Effects of the film thickness on optical constants of transparent CdS thin films deposited by chemical bath deposition

F. YAKUPHANOGLU^{a*}, C. VİSWANATHAN^b, P. PERANANTHAM^b, D. SOUNDARRAJAN^b ^aPhysics Department, Faculty of Arts and Science, Firat University, 23119 Elazig-Turkey ^bReseach Scholar, Department of Physics, Bharathiar University, Coimbatore-641 046 India

The optical constants and band gaps of the CdS thin films deposited by chemical bath have been calculated in the spectral wavelength range 400–1000 nm from the transmittance and reflectance measurements of normally-incident light. The CdS thin films exhibit good transparent behavior due to high transmittance values. The optical band gaps of the films were respectively found to be 2.34, 2. 41 and 2.46 eV for 100, 125 and 152 nm thicknesses. The increase in film thickness leads to an increase in optical band gap of the films. The refractive index values of the thin films changed significantly with film thickness. The dielectric constant of the films was analyzed using Standard Drude model. The optical carrier concentration and mobility values for the CdS thin films were determined and the obtained values changed with film thickness. It is shown that the film thickness modifies the optical constants and band gaps of the CdS films.

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1. Introduction

Cadmium sulphide (CdS), a wide energy gap semiconductor has emerged as an important material due to its applications in photovoltaic cell and optoelectronic devices [1–15]. CdS is naturally an n-type material with an optical band gap of 2.4 eV [16-17] and this is one of the metal chalcogenide semiconductors (II-VI) used in solar cells. Thin films of CdS are of considerable interest for their efficient use in the fabrication of solar cells [18]. The optical and structural properties of vacuum evaporated thin films of CdS are very sensitive to the deposition conditions as substrate temperature [19] and subsequent heat treatment [20]. The thin films of CdS have bee prepared using various methods such as chemical vapor deposition, electrodeposition, spray pyrolysis, dip growth, electroless deposition, successive ionic adsorption and reaction, and chemical bath deposition [21-27].

Chemical bath deposition (CBD) is widely used as a method for preparation of thin film materials. The CBD method consists of preparing a chemical bath of a salt which contains cadmium cations, and anions of either sulphates, nitrates, chlorides or acetates [28]. Optical properties of semiconductor films depend on the film thickness for their preparations and thus, optical properties of CdS thin films can be modified by preparing thin films having different thickness.

In present study, CdS thin films were prepared by chemical bath deposition to improve the optical constants and optical band gap. The aim of the present work is to study the dependence of optical constants of film thickness. Because, the evaluation of refractive indices of optical materials is of considerable importance for applications in integrated optic devices such as switches, filters and modulators, etc., where the refractive index of a material is the key parameter for device design. Furthermore, the optical absorption edge is one of the most important factors which determine the use of a thin film material for optical applications.

2. Experimental

2.1 Preparation of CdS thin films

CdS films can be deposited on Corning glass 7059 substrates cleaned with carbon tetrachloride, acetone, and isopropyl alcohol and rinsed with distilled water. The chemical bath was an aqueous solution of CdCl₂, KOH, NH_4NO_3 , and $CS(NH_2)_2$ with molar concentrations as cadmium chloride 0.074g(CdCl₂), potassium follows: hydroxide 1.4g(KOH), ammonium nitrate 2.4g(NH₄NO₃), and thiourea $0.304g(CS(NH_2)_2)$. In this process, thiourea acts as catalytic reagent. The glass is supported by Teflon holder and immersed into the chemical bath with continuous agitation during film deposition. The film deposition starts when the precursor thiourea is added. In this modality, the chemical bath solution is stirred meanwhile glass substrates are immersed into the bath. Bath solution is maintained at 75° C and deposition times vary for 15, 30 and 45 minutes. Optical spectrums of the thin films were recorded by Shimadzu UV-VIS-NIR 3600 spectrophotometer at room temperature. The optical absorption, transmittance .and reflectance spectra were analyzed to determine the optical constants such as refractive index, n extinction coefficient, k and absorption coefficient α . Analysis of the absorption coefficient was also carried out to determine optical band gap and nature of transitions.

3. Results and discussion

3.1. Determination of the optical band gap of the CdS thin films

The spectrums of absorption A, transmittance T and reflectance R of CdS thin films having thickness are shown in Fig. 1 (a-c). These spectrums of the thin films were significantly changed with the film thickness. Transmittance spectrums are analyzed into two regions, which are λ >300 nm and λ <300 nm. In region for λ <300 nm, the films indicates a good absorber behavior as the total of transmittance and reflectance is lower than unity. Whereas, in region for λ >300 nm the films exhibit good transparent behavior due to high transmittance values. As seen in T spectrums, the optical band edge increases with the film thickness. In semiconductor materials, the absorption due to the band to band transitions that determine the optical band gap E_g is expressed by the following relation [29],

$$(\alpha h\nu) = A(h\nu - E_g)^m \tag{1}$$

where m is a constant which determines type of the optical transition (m=1/2 for allowed direct transitions and m=2 for allowed indirect transitions). The optical band gaps from the plots of $(\alpha hv)^2$ and $(\alpha hv)^{1/2}$ vs. photon energy, as shown in Fig. 2 (a-c). The direct optical band gap values of the films were determined by a least squares fit and are given in Table 1. Absorption spectrums of the thin films show that the direct transitions are taking place. The absorption edge of the thin films shifts to higher energy values due to the film thickness. This suggests that the increase in film thickness leads to an increase in optical band gap. The increase in the optical band gap can be attributed to the broadening of energy band with increasing film thickness. It is evaluated that the film thickness becomes important parameter the for modification of the optical band gap of the thin films. Absorption spectrums indicate that the film thickness increases absorbance due to scattering losses. This increase in the absorbance cause large variations in the optical edge of the films. The thickness of the film causes a shift in the optical absorption edge therefore change in the band structure of the films [30].

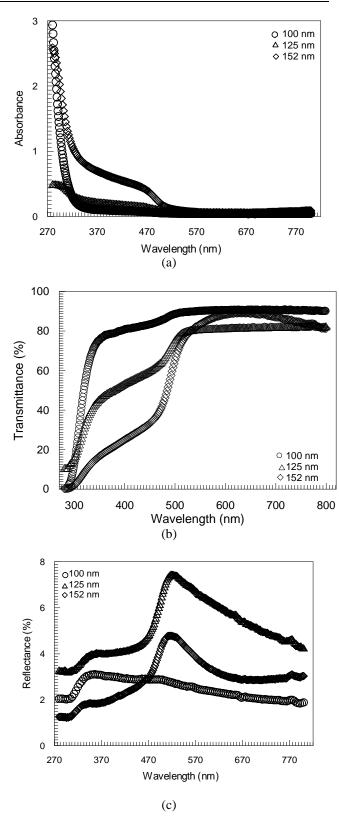


Fig. 1. Absorption, transmittance and reflectance spectra of CdS thin films.

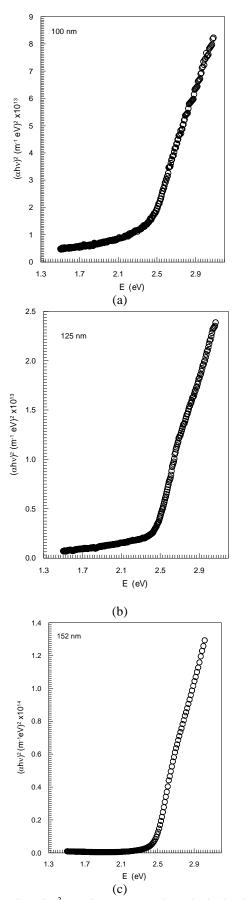


Fig. 2. The $(\alpha h v)^2$ vs. photon energy plots of CdS thin films.

3.2. Refractive index dispersion analysis of the CdS thin films

The refractive index of the films was calculated from reflectance spectrums [31]. The refractive index n of the films as a function of wavelength is shown in Fig. 3. It is seen that after 500 nm, the n values are decreased with increasing wavelength and the refractive index curves indicate the normal dispersion behaviour. The refractive index of the films changes with film thickness. The n curves show a peak at visible region and the intensity and position of the peak change with film thickness. The presence of this peak is due to optical transition from valence band to conduction band. The shifting of the peak position is indicative of variation in the optical band gap of the thin films. The refractive index values of the films are lower than that of vacuum evaporated CdS films and CdS films obtained from an ammonia-free chemical bath deposition process [32-34]. This suggests that the preparation process of the films and film thickness affect significantly the refractive index parameter.

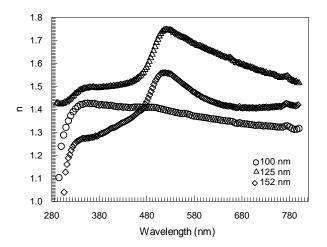


Fig. 3. Variation of n with wavelength for the CdS thin films.

The complex dielectric function can be used to study the optical properties of the thin films. The dielectric constant can be defined as, $\varepsilon(\omega)=\varepsilon_r(\omega)+i\varepsilon_i(\omega)$ and real and imaginary parts of the dielectric constant are related to the n and k values and these values are calculated using the formulas [30],

$$\varepsilon_1(\omega) = n^2(\omega) - k^2(\omega) \quad \varepsilon_2(\omega) = 2n(\omega)k(\omega)$$
(2)

The real and imaginary of the dielectric constant for the thin films were calculated and are given in Figs 4 (a-b). The ε_1 values increase up to certain photon energy and then decreases with increasing photon energy. The ε_1 values of the films with change film thickness. But, ε_2 values increase significantly with photon energy and tends to be constant. After 2.4 eV photon energy, the ε_2 values increases with increasing film thickness. The film thickness causes important changes in real part and imaginary parts of the dielectric constant. The dielectric constant of the films can be analyzed using Standard Drude model given by [35]

$$\varepsilon_D(E) = -\frac{E_D^2}{E^2 + iE_{\gamma}E} \tag{3}$$

where E_D is the Drude energy and $E\gamma$ is the relaxation energy. The real part of dielectric constant is expressed as,

$$\varepsilon_1(E) = \varepsilon_{opt} - \frac{E_D^2}{E^2 + E_{yt}^2} \tag{4}$$

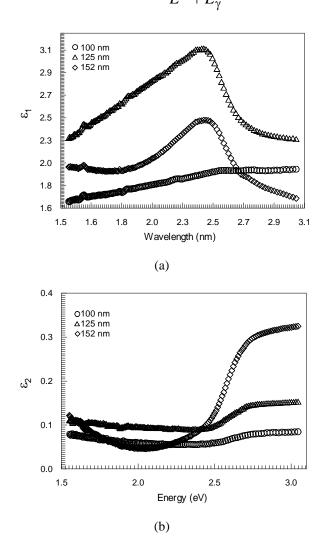


Fig. 4. Plots of ε_1 *and* ε_2 *versus wavelength of the CdS thin films.*

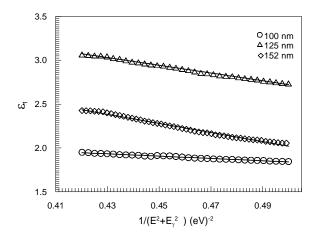


Fig. 5. Plots of ε_1 versus $1/(E^2+E\gamma^2)$ of the CdS thin films.

where ε_{opt} is the optical dielectric constant. Fig. 5 shows the plots of ε_1 versus $1/(E^2+E\gamma^2)$ for the films. The ε_{opt} values can be obtained from intercept of Fig. 5 and are given in Table 1. These values increase with film thickness. The plasma energy for the films were calculated from Fig. 4, where $\varepsilon_1=0$ E_p for films. The Drude E_D and plasma E_p energy values were determined and are given in Table 1. The plasma energy values of the films change with film thickness. The plasma frequency is determined by the well-known relation,

$$\omega_p^2 = \frac{N_{opt} e^2}{\varepsilon_{opt} \varepsilon_o m^*} \tag{5}$$

where N_{opt} is the optical carrier concentration and m^{*} is the effective mass of the electrons. The N_{opt} values for the films were calculated using Eq. 5 and are given in Table 1. The optical carrier concentration values changes with film thickness. The highest value was found for the film having thickness of 125 nm. The optical mobility of the films can be obtained using the following relation,

$$\mu_{opt} = \frac{e\tau}{m^*} \tag{6}$$

where t is the relaxation time. The μ_{opt} values for the film were calculated using Eq. 7 and are given in Table 1. The optical mobility values of the CdS films increase with the film thickness.

t (nm)	$E_g(eV)$	$E_p(eV)$	$E_{\gamma o}(eV)$	\mathcal{E}_{opt}	$E_D(eV)$	$\mu_{opt}(cm^{-2}/V.s)$	$N_{opt}(cm^{-3})$
100	2.34	0.87	5.8	2.49	10.23	0.94	2.89×10^{20}
125	2.41	4.90	4.134	4.61	3.98	1.33	1.69×10^{22}
152	2.46	0.33	1.96	4.92	4.53	2.80	8.22×10^{19}

Table 1 The optical parameters of CdS films

4. Conclusions

The optical constants and band gaps of the CdS thin films deposited by chemical bath have been computed. The optical band gaps and refractive index values of the films changed with film thickness. The dielectric constant of the films was analyzed using Standard Drude model. It is shown that the film thickness modifies optical constants and band gaps of the CdS thin films.

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References

- P. O'Brien, T. Saeed, J. Crystal Growth 158, 497 (1996).
- [2] M. Kostoglou, N. Andritsos, A.J. Karabelas, Thin Solid Films 387, 115 (2001).
- [3] S. S. Kale, U. S. Jadhav, C. D. Lokhande, Indian J. Pure Appl. Phys. 34, 324 (1996).
- [4] J. Herrero, M. T. Gutierrez, C. Guillen, J. M. Dona, M. A. Martinez, A. M. Chaparro, R. Bayon, Thin Solid Films 361–362, 28 (2000).
- [5] J. M. Dona, J. Herrero, J. Electrochem. Soc. India 139, 2810 (1992).
- [6] U. Pal, R. Silva-Gonzalez, G. Martinez-Montes, M. Gracia-Jimenez, M.A. Vidal, Sh. Torres, Thin Solid Films **305**, 345 (1997).
- [7] M. E. Calixto, P. J. Sebastian, Sol. Energy Mater. Sol. Cells 59, 65 (1999).
- [8] J. He, X.-N. Zhao, J.-J. Zhu, J. Wang, J. Crystal Growth 240, 389 (2002).
- [9] C. Guillen, M.A. Martinez, J. Herrero, Thin Solid Films 335, 37 (1998).
- [10] P. N. Gibson, M. E. Ozsan, D. Lincot, P. Cowache, D. Summa, Thin Solid Films **361–362**, 34 (2000).
- [11] K. L. Choy, B. Su, Thin Solid Films 388, 9 (2001).
- [12] R. Ortega Borges, D. Lincot, Journal of Electrochemical Society of India 144, 4081 (1997).
- [13] M. T. S. Nair, P. K. Nair, R. A. Zingaro,
 E. A. Meyers, J. Appl. Phys. 75(3), 1557 (1994).
- [14] S. G. Munde, M. P. Mahabole, R. S. Khairnar, J. Instrum. Soc. India **30**(1), 25 (2000).
- [15] T. L. Chu, S. S. Chu, C. Ferekides, C. Q. Wu, J. Britt,

C. Wang, J. Appl. Phys. 70(12), 7608 (1991).

- [16] S. Mathew, P. S. Mukerjee, K. P. Vijayakumar, Thin Solid Films 254, 278 (1995).
- [17] T. Hayashi, T. Nishikura, T. Suzuki, Y. Ema, J. Appl. Phys. 64(7), 3542 (1988).
- [18] T. L. Chu, S. S. Chu, J. Britt, C. Ferekids, C. Wang, C. Q. Wu, H. S. Ullal, IEEE Electron. Dev. Lett. EDL-13, 303 (1992).
- [19] J. Britt, C. Ferekids, Appl. Phys. Lett. 62, 2851 (1993).
- [20] V. Singh, B. Pal Singh, T.P. Sharma, R.C. Tyagi, Optical Materials 20, 171 (2002).
- [21] M. Kostoglou, N. Andritsos, A.J. Karabelas, Thin Solid Films 387, 115 (2001).
- [22] R.K. Nkum, A.A. Adimado, H. Totoe, Mater. Sci. Eng., B 55, 102 (1998).
- [23] S. Mahanty, D. Basak, F. Rueda, M. Leon, J. Electron. Mater. 28, 559 (1999).
- [24] C. Guillén, M.A. Martinez, J. Herrero, Thin Solid Films 335, 37 (1998).
- [25] K. Senthil, D. Mangalaraj, S.K. Narayandass, Appl. Surf. Sci. 476, 169 (2001).
- [26] R.S. Mane, C.D. Lokhande, Mater. Chem. Phys. 65, 1 (2000).
- [27] A. E. Rakhshani, A.S. Al-Azab, J. Phys., Condens. Matter 12, 8745 (2000).
- [28] J. L. Martinez, G. Martinez, G. Torres-Delgado, O. Guzman, P. Del Angel, O. Zelaya-Angel, R. Lozada-Morales, Journal of Materials Science: Materials In Electronics 8, 399 (1997).
- [29] N. F. Mott, E. A. Davis, Electronic process in non-Crystalline Materials, Calendron Press, Oxford, 1979
- [30] F. Yakuphanoglu, M. Sekerci, A. Balaban, Optical Materials 27, 1369 (2005).
- [31] F. Yakuphanoglu, Optical Materials 29, 253 (2006).
- [32] U. Pal, R. Silva-Gonzalez, G. Martinez-Montes, M. Gracia-Jimenez, M. A. Vidal, Sh. Torres, Thin Solid Films 305, 345 (1997).
- [33] M. G. Sandoval-Paz a, M. Sotelo-Lermab, A. Mendoza-Galvan a, R. Ramírez-Bon Thin Solid Films 515, 3356–3362 (2007)
- [34] K. Senthil, D. Mangalaraj, Sa. K. Narayandass, Sadao Adachi, Materials Science and Engineering B78, 53–58 (2000).
- [35] I. Hamberg, C. G. Granqvist, J .Appl. Phys. 60, R123 (1986).

^{*}Corresponding author: fyhanoglu@firat.edu.tr fyhan@hotmail.com;