

OPTICAL CONSTANTS OF $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ FILMS DEPOSITED BY FLASH EVAPORATION

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The $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($0 < x < 0.3$) thin films were deposited onto glass substrates by the flash evaporation technique. The optical properties of the films were characterized by the method of normal incidence transmittance and reflectance at room temperature. The absorption coefficient and the energy band gaps values of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($0 < x < 0.3$) alloys were extracted from the optical measurements. The extinction coefficient of the thinnest film CuInSe_2 was modelled in the 0.85-3.1 eV photon energy range using the Adachi's model for the optical properties of semiconductors and the simulated annealing algorithm. A good agreement with the experimental data was obtained, and the model parameters (strength, threshold energy, and broadening) were determined.

1. Introduction

CuInSe_2 (CIS), CuGaSe_2 (CGS), and their alloys (CIGS) are prototype chalcopyrite semiconductors that are key materials for thin-film solar cell applications. CIS-based cells currently hold the world-record energy conversion efficiency (19.5-19.9%) for thin film technologies [1, 2]. For a photovoltaic material, optical reflectance and absorbance are the cornerstones for optical losses and photo-generation; therefore, they establish the link between the optical properties and photo-response of solar cells [3]. Precise knowledge of the optical properties of CIGS films is an essential factor in characterizing and modelling CIGS-based solar cell devices. Therefore, a detailed study of the physical properties of CIGS films is important. However, so far very little is known about CIGS films in general and, in particular about the films with small content of Ga ($x \leq 0.35$) which show the highest energy conversion efficiency (19.5-19.9%) [1, 2]. Some optical properties of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin films with x from 0 to 1.0 have been determined using transmittance and reflectance measurements [3-6] and by spectroscopic ellipsometry [7-11]; however, data on CIGS films with $x \leq 0.3$ are quite scarce. Main attention has been paid to $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ films with x of about 0.2 [3-5, 7]; values of the energy gap [3-5, 7], as well as the refractive index and extinction coefficient [3, 5], were estimated. In addition, an important discrepancy was found in the extinction coefficient $k(\lambda)$ values obtained from the measurements of the normal incidence transmittance and reflectance reported by Paulson [8] and by Orgassa [3] for CIGS thin films in a spectral range of 1-2 eV and those listed in [12, 13] for bulk crystals (single and polycrystals) obtained from ellipsometry measurements.

In the present study, the room temperature spectral transmittance and reflectance at normal incidence of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ films with x 0; 0.11; 0.14 and 0.29 were measured in the spectral range from 0.8 to 3.1 eV. The spectral dependences of the optical constants (both the refractive index and the extinction coefficient) were determined as well as the energy gap of the films studied. In the case of $x=0$ with lowest thickness, the modelling of the extinction coefficient was also performed and the interband transition energies values were estimated.

2. Experimental

$\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin films used in this study were deposited onto soda-lime glass (SLG) substrates by the flash evaporation technique [14] controlling the crucible intensity (evaporation temperature), the substrate temperature, and the period of oscillating sample holder. An oscillating sample-holder was used in order to improve the uniformity in thickness and in composition of the films. As a source material, direct synthesis from high pure elements in stoichiometric quantities was used. The grain size of the $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ powder used ranged within 100 and 200 μm . The evaporation temperature was kept at 1150°C, and the substrate temperatures were $335 \pm 5^\circ\text{C}$ and $376 \pm 5^\circ\text{C}$ for the deposition of the films.

The structure of the thin films was analyzed by grazing angle X-ray diffraction (GXR) with an X'Pert PRO theta/theta diffractometer. The compositional measurements summarized in Table 1 were carried out by energy dispersive X-ray analysis (EDX) using a Hitachi S3000N scanning electron microscope (SEM). All thin-film samples showed compositions close to the stoichiometric values, although Cu-deficiency was observed. It is worth mentioning that the films fabricated by vapor deposition techniques in the high-efficiency CIGS solar cells are always Cu-deficient [1, 15, 16].

Table 1. Compositional measurements of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ thin films.

X	Elements				Thickness (Å)	Subst. Temp. (°C)
	Cu	Ga	In	Se		
0 Cr2	22.4	-	28.3	49.4	2850	335
0.11 EvJ-06	23.7	3.4	27.7	45.2	6800	336
0.14 EvJ-07	22.2	4.2	26.5	47.1	7100	333
0.29 EvJ-28	20.3	8.8	21.4	49.5	6100	376

The transmission and reflection spectra in the UV/VIS/NIR regions of the films were measured in a wavelength range of 400-1500 nm using a Perkin Elmer Lambda-9 dual-beam spectrophotometer with an integrating sphere. The film thickness d_f must be determined very accurately, as it is a critical parameter in the computation of the optical constants [8]. We measured d_f using a Talystep 223-17 profile system.

3. Results and discussion

The spectral distribution of the optical transmission (T) and reflectivity (R) at near normal incidence of the CIGS films are presented in Fig. 1.

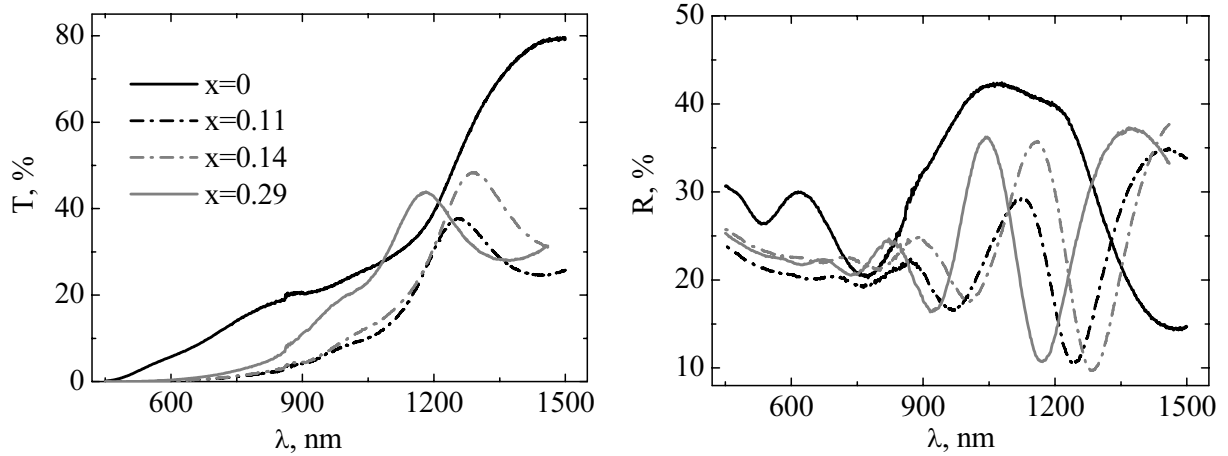


Fig. 1. Transmittance and reflectance from normal incidence of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films at 300 K.

To obtain the optical constants from measurements of the normal incidence transmittance T and reflectance R of a thin absorbing film on a nonabsorbing substrate (glass) in the air interface, the model was used that is given by a stack of plane-parallel flat layers with abrupt interfaces on which a plane wave is incident along the surface normal [3]. This model system allows formulating analytical expressions for the optical transmittance $T(n, k, d, s)$ and reflectance $R(n, k, d, s)$ in terms of the optical constants of a thin film $n(\lambda)$ and $k(\lambda)$, the film thickness d , the refractive index of the transparent substrate s , and implicitly the wavelength of light λ [9].

The theoretical expressions for T and R in this model are given by [17, 18]

$$T = \frac{Ax}{B - Cx \cos \varphi + Dx^2}, \quad (1)$$

$$R = \frac{A' + B'x^2 + (2C' \cos \varphi + 4D' \sin \varphi)x}{E' + F'x^2 + (2G' \cos \varphi + 4H' \sin \varphi)x}, \quad (2)$$

where

$$\begin{aligned} A &= 16n^2s, & A' &= \left[(n-1)^2 + k^2 \right] \left[(n+s)^2 + k^2 \right], \\ B &= (n+1)^3(n+s^2), & B' &= \left[(n+1)^2 + k^2 \right] \left[(n-s)^2 + k^2 \right], \\ C &= 2(n^2-1)(n^2-s^2), & C' &= (n^2+k^2)(1+s^2) - (n^2+k^2)^2 - s^2 - 4sk^2, \\ D &= (n-1)^3(n-s^2), & D' &= k(s-1)(n^2+k^2+s), \\ \varphi &= \frac{4\pi nd}{\lambda}, & x &= \exp\left(-\frac{4\pi kd}{\lambda}\right), \\ E' &= \left[(n+1)^2 + k^2 \right] \left[(n+s)^2 + k^2 \right], & F' &= \left[(n-1)^2 + k^2 \right] \left[(n-s)^2 + k^2 \right], \\ G' &= (n^2+k^2)(1+s^2) - (n^2+k^2)^2 - s^2 + 4sk^2, & H' &= k(s+1)(n^2+k^2-s). \end{aligned}$$

Measuring the film thickness d and using the value 1.51 for the index s of the substrate, we determine the optical constants n and k for each single wavelength by solving the equation system

$$T(n, k) - T_{\text{exp}} \leq \Delta T, \quad (3)$$

$$R(n, k) - R_{\text{exp}} \leq \Delta R, \quad (4)$$

where T_{exp} , T , R_{exp} , and R are the experimental and theoretical values of transmittance and reflectance data, respectively; ΔT and ΔR are the spectral resolutions.

An unfortunate complication [19] associated with these relations (3) and (4) is the existence of multiple solutions for singular values of T_{exp} , R_{exp} , and d . Also, the curve evaluated for $n(\lambda)$ features discontinuities at specific wavelengths which is typical for the method of normal incidence transmittance and reflectance [3, 6, 19]. It could be explained [3, 6] by some discrepancies between the theoretical model and the experimental data or/and by the presence of a significant amount of a secondary phase in the absorbing film.

To exclude multiple solutions of equation system (3)-(4) and taking into account reported values of the CIGS optical constants [3, 6, 10, 12, 13], we performed computation in a region of 2.5-3.5 for n and in a region of 0-1.5 for k allowing a variation of thickness by $\Delta d = 25$ nm. Calculated values of n and k of the CIGS ($x = 0$) film are plotted in Fig. 2. Unfortunately, there are some spectral regions in which solutions of equation system (3)-(4) cannot be found in the above regions and curves $n(\lambda)$, $k(\lambda)$ exhibit some discontinuities. Nevertheless, the deduced values of $n(\lambda)$ are in a satisfactory agreement with those previously determined by spectroscopic ellipsometry both for single crystals [12, 13] and for polycrystalline films [8].

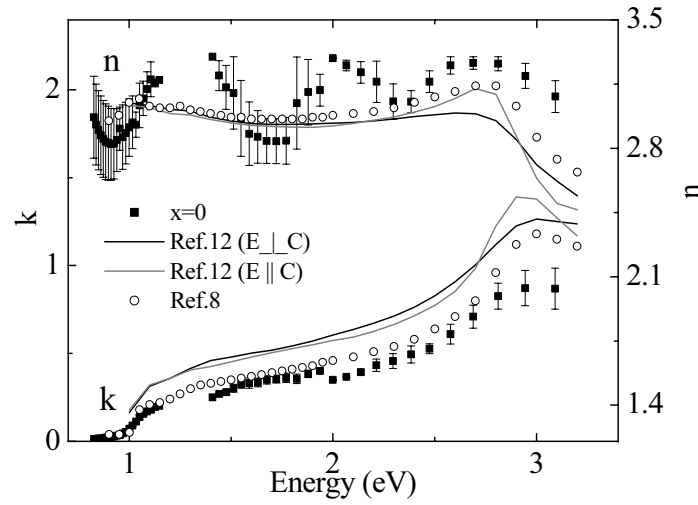


Fig. 2. Solution branches for refractive index n and extinction coefficient k of CuInSe_2 ($x = 0$). The closed squares, open circles, and lines represent our results and the data taken [8] and [12], respectively.

However, our values of the extinction coefficient $k(\lambda)$ are in agreement with that reported by Paulson [8] for CIGS thin films in a spectral range of 1-2 eV and lower by a factor of 1.5 than those listed in [12, 13] for bulk crystals. The same difference between data of the extinction coefficient $k(\lambda)$ obtained from ellipsometry measurements and the measurements of the normal incidence transmittance and reflectance of CIGS thin films was observed in [3] and references therein. This discrepancy could be due to the following: first, the films were measured as grown with a surface roughness, while the bulk samples were measured after the surface had been polished; second, the grain size in the films is much lower than in the bulk samples.

The spectral dependence of extinction coefficient of the thinnest sample CIGS ($x = 0$) was modeled using the Adachi's model for interband transitions [20]. In this model, the complex dielectric function as a function of energy, $E = \hbar\omega$, can be described by the sum of two terms, $\epsilon_0(E)$ and $\epsilon_1(E)$, corresponding to the one-electron contributions at the $E_{0\alpha}$ and E_I critical point (CP), respectively, where $\alpha = a, b, c$ refers to the triple valence band splitting level in chalcopyrites and E_{IA} refers to energy transitions after the main one. It is worth mentioning that in our case, splitting among the E_0 CPs is not observed and they were treated as single degenerate. In this way, the contribution of the three-dimensional (3D) M_0 CP E_0 and of the two-dimensional (2D) M_1 CP E_I to $\epsilon(E)$ are given by [20-22]

$$\varepsilon_0(E) = AE_0^{-3/2} \chi_0^{-2} \left[2 - (1 + \chi_0)^{1/2} - (1 - \chi_0)^{1/2} \right], \text{ with } \chi_0 = \frac{E + i\Gamma}{E_0} \quad (5)$$

$$\varepsilon_1(E) = \frac{C}{(1 - \chi_1^2) - i\chi_1\gamma}, \text{ with } \chi_1 = \frac{E}{E_1}, \quad (6)$$

where A (C) and Γ (γ) are the strength and damping constants for the E_0 (E_1) transitions, respectively. The contribution of the interband transitions higher than E_1 was taken into account by adding the nondispersive term $\varepsilon_{1\infty}$ to the real part of the model function $\varepsilon(E)$ [20-22].

The simulated annealing (SA) algorithm [22, 23] has been used to obtain those model parameters through the minimization of the following objective function

$$F = \sum_{i=1}^N \left(\frac{k(\omega_i)}{k^{\text{expt}}(\omega_i)} - 1 \right)^2, \quad (7)$$

where the summation is performed over the available range of experimental points, and $k^{\text{expt}}(\omega_i)$, $k(\omega_i)$ are the experimental and theoretical values of the extinction coefficient at ω_i point, respectively. The theoretical values of the extinction coefficient were computed from

$$k = \left(((\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1) / 2 \right)^{1/2},$$

where ε_1 and ε_2 are the real and imaginary part of the complex dielectric function determined in (5)-(6).

A good agreement between our calculations and the experimental data can be observed for CIGS ($x = 0$) (Fig. 3). We obtained following sets of parameters E_0 , Γ , A , (1.01 eV, 0.02 eV, 4.4 eV^{3/2}), E_1 , γ , C , (2.82 eV, 0.28, 0.98) and $\varepsilon_{1\infty}$ (5.2). Despite the discrepancy in $k(\lambda)$, our calculated values of energy transitions E_0 , E_1 are in a good agreement with those previously determined for single crystals by Kawashima et al. [20] ($E_0 = 1.04$ eV, $E_1 = 2.92$ eV), Alonso et al. [12], ($E_0 = 1.04$ eV, $E_1 = 2.90$ eV), and specially for polycrystals by Alonso et al. [13] ($E_0 = 1.01$ eV, $E_1 = 2.89$ eV). The energy threshold of the fundamental absorption edge, $E_0 = E_g$, can be well identified in spectrum (Fig. 3) and could be related to an electronic transition at the Γ point, corresponding to a direct transition from the valence band maximum to the conduction band minimum. We assume that E_1 transition can be related to N -type transitions after references [12, 13, 20].

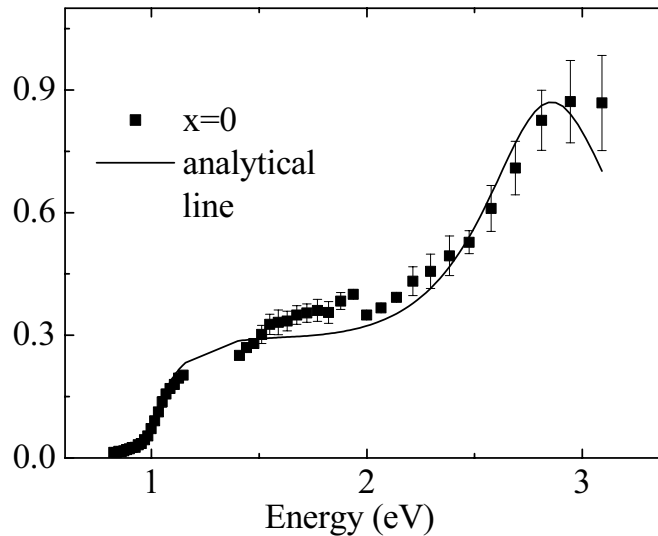


Fig. 3. Extinction coefficient vs. energy for $x = 0$ thin film. The squares represent the experimental data, while the solid line corresponds to the theoretical fits including E_{0A} and E_1 interband transitions.

The real and imaginary refraction index n and extinction coefficient k are the fundamental properties. However, a device physicist, who wants to assess the influence of the chalcopyrite optical properties on the solar cell device properties, would prefer to know the optical absorption coefficient α . The spectral dependence of $\alpha(\lambda) = (4\pi/\lambda)k(\lambda)$, where λ is the wavelength of light in the vacuum, is presented in Fig. 4a for $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($x = 0, 0.3$). The spectrum shifts toward the higher energy as the content of Ga increases indicating an increase in the optical gap.

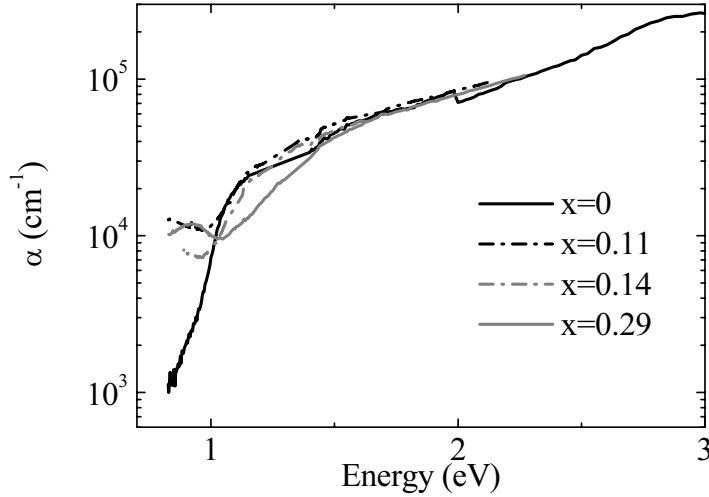


Fig. 4a. Absorption coefficient α for $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films: $x = 0, 0.11, 0.14, 0.29$.

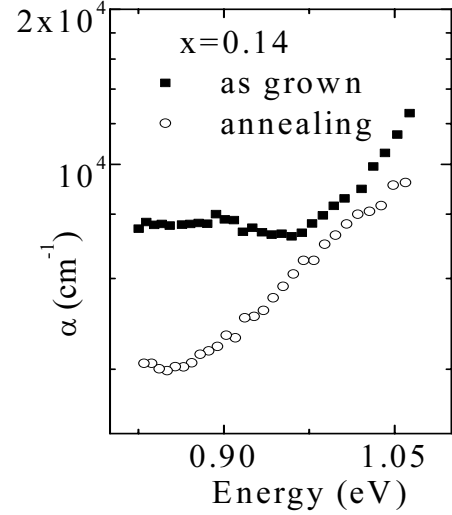


Fig. 4b. Absorption coefficient α below the band gap for $x=0.14$ thin film.

The studied samples with $x > 0$ show a significant absorption tail below the fundamental gap edge (Fig. 4a). The tail can be related to the presence of defects and grain boundaries in polycrystalline material deviation from stoichiometry and/or the secondary phase at grain boundaries and free surfaces [6]. Annealing leads to decreasing of the tail (Fig. 4b) which could be considered as improving of quality of the films studied.

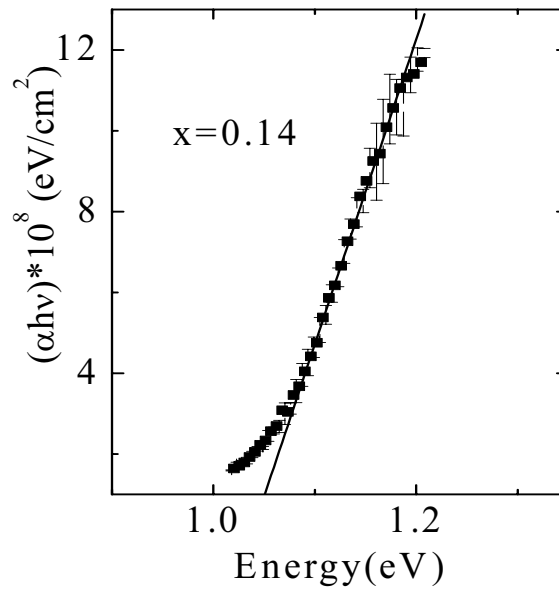


Fig. 5. Plot of the square of the absorption coefficient of $x=0.14$ thin film against photon energy.

For direct band gap semiconductors

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \quad (8)$$

where $h\nu$ is the characteristic energy of a photon, and A is a temperature independent constant that depends on the effective mass and the refractive index.

In our films, the $(\alpha h\nu)^2$ spectra show a linear dependence on photon energy over an appreciable energy range, revealing the existence of direct band gap in CIGS solid solutions. The plot points of each film fit well a straight line irrespective of the Ga content. One representative fit to the absorption data (sample $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ with $x = 0.14$) is shown in Fig. 5. From the extrapolation of $(\alpha h\nu)^2$ vs $h\nu$ curves to $(\alpha h\nu)^2 = 0$, the value of E_g was estimated. The values were 1.00, 1.04, 1.03, and 1.32 eV for the band gaps of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ with $x = 0, 0.11, 0.14$, and 0.3 , respectively. It should be noted that value of band gap for CIGS($x=0$) obtained from absorption coefficient is in a good agreement with the value 1.01 determined above from the modeling of extinction coefficient. The value of E_g for CIGS ($x = 0$) amounting to 1.32 eV is high compared to the previously reported in [24] and might be caused by a small Cu concentration ($\text{Cu} \approx 0.81$) in the sample under study. It is well known that the Cu-poor CIGS materials [10, 24] show an increase in the band gap due to the reduction in repulsion between Cu $3d$ and Se $4p$ states in the valence band and an increase in the perturbation potential due to lattice deformation.

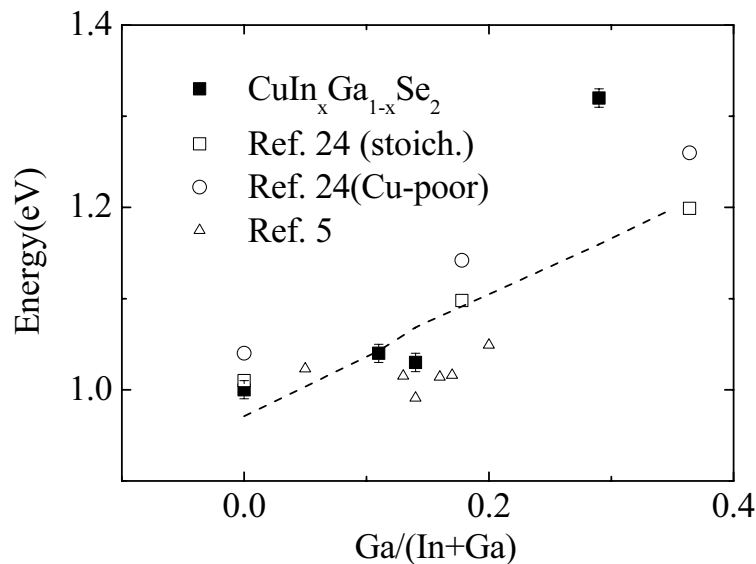


Fig. 6. Compositional dependence of the band gap in $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ alloys. The closed squares, open and closed circles, and open triangles represent our results and the data taken from [24] and [5], respectively. The dashed line shows the best fit of (9) to our results and the published data for the band gap values.

Figure 6 shows the variation of the optical band gap for the Ga content. The data of the optical band gap for $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ alloys based on ellipsometry measurements for Cu stoichiometric and Cu-poor ($\text{Cu}_{0.9}\text{In}_{1-x}\text{Ga}_x\text{Se}_2$) films [24] and absorption spectra of the films [5] are also presented in Fig. 6. The values of E_g of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ films are found to increase linearly with increasing Ga content in the range of $x \leq 0.35$ (Fig. 6) and may be expressed as

$$E_g(x) = 0.972 + 0.69x. \quad (9)$$

Equation (9) gives the room temperature $E_g = 0.97$ and 1.66 eV for CuInSe_2 and CuGaSe_2 , respectively, which is in a good agreement with the band gap of the endpoint compounds.

4. Conclusions

Thin films $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($0 < x < 0.3$) deposited onto soda-lime glass substrates by the flash evaporation technique were characterized by the method of normal incidence transmittance and reflectance at room temperature. The absorption coefficients and values of band gaps of $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($0 < x < 0.3$) alloys were extracted from the optical measurements. The extinction coefficient of the thinnest film $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ ($x=0$) was modelled in the 0.85-3.1 eV photon energy range using the Adachi's model for the optical properties of semiconductors and the SA algorithm. A good agreement with the experimental data was obtained, and the model parameters (strength, threshold energy, and broadening) were determined. The obtained optical constants for $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ solid solutions can be useful for optical modelling of the thin-film solar cells based on these alloys.

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