4.06**	**0.185**	
Sintered at 400°C	**600**	**76.72**	**11.77**	**2.282**	**0.0813**	**5.06**	**0.366**	**2.42**
	700	**76.53**	**11.86**	**2.249**	**0.0855**	**4.98**	**0.382**	
	800	**77.91**	**11.25**	**2.198**	**0.0988**	**4.79**	**0.433**	
	1000	**78.64**	**10.93**	**2.166**	**0.118**	**4.66**	**0.564**	
Sintered at 600°C	**600**	**57.75**	**18.4**	**2.544**	**0.136**	**6.237**	**0.678**	**2.35**
	700	**58.62**	**18.19**	**2.505**	**0.141**	**6.116**	**0.698**	
	800	**61.58**	**17.36**	**2.442**	**0.159**	**5.894**	**0.769**	
	1000	**64.02**	**16.62**	**2.392**	**0.185**	**5.621**	**0.878**	
Doped at 0.5%	**600**	**37.95**	**19.97**	**2.64**	**0.006**	**6.44**	**0.033**	**3.45**
	700	**44.97**	**20.32**	**2.62**	**0.005**	**6.57**	**0.027**	
	800	**51.75**	**20.60**	**2.60**	**0.004**	**6.72**	**0.020**	
	1000	**64.44**	**16.48**	**2.37**	**0.002**	**5.60**	**0.0095**	
Doped at 0.8 %	**600**	**47.67**	**20.15**	**2.59**	**0.004**	**6.91**	**0.020**	**3.28**
	700	**53.91**	**19.26**	**2.56**	**0.003**	**6.93**	**0.015**	
	800	**61.05**	**17.52**	**2.42**	**0.002**	**6.95**	**0.010**	
	1000	**76.29**	**11.96**	**2.06**	**0.0006**	**4.23**	**0.0024**	

Conclusion

Screen printed CdS films have good transmittance for light waves in the visible range which make them a good choice to be applied as n-type window layer in the solar cells. Also, the band gap was found to be around 2.4 eV which is the characteristics value of CdS compounds energy band gap. And this energy gap can be made to have a higher value by doping the CdS films with $CuCl_2$.

The optical constants of the Cds films are affected strongly by sintering temperature and by doping CuCl2 concentration ratio.

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دراسة الخواص الضوئية لافلام كبريتيد الكادميوم المحضرة بطريقة الطباعة الشبكية

عبدالله عمر علي، محمد سيف مقبل وخالد مثنى حبيب
قسم الفيزياء، كلية التربية - زنجبار، جامعة عدن
قسم الفيزياء، كلية التربية - الضالع، جامعة عدن
قسم الفيزياء كلية التربية – صبر، جامعة عدن
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الملخص

قمنا بتحضير نوعين من أفلام مادة كبريتيد الكاديميوم بواسطة طريقة "الطباعة على الشبكة" مطعمة وغير ومطعمة ثم قمنا بدراسة الخصائص الضوئية لهذه الأفلام بواسطة جهاز المطياف الضوئي والمسمى(UV/Visible-spectrophotometer) وذلك عبر تحليل طيف النفاذية, (Transmittance) وطيف الانعكاسية, (Reflectance) أظهرت الأفلام غير المطعمة والمسخنة نتائج لخاصية النفاذية عالية حيث تراوحت قيمة النفاذية بين 60% إلى 90% وانخفضت فجوة الطاقة لهذه الأفلام من 2.44 إلكترون فولت إلى 2.35 إلكترون فولت مع زيادة التسخين، وبالمقابل أظهرت العينات المطعمة قيم نفاذية حوالي (70%) وانعكاسية (20%) وارتفاع فجوة الطاقة إلى 3.45 إلكترون فولت, مما يدل على إمكانية استخدام هذه العينات كطبقة نافذة (windows layer) من نوع n في تركيب الخلايا الشمسية. وقمنا أيضا بحساب الثوابت الضوئية مثل ثابت الانكسار وثابت الإخماد وثابتا العازلية للأفلام.

الكلمات المفتاحية: أفلام كبريتيد الكادميوم، الخصائص الضوئية، تحضير أفلام بطريقة الطباعة على الشبكية.