Optical properties of flash - evapored $CuInSe_2$ thin films

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Abstract - *$CuInSe_2$ thin films (CIS) are fabricated by flash evaporation in vaccum from a single source. Their optical properties are investigated by spectrophotometry in the range 0.3-2.5 µm. The interpretation of these results are based on the Mueller numerical method of resolution of nonlinear equations. We have determined the optical constants. The optical energies gap are deduced for different thicknesses of thin films.*

Résumé - *Les couches minces de $CuInSe_2$ ou CIS sont fabriquées par évaporation flash sous vide avec une seule source. Les propriétés optiques ont été étudiées par spectrophotométrie dans le domaine 0.3-2.5µm. Nos équations étant non linéaires, ont été résolues par la méthode de Mueller. Nous avons calculé les constantes optiques et déduit les gap optiques d'énergie pour les différentes épaisseurs considérées.*

Key words: Flash evaporation - Thin films - Optical constants - Energies gap - Index of refraction - Extinction - Absorption - Reflection - Transmission - Spectrum.

1. INTRODUCTION

$CuInSe_2$ which is promising for photovoltaic applications [1], presents a direct band gap. It is an ideal material for high efficiency solar cells. $CuInSe_2$ films are prepared by flash evaporation in vaccum from a single source. The successful preparation of CIS thin films depends on the fabrication conditions [2].

The aim of the present paper is to calculate the optical constants: the index of refraction $n(\lambda)$ and the extinction coefficient $k(\lambda)$, using the Mueller numerical method of resolution of nonlinear equations[3, 4].

The absorption coefficient $\alpha(\lambda)$ and optical energies gap were also determined.

2. THEORY AND EXPERIMENTS

It is a question of resolving the systeme of nonlinear equations:

$$R_{exp} - R_{the}(n, k, \lambda) = 0 \qquad (1)$$

$$T_{exp} - T_{the}(n, k, \lambda) = 0 \qquad (2)$$

where $R_{exp}\,(T_{exp})$ and $R_{the}\,(T_{the})$ are the experimental reflection (transmission) and the theoretical reflection (transmission), and determining the spectral distribution of both n and k for $CuInSe_2$ films.

The reflection coefficient R and transmission coefficient T at normal incidence on plane-parallel surfaces absorbing film bounded by two transparent and non-absorbing media (air and substrate) are given by :

$$R = \frac{\left[\left(g_0^2 + h_0^2\right)e^{\alpha d} + \left(g_1^2 + h_1^2\right)e^{-\alpha d} + A\cos(2\delta) + \sin(2\delta)\right]}{\left[e^{\alpha d} + \left(g_0^2 + h_0^2\right)\left(g_1^2 + h_1^2\right)e^{-\alpha d} + A\cos(2\delta) + \sin(2\delta)\right]} \qquad (3)$$

$$T = \frac{\left[\left(1 + g_0^2\right)^2 + h_0^2\right] . \left[\left(1 + g_1^2\right)^2 + h_1^2\right]}{\left[e^{\alpha d} + \left(g_0^2 + h_0^2\right)\left(g_1^2 + h_1^2\right)e^{-\alpha d} + A\cos(2\delta) + \sin(2\delta)\right]} \qquad (4)$$

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with :

$$g_0 = \frac{\left[1 - n^2 - k^2\right]}{\left[(1+n)^2 + k^2\right]} \qquad k_0 = \frac{2k}{(1+n)^2 + k^2} \qquad g_1 = \frac{\left(n^2 - n_s{}^2 + k^2\right)}{(n+n_s)^2 + k^2}$$

$$h_1 = \frac{-2 n_s k}{(n+n_s)^2 + k^2} \qquad A = 2\left(g_0 g_1 + h_0 h_1\right) \qquad B = 2\left(g_0 h_1 + g_1 h_0\right)$$

$$C = 2\left(g_0 g_1 - h_0 h_1\right) \qquad \alpha = \frac{4\pi k}{\lambda} \qquad \delta = \frac{2\pi n k}{\lambda}$$

Where n and n_s are respectively the refractive indices of film and substrate, k is the extinction coefficient, α is the absorption coefficient of the film, λ is the wavelength and δ is the phase difference introduced in the ray when it traverses the film once.

Figures 1, 2, 3 and 4, show the experimental spectra of the reflection R and transmission T at normal incidence of light in the visible and near infrared region, recorded at room temperature for different thicknesses of thin films in the range 0.3 – 3 µm using spectrophotometer Beckman model UV 5240.

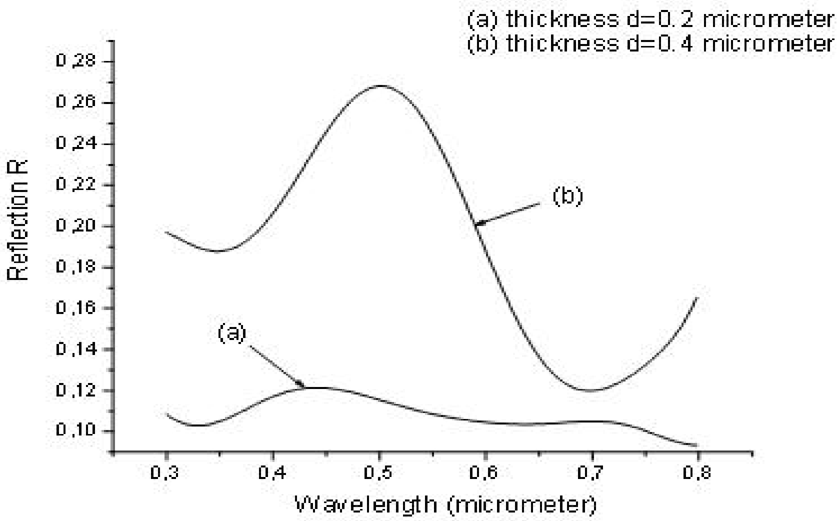

Fig. 1: Reflection spectrum of thin films $CuInSe_2$ in the visible range for the thickness equal to 0.2 and 0.4 µm

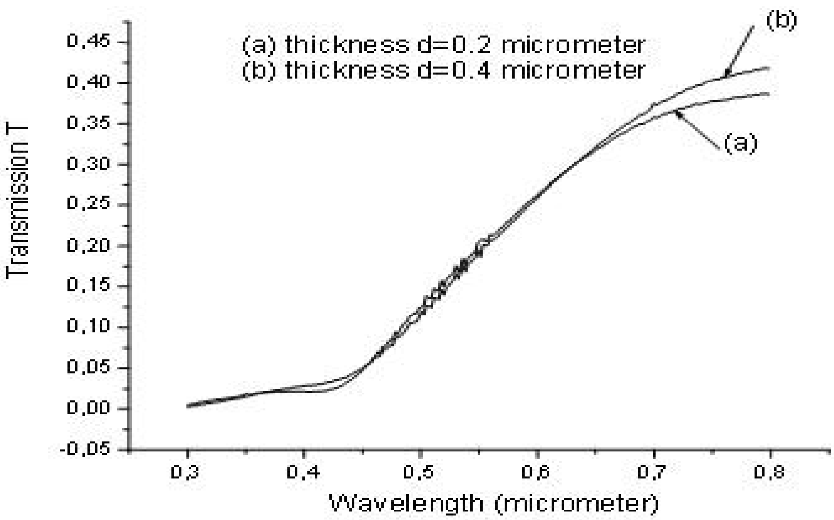

Fig. 2: Transmission spectrum of thin films $CuInSe_2$ in the visible range for the thickness equal to 0.2 and 0.4 µm

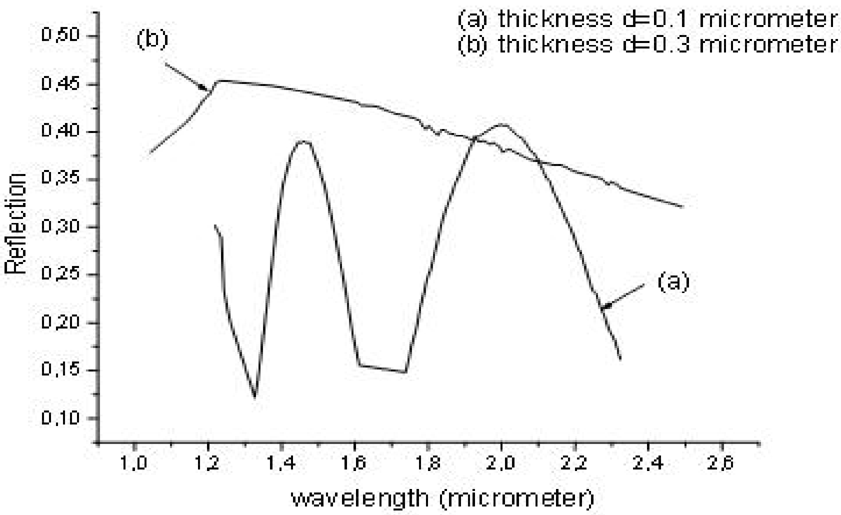

Fig. 3: Reflection spectrum of thin films $CuInSe_2$ in the near infrared range for the thickness equal to 0.1 and 0.3 µm

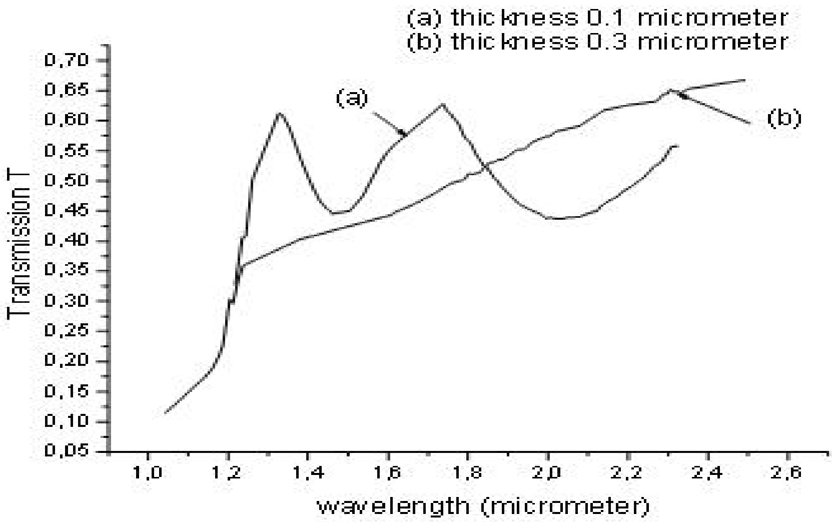

Fig. 4: Transmission spectrum of thin films $CuInSe_2$ in the near infrared range for the thickness equal to 0.1 and 0.3 µm

3. RESULTS AND DISCUSSION

The expressions of $R = R(n,k,\lambda)$ and $T(n,k,\lambda)$ are complicated. Also, we use the expressions suggested by [5], $(1+R)/T$ and $(1-R)/T$, because they are more practical and useful.

All these spectra exhibit a middle and strong absorption in the visible while a weak absorption the near infrared range.

1- In the visible région, the $\exp(\alpha\delta)$ term dominates and hence the expressions of R and T reduce to:

$$R = \frac{(1-n^2)+k^2}{1+n^2+k^2} \tag{5}$$

$$T = \frac{16\, n_s\,(n^2+k^2)\,e^{-\alpha\delta}}{(1-R^2)\,e^{-\alpha\delta}} \tag{6}$$

n and n_s are the refraction indices of film and substrate respectively. k is the extinction coefficient and α is the absorption coefficient of the film. Combining equations (5) and (6) gives:

$$n = \frac{\left[1 + \left[1 - \left(\frac{(1-R)}{(1+R)}\right)^2 \left(1 + k^2\right)\right]^{1/2}\right]}{\left(\frac{(1-R)}{(1+R)}\right)} \qquad (7)$$

$$k = (\lambda / 4\pi\delta)\, \mathrm{Ln}\left(\frac{(1-R)^2}{T}\right) \qquad (8)$$

2- In the infrared region, there is a weak absorption and $k^2 << n^2$ implies:

$$\frac{(1+R)}{T} = \left(1/4\, n_s\, n^2\right)\left[A_1 + B_1 k + C_1 k^2 + D_1 k^3 + \ldots\right] \qquad (9)$$

$$\frac{(1-R-T)}{T} = \left(1/2\, n_s\, n^2\right)\left[B_2 k + C_2 k^2 + D_2 k^3 + \ldots\right] \qquad (10)$$

with

$$A_1 = \left(1+n^2\right)\left(n^2 + n_s^2\right) + \left(1-n^2\right)\left(n^2 - n_s^2\right)\cos(2\delta)$$

$$B_1 = 2n_s\left(1+n^2\right)2\delta - \left(1-n^2\right)\sin(2\delta)$$

$$C_1 = \left(2/n^2\right)\left[\left(1+n^2\right)\left(n^2+n_s^2\right)\delta^2 + \left(n^4 - n_s^4\right)\sin^2\delta\right]$$

$$D_1 = \left(2n_s / n^2\right)\left[\frac{4\left(1+n^2\right)\delta^3}{3 - 2\delta + \sin(2\delta)}\right]$$

$$B_2 = \left(n^2 + n_s^2\right)2\delta + \left(n^2 - n_s^2\right)\sin(2\delta)$$

$$C_2 = 4\, n_s\left(\delta^2 - \sin^2\delta\right)$$

$$D_2 = \left(1/n^2\right)\left[4\left(n^2 + n_s^2\right)\delta^3 - n_s^2\left(2\delta - \sin(2\delta)\right)\right]$$

At a first order, equations (9) and (10) can be written:

$$\frac{(1+R)}{T} = \left(1/4\, n_s\, n^2\right)\left[A_1 + B_1 k\right] \qquad (11)$$

$$\frac{(1-R-T)}{T} = \left(1/2\, n_s\, n^2\right)\left[B_2 k\right] \qquad (12)$$

from (12) $$k = 2n_s n^2 \frac{(1-R-T)}{(T\,.\,B_2)} \qquad (13)$$

Thus :

$$\frac{(1+R)}{T} = \left(1/4\, n_s\, n^2\right)\left[A_1 + B_1\left[2n_s n^2 \frac{(1-R-T)}{(T\,.\,B_2)}\right]\right] \qquad (14)$$

The optical function is defined as

$$f_2(n,\lambda) = \frac{(1+R_{th})}{T_{th} - (1+R_{exp})/R_{exp}} = 0 \qquad (15)$$

At second order, we obtain:

$$k = (B_2 / 2C_2)\left[\left[1 + 8n_s n^2 C_2 / B_2^2 \left((1-R-T)/T\right)\right]^{1/2} - 1\right] \qquad (16)$$

and the optical function

$$f_3(n,\lambda) = \left(1 + \frac{R_{th}}{T_{th}}\right) - (1+R_{exp})/R_{exp} = 0 \qquad (17)$$

$$f_3(n,\lambda) = A_1 + B_1 k + C_1 k^2 - 4 n_s n^2 . (1 + R_{exp}) / R_{exp} = 0 \quad (18)$$

We define also $f_4(n,\lambda)$ and $f_5(n,\lambda)$.

The resolution of equation $f_3(n,\lambda) = 0$ give the approximation value of the refractive indice $n(\lambda)$ of film.

4. DETERMINATION OF OPTICAL CONSTANTS

In the range 0.3 - 0.8 µm, we utilise equations (7) and (8) to calculate $n(\lambda)$ and $k(\lambda)$ [6] for different thicknesses. Their spectra are showed in figures 5 and 7 as function of wavelength. While in the range 0.8 - 2.5 µm corresponding to a weak absorption $n(\lambda)$ and $k(\lambda)$ are determined by Mueller method.

Knowing approximative values of $k(\lambda)$ and $n(\lambda)$ given by equations (16) and (17) in this range, we can calculate exactly n and k from equations $f_4(n,\lambda)$ and $f_5(n,\lambda)$ respectively, using the computer. The calculated spectra of $n(\alpha)$ and $n(\lambda)$ by the Mueller numerical method, for different thicknesses are represented in figures 6 and 8 as function of wavelength.

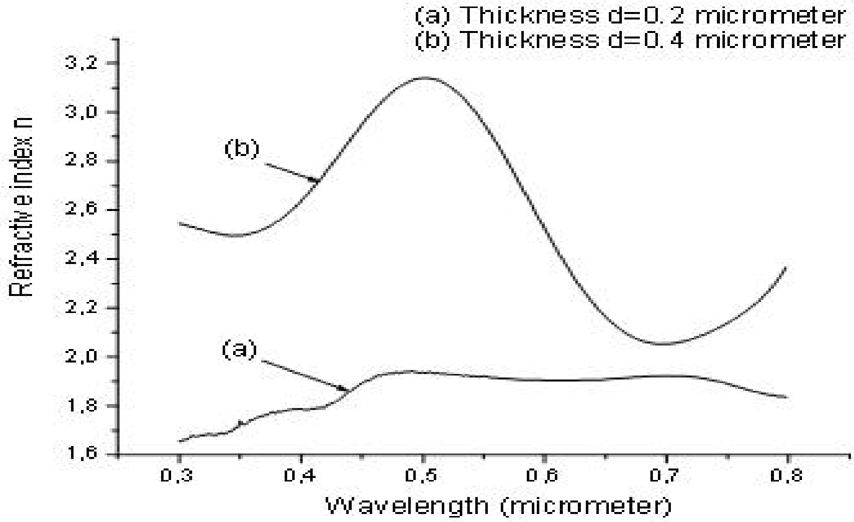

Fig. 5: Refractive index refraction of thin films $CuInSe_2$ in the visible range for the thickness equal to 0.2 and 0.4 µm

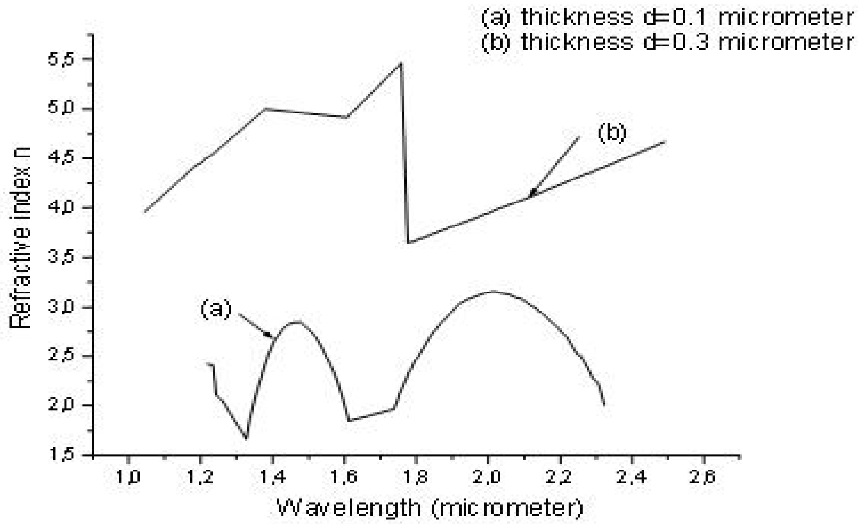

Fig. 6: Refractive index refraction of thin films $CuInSe_2$ in the near infrared range for the thickness equal to 0.1 and 0.3 µm

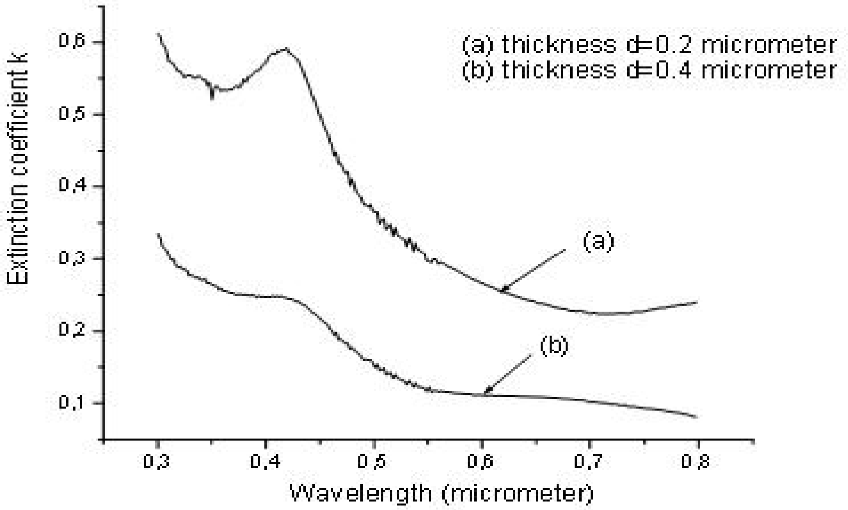

Fig. 7: Extinction coefficient of thin films $CuInSe_2$ in the visible range
for the thickness equal to 0.2 and 0.4 µm

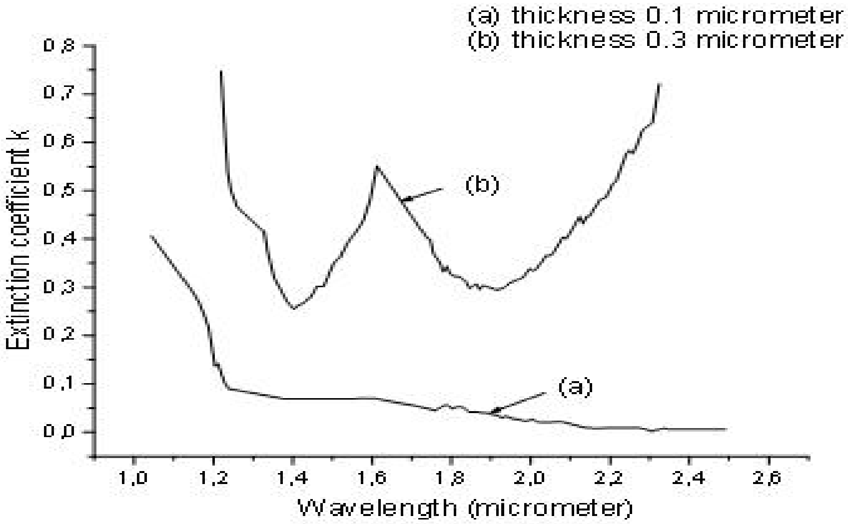

Fig. 8: Extinction coefficient of thin films $CuInSe_2$ in the near infrared range
for the thickness equal to 0.1 and 0.3 µm

The k values for thicknesses 0.2 and 0.40 µm are high in the 0.3 - 0.45 µm, decrease and remain constant for 0.45 - 0.8 µm. While in infrared range k is small for thickness 0.3 µm and reveals so a spectral singularity for thickness 0.1 µm. This can be attributed to physical imperfections which were not taken into account in the calculations [7].

However the refractive index shows a maximum at 0.5 µm and then decreases for thickness 0.4 µm. For thickness 0.2 µm, it fluctuates around 1.7 and for thickness 0.1 µm and 0.3 µm, n presents the same trend that k.

The film absorption coefficient α was extracted from R and T measurements [5].

Curves of α vs photon energy for four films with different thicknesses were shown in figures 9 and 10. For direct transition materials, the absorption coefficient α is given by $\alpha E = A\left(E - E_g\right)^{1/2}$, where E is the photon energy and E_g is the band gap energy. The optical energy gap was calculed by extrapoling the linear portion of the absorption spectrum to E = 0.

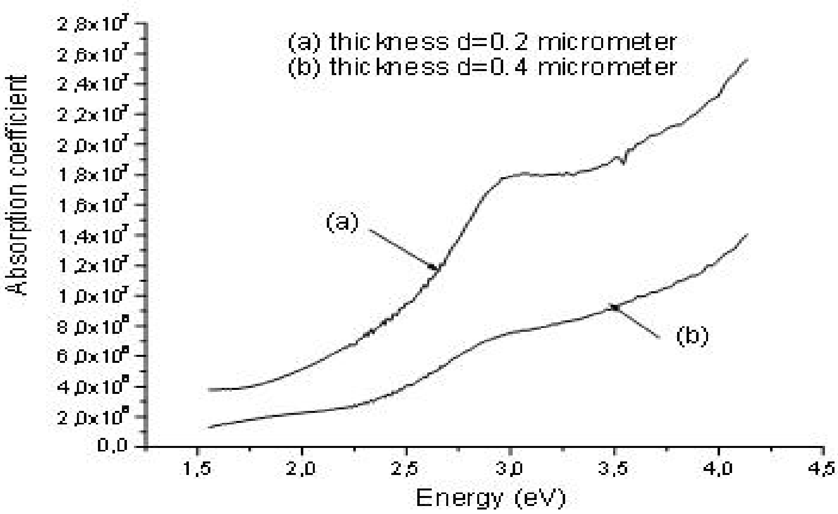

Fig. 9: Absorption coefficient of thin films $CuInSe_2$ for the thickness equal to 0.2 and 0.4 µm

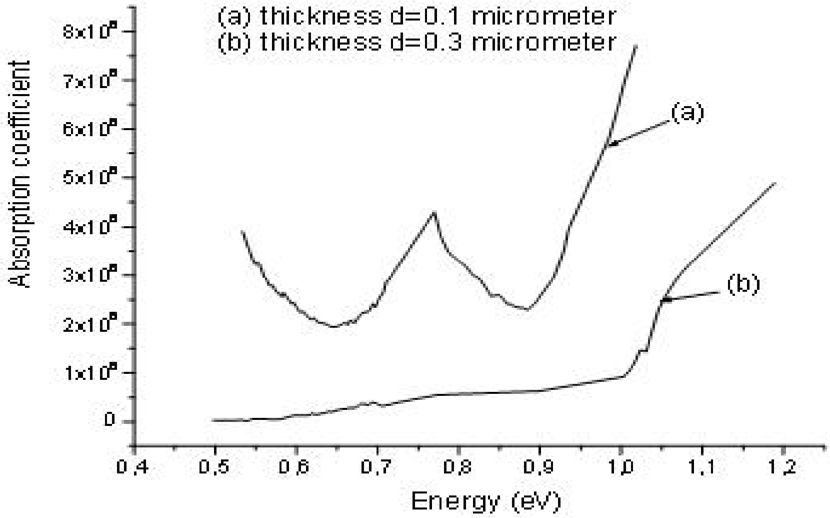

Fig. 10: Absorption coefficient of thin films $CuInSe_2$ for the thickness equal to 0.1 and 0.3 µm

Thus we obtain:

$E_g = 0.98$ eV for $\delta = 0.1$ µm $E_g = 0.97$ eV for $\delta = 0.2$ µm

$E_g = 1.02$ eV for $\delta = 0.3$ µm $E_g = 1.03$ eV for $\delta = 0.4$ µm

in good agreement with the published data [6].

REFERENCES

[1] D. Haneman, Crit. Rev. Sold State mater, Sci.14, p. 377, 1988.
[2] H. Lhwang, C.C. Tu, J.S. Maa and C.Y. Sun, Sol. Ener. Mater. 2, pp. 433 – 446, 1980.
[3] S. Belgacem, R. Bennaceur, Rev. Phys. Appl. 25, p. 1245, 1990.
[4] J. Vignes, Algorithmes Numériques, Tome 2, 1980.
[5] S.G. Tomlin, Journal Phys. d, 5, p. 852, 1972.
[6] G.B. Dubrovski and V.K. Subashiev, Sov. Phys. Solid State, 11, p. 2212, 1963.
[7] J.M. Pawlikowski, Thin Solid Films, 125, p. 213, 1985.
[8] H. Soliman, Journal of Materials Sciences, 23, pp. 4071 – 4075, 1988.
[9] M. El-Nahass, H.S. Soliman, N. El-Kadry, A.Y. Morsy and S. Yaghmour, J. Mater. Sci. Lett., 7, p. 1050, 1988.