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STUDY OF OPTICAL PARAMETERS OF CHEMICAL BATH DEPOSITED $Cd_{1-X}Zn_XS$ THIN FILMS

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Abstract. The Chemical Bath Deposition Method (CBD) was employed for deposition of $Cd_{1-x}Zn_xS$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0) thin films. The chemically deposited $Cd_{1-x}Zn_xS$ thin films were characterized by using UV-Visible spectrophotometer. Transmission spectra show the blue shifting of absorption edge as the Zn content increased. The x = 0.8 composition shows maximum 78 % transmittance. The reflection in the blue portion of the incident spectrum was decreased as the Zn content increased. The $(\alpha h\nu)^2$ versus photon energy *(hν)* curves shows tuning of band gap with Zn content. The observed band gap was 3.9 eV in the x = 0.8 composition. The effect of composition on refractive index, absorption index and other optical dispersion parameters were also investigated. The calculated values of average excitation energy E_o approximately obey the empirical relation (E_o=1.2 E_g) obtained from single oscillator model.

1. Introduction

Now solar cell devices plays vital role in converting solar energy into usable form. The selection of window material is often important in the fabrication of low cost, high efficiency solar cell devices. Cadmium sulphide (CdS) is a low direct band gap (E_g= 2.42 eV) n-type semiconductor and widely used as window layer material in solar cell devices (Tuttle J.R. et al., 1996 [1]). CdS absorbs blue portion of solar radiations and decrease the current density of solar cells (Chavhan S.D. et al., 2008 [2]). Addition of Zn to widely used CdS window material improves the electrical and optical properties. The CdZnS provides the wider band gap and higher optical transmittance as compared to CdS. The wider band gap and higher optical transmittance are essential requisite in solar cell applications (Chavan S.D. et al., 2005 [3]). The CdZnS is II-VI compound semiconductor potentially used as window material for fabrication of p-n junction without lattice mismatch in CdTe or $CuIn_xCa_{1-x}$ Se_2 solar cell devices (Ilican S. et al., 2007 [4]).

The knowledge of optical parameters such as optical band gap, reflectivity, optical transmittance, refractive index and dielectric constants etc. are essential prerequisite in using the suitable material for device applications

A number of thin film deposition techniques are available. Of the most, Chemical Bath Deposition (CBD) is practically attractive because of its simplicity in comparison with other techniques, requiring vacuum conditions and complex instrumentations. Production of large surface area CdS thin films by easy and low cost techniques for industrial use, is still of great importance (Rakhshani et al., 1998 [5]). CBD is fast, simple, inexpensive, non-vacuum and suitable for mass production.

The objective of the present study is to synthesize $Cd_{1-x}Zn_xS$ thin films by using chemical bath deposition technique (CBD). The prepared thin films are characterized by using UV-Visible spectrophotometer to study the effect of Zn content on the optical properties and optical constants like refractive index, extinction coefficients and dielectric constants etc. of $Cd_{1-x}Zn_xS$ thin films.

2. Experimental

In order to prepare $Cd_{1-x}Zn_xS$ thin films, the aqueous solution of Cadmium Chloride $CdCl_2$, Zinc Chloride $ZnCl_2$ and thiourea NH_2CSNH_2 were used as the precursor solutions. The stock solutions of $CdCl_2$ (0.05 M), $ZnCl_2$ (0.05 M) and NH_2-CS-NH_2 (0.1 M) were prepared. The experimental solutions with different volume proportions were taken in reaction beaker for deposition of $Cd_{1-x}Zn_xS$ thin films as shown in following Table 1.

Table 1. The experimental solutions with different volume proportions.

Composition x	$CdCl_2$, ml	$ZnCl_2$, ml	NH_2CSNH_2, ml
0.0	10	0	10
0.2	8	2	10
0.4	6	4	10
0.6	4	6	10
0.8	2	8	10
1.0	0	10	10

The pH of the solution was adjusted to 11 by adding the aqueous NH_3. The reaction beaker was kept in temperature bath, maintained at constant 80 °C. Glass substrates were cleaned by 24 hr immersion in chromic acid, rinsed with acetone and distilled water.

All the chemicals and reagents used were of analytical grade. The experimental glass substrates were mounted on substrate holder and immersed in the reaction beaker. The substrate holder was rotated at slow speed (45 rpm) by means of DC geared motor for 25 to 30 minutes.

The pH of the precursor, reaction temperature, rotation speed and dipping time of the substrate were kept constant throughout the experiment at optimized values. The thin, uniform $Cd_{1-x}Zn_xS$ films were obtained at the end of the reaction process. The prepared $Cd_{1-x}Zn_xS$ thin films were rinsed with deionized water to remove the loosely bound particles and annealed at 100 ^oC. The synthesized $Cd_{1-x}Zn_xS$ films are characterized by using UV-Visible spectrophotometer.

Two different methods were used for thickness measurements: the “Weighting difference method” and the “Optical interference fringes method”. The weighting difference method gives an approximate value for thickness of the prepared films. A digital balance with accuracy of (= 0.1 x 10^3 gm) was used for weighting the bulk content of deposited material on the substrate (Nathera A. et al., 2012 [6]).

The optical band gap was determined by using relation (Jauc J., 1974 [7]):

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

where A is the energy independent constant; E_g is the optical band gap; n is the constant which can determine types of optical transitions. The wavelength dependence of optical constants such as extinction coefficients (k), refractive index (n), real and imaginary parts of dielectric constant (ε_1) and (ε_2) were calculated using fowling relations (Abeles F., 2007 [8]):

$$n = \frac{1+R}{1-R} + \left\{ \frac{4R}{(1-R)^2} - k^2 \right\}^{1/2}, \tag{2}$$

where R is the reflectance; and K is extinction coefficient,

$$k = \frac{\alpha\lambda}{4\pi}, \tag{3}$$

where α is absorption coefficient.

3. Results and discussion

Absorbance data of $Cd_{1-x}Zn_xS$ thin films was recorded by using UV-Visible spectrophotometer (Systronics Double Beam 2201).

Figure 1 is the plot of transmission versus wavelength. The transmission curves show the blue shifting of absorption edge (approximately from 450 – 350 nm). From Fig. 1, it is clear that, the optical transmittance is maximum in the visible region (450 - 800 nm) and found increased from 5 to 78 % with Zn content. In the composition x= 0.8, the observed transmittance was 78 %.

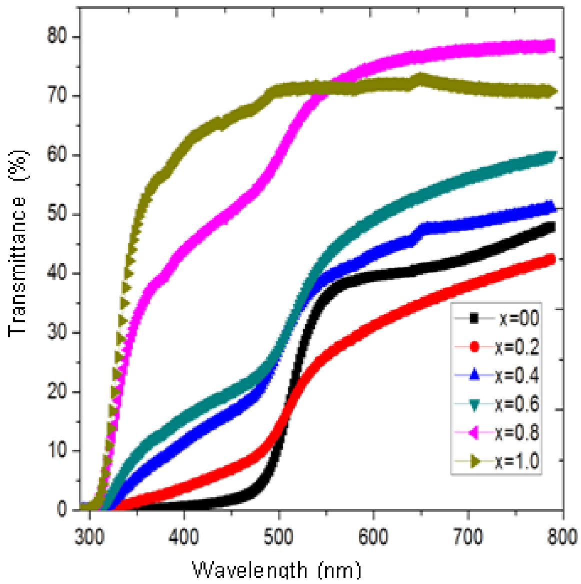

Fig. 1. Percent transmittance plotted versus wavelength for $Cd_{1-x}Zn_xS$ thin films.

Figure 2 shows the variation of optical reflection with wavelength. The reflection is found decreased from 0.02 to 0.005 (a.u.) in the visible and near infrared region. It supports the antireflection property of the $Cd_{1-x}Zn_xS$ thin films. In the compositions x=0.8 and 1.0, the optical reflectance was significantly decreased in the blue portion of the incident spectrum. Blue shifting of absorption edge indicate the decrease in optical absorption in the blue portion of the solar spectrum. (Borse S.V. et al., 2007 [9]).

The variation of film thickness with composition x is displayed in Table 2. Thickness of the films was found decreased from 6.63 to 1.13 µm.

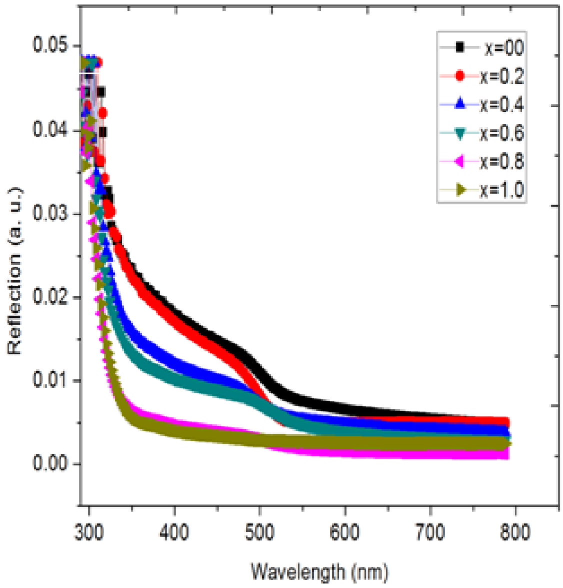

Fig. 2. Reflection versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

Table 2. Variations of optical parameters with Zn content.

Composition of $Cd_{1-x}Zn_xS$ film	Thickness, µm	Band gap E_g, eV	Refractive index (n) at 450 nm	Absorption index (k) at 450 nm	ε_1 at 450 nm	ε_2 at 450 nm
0.0	6.3	2.427	1.20	0.045	1.46	0.021
0.2	4.3	3.4	1.27	0.029	1.61	0.05
0.4	2.13	3.7	1.212	0.019	1.64	0.109
0.6	2.13	3.8	1.21	0.0144	1.48	0.073
0.8	1.67	3.9	1.129	0.014	1.27	0.0301
1.0	1.13	3.85	1.123	0.0091	1.25	0.030

The annealing effect shows that, band gap of CdS ($Cd_{1.0}Zn_{0.0}S$) is 2.47 eV which is larger than 2.42 eV of the bulk CdS material. The variation of band gap with Zn content was shown in Table 2. The band gap was increased with Zn content from 2.427 to 3.9 eV. In the composition x=0.8, the band gap was found to be 3.9 eV.

The dispersion of incident photon energy plays the important role in determining the optical property of the material. The knowledge of variation of refractive index helps to investigate the average excitation energy (E_o) and dispersion energy (E_d) of the deposited material.

The variation of refractive index (n) and extinction coefficient (k) with wavelength of the $Cd_xZn_{1-x}S$ films are presented in Figs. 4 and 5 respectively.

The refractive index of the deposited films significantly changes with the film composition. In the low wavelength region the values of refractive index for deposited films are higher and then decreased after 350 nm. The effect of Zn content of the deposited $Cd_{1-x}Zn_xS$ films on n and k was clearly illustrated from Figs. 4 and 5.

The extinction coefficient (k) shows similar nature of variation, however the k has less value as compared to n. The observed values of n and k at wavelength 450 nm were presented in Table 2.

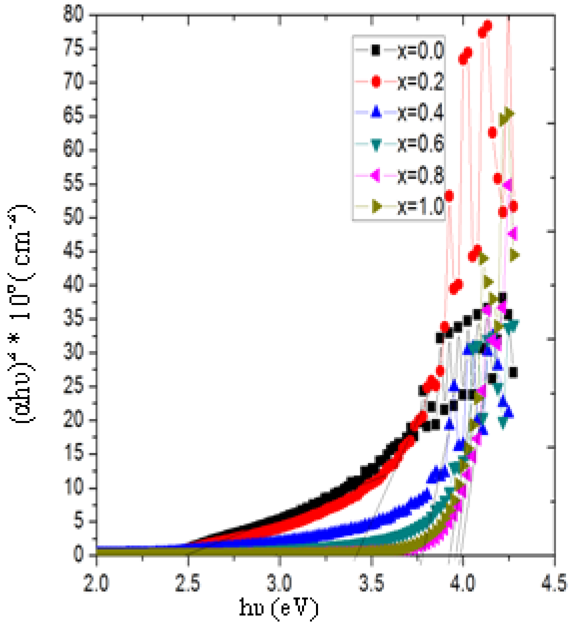

Fig. 3. plot of $(\alpha h\nu)^2$ versus $h\nu$ of $Cd_{1-x}Zn_xS$ thin films.

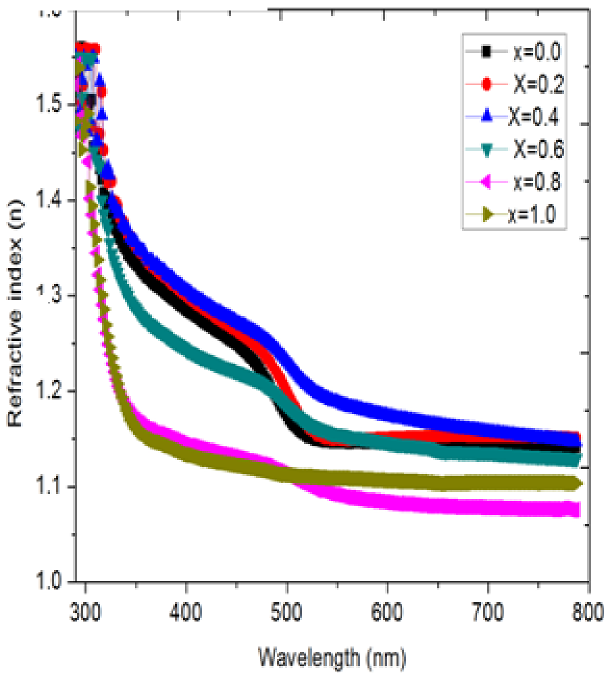

Fig. 4. Plot of refractive index (n) versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

The investigation of complex dielectric constant is very important as it provides information about electronic structure of the deposited material onto the substrate. The dielectric constant is given as, $\varepsilon(\omega) = \varepsilon_1(\omega)+i\varepsilon_2(\omega)$, where, real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of dielectric constant are related to the n and k values respectively. The ε_1 and ε_2 were calculated using formulas:

$$\varepsilon_1 = n^2 - k^2, \quad (4)$$

$$\varepsilon_2 = 2nk. \quad (5)$$

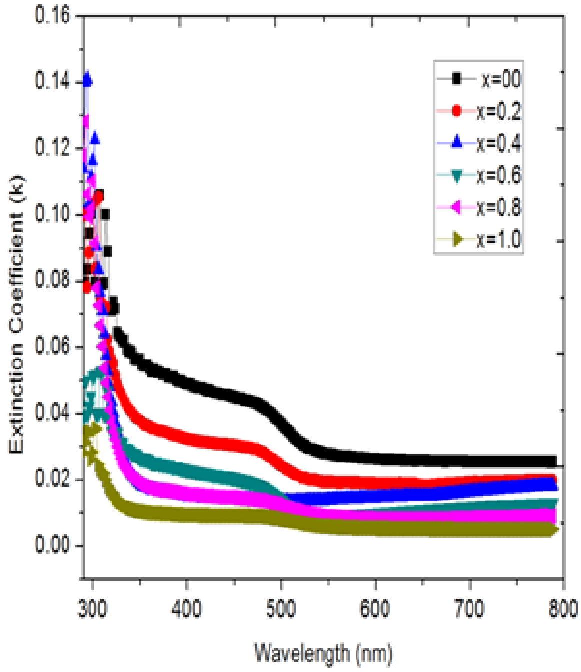

Fig. 5. Plot of extinction coefficient (k) versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

From the Figs. 6 and 7, it is concluded, that both ε_1 and ε_2 decrease from 0.45 to 0.025 and 2.4 to 1.2 respectively. The observed values of ε_1 and ε_2 at wavelength 450 nm were presented in Table 2.

The variation of ε_1 as a function of wavelength 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 and hence the thickness of the deposited thin films. The change of Zn content in $Cd_{1-x}Zn_xS$ thin films causes the important change in dielectric constants.

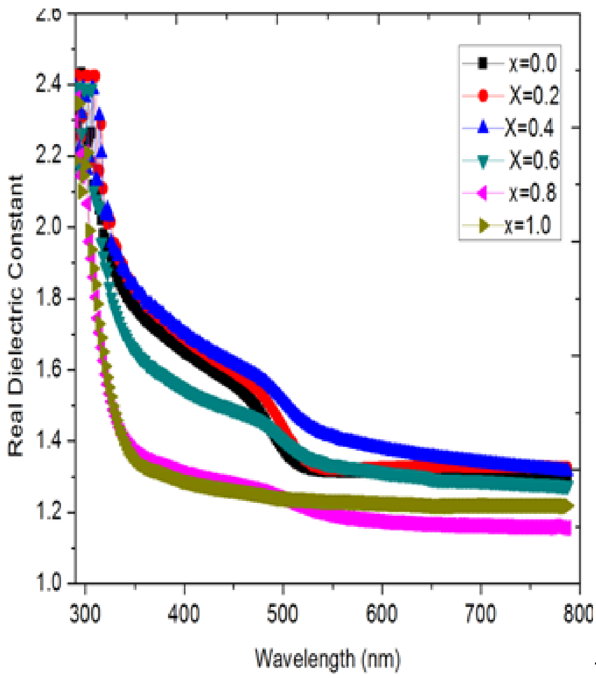

Fig. 6. Plot of real part of dielectric constant (ε_1) versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

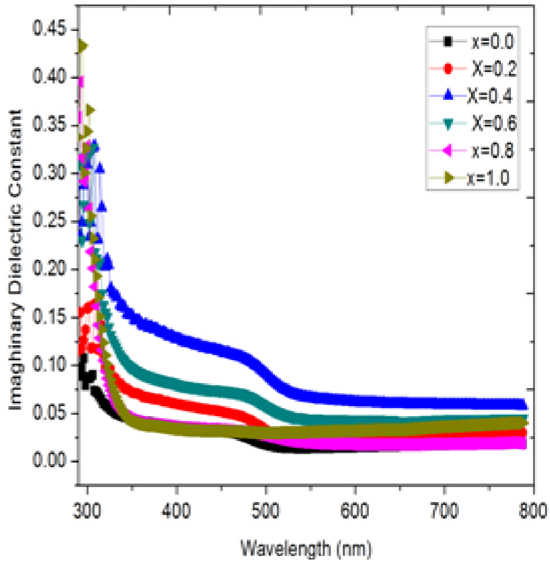

Fig. 7. Plot of imaginary part of dielectric constant (ε_2) versus wavelength of $Cd_{1-x}Zn_xS$ thin films.

The approximate relation between refractive index n, average excitation energy for electronic transition (E_o), the dispersion energy (E_d) and incident photon energy $(h\nu)$ was described by Wemple and DiDomenico (Wemple S.H., 1971 [10]) means of single oscillator:

$$n^2 - 1 = E_d E_o/(E_o^2 - (h\nu)^2). \quad (6)$$

Plot of $(n^2-1)^{-1}$ against $(h\nu)^2$ gives the oscillator parameters E_o and E_d which are determined by fitting a straight line to the points and shown in Fig. 8.

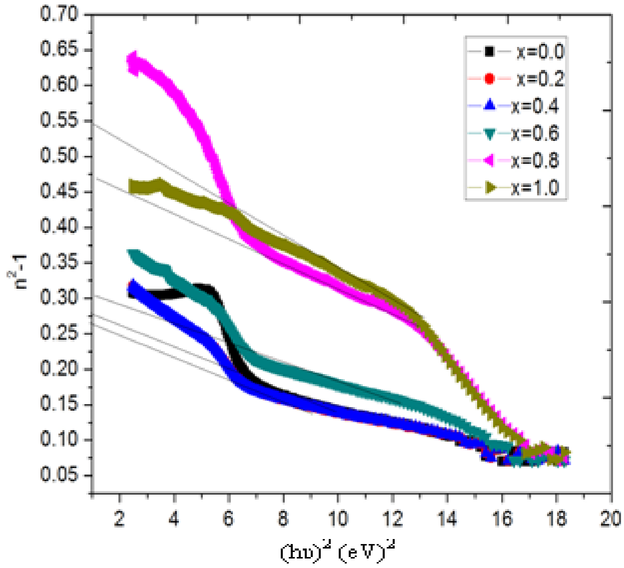

Fig. 8. Plot of $(n^2-1)^{-1}$ versus $(h\nu)^2$ of $Cd_{1-x}Zn_xS$ thin films.

The values of E_o and E_d can be directly determined from the gradient $(E_oE_d)^{-1}$ and intercept on vertical axis, (E_d/E_o). The values obtained for dispersion parameters, E_o and E_d are displayed in Table 3. Caglar M. et al. (2006) [11] and Ilican S. (2006) [12] reported that the oscillator energy E_o was related to lowest direct band gap empirically by E_o= 1.2 E_g. The calculated values of E_o satisfies the empirical relation approximately obtained from single oscillator model.

Table 3. Variations of oscillator parameters with composition.

Composition of $Cd_{1-x}Zn_xS$ film	E_o, eV	E_d, eV	M_{-1}	M_{-3}, $(eV)^{-2}$
0.0	3.72	23.1	6.71	0.49
0.2	4.082	25.9	6.31	0.38
0.4	4.08	26	6.32	0.38
0.6	4.378	22	5.0	0.26
0.8	5.17	14.78	2.89	0.118
1.0	5.26	14	2.66	0.096

The moments M_{-1} and M_{-3} of the optical transitions can be obtained from relationships:

$$(E_o)^2 = M_{-1}/M_{-3}, \tag{7}$$

$$(E_d)^2 = M^3_{-1}/M_{-3}\,. \tag{8}$$

The calculated values of E_o, E_d and M_{-1}, M_{-3} were found decreased with Zn content. As compared with values reported (Ilican S. et al., 2006), the obtained values of E_o, E_d and M_{-1}, M_{-3} are found higher. This may be because of technique of deposition. The values of moments of optical transitions are tabulated in Table 3. Table 3 shows the decreasing trend with Zn content.

The compositional and structural studies are the future scope of the work, to confirm the initial and final content of elements.

4. Conclusions

The transparent $Cd_{1-x}Zn_xS$ thin films have been synthesized by low cost simple Chemical Bath Deposition Technique. It was concluded that, Zn content changes the optical properties of the $Cd_{1-x}Zn_xS$ thin films. The film of composition x= 0.80 and 1.0 gives maximum 78 % transmittance. The maximum transmittance and low reflection property indicate that the prepared thin films are antireflective. The band gap shows the increasing trend with Zn content. The film composition x = 0.8 shows maximum 3.9 eV band width. The variation of ε_1 as a function of wavelength follows the similar behavior as n whereas the variation of ε_2 follows the behavior of *k*. The values of E_o, E_d and M_{-1}, M_{-3} decreased with concentration of Zn. The calculated values of average excitation energy E_o approximately obey the empirical relation obtained from single oscillator model.

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References

[1] J.R. Tuttle, J.S. Ward, A. Dude, T.A. Berens, M.A. Contreras, K.R. Ramanathan, A.L. Tennant, J. Keane, E.D. Cole, K. Emery, R. Noufi, In: *Proceedings of MRS Meeting* (Cambridge University Press, 1996), Vol. 426, p. 143.

[2] S.D. Chavhan, S. Senthilarasu, L.S. Hyoung // *Applied Surface Science* **254** (2008) 4539.
[3] S.D. Chavan, R.P. Sharma // *J. Phys. Chem. Solids* **66** (2005) 1721.
[4] S. Ilican, M. Caglar, Y. Caglar // *Advanced Materials* **9 (5)** (2007) 1414.
[5] Y. Rakhshani Makdisi, Ramazaniyan // *J. Applied Phys.* **83** (1998) 1049.
[6] A. Nathera, A. Tememee, M.N. Saeed, M.A. Sundus, A. Dujayli, T. B. Chiad // *Advances in Materials Physics and Chemistry* **2** (2012) 69.
[7] J. Jauc, *Amorphous and Liquid Semiconductors* (Plenum Press, New York, 1974).
[8] *Optical Properties of Solids*, ed. by F. Abeles (North-Holland Pub. Co., Amsterdam; American Elsevier, New York, 1972).
[9] S.V. Borse, S.D. Chava, R.P. Sharma// *Journal of Alloys and Compounds* **436** (2007) 407.
[10] S.H. Wemple, M. DiDomenico // *Phys. Rev. B* **3 (4)** (1971) 1338.
[11] S. Ilican, M. Zor, Y. Caglar, M. Caglar // *Optica Applicata* **36 (1)** (2006) 29.
[12] S. Ilican, Y. Caglar, M. Caglar // *Physica Macedonica* **56** (2006) 43.