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Variable-Angle Spectroellipsometric Characterization of CdS Thin Films

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Abstract: In this work, CdS thin films produced by ultrasonic spray pyrolysis technique. The optical properties of CdS thin films were investigated using spectroscopic ellipsometry and UV-VIS Spectrophotometer. The optical properties of CdS thin films coated glass substrates were evaluated by variable-angle spectroscopic ellipsometry. Variable angle spectroscopic ellipsometry was used for thickness and optical constant calculations. Multiple angle measurements were taken in the most sensitive angle of incidence region. Appropriate incident angle were obtained as experimental using graph of ψ and Δ. Cauchy-Urbach model was used to determine the thickness, refractive index and extinction coefficient for CdS thin films. Also, transmittance measurements and band gap values of the films was examined by UV-VIS spectrophotometer and optical method, respectively. Finally, the incidence angle effects were discussed on the optical properties of CdS thin films such as thickness and optical constant (refractive index and extinction coefficient).

Key words: CdS thin film, spectroscopic ellipsometry, thickness, optical constants and transmittance

CdS İnce Filmlerinin Değişik Açılarda Spektroelipsometrik Karakterizasyonu

Özet: Bu çalışmada, CdS ince filmleri ultrasonik kimyasal püskürtme tekniği kullanılarak üretildi. CdS ince filmlerinin optik özellikleri spektroskopik elipsometre ve UV-VIS spektrofotometre kullanılarak belirlendi. Cam tabanlar üzerine depolanan CdS ince filmlerinin optik özellikleri değişken açılardaki spektroskopik ellipsometre ölçüleri kullanılarak incelendi. Kalınlıkların ve optik sabitlerin hesaplamaları değişken açılardaki elipsometrik ölçümler kullanılarak yapıldı. En duyarlı gelme açısını belirlemek için çeşitli açılarda ölçümler yapıldı. Uygun gelme açısı, ψ ve Δ grafikleri kullanılarak deneysel olarak elde edildi. CdS ince filmlerinin kalınlıklarını, kırılma indisi ve sönüm katsayısı değerlerini belirlemek için Cauchy-Urbach modeli kullanıldı. Ayrıca, geçirgenlik ölçümleri ve bant aralığı değerleri sırasıyla UV-VIS spektrofotometre ve optik metot kullanılarak belirlendi. Sonuç olarak, CdS ince filmlerinin kalınlık ve optik sabitler (kırılma indisi ve sönüm katsayısı) gibi optik özelikleri üzerine gelme açısının etkileri tartışılmıştır.

Anahtar kelimeler: CdS ince filmleri, spektroskopik elipsometre, kalınlık, optik sabitler, geçirgenlik

1. Introduction

CdS is one of the most interesting II-VI semiconductors owing to its interesting optical, electrical and optoelectronic properties. CdS thin films have been used in a large variety of applications such as electronic, optoelectronic devices and photovoltaic applications [1, 2]. There are several techniques for process CdS thin films, such as chemical bath deposition [3, 4], thermal evaporation [5, 6], vacuum evaporation [7], spray pyrolysis [8-10]. Among these techniques, spray pyrolysis is a simple, inexpensive, non-vacuum and suitable technique to prepare large area. Also, this technique is used to obtain homogeneous, adherent and stoichiometric thin films.

The optical parameters such as thickness, refractive index, extinction coefficient, absorption coefficient and transmittance are necessary to study various technology application that use semiconductor thin films. For this reason, the thin film technologies need the films with the well examined these physical parameters. These parameters of thin films are determined from spectroscopic ellipsometry [11-14]. Spectroscopic ellipsometry technique is used in practice and it is one of the nondestructive methods. Also, several methods can be used to determine these optical parameters such as PUMA [15], Swanepoel-Heavens's method [16] and envelop method [17].

In this work, CdS thin films were produced by the ultrasonic spray pyrolysis technique (USP), and optical properties of the films were characterized using spectroscopic ellipsometry (SE) and UV-VIS spectrophotometer. The thickness and optical constants of such as refractive index, extinction coefficients are obtained using variable-angle SE data. Besides, the effect of the variable-angle SE on the thickness and optical constants of CdS films is investigated.

2. Experimental procedure

CdS thin films were grown on glass substrate using USP technique. Spray solution was prepared by mixing the appropriate volumes of $CdCl_2.2H_2O$ (0.1 M) and $CS(NH_2)_2$ (0.1 M) dissolved in a deionized water. The substrate temperature was fixed at 320±5 °C and was controlled a thermocouple. The solution flow rate and gas pressure were kept constant at 5 ml.min^{-1} and 1 bar. Air was used as the carrier gas and the nozzle to substrate distance was 28 cm.

After deposition of CdS thin films, the optical properties were investigated. Optical transmittance and absorbance data were obtained with a UV-VIS Shimadzu 25500 double beam spectrophotometer and ellipsometric measurements were carried out by PHE 102 spectroscopic ellipsometer over a spectrum wavelength range 250-2300 nm with a polarizer-sample-analyzer configuration. But, the investigation of CdS thin films has been performed in the wavelength range of 1200-1600 nm where Cauchy-Urbach model has been used to obtain the thickness and the optical constants. This wavelength range corresponds to a region where all films are transparent or weakly absorbing. So, Cauchy-Urbach model can be used to these films in this wavelength range.

The thickness and the optical constants (refractive index and extinction coefficient) of the films were obtained by analyzing the measured variable-angle ellipsometric spectra (Ψ and Δ) though the Cauchy-Urbach model.

3. Results and discussions

Ellipsometry is one of the most advantaged techniques that is used to polarized light to characterize thin film and bulk materials. SE is very sensitive to the film thickness and optic constants, especially semiconductors. Besides, SE can be used to characterize composition, roughness, crystalline nature and other material properties [18-20]. As an optical technique, SE is non-destructive and contactless. Upon the analysis of the change of polarization of light, SE can be give information about layers.

In SE measurements, Ψ and Δ spectra are recorded at each wavelength and angle of incidence [21]. These two parameters are related to the optical and structural properties of the sample through the following expression [22]:

$$\rho = R_p / R_s = \text{tg}\,\Psi \exp(i\Delta) \tag{1}$$

where R_p and R_s are the complex reflection coefficients for the light being polarized parallel (p) and perpendicular (s) to the plane of incidence, respectively. Δ reflects the change in the phase difference between the incident and reflected waves for respectively p-polarized and s-polarized components. The values of Δ vary from zero to 360°. Ψ describes the orientation of the ellipse and $tg\Psi$ is the absolute value of R_p/R_s [23, 24]. The fundamental equation for the complex reflectance ratio ρ is also described as follows:

$$\rho = f(n_1, n_2, n, \varphi, t, \lambda, k) \tag{2}$$

where n_1, n_2 and n represent the refractive index of air, substrate and film, respectively. φ and λ represent the incident angle and wavelength of incident light, respectively. t and k the thickness and extinction coefficient of thin film, respectively [25].

Ellipsometry does not measure optical constants or film thickness directly; however Ψ and Δ can be represented as mathematical functions relating these material characteristics. Hence, a mathematical analysis called model-dependent analysis must be performed to determine real parameters from the measured ellipsometric data. Also, finding the best match between the model and the experiment is typically achieved through regression. An estimator, like the Mean Squared Error (MSE), is used to quantify the difference between curves. The unknown parameters are allowed to vary until the minimum MSE is reached. The best answer corresponds to the lowest MSE.

Numerous material parameters can potentially be determined through SE analysis, including layer thickness, surface and/or interfacial roughness, optical constants and void fraction, using optical physics (Fresnel reflection coefficients, Snell's law, etc.) In order to extract useful information about a sample (thicknesses and optical constants of the layers) the experimental data are compared with the data generated using a model which describes the structure of the sample and its optical response [26].

The optical constants play an important role in optical communication and designing of the optical devices, because they are closely related to the electronic polarizability of ions and the local field inside materials. Cauchy model, which is suitable for semiconductors, was used to extract the optical constants of the CdS thin films. The following formulas were used to define the refractive index (n) and extinction coefficient (k) of the Cauchy material [27]:

$$n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \tag{3}$$

$$k(\lambda) = \alpha \exp \beta \left[12.400 \left(\frac{1}{\lambda} + \frac{1}{\gamma} \right) \right] \tag{4}$$

where *A*, *B*, *C*, α, β and γ are model parameters. Some works showed that Cauchy model is suitable for CdS thin film ellipsometric characterization [28, 29]. Variable angle spectroscopic ellipsometry measures changes in polarization of light as a function of angle and wavelength when light is reflected from or transmitted through a sample.

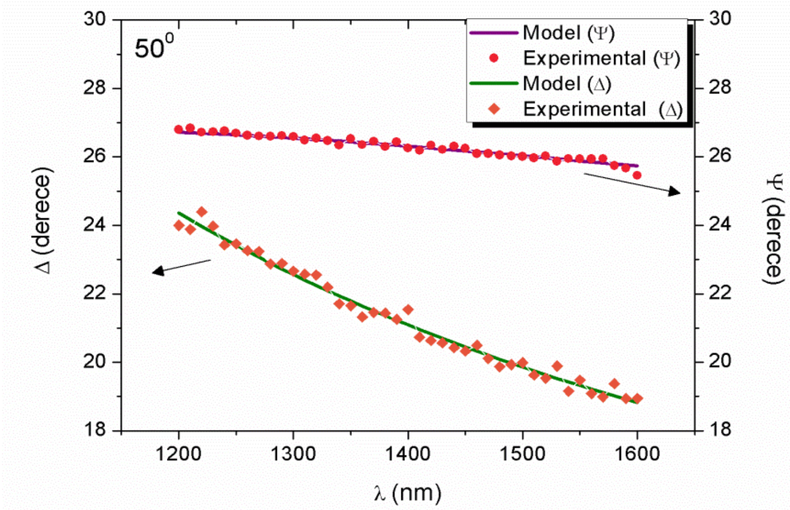
So, this work investigates the effectiveness of different angle that can be applied to the analysis of CdS thin films. Ellipsometric Ψ and Δ data were acquired at three angles of incidence (50°, 60° and 70°) over the spectral range 1200-1600 nm in step 10 nm. Multiple angles and wavelengths were fit simultaneously in the Cauchy-Urbach optical model. At each measured wavelength Ψ and Δ data are measured at multiple angles. This helps greatly in adding information about film thickness, refractive index and extinction coefficient for CdS thin films.

Cauchy-Urbach model determined an approximate film thickness and refractive index it is desirable to find a region of the measured spectral range where the film nearly transparent. This allows simpler models with fewer parameters to be used in the fitting the data. Fig. 1 shows Ψ and Δ fits to the experimental data over the spectral range 1200-1600 nm at different incidence angles. Also, thicknesses and model parameters are given in Table 1. The measured values were best fitted using Cauchy-Urbach dispersion model. A good fit is found between experimental and model data. However, there are some small deviations on Ψ and Δ values between model and experimental data. This is probably due to the depolarizing effect of roughness, grain boundaries and morphologies of the films which affect the experimental data. Backside reflection of glass substrates may also cause deviations on fitted values.

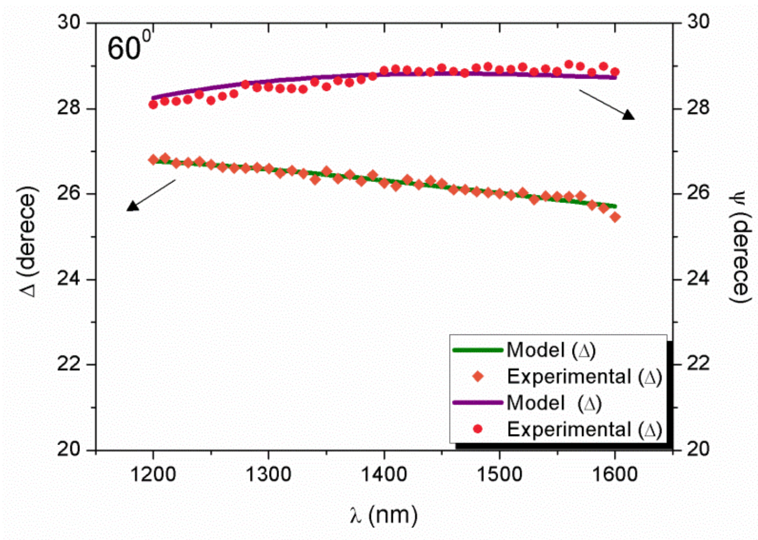
Table 1. The thickness and SE parameters of CdS thin films at different incidence angles

Sample	**t (nm)**	**A**	**B($\times10^{-2}$) (nm^2)**	**C($\times10^{-2}$) (nm^2)**	**α**	**β**	**MSE**
50°	139.04	2.349	0.019	0.14	0.48	1.5	0.01
60°	139.09	2.347	0.018	0.12	0.31	1.3	0.01
70°	137.06	2.339	0.015	0.10	0.56	1.6	0.03

Refractive index n (λ) and extinction coefficient k (λ) spectra of the CdS films are shown in Fig. 2 and Fig. 3, respectively. Fig. 2 is observed that the variation of refractive index with wavelength where the solid curve reperesents the Cauchy fit and refractive index of all deposited films decreases slightingly from 50° to 70°. Also, the data followed the relation Eq. (3) for the CdS films, implying that the films had normal dispersion for the entire range of wavelength studied.



(a)



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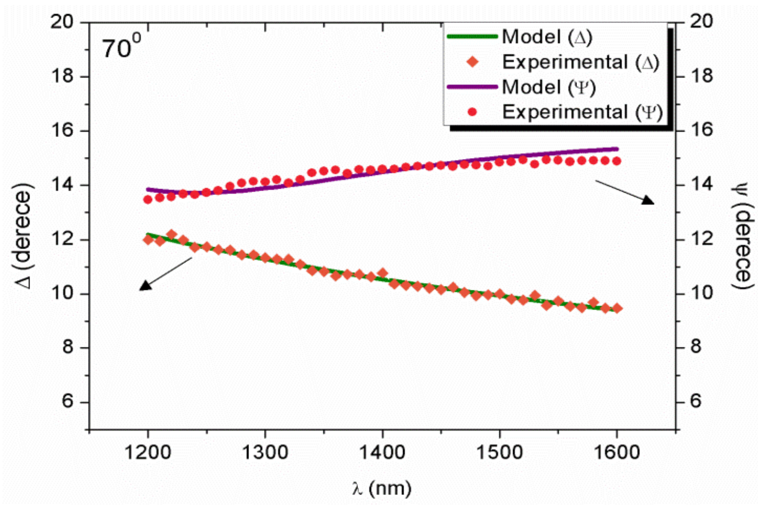

(c)

Figure 1. SE spectra (Δ and Ψ) (a) 50°, (b) 60° and (c) 70° of CdS thin films at different incidence angles

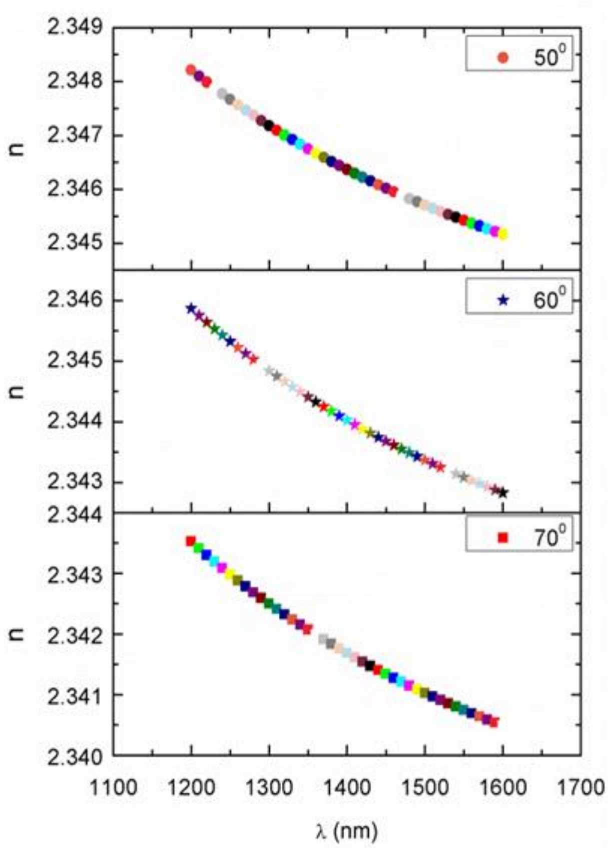

Figure 2. Refractive index (*n*) spectra of CdS thin films

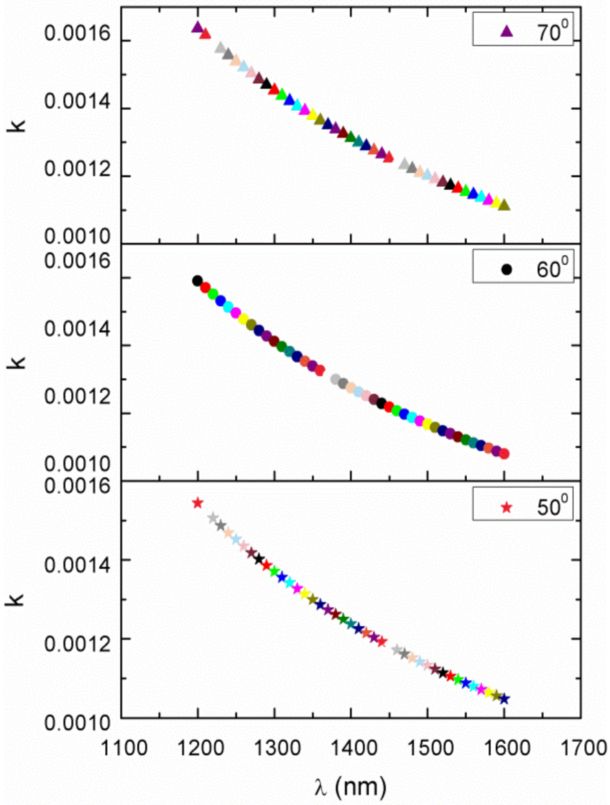

Figure 3. Extinction coefficient (*k*) spectra of CdS thin films.

Fig. 4 shows the transmittance and absorbance spectra of CdS thin films, measured in the wavelengths between 300-900 nm. The optical transmittance falls very sharply near the UV region due to the onset of fundamental absorption. The spectra showed an average transmittance ~60 %.

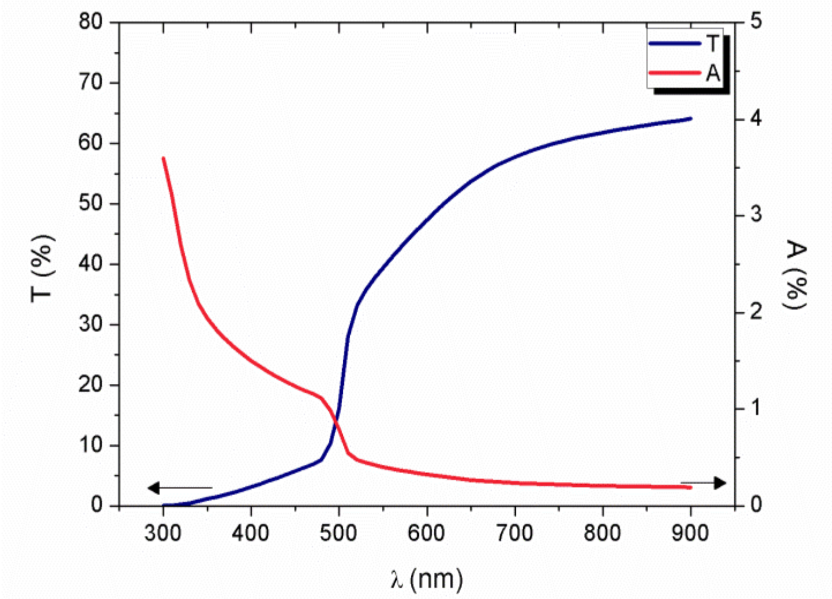

Figure 4. Transmittance spectra of CdS thin films

The absorption coefficient (α), in the strong absorption region was calculated from the transmittance spectra data;

$$\alpha = -\left(\frac{1}{t}\right)\ln T \qquad (5)$$

where t is the thickness and T is the transmittance of the film. Fig. 5 shows the spectral dependence of absorption coefficient in CdS thin films. It could be observed that the absorption coefficient increased with the increase of photon energy and showed band tails in the different energy region. This indicated that is a high concentration of impurity states causing the band structures to perturb, resulting in a prolonged tail extending into the energy gap in the thin films [30]. An exponential increase in the absorption edge follows the Urbach equation [31];

$$\alpha = \alpha_0 exp\left[\frac{h\nu - E_1}{E_0}\right] \qquad (6)$$

where E_0 and α_0 are characteristic parameters of the material, represented as the Urbach energy width of the exponential tail and Urbach absorption energy. According to Eq. (6), the plot of lnα as a function of photon energy, E gives a straight line converges at a point E_1 called as 'focal point'. The Urbach tail was observed for CdS thin films and Urbach energy is calculated as 281 meV.

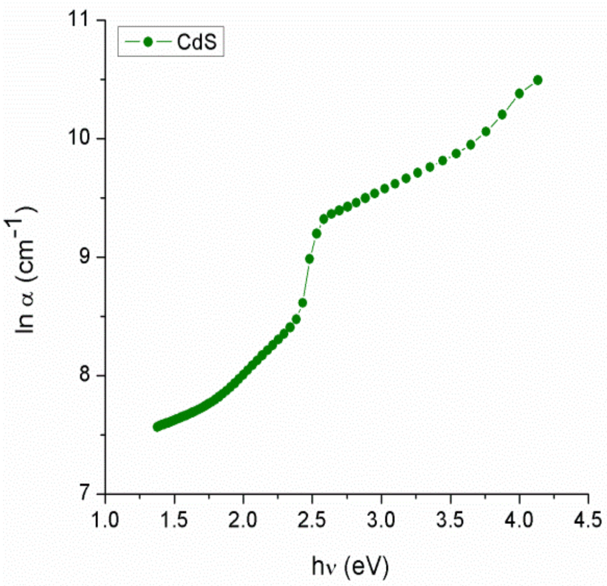

Figure 5. Variation of absorbtion coefficient as a function of photon energy

The energy band gap of the CdS films can be calculated from the absorption coefficient, (α) on the photon energy ($h\nu$). The direct and indirect nature of optical transition between parabolic bands can be studied using the relation [32];

$$\alpha h\nu = A\left(h\nu - E_g\right)^n \tag{7}$$

where A is a constant, E_g is the optical energy band gap, $n=1/2$ and $3/2$ for direct allowed and direct forbidden transitions, respectively. Further, the value of n=2 and 3 for the indirect allowed and indirect forbidden transitions respectively. In this work, the variation of absorption coefficient with the photon energy followed the above relation for n=1/2 indicating that the transition must correspond to a directly allowed electronic transition. Fig. 6 shows a plot of $(\alpha h\nu)^2$ versus $h\nu$ and the energy band gap was calculated by extrapolation of the linear portion of $(\alpha h\nu)^2$ versus $h\nu$ plot onto the energy axis. The energy band gap value of CdS thin films was determined as 2.38 eV.

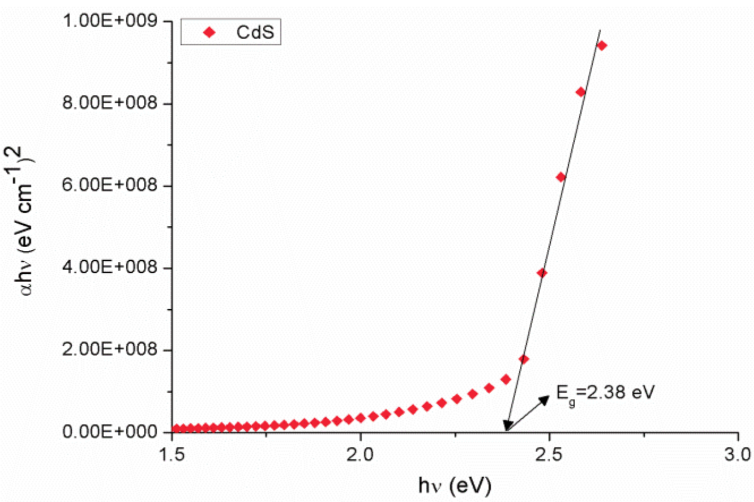

Figure 6. $(\alpha h\nu)^2$~$h\nu$ variations of CdS thin films

4. Conclusion

In conclusion, CdS thin films were successfully prepared by ultrasonic spray pyrolysis on glass substrate. The optical constants of the films were characterized by using spectroscopic ellipsometer. It was found that the three different incident angles could be used to fit the experimental data in the thin film studied. Cauchy-Urbach model fitted well the spectroscopic ellipsometric data (Ψ and Δ) at different incidence angles. The thickness, refractive index and extinction coefficient were found to be dependent on variation of angle of incidence. The best fit was determined optimal angle of incidence at 50° and 60°. The thickness of the films was measured as 139±2 nm. The refractive indices of CdS thin films showed a normal dispersion behavior and the values were in the range of 2.3~2.4, which are reasonable for CdS thin films. The optical properties of the films were determined by using optical transmittance and absorption spectra. The CdS thin films had an absorption coefficient and Urbach energy (E_0=281 meV) was calculated. Also, the optical band gap value was determined as 2.38 eV.

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References

[1] Chu T.L., Chu S.S., 1993. Efficient thin film CdS/CdTe solar cells, *Progress Photovoltaics*, 1: 31-42.

[2] Davis A., Vaccoro K., Dauplaise, Waters W., Lorenzo J., 1999. Optimization of chemical bath-deposited cadmium sulfide on InP using a novel sulfur pretreatment, *Journal of Electrochemical Society*, 146: 1046-1053.

[3] Vigil O., Riech I., Garcia-Rocha M., Zelaya-Angle O., 1997. Characterization of defect levels in chemically deposited CdS films in The cubic-to hexagonal phase transition, *Journal of Vacuum Science Technology A*, 15: 2282-2286.

[4] Yu I., Isobe T., Senna M., 1995. Preparation and properties CdS thin films comprising nano-particles by a solution growth technique, *Material Research Bulletin*, 30: 975-985.

[5] Mahdi M.A., Hassan J.J., Kasim S.J., Ng S.S., Hassan Z., 2014. Optical properties of CdS micro/nanocrystalline structures prepared via a thermal evaporation method, *Materials Science in Semiconductor Processing*, 26: 87–92.

[6] Smith G. B., Ignatiev A., Zajac G., 1980. Solar Selective Black Cobalt: Preparation, Structure and Thermal Stability, *Journal of Applied Physics*, 51:4186-4196.

[7]Lepek M., Dogil B., Ciecholewski R., 1983. A Study of CdS thin film deposition, *Thin Solid Films*, 109: 103-107.

[8] Ahmed-Bitar R.N., 2000. Effect of doping and heat treatment on the photoluminescence of CdS films deposited by spray pyrolysis, *Renewable Energy*, 19: 579-586.

[9] Ashour A., 2003. Physical properties of spray pyrolysed CdS thin films, *Turkish Journal of Physics*, 27: 551-558.

[10] Mathew S., Mukerjee P.S., Vijayakumar K.P., 1995. Optical and surface properties of spray-pyrolysed CdS thin films, *Thin Solid Films*, 254: 278-284.

[11]Podesta A., Armani N., Saltavi G., Romeo N., Bosio A., Prato M., 2006. Influence of fluorine doping on the optical properties of CdS thin films for photovoltaic applications, *Thin Solid Films*, 511-512: 448-452.

[12]Mathew S., Mukerjee P.S., Vijayakumar K.P., 1995. Optical and surface properties of spray-pyrolysed CdS thin films, *Thin Solid Films*, 254: 278-284.

[13] Senthil K., Mangalaraj D., Narayandass Sa.K., Adachi S., 2000. Optical constants of vacuum-evaporated cadmium sulphide thin films measured by spectroscopic ellipsometry, *Material Science Engineering B*, 78: 53-58.

[14] Sridharan M., Narayandass Sa.K., Manglanaj D., Lee H.C., 2002. Characterization of vacuum evaporated polycrystalline Cd0.96Zn0.04Te thin films by XRD, Raman scattering and spectroscopic ellipsometry, *Crystal Research Technology*, 37:964-975.
[15] E Birgin. G., I Chambouleyron. and Martınez J. M., 1999. Es-timation of the optical constants and the thickness of thin films using unconstrained optimization, *Journal of Computational Physics*, 151(2): 862- 880.
[16] Swanepoel R., 1983. Determination of the thickness and optical constants of amorphous silicon, *Journal of Physics E: Scientific Instruments*, 16: 1214-1222.
[17] Gencyılmaz O., Karakaya S., F Atay., Ozbas O., and Akyuz I., 2012. Structural and optical properties of transparent polycrystalline ZnO films, AIP Conf. Proc., 1476: 216-220.
[18] Liu A., Xue J., Meng X., Sun J., Huang Z., Chu J., 2008. Infrared optical properties of Ba(Zr0.20Ti0.80)O3 and Ba(Zr0.30Ti0.70)O3 thin films prepared by sol–gel method, *Applied Surface Science*, 254: 5660-5663.
[19] Xu J., Gao C., Zhai J., Yao X., Xue J., Huang Z., 2006. Structure-related infrared optical properties of Ba(ZrxTi1-x)O3 thin films grown on Pt/Ti/SiO2/Si substrates by low-temperature processing, *Journal of Crystal Growth*, 291: 130-134.
[20] Huang Z., Chu J., 2001. The refractive index dispersion of Hg1-xCdxTe by infrared spectroscopic ellipsometry, *Infrared Physics Technology*, 42:77-84.
[21] Shan F.K., Z. Liu F., Liu G.X., Shin B.C., Yu Y.S., Kim S.Y., Kim T.S., 2004. spectroscopic ellipsometry characterization of Al-doped ZnO thin films deposited by pulsed laser deposition, *Journal of the Korean Physical Society*, 44 (5): 1215-1219.
[22] Azzam R.M.A., Bashara N.M., Ellipsometry and Polarized Light, North-Holland, New York, 1977.
[23] Khoshman J.M., Kordesch M.E., 2005. Spectroscopic ellipsometry characterization of amorphous aluminum nitride and indium nitride thin films, *Physica Statatus Solidi*, C2(7): 2821-2827.
[24] Goyal D.K., Pribil G.K., Woollam J.A., Subramanian A., 2008. Detection of ultrathin biological films using vacuum ultraviolet spectroscopic ellipsometry, *Material Science Engineer B.*, 149: 26-33.
[25] Mansour M., Naciri A.E., Johann L., Duguay S., Grob J.J., Stchakovsky M., Eypert C., 2006. Dielectric function of germanium nanocrystals between 0.6 and 6.5 eV by spectroscopic ellipsometry, *Journal of Physics and Chemistry Solids*, 67:1291-1300.
[26]Jellison G.E., 2004. Generalized ellipsometry for materials characterization, *Thin Solid Films* 450: 42-47.
[27] Khoshman J.M., Kordesch M.E., 2005. Bandgap engineering in amorphous BexZnyO thin films *Journal of Non-Crystal Solids*, 351:3334-3340.
[28] Castilloa S.J., Mendoza-Galvánc A., Ramírez-Bonc R., Espinoza-Beltránc F.J., Sotelo-Lermab M., González-Hernándezc J., Martínez G., 2000. Structural, optical and electrical characterization of In/CdS/glass thermally annealed system, *Thin Solid Films*, 373: 10-14.
[29] Podesta A., Armani N., Salviati G., Romeo N., Bosio A., Prato M., 2006. Influence of the fluorine doping on the optical properties of CdS thin films for photovoltaic applications, *Thin Solid Films*, 511: 448-452.
[30] Parmenter R.H., 1955. Energy levels of a disordered alloy, *Physics Review Letters*, 97: 587-698.
[31] Melsheimer J., Ziegler O., 1985. Band gap energy and Urbach tail studies of amorphous, partially crystalline and polycrystalline tin dioxide, *Thin Solid Films*, 129: 35-37.
[32] Tan S.T., Chen B.J., Sun X.W., Fan W.J., Kwok H.S., Zhang X.H., Chua S.J., 2005. Blueshift of optical band gap in ZnO thin films grown by metal-organic chemical-vapor deposition, *Journal of Applied Physics*, 98:013505(1-5).

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