INFLUENCE OF SUBSTRATE TEMPERATURE ON THE STRUCTURAL AND OPTICAL PROPERTIES OF CdS THIN FILMS

Najiba Abdullah Hasan, Salah Qaduri Hazaa[a], Ameer Abdul Hussain Salih, Saba Jameel Hasan

Physics Department, Education College, Al-Mustansiriyah University, Baghdad, Iraq
[a]Email: salehhazaa@yahoo.com

ABSTRACT

CdS thin films were deposited on glass substrates at different temperatures by chemical spray pyrolysis. The prepared films were characterized by X-ray diffraction (XRD), Atomic Force Microscopy (AFM) and UV-Visible spectrophotometer. X-ray diffraction study shows a phase transition from cubic to hexagonal phase with the increase in substrate temperature from 200 °C to 400 °C and improves the crystalline of films. AFM analysis shows that the root mean square (RMS) surface roughness ranges from 15 nm for 200 °C films to 24.9 nm for 400 °C films. Optical characterization indicates that deposited film by chemical spray pyrolysis at different temperatures has a small decrease in band gap, which can be related to a phase change from cubic to hexagonal phase.

Keywords: CdS thin films, spray pyrolysis, structural properties, optical properties.

I. INTRODUCTION

Among wide band gap II-VI semiconductors, cadmium sulphide (CdS) with its direct band gap of 2.42eV at room temperature is a promising material and is applied in various applications such as solar cells, thin film transistors, light emitting diodes and photonic devices (Saikia, et al., 2010, Sanap and Pawar, 2009, Khan, et al., 2010, Ezenwa and Ekpunobi, 2010). Polycrystalline CdS thin films are widely used as window material (Tepantl´an, 2008) in several heterojunction solar cells because of its optical and electrical properties (Khan, et al., 2010) .

There are different deposition techniques to prepare thin films in which the deposition temperature is one of the main parameters that should be controlled to get high quality. These methods include thermal evaporation (Khan, et al., 2010, Sahay, et al., 2007), spray pyrolysis (SP) (Tepantl´an, 2008, Raji, et al., 2005), chemical bath deposition (CBD) (Ezenwa and Ekpunobi, 2010, Patil, et al., 2011), and dc magnetron sputtering (Abduev, et al., 2010).

It is known that CdS thin films can exist in either cubic or hexagonal phase or as a mixture of both. Recently, a transition from the cubic to the stable hexagonal phase on thermal annealing and a consequent change in the optical band gap have been reported (Ikhmayies and Bitar, 2010, Melo, et al., 1994) for their chemical bath deposited CdS thin films.

The aim of this work is to obtain CdS films on glass substrates at different temperatures using spray pyrolysis and to investigate the influence of the substrate temperature on their structural, morphological and optical properties.

II. THEORY

When one observes the optical transmittance and absorbance spectra of thin films, it is clear that the transmittance values increase with increasing wavelength and thickness of films, and absorbance decreases with increasing wavelength and thickness of films. The nature of the transition (direct or indirect) is determined by the relations (Liu, et al., 2010, Gumus, et al., 2006)

$$\alpha h\upsilon = A(h\upsilon - E_g)^r, \qquad (1)$$

$$\alpha = \frac{\ln\left(\frac{1}{T'}\right)}{t}, \qquad (2)$$

where A is a constant, $h\nu$ the photon energy, E_g the optical energy gap, α the absorption coefficient, t the thickness of the film, T' the transmittance, and r a constant which depends on the type of the electronic transitions, where r is equal to 1/2, 3/2, 2 and 3 for allowed direct, forbidden direct, indirect allowed and indirect forbidden transitions, respectively.

The absorption coefficient near the band edge shows an exponential dependence on photon energy (Urbach, 1953)

$$\alpha = \alpha_0 \exp(h\upsilon / E_u), \qquad (3)$$

where α_o is a constant, and E_u is called the Urbach energy. The Urbach energy of a thin film depends on the structural defects, and dislocation density. Some defects are formed during the formation of the films, and these defects produce localized states in the band gap. The Urbach energy is interpreted as the width of the tails of localized states. Thus, a plot of ln α against $h\nu$ should be linear, and the Urbach energy can be calculated from the reciprocal slope of the linear portion.

From the Urbach energy, the steepness parameter β can be calculated using the relation (Park, 2011)

$$\beta = k_B T / U_r, \qquad (4)$$

where k_B is Boltzman's constant and T is the absolute temperature. The steepness parameter characterizes the broadening of the absorption edge due to the electron-phonon interaction or excitation-phonon interaction (Dhanya and Menon, 2011).

The refractive index of a solid and in thin films gives information on the electronic polarizability, local field and for determining the density of colors inside the material (Mahdi, et al., 2009). Thus, it is important to determine optical constants of films, the complex optical refractive index (ň) of the films is described by the equation (Mahdi, et al., 2009):

$$\check{n} = n + ik, \qquad (5.a)$$

where n is the real part and k is the imaginary part (extinction coefficient) of the complex refractive index. The real refractive index n and the extinction coefficient k of the sample can be obtained from the equation (Abeles, 1972)

$$n = \frac{1+R}{1-R} + [(\frac{1+R}{1-R})^2 - (k^2 - 1)]^{\frac{1}{2}}, \qquad (5.b)$$

where

$$k = \frac{\alpha\lambda}{4\pi}. \qquad (6)$$

and R is the reflectance. The complex dielectric constant is defined as (Abeles, 1972)

$$\varepsilon = \varepsilon_r + i\varepsilon_i, \qquad (7)$$

where ε_r and ε_i are the real and imaginary parts of the dielectric constant, respectively, and are related to the n and k in eqs. (5) and (6) by the relations

$$\varepsilon_r = n^2 - k^2, \qquad (8)$$

$$\varepsilon_i = 2nk. \qquad (9)$$

III. EXPERIMENTAL DETAILS

CdS thin films were prepared on glass substrates by spray pyrolysis technique. The experimental setup is similar to that described in Hazaa (2013) and Raji, et al. (2005). The CdS thin films were prepared by spraying an aqueous solution of 0.1 M cadmium chloride ($CdCl_2$) and 0.1 M thiourea (CH4N2S) on a glass substrate kept at 200°C, 300 °C and 400 °C and controlled through a thermocouple.

The X-ray diffraction patterns of the films were recorded with a JEOL 60 PA X-ray diffractometer operating with a 0.15418 nm monochromatized Cu –K_{α} radiation at 40 kV and 30 mA with Ni filter. The surface morphology of the thin films was investigated using Atomic Force Microscopy (AFM). The value of root mean square roughness was calculated from the heights in the AFM image using the commercial software.

Transmittance T and absorbance A of the spectra of the prepared samples were measured by normal incidence of light using a double-beam spectrophotometer in the wavelength range 300-900 nm using a blank substrate as the reference position. The thickness of deposited films of about (390±5) nm were measured by weight difference method.

IV. RESUITS AND DISCUSSION

a. Structural and Morphological Properties

The XRD patterns of the CdS films deposited onto glass substrates at different temperatures by chemical spray pyrolysis are shown in Figure 1. XRD analysis reveals that films deposited are polycrystalline in nature. For the CdS films deposited at low temperature 200^{o}C, very small peaks are observed at 2θ = 26.504°, 30.967°, 43.856° which belong to (111), (200), (220) cubic CdS phase respectively, and a peak at 2θ =38.26° which belong to the CdO phase.The XRD spectra show that films obtained at 200^{o}C consist mostly of cubic structure with a crystallite size (calculated from the Scherrer equation) of 11.9 nm. It is also observed that as substrate temperature increases (from 200 ^{o}C to 300^{o}C), the X-ray peaks become more prominent, new peaks appear and others disappear with the variation in the substrate temperature; these variations may be related to the phase transition from a cubic to a mixture of two phases (cubic and hexagonal), and a crystallite size of 14.1 nm.

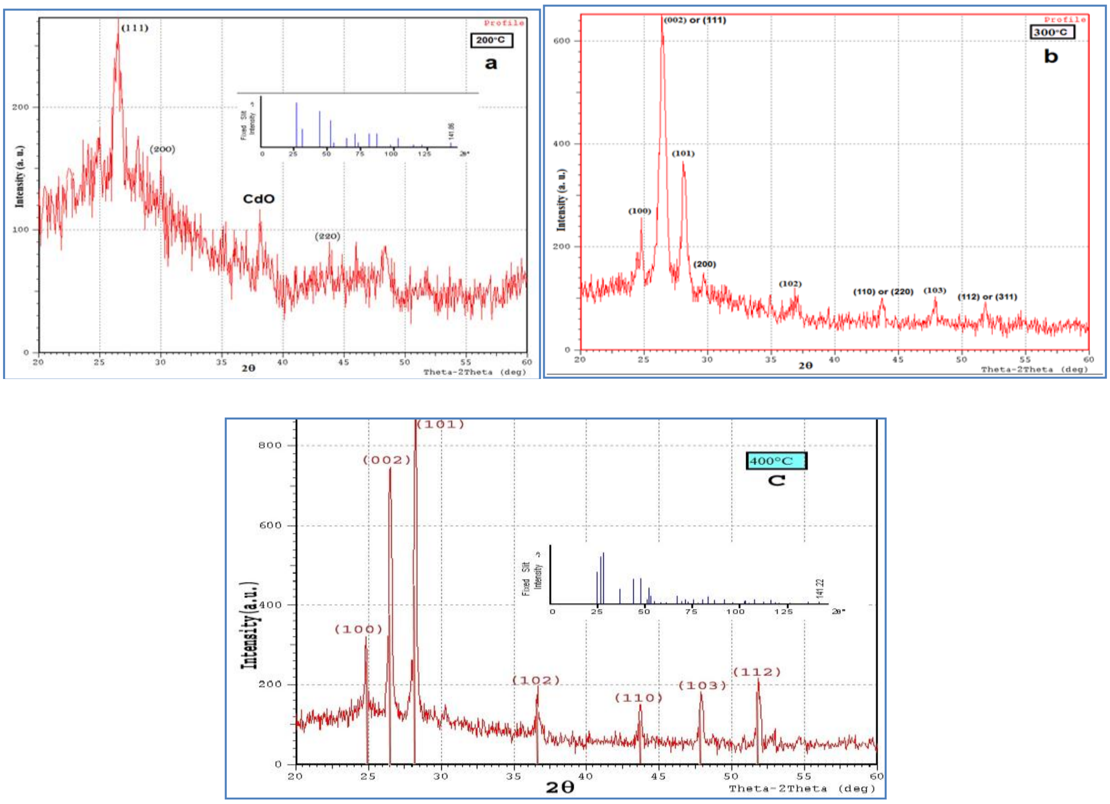

Figure 1. X–ray diffraction of CdS at different temperatures.

The variations of the intensities of Bragg peaks and their widths at half maximum (FWHM) with substrate temperature are evidence of the changes in grain size. The narrowing of the lines of crystal growth at the higher substrate temperature (i.e. the decrease in FWHM) means that the grain size increases. The shifts of the positions of the peaks refer to changes in lattice spacing and the lattice parameters as shown in Table I. Increasing the substrate temperature from 200ºC to 400ºC makes a cubic peak vanish. For the film obtained at 400°C the only hexagonal phase is observed and a crystallite size of 36.9 nm with a preferential orientation along the (101) direction. From these results it is confirmed that increasing the deposition temperature promotes phase transformation from cubic to hexagonal and improves the crystalline structure in CdS films, and also causes a variation in lattice parameters, as shown in Table II. The same result was observed by other authors (Ikhmayies and Bitar, 2010, Acosta, et al., 2004).

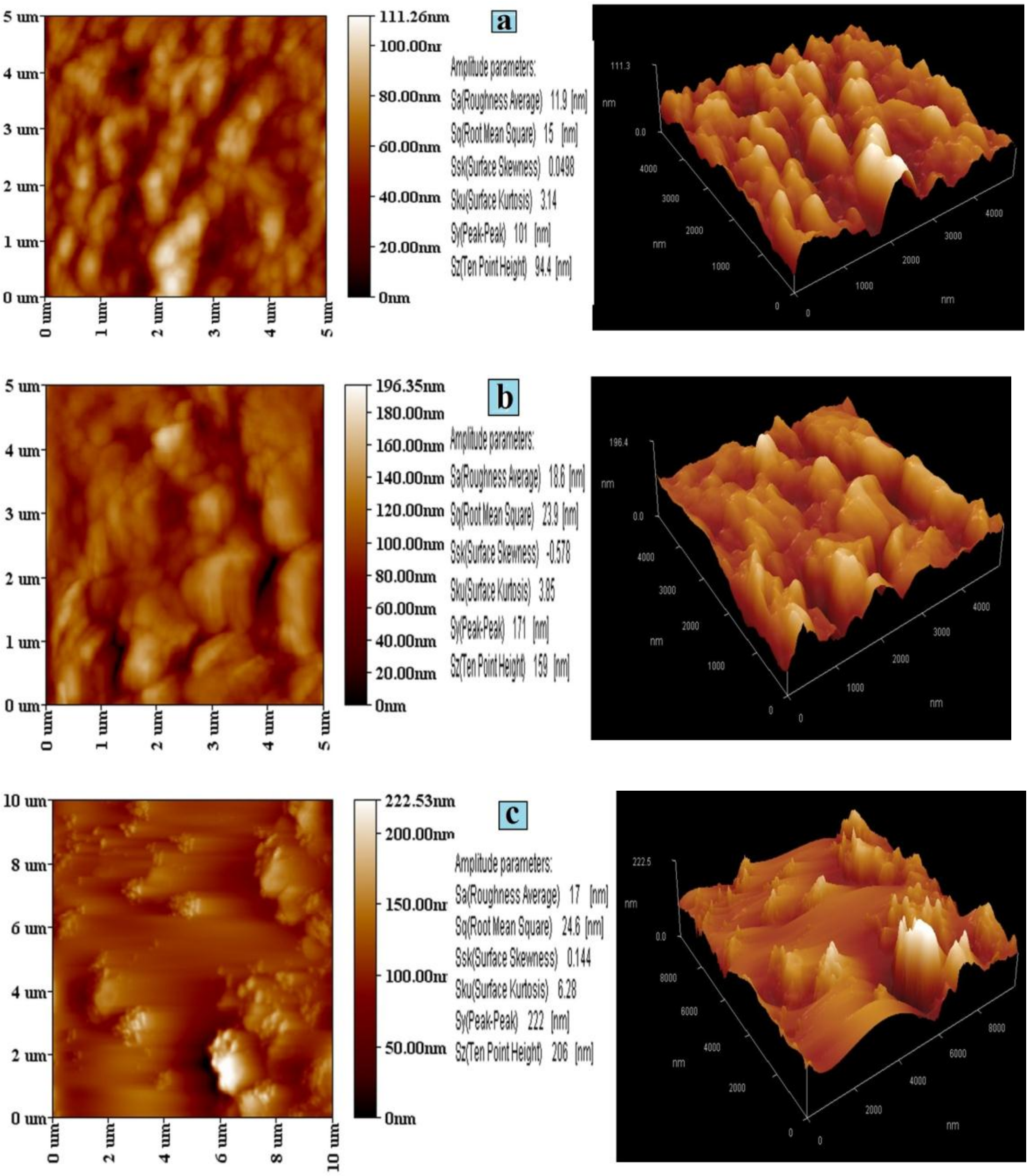

Figure 2. AFM images of CdS at different temperatures.

Figures 2 a–c show the three-dimensional and two-dimensional AFM images for CdS thin films deposited at various substrate temperatures. AFM analysis shows that the root mean square (RMS) surface roughness ranges from 15-24.9 nm as shown in Table I. AFM images also reveal that films become rougher and the surface more inhomogeneous with the increase of substrate temperature.

b. Optical Properties

The optical band gap of the material has been determined from the transmittance T vs. wavelength plot shown in Figure 3. The fundamental absorption, which corresponds to electron excitation from the valence band to the conduction band, can be used to determine the nature and value of the optical band gap. The film prepared at lower temperature (200ºC) shows higher transmittance than the film prepared at 400ºC, which may be due to either more light scattering or rougher surfaces or the transition of the CdS phase from the cubic to hexagonal structure (Liu, et al., 2010). Using the transmittance data, the absorption coefficient (α) was calculated using Equation (2).

Table I. Changes in lattice spacing and lattice parameters.

Temperature		200 ºC	300 ºC	400 ºC	ASTM
d	$d_{(111)}$	3.36024	3.35911	---------	3.16275
	$d_{(101)}$	---------	---------	3.35357	3.3599
FWHM (°)	(111)	0.6875	0.5789	---------	--------
	(002)	---------	---------	0.2213	--------
G (nm)		11.9	14.1	36.9	--------
RMS (nm)		15.0	23.9	24.6	--------
E_g (eV)		2.460	2.435	2.420	--------

The plots of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ are shown in Figure 4. The linear nature of the plots indicates the existence of direct transitions. The values of direct optical band gap E_g were obtained by extrapolating the straight portion to the $h\upsilon$ axis at $(\alpha h\upsilon)^2 = 0$. The values of optical energy band gap were determined and are given in Table I. A slight decrease in the optical band gap energy with substrate temperature was observed by different authors such as. (Liu, et al.,2010) This decrease can be related to the phase change from cubic to mixed (cubic and hexagonal) and to hexagonal phase.

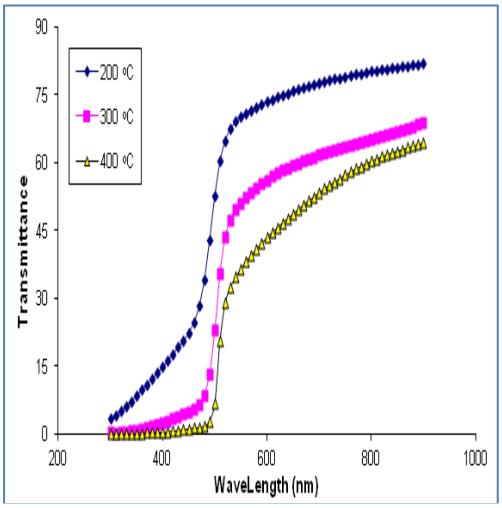

Figure 3. Transmittance spectra of CdS at different temperatures.

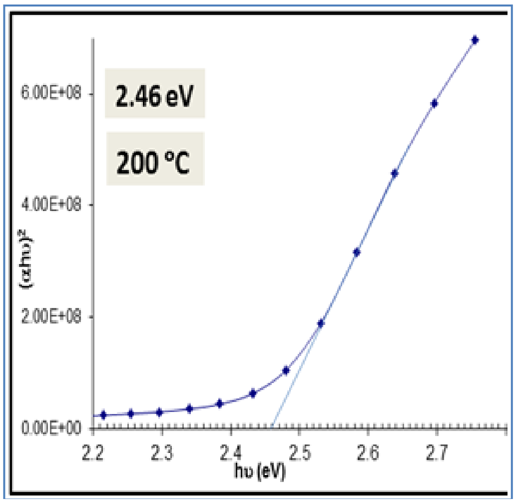

Figure 4. The plots of $(\alpha h\upsilon)^2$ vs. $h\upsilon$ of CdS.

Figure 5 shows the refractive index vs. hυ of CdS at different temperatures, while Figure 6 shows extinction coefficient vs. hυ of CdS at different temperatures. The dependence of the real and the imaginary parts of dielectric constant on wavelength are shown in Figures 7 and 8. The real and imaginary parts follow the same pattern and it is seen that the values of the real part are higher than the imaginary part.

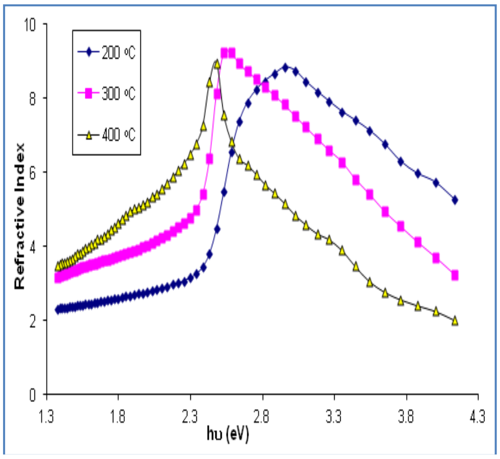

Figure 5. Refractive index vs. $h\upsilon$ of CdS at different temperatures.

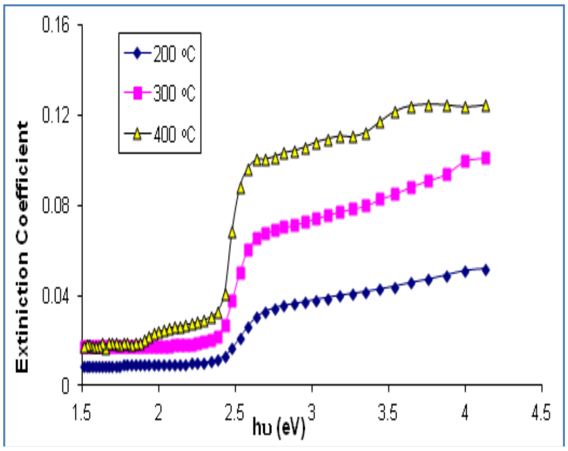

Figure 6. Extinction coefficient vs. $h\upsilon$ of CdS at different temperatures.

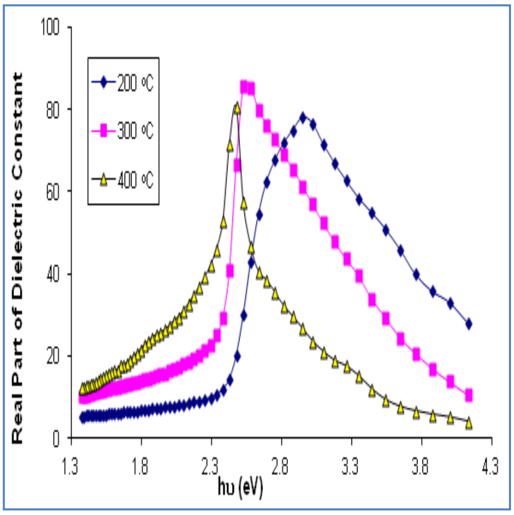

Figure 7. Real parts of dielectric constant vs. wavelength of CdS at different temperature

.

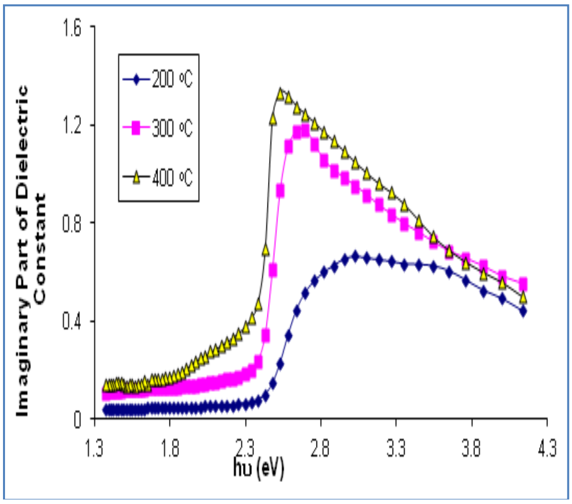

Figure 8. Imaginary parts of dielectric constant vs. wavelength of CdS at different temperature.

Table II. Variation in lattice parameters with temperature.

T (ºC)	Structure	2θ (º)		(hkl)	Lattice Constant (nm)			
		ASTM	Obs.		*a* ASTM	*a* Obs.	*c* ASTM	*c* Obs.
200	β-CdS Cubic	26.514	26.504	(111)	5.818	5.820	---	---
		30.709	30.967	(200)				
		43.983	43.856	(220)				
300	β-CdS Cubic	26.514	26.514	(111)	5.818	5.818	---	---
		30.709	29.752	(200)				
		43.983	43.719	(220)				
400	α- CdS Hexagonal	24.807	24.877	(100)	4.1409	4.1320	6.7198	6.7071
		26.507	26.558	(002)				
		28.182	28.243	(101)				

CONCLUSIONS

The experimental results show that the substrate temperature influences the properties of semiconducting thin films of CdS. Change of state from phase cubic to hexagonal and increase in grain size were observed with the increase of the substrate temperature. Morphological changes such as shape of grains, surface roughness, were also observed with the increase of the substrate temperature. The optical properties are also sensitive to these changes.

REFERENCES

Abduev, A. Kh., Akhmedov, A. K., Asvarov, A. Sh., Abdullaev, A. A., and Sulyanov, S. N., 2010, "Effect of growth temperature on properties of transparent conducting gallium doped ZnO films", *Semiconductors*, **44**(1), 32–36.

Abeles, F., 1972, “Optical Properties of Solids,” Amsterdam: North–Holland.

Acosta, D. R., Maganã, C. R., Martínez, A. I., Maldonado, A., 2004, "Structural evolution and optical characterization of indium doped cadmium sulfide thin films obtained by spray pyrolysis for different substrate temperatures", *Solar Energy Mater. Solar Cells*, **82** , 11-20.

Dhanya, I. and Menon, C.S., 2011, *J. Chemistry*, **1** (4), 1686.

Ezenwa, I.A. and Ekpunobi, A.J., 2010, "Deposition and characterization of CdS thin film by chemical bath method," *The Pacific Journal of Science and Technology*, **11** (2), 435-440.

Gumus, C., Ozkendir, O.M., Kavak, H., Ufuktepe, Y., 2006 ,"Structural and optical properties of zinc oxide thin films prepared by spray pyrolysis method", *Journal of Optoelectronics and Advanced Materials*, **8**(1), 299-303.

Hazaa, S.K., 2013, “The determination of optical band and optical constants of Mno2 thin films prepared by spray pyrolysis”, *Berkala Fisika Indonesia*, **5** (1), 1-6.

Ikhmayies, S. J., and Bitar, A.R. N., 2010, "The influence of the substrate temperature on the photovoltaic properties of spray-deposited CdS:In thin films", *Applied Surface Science*, **256**, 3541–3545.

Khan, Z. R., Zulfequar, M., Khan, M. S., 2010, "Effect of thickness on structural and optical properties of thermally evaporated cadmium sulfide polycrystalline thin films", *Chalcogenide Letters*, **7** (6) June, 431-438.

Liu, F., Lai, Y. , Liu, J., Wang, B., Kuang, S., Zhang, Z., Li, J., Liu, Y., 2010, "Characterization of chemical bath deposited CdS thin films at different deposition temperatures", *Journal of Alloys and Compounds*, **493**, 305–308.

Mahdi, M. A., Kasem ,S. J., Hassen, J. J., Swadi, A. A., Al-Ani, S. K. J. , 2009, "Structural and optical properties of chemical deposition CdS thin films", *International Journal Nanoelectronics and Materials*, **2** , 163-172.

Melo, O. De, Hernández L., Angel, O. Z., Morales, R. L., Becerril, M., and Vasco, E., 1994, "Low resistivity cubic phase CdS films by chemical bath deposition technique", *Applied Physics Letters*, **65** (10), 1278-1280.

Patil, B. N., Naik, D. B. , Shrivastava, V. S., 2011, "Synthesis and characterization of Al doped CdS thin films grown by chemical bath deposition method and its application to remove dye by photo catalytic treatment ", *Chalcogenide Letters* , **8** (2), 117 – 121.

Raji, P., Sanjeevirja, C., and Ramachandran, K., 2005, "Thermal and structural properties of spray pyrolysed CdS thin film", *Bull. Material Science*, **28** (3), 233–238.

Sahay, P. P., Nath, R. K., Tewari, S., 2007, "Optical properties of thermally evaporated CdS thin films", *Crystal Research and Technology*, **42**, (3), 275–280.

Saikia, D., Gogol, P. K., Saikia, P. K., 2010, "Structural and optical properties of nanosructured CdS thin films deposited at different preparative conditions", *Chalcogenide Letters* , **7** (5), 317 – 324.

Sanap, V. B., and Pawar, B. H., 2009, "Growth and characterization of nanosructured CdS thin films by chemical bath deposition technique", *Chalcogenide Letters*, **6** (8), 415 – 419.

Tepantl´an, C. S., 2008, "Structural, optical and electrical properties of CdS thin films obtained by spray pyrolysis", *Revista Mexicana de Fi´sica*, **54** (2), 112–117.

Urbach, F., 1953, *Phys. Rev.*, **92,** 1324.