OPTICAL PARAMETERS OF SPRAY-DEPOSITED CdS:In THIN FILMS

Shadia J. Ikhmayies

Al Isra University, Faculty of Information Technology, Department of Basic Sciences-Physics, Amman 11622, Jordan.

Keywords: Cadmium sulfide, Thin films, Solar cells, Spray pyrolysis, Optical parameters.

Abstract

Cadmium sulfide (CdS) continues to hold an important position among the solar cell materials and optoelectronic materials. It is usually used as window layer in the CdS/CdTe thin film solar cell. Indium doping of CdS increases its conductivity, which results in a lower series resistance of the solar cell. Optimizing the optical parameters of this material is important in getting high performance solar cells and in the use of the material in optoelectronic devices. In this work, polycrystalline indium doped cadmium sulfide (CdS:In) thin films were produced by the spray pyrolysis (SP) technique on glass substrates. Transmittance of the films was measured at room temperature in the wavelength range 400-1100 nm and used to deduce the optical parameters such as the absorption coefficient, extinction coefficient, refractive index, real and imaginary parts of the dielectric constant. The refractive index dispersion was analyzed by the single oscillator model and the oscillator parameters were computed.

Introduction

Cadmium sulfide (CdS) which belongs to the II–VI group compounds is an n-type semiconductor with a direct bandgap E_g = 2.42 eV at room temperature. CdS thin films are usually used as a window layer in the CdS/CdTe thin film solar cells. But undoped CdS thin films generally have high electrical resistivity. An effective way to produce less resistive films is doping indium into these films [1]. The knowledge of the optical properties of these indium doped (CdS:In) films is very important in many scientific, technological and industrial applications in the field of optoelectronic devices, particularly solar cells. There are different techniques to produce CdS thin films such as chemical bath deposition (CBD) [2,3,4], thermal evaporation [5,6], electrodeposition [7], and spray pyrolysis (SP) [1,8,9]. The SP is used in the present work because it is a simple and inexpensive technique. It enables intentional doping and the production of large area films.

The evaluation of the optical parameters and dispersions constants of CdS is of considerable importance for applications in optoelectronic devices and solar cells, where the refractive index of a material is the key parameter for device design. The objective of this work is to deduce the optical parameters and dispersive constants of CdS:In thin films prepared by the SP technique on glass substrates. The extinction coefficient, refractive, index, the real and imaginary parts of the dielectric constant are calculated and discussed. The refractive index dispersions data of the produced films obeyed the single oscillator model, and the oscillator parameters were computed.

Experimental Procedure

The CdS:In thin films were prepared by spraying an aqueous solution of approximately stoichiometric ratios of the hydrated cadmium chloride ($CdCl_2.H_2O$) and thiourea [$(NH_2)_2CS$]

on glass substrates kept at 490°C. Indium chloride ($InCl_3$) was used as a dopant source with a ratio [Cd]/[In] = 1×10^{-4} in the starting solution. The solution flux was about 12.4 ml/min at a constant nitrogen flux of 5Kg/cm^2, where nitrogen is the carrier gas.

Transmission spectra of the prepared films were measured at room temperature by normal incidence of light, using a double beam UV-1601 PC Shimadzu spectrophotometer, in the wavelength range 400–1100 nm, using a blank glass substrate as a reference position. The microstructure of the films was determined by scanning electron microscopy (SEM), and the composition was determined by energy dispersive analysis of X-ray (EDAX). SEM observations and EDAX analysis were taken by FEI scanning electron microscope (Inspect F 50) which is supported by X-ray energy dispersive spectroscopy. The thickness of the films was determined by using transmittance and Lambert law of absorption in a semiconductor.

Results and Discussion

Polycrystalline CdS:In thin films of thickness 275–300 nm were produced by the SP technique on glass substrates at a substrate temperature of 490°C. Figure 1 depicts the SEM micrograph of one of the films, where the surface of the film appears to be compact, uniform, and fully covered with material. Polycrystalline nature of the film is apparent, where grains of different sizes and shapes can be easily distinguished.

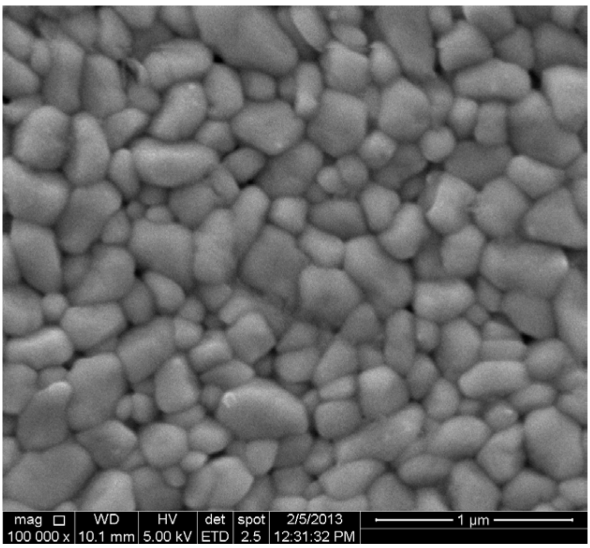

Figure 1. SEM micrograph of one of the as-deposited CdS:In thin films.

Transmission measurements are performed at room temperature in the range of 400–1100 nm to obtain information on the optical parameters of the CdS:In thin films obtained at the same conditions. The transmission spectra of three films of thickness 275–300 nm are shown in Figure 2. The transmittance of the films in the visible and near infrared region is in the range 72–89%.

The spectra show a sharp fall at the band edge, which is an indication of the good crystallinity of the films which is apparent in Figure 1.

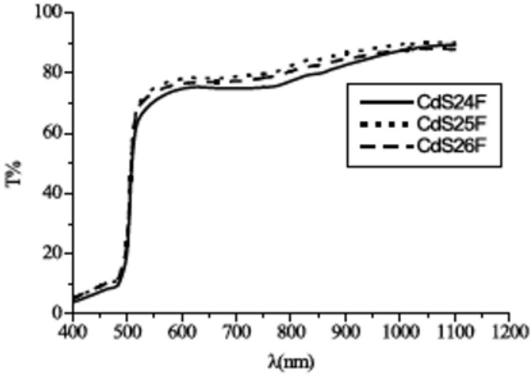

Figure 2. Optical transmittance against wavelength of the as-deposited CdS:In thin films of approximately the same thickness. Note: The legend displays the names of the samples.

To find the optical parameters the reflectance was deduced from the transmittance and plotted in Figure 3 against the photon's energy hv. The sharp increase in reflectance at about 2.5 eV corresponds to the characteristic bandgap of CdS:In. Reflectance in the near infrared and visible regions before the absorption edge is in the range 0.094–0.362

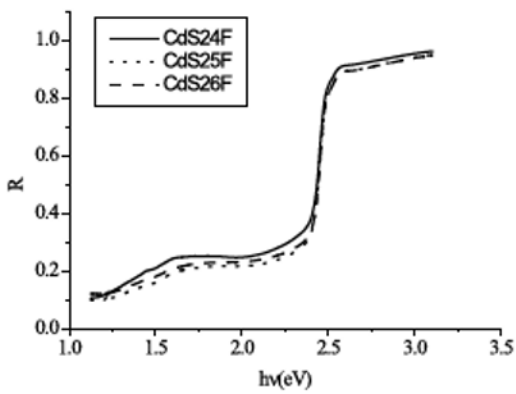

Figure 3 Reflectance against photon's energy for CdS:In thin films of approximately similar thickness.

The refractive index and the extinction coefficient were deduced from the relation that relates them with reflectance. This relation defines the reflectance of a film for a light wave incident normally from air, with refractive index $n_0 = 1$, on a medium of complex refractive index $n^* = n + ik$ and it is given by [10]

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

where n is the refractive index and k the extinction coefficient of the film. The value of the absorption coefficient α can be calculated from the transmittance data, and the extinction coefficient can be calculated using the relation

$$k = \frac{\lambda\alpha}{4\pi} \tag{2}$$

where λ is the wavelength in free space. Solving equation (1) for the refractive index n gives;

$$n = \frac{(1+R) + \left[(1+R)^2 - (1-R)^2(1+k^2)\right]^{1/2}}{1-R} \tag{3}$$

Figure 4 depicts the extinction coefficient of the three aforementioned films as a function of photon's energy hν. As the figure shows, in the region of weak absorption (before the absorption edge) k varies in the range 0.031–0.066. The value $k = 0.066$ is much larger than that of bulk CdS ($k = 0.0186$). This is because the extinction coefficient depends on the inherent properties and surface morphology of the films [8], and in the case of polycrystalline films, extra absorption of light occurs at the grain boundaries, which leads to non-zero value of k for photon energies smaller than the fundamental absorption edge [5]. After the absorption edge k sharply increases in accordance with the bandgap energy, then a knee is observed after which a slow increase in k is observed, and k reaches values in the range 0.31–0.34.

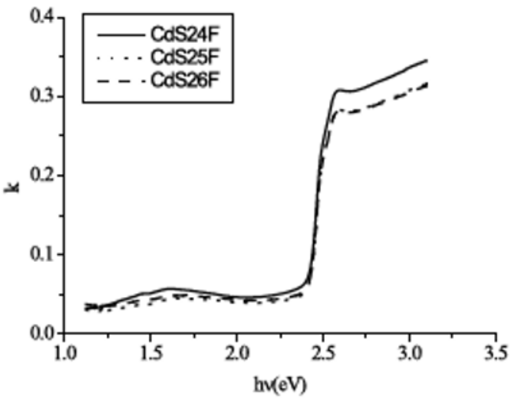

Figure 4 Extinction coefficient of the three spray-deposited CdS:In thin films of approximately the same thickness.

Figure 5 depicts the refractive index n as a function of hv for the same set of CdS:In thin films. From the figure, it can be seen that the values of n in the region of weak absorption (before the fundamental absorption edge) is in the range 1.384-2.556 for the energy range 1.127–2.396, after which it strongly increases with hv, where a knee is observed and strong increase in n continues. The maximum value of n in the region of weak absorption is consistent with that obtained by Sahay et al.[5] which is 2.53 to 2.64 for films of thickness in the range 25–100 nm.

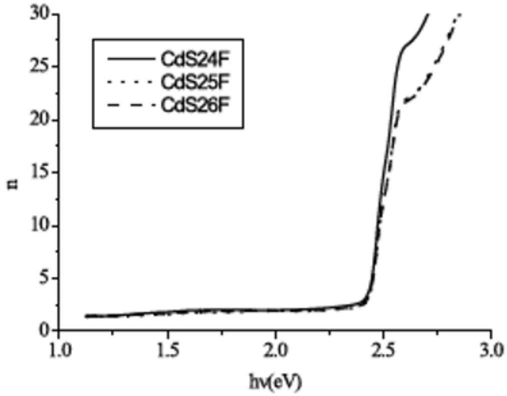

Figure 5 Refractive index against photon's enrgy of CdS:In thin films of approximately the same thickness.

Below the absorption edge, refractive index dispersion can be analyzed by the single oscillator model. So the obtained data of refractive index n is also analyzed to yield the long wavelength refractive index (n_∞) together with the average oscillator wavelength (λ_0) for CdS:In thin film using the following relation [11]

$$\frac{n_\infty^2-1}{n^2-1}=1-\left(\frac{\lambda_0}{\lambda}\right)^2 \tag{5}$$

The relation between $\left(n^2-1\right)^{-1}$ and λ^{-2} is shown in Figure 6. The figure also shows the linear fits in the linear part of each curve, where λ_0, n_∞ and $n_\infty^2=\varepsilon_\infty$ are evaluated from the fit parameters and listed in table I. From these values, the average excitation energy for electronic transitions $E_0=hc/\lambda_0$, and the dispersion energy which is a measure of the strength of interband optical transitions $E_d=E_0\left(n_\infty^2-1\right)$ are also calculated and listed in table I. The moments $M_{-1}=E_0^2M_{-3}$ and $M_{-3}=E_d/E_0^3$ of the optical transitions are calculated and inserted in table I too.

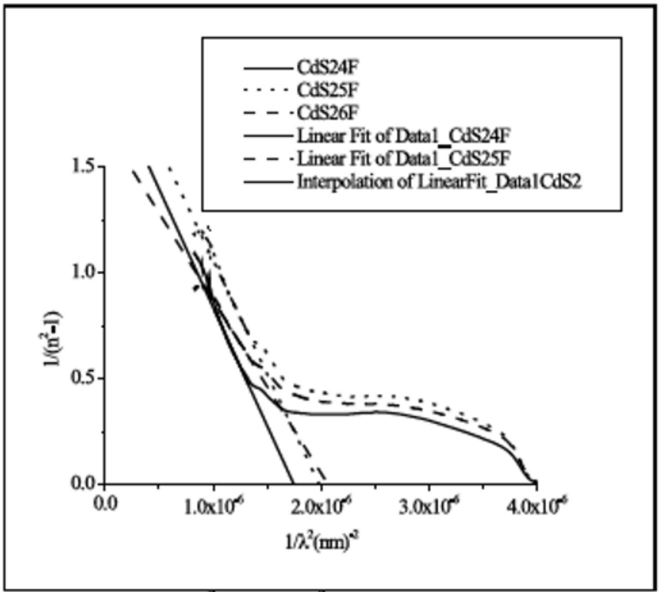

Figure 6. The relation between $1/(n^2-1)$ and $1/\lambda^2$ for CdS:In thin films of approximately the same thickness with the linear fits.

Table I. The oscillator parameters of CdS:In thin films of thickness 275-300 nm.

Sample	n_∞	ε_∞	λ_0(nm)	E_0(eV)	E_d(eV)	M_{-1}	$M_{-3}(eV)^{-2}$
CdS24F	1.229	1.511	756.1	1.640	0.839	0.511	0.190
CdS25F	1.211	1.468	709.8	1.747	0.817	0.468	0.153
CdS26F	1.261	1.591	695.9	1.782	1.053	0.591	0.186

The investigation of complex dielectric constant is very important as it provides information about electronic structure of the deposited material [12]. The complex dielectric constant ε^* is given by the relation $\varepsilon^* = \varepsilon_1 + \varepsilon_2 i$, where ε_1 is the real part and ε_2 is the imaginary part. The real part is the normal dielectric constant and imaginary part represents the absorption associated with free carriers [5]. The variation of ε_1 as a function of photon's energy hν follows the similar behavior as n whereas the variation of ε_2 follows the behavior of k. The extinction coefficient k and ε_2 are related to absorption coefficient α [12].

Figure 7 displays the relation between the real part of the dielectric constant ε_1 and photon's energy hν. It varies from 1.916–6.913 in the energy range 1.129–2.389 eV. This value is in good agreement with that obtained by Sahay et al. [5] for CdS films of different thicknesses (25–100 nm), where they got a peak value of 6.62 for wavelength values 300–1100 nm (1.127–4.133 eV), where it increases with hν.

Figure 8 depicts the relation between the imaginary part ε_2 of the dielectric constant with photon's energy hν. The value of ε_2 is approximately zero before the fundamental absorption edge. In the region of the absorption edge ε_2 sharply increases with hv, where the rapid increase at the edge is typical for direct bandgap materials. A knee appears at 2.58 eV for two films and at 2.59 eV for the other film after which a change in the rate of increase occurs. The values of hv at the knee correspond to the fundamental absorption edge E_g known as the optical bandgap energy, which can be assigned to the hexagonal phase of the CdS:In films, because at high substrate temperatures this phase is the predominant phase [9]. This value is in good agreement with that obtained by Sahay et al. [5] for the CdS films of different thicknesses (25–100 nm), where they got a peak value of 6.0 for wavelength values 300–1100 nm (1.127–4.133 eV).

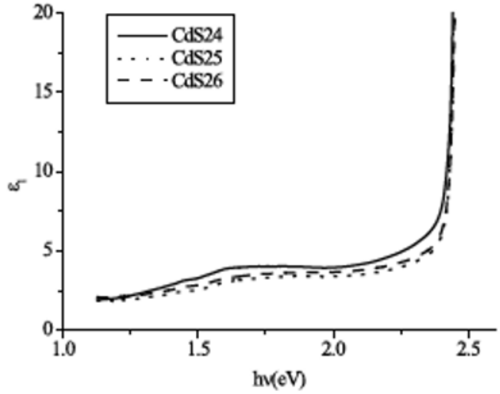

Figure 7 The real part of the dielectric constant against photon's energy for CdS:In thin films of approximately the same thickness.

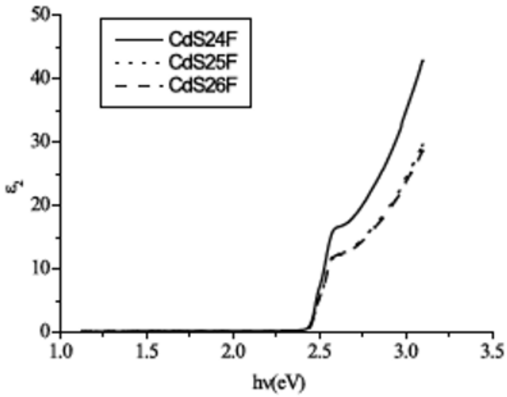

Figure 8 The imaginary part of the dielectric constant against photon's energy for CdS:In thin films of the same thickness.

Conclusions

CdS:In thin films prepared by the SP technique on glass substrates have been characterized using SEM, EDAX and optical transmittance measurements. Optical parameters such as extinction coefficient, refractive index, real and imaginary parts of the complex dielectric constant were deduced from the reflectance, and the variations of these with incident photon energy have been studied. From the dispersion of the refractive index, the oscillator parameters were calculated. These results are important for the use of CdS:In thin films in the development of solar cells and optoelectronic devices.

References

1. F. Atay et al., "The effect of In doping on some physical properties of CdS films", *Materials Science in Semiconductor Processing*, 6 (2003), 197–203.
2. G. Sasikala, P. Thilakan, C. Subramanian, "Modification in the chemical bath deposition apparatus, growth and characterization of CdS semiconducting thin films for photovoltaic applications", *Solar Energy Materials & Solar Cells*, 62 (2000), 275–293.
3. P. K. Nair, M. T. S. Nair, and J. Campos, "Photocurrent response in chemically deposited CdS thin films", *Solar Energy Materials*, 15 (1987), 441-452.
4. A. Kariper et al., "The structural, electrical and optical properties of CdS thin films as a function of pH", *Materials Chemistry and Physics*, 129 (2011), 183– 188.
5. P. P. Sahay, R. K. Nath, and S. Tewari, "Optical properties of thermally evaporated CdS thin films", *Cryst. Res. Technol.*, 42 (3) (2007), 275 – 280.
6. N.A. Shah et al., "Physical properties and characterization of Ag doped CdS thin films", *Journal of Alloys and Compounds*, 512 (2012), 27– 32.
7. Figen Kadirgan et al., "Properties of electrodeposited cadmium sulfide films for photovoltaic devices with comparison to CdS films prepared by other methods", *Turk. J. Chem.*, 24 (2000), 21– 33.
8. Nitu Badera et al., "Quenching of photoconductivity in Fe doped CdS thin films prepared by spray pyrolysis technique", *Applied Surface Science*, 254 (2008), 7042–7048.
9. Shadia. J. Ikhmayies and Riyad N. Ahmad-Bitar, "The influence of the substrate temperature on the photovoltaic properties of spray-deposited CdS:In thin films", *Applied Surface Science*, 256 (2010), 3541–3545.
10. Saeed Salem Babkair, Najat Mohammad Al-Twarqi, and Azhar Ahmad Ansari, "Optical characterization of CdTe films for solar cell applications", *Karachi University Journal of Science* 39 (2011), 1-5.
11. Ebru Şenadım Tüzemen et al., "Dependence of film thickness on the structural and optical properties of ZnO thin films", *Applied Surface Science* 255 (2009), 6195–6200.
12. L. S. Ravangave and U. V.Biradar, "Study of optical parameters of chemical bath deposited $Cd_{1-x}Zn_xS$ thin films, *GRA-Global Research Analysis*, 2 (1) (2013), 185–188.