A Comparison between the Electrical and Optical Properties of CdS: In Thin Films for Two Doping Ratios

Shadia J. Ikhmayies [a,*], Riyad N. Ahmad-Bitar [b]

[a] Physics Department, Faculty of Basic Sciences, Applied Science Private University, Amman, Jordan.

[b]Physics Department, Faculty of Science, University of Jordan, Amman-Jordan.

Abstract

Indium-doped cadmium sulphide CdS:In thin films were prepared by the spray pyrolysis (SP) technique on glass substrates at a substrate temperature T_s = 490˚C. A comparison between the electrical and optical properties of the films for two different doping ratios was made through measuring and analyzing the transmittance curves, photoluminescence spectra (PL) and I-V plots. It was found that the higher doping ratio results in a decrease in the transmittance and PL signal, and a slight increase in the optical bandgap energy. Also it results in a considerable reduction of the resistvity of the films. So choosing the proper doping ratio is important to produce high quality CdS:In thin films suitable for the use as windows in CdS/CdTe solar cells.

1. Introduction

Thin films of CdS have been extensively studied due to the variety of applications in optoelectronic devices. In particular heterojunction solar cells with a narrow bandgap base and a wide bandgap window such as CdS/CdTe and CdS/CuInSe solar cells [1].

There are several methods for depositing CdS thin films, such as; vacuum evaporation (VE) [2-4], chemical bath deposition (CBD) [1, 5, 6], spray pyrolysis (SP) [7-11], etc. However, the SP technique is a very low cost and simple technique that enables intentional doping and getting large area and uniform thin films [8].

In this work CdS:In thin films were produced by the SP technique, and a comparison between the effects of two different doping ratios on the electrical and optical properties of the films were investigated. The resistivity of the films was determined from the I-V plots which are linear. The optical bandgap energy was estimated from the transmittance curves and the PL spectra were recorded, deconvoluted and investigated.

2. Experimental Part

The precursor solution of CdS:In thin films was prepared by dissolving 2.06×10^{-2} moles of extra pure $CdCl_2 \cdot H_2O$ (MERCK Art. 2011) and 2.24×10^{-2} moles of thiourea $(NH_2)_2CS$ (>97% S) in 350 ml of distilled water.

Indium chloride $InCl_3$ (MERCK Art.12471) was used as a doping compound. The ratio of the concentration of indium ions to that of cadmium ions in the solution which is not necessarily the same as their ratio in the films was considered as an estimation of the doping ratio. Two doping ratios were considered; 1.0×10^{-4} (light doping) and 1.5×10^{-2} (heavy doping). The solution was sprayed intermittently by using the spraying system described in [8] on glass substrates that were ultrasonically cleaned with methanol at a substrate temperature T_s= 490˚C.

The transmittance of the films was measured by using a double beam Shimadzu UV 1601 (PC) spectrophotometer with respect to a piece of glass of the same kind of the substrates in the wavelength range 400-1100 nm. The films' thickness was estimated by using Lambert law for absorption in a semiconductor. That is by making use of the relative transmittance through each film at a certain wavelength. The produced films have a thickness restricted in the range 0.2-1.0 μm.

The PL spectra were recorded at T= 23K by a system which consists of an Air Product He cryostat DISPLEX DE-202 capable of cooling down to 10 K, where the Ar ion laser of wavelength 488 nm was used as an excitation source. The laser power was 10 mW and the diameter of the laser beam on the sample was about 2 mm. The PL signal was collected by a multi-channel optical spectrometer (an Avantes Fiberoptic Spectrometer AVS-S2000) which hosts two gratings. The first grating has a range: 640 – 1280 nm and the second grating has a range: 190-860 nm. The spectrometer resolution (FWHM) ranges

Corresponding Author. shadia_ikhmayies@yahoo.com

from 0.3 - 10 nm depending on the recorded region and the grating.

Aluminum was chosen to make the contacts, where two strips were deposited on the surface of the film by vacuum evaporation. The contacts have a thickness of more than 0.4 μm, a length of 1 cm, a width of 1 mm, and a separation of 2-3 mm. The I-V measurements were taken by using a Keithley 2400 Source Meter, which was interfaced by an IBM personal computer and capable of measuring 10^{-11}A. The samples were placed in a brass cell that had a cover to enable measurements in the dark.

3. Results and Discussion

3.1. Electrical Properties

The I-V characteristics of indium-doped CdS:In thin films were taken in the dark at room temperature. The measurements were taken in the voltage range 0-10 V, and the curves are linear, which indicates the ohmic behavior of the contacts.

The I-V plots for two films with the doping ratios 10^{-4} and 1.5×10^{-2} were displayed in Figure 1. From the plot the resistivity was $\rho = 4.63 \times 10^{7}$ Ω.cm for the film of doping ratio 10^{-4} and $\rho = 900$ Ω.cm for the 1.5×10^{-2} doping ratio. So a huge decrease in the resistivity had occurred in the film of the higher doping ratio.
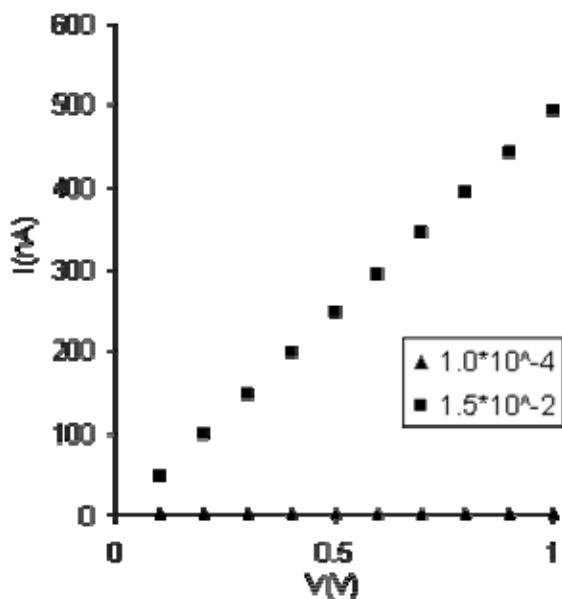

Figure 1. The I-V plots for CdS:In thin films of different doping ratios.

These results can be interpreted in terms of the decrease in the barrier height caused by doping. Josh et al [12] say that the decrease in the barrier height ϕ and hence the increase in the conductivity of the films can be explained on the bases of Waxman et al as,

$$\phi = kT \log(\frac{n_1}{n_2}) \qquad \textbf{(1)}$$

where n_1 and n_2 are the numbers of carriers in the crystallite and in the grain boundary regions respectively. Indium will increase the number of charge carriers, because indium impurity atoms serve as strong donor impurities. If we assume the same extent of increase in the two regions (crystallite and grains), then ϕ will continue to decrease with increasing indium concentration.

The current will not continue increasing by increasing the concentration of indium atoms in the films, but beyond a certain limit the indium atoms will be incorporated in the crystal lattice as electrically inactive impurities (neutral impurity centers). The observations of Joshi et al [12] confirmed this thing. They observed that the Hall coefficient decreased with increasing indium content and finally saturates for large indium content.

3.2. 3.2 Optical Properties

3.2.1 Transmittance and Bandgap Energy

The transmittance of CdS:In thin films was measured at room temperature in the wavelength range 400-1100 nm and shown in Figure 2a for a film of thickness 0.5 μm. As we see there is a dependence of transmittance on the doping ratio; that is it reaches about 84% for the lower doping ratio, and about 72% for the higher doping ratio. The decrease in transmittance with doping is expected, because doping increases the number of charge carriers which increases the absorption in the films, and then decreases the transmission of light.

Figure 2b depicts the absorption coefficient of the two curves shown in Figure 2a. It is noticed that the absorption edge of the film of the higher doping ratio is red-shifted with respect to that of the film of the lower doping ratio. This is mainly due to the formation of band tails in doped semiconductors, which causes a strong modification of the joint density of states and, consequently the absorption spectrum [13].

The value of the optical energy bandgap was estimated from the plots of $\alpha h \nu$ versus $h \nu$ shown in Figure 3, where α is the absorption coefficient, h is Planck's constant and ν is the frequency of the radiation. Since the plots are linear, the direct nature of the optical transition is confirmed. The estimated values of the bandgap energy for films of different thickness are summarized in table 1. As we see in the table it is noticed that the bandgap energy was slightly larger for the higher doping ratio. The increase in E_g is due to the increase in the carrier concentration with doping, and can be attributed to the Moss-Burstein shift.
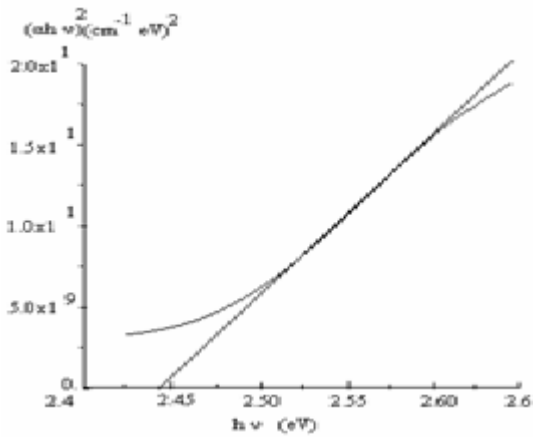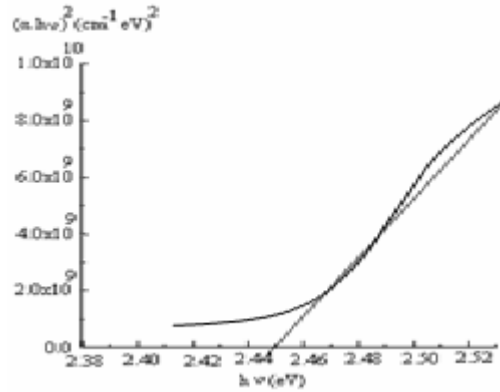
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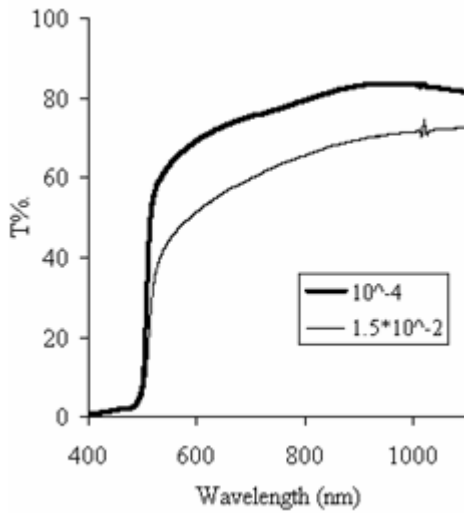
(a)
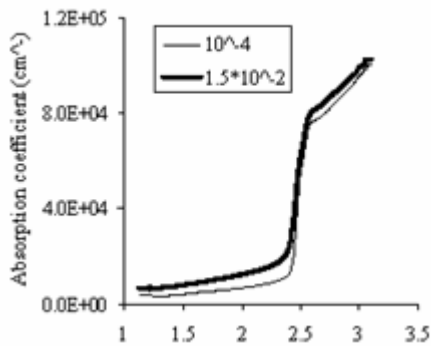
(b)

Figure2 a) The transmittance curves of CdS:In thin films of the two doping ratios. b) Absorption coefficient against energy for the transmittance curves in a.

(a)

(b)

Figure 3 Plots of $(\alpha h\nu)^2$ versus $h\nu$ for two films of thickness 0.50μm. (a) Doping ratio is 1.5×10^{-2}. (b) Doping ratio is 10^{-4}.

Table 1.The bandgap energy of CdS:In thin films of different thickness.

t(nm)	E_g(eV) for the 10^{-4} doping ratio	E_g(eV) for the 1.5×10^{-2} doping ratio
150	2.43	2.44
300	2.44	2.45
500	2.44	2.45

3.2.2 Photoluminescence

Figure 4 shows the PL spectra of two CdS:In thin films of different doping ratios. As the figure shows the PL signal had decreased with doping. A deconvolution peak fit was made (Figure5) to compare the effect of the two doping ratios on the PL spectra. The peak parameters obtained from the fit are inserted in table 2. At the higher doping ratio two peaks in the yellow region are attenuated and slightly red shifted, but the peak at 2.032 eV had slightly blue shifted and practically disappeared. The peak at 1.910 eV had completely disappeared and the peak at 1.961 eV had enhanced and blue-shifted. The peaks at 1.758 and 1.830 eV in the red region had completely disappeared, the peak at 1.712 eV had attenuated and two new peaks in the red region appeared which are 1.635 (but it is very weak) and 1.796 eV. The peak in the infrared region centered at 1.055 eV in Figure 4b was attenuated to more than half its original intensity.

Indium as other impurities (Fe and Zn) exhibits a quenching effect on the luminescence peak in mixed sulfide films were the In:Cd ratio is varying locally. This result was consistent with the results of Ahmed-Bitar [7] where he studied the PL with the doping ratio and he had a greatest signal for the undoped sample, and then the PL signal decreases with the doping ratio. He interpreted this result by saying that the doping level was found to produce structural changes which affect radiative transitions differently.

The disappearance of some peaks may mean that some defects had disappeared or reduced such as $I_{Cd}^{+} - V_{Cd}^{-}$ which is expected to be responsible about the orange emission and V_{Cd}^{2-} which is expected to be responsible about the infrared emissions. The new peaks and those that are enhanced are most probably associated to doping; that is new radiative transitions between doping levels and acceptor levels and/ or the valence band had

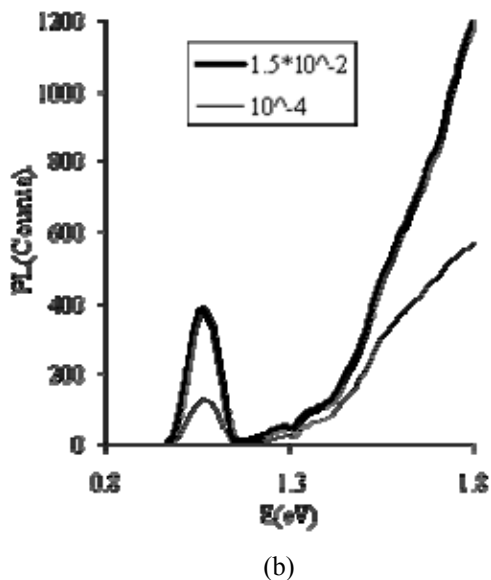taken place. The red shift of some peaks is related to doping and it increases with doping [13].
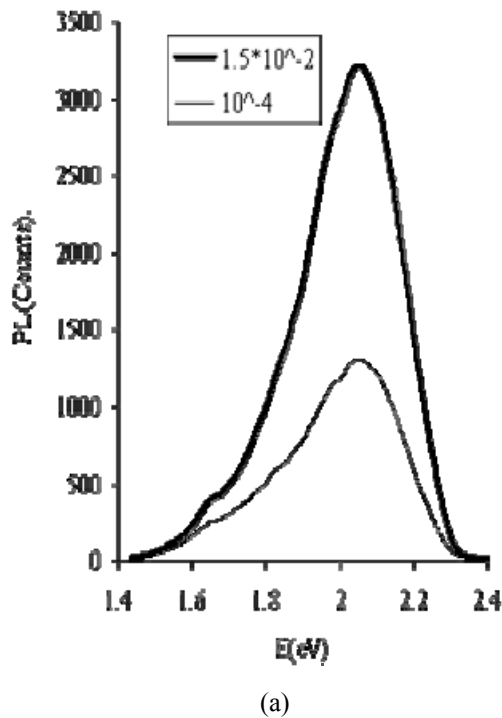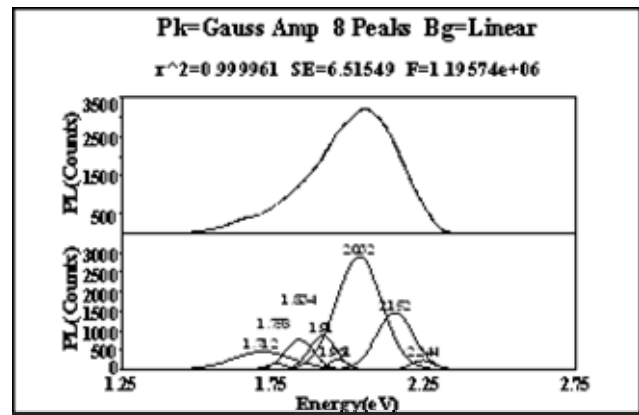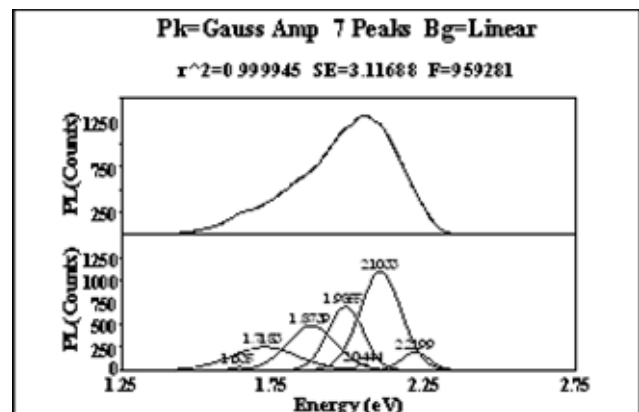

(a)

(b)

Figure 4 The PL spectra of CdS:In thin films of different doping ratio. a) Taken by the 2nd grating. b) Taken by the 1st grating.

(a)

(b)

Figure 5 A deconvolution peak fit of the PL spectra in Figure 4a. a) Doping ratio is 10^{-4}. b) Doping ratio is 1.5×10^{-2}.

Table 2. Peak parameters obtained from the deconvolution peak fit in Figure5.

No	Position for the 10^{-4}	Amplitude	Position for the 1.5×10^{-2}	Amplitude
1			1.635	30
2	1.712	448	1.718	251
3	1.758	132		
4			1.796	181
5	1.834	757		
6			1.874	488
7	1.910	862		
8	1.961	267	1.986	702
9	2.032	2916	2.044	69
10	2.152	1458	2.103	1089
11	2.244	224	2.220	198

4. Conclusions

Indium-doped cadmium sulphide thin films were prepared by the spray pyrolysis technique with two different doping ratios on glass substrates at a substrate temperature $T_s = 490°C$. A comparison between the effects of two different doping ratios on the electrical and optical properties of the films had been investigated. Higher doping had improved the electrical properties by

decreasing the resistivity of the films and slightly increased the bandgap energy. It attenuated the PL signal and caused the disappearance of some peaks and the appearance of new peaks, which means that doping levels had a significant role in the produced PL signal.

Acknowledgement

References

[1] H. Ariza-Calderon, R. Lozada- Morales, O. Zelaya-Angel, J. G Mendoza- Alvarez and L. Baños, "Photoluminescence measurements in the phase transition region for CdS thin films". J. Vac. Sci. Technol. A. Vol. 14, No.4, 1996, 2480-2482.

[2] M. Lepek, B. Dogil and R. Ciecholewski, "A Study of CdS thin film deposition". Thin Solid Films. Vol. 109, 1983, L103-L107.

[3] E. Bertran, J. L. Morenza, J. Esteve and J. M. Codina, " Electrical Properties of Polycrystalline Indium-Doped Cadmium Sulfide Thin Films". J. Physics. D. Vol. 17, No. 8, 1984, 1679-1685.

[4] D Patidar, R Sharma, N Jain, T P Sharma and N S Saxena, "Optical properties of thermally evaporated CdS thin films". Cryst. Res. Technol. Vol. 42, No. 3, 2007, 275–280.

[5] O. De. Melo, L. Hernández., O. Zelaya-Angel, R. Lozada-Morales, M. Becerril, and E. Vasco, "Low Resistivity Cubic Phase CdS Films by Chemical Bath Deposition Technique". Appl. Phys. Lett. Vol. 65, No. 10,1994, 1278-1280.

[6] O. Vigil, I. Riech, M. Garcia-Rocha, O. Zelaya-Angle, "Characterization of defect levels in chemically deposited CdS films in the cubic-to hexagonal phase transition". J. Vac. Sci, Technol. A. Vol. 15, 4, 1997, 2282-2286.

[7] Riyad. N. Ahmed-Bitar, "Effect of dopping and heat treatment on the photoluminescence of CdS films deposited by spray pyrolysis". Renewable Energy. Vol. 19, 2000, 579-586.

[8] Ikhmayies J. Shadia. Production and Characterization of CdS/CdTe Thin Film Photovoltaic Solar Cells of Potential Industrial Use. Ph.D Thesis, University of Jordan, Amman, Jordan, 2002.

[9] G. G. Slawh, W. Z. Manookian, and W. S. A. Abdul Ghafor, "Optical and Electrical Properties of CdS Thin Films Prepared by Spraying Pyrolysis Technique". Iraqi Soc. Of Phys. And Math., J. Math. Phys. Vol. 12, No.1,1991, 91-98.

[10] A. Ashour, "Physical Properties of Spray Pyrolysed CdS Thin Films". Turk J Phys. Vol. 27, 2003, 551-558.

[11] P Raji, C Sanjeeviraja and K Ramachandran, "Thermal and structural properties of spray pyrolysed CdS thin. Bull. Mater. Sci. Vol. 28, No. 3, 2005, 233–238.

[12] J. C. Joshi, , B. K. Sachar and Partap Kumar, "Electrical Transport Properties of Heavily Indium Doped Polycrystalline CdS Films". Thin Solid Films. Vol. 88, No. 3, 1982, 189-193.

[13] G.Perna, V.Capozzi, M.Ambrico, V.Augelli, T.Ligonzo, A.Minafra, L.Schiavulli and M.Pallara, "Structural and optical characterization of undoped and indium-doped CdS films grown by pulsed laser deposition". Thin Solid Films. Vol. 453-454, 2004, 187-194.