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Citation: *J. Appl. Phys.* **102**, 113503 (2007); doi: 10.1063/1.2817896

View online: <http://dx.doi.org/10.1063/1.2817896>

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Optical constants of CuGa_5Se_8 crystals

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(Received 25 June 2007; accepted 2 October 2007; published online 4 December 2007)

Spectral dependence of the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the complex dielectric function, complex refractive index, absorption coefficient, and normal-incidence reflectivity of CuGa_5Se_8 crystals with slightly different Cu contents are modeled using Adachi's model for interband transitions. The results are in good agreement with the experimental data over the entire range of photon energies. The model parameters are determined using the simulated annealing algorithm.

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I. INTRODUCTION

Thin film photovoltaic cells based on $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ show an efficiency up to 19.3%.¹ The layers of Cu ($\text{In}_x\text{Ga}_{1-x}$)₃Se₅ might play an important role in the optimization of the efficiency of the $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ -based solar cells.^{2,3} CuGa_5Se_8 , as well as CuGa_3Se_5 and CuIn_3Se_5 , belong to the family of Cu-deficient ordered vacancy compounds (OVCs) and attract some attention as a perspective material for application in high efficiency photovoltaic devices and in nonlinear optics and therefore a detailed study of their various physical properties is of great interest. However, so far the characteristics of such OVCs have not yet been well studied. Some structural, optical, and electrical properties of CuGa_5Se_8 (G58) crystals were reported⁴⁻⁶ and the band gap values E_g were determined.^{4,5}

Spectroscopic ellipsometry is a powerful and appropriate technique for determining the optical functions of bulk and thin-film materials. Recently, ellipsometric investigations of CuGa_5Se_8 crystals have been reported and the energies corresponding to the fundamental gap and higher critical points have been determined; a linear correlation of the fundamental gap values with Ga/Cu atomic ratio content has been deduced.⁷

The main aim of this work is to model the optical constants of CuGa_5Se_8 crystals with different deviation from stoichiometry and, through the analysis of their optical functions, to clarify the optical properties of nearly stoichiometric and Cu-poor CuGa_5Se_8 crystals.

II. EXPERIMENTAL METHODS

CuGa_5Se_8 crystals have been grown by the Bridgman method. The compositional measurements were carried out by energy dispersive x-ray microanalysis (EDAX) and the samples used for the optical study showed nearly stoichiometric composition (Table I, G58S) and some deviation from stoichiometry (Table I, G58T and G58B). The structural analysis was performed by x-ray diffraction measurements and found that the ingots of G58 were polycrystalline single phase with tetragonal structure. The optical measurements using a variable-angle spectroscopic ellipsometer were performed at room temperature in the photon energy range from 0.8 to 4.4 eV at two angles of incidence (55° and 65°).⁷ In order to reduce surface layer artifacts, our samples were specially prepared, as described in Ref. 8.

III. THEORETICAL MODEL

Adachi's model of the dielectric function has been successfully applied to model the dielectric function as well as optical constants of III-V and I-III-V₂ compounds.⁹⁻¹² The complex dielectric function as a function of energy $E = \hbar\omega$ is described by the sum of $\varepsilon_0(E)$ and $\varepsilon_1(E)$ terms, corresponding to one-electron contributions at critical points (CP's) E_0 and $E_{1\beta}$, where $\beta = (A, B)$,

$$\varepsilon(E) = \varepsilon_0(E) + \varepsilon_1(E). \quad (1)$$

The contributions of the three-dimensional M_0 CP's $E_{0\alpha}$ and of the two-dimensional M_0 critical points $E_{1\beta}$ are given by^{11,12}

$$\varepsilon_0(E) = \sum_{\alpha=A,B,C} A_{0\alpha} E_{0\alpha}^{-3/2} f(\chi_{0\alpha}), \quad (2)$$

where

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TABLE I. Composition data of the studied samples carried out by EDAX.

Samples	Cu (at. %)	Ga (at. %)	Se (at. %)	Ga/Cu	Se/Cu
CuGa ₅ Se ₈ (G58T)	6.29	39.60	54.11	6.3	8.6
CuGa ₅ Se ₈ (G58B)	8.73	37.05	54.22	4.2	6.2
CuGa ₅ Se ₈ (G58S)	7.15	31.33	61.52	4.4	8.6

$$f(\chi_{0\alpha}) = \chi_{0\alpha}^{-2} [2 - (1 + \chi_{0\alpha})^{1/2} - (1 - \chi_{0\alpha})^{1/2}],$$

$$\chi_{0\alpha} = \frac{E + i\Gamma}{E_{0\alpha}},$$

$$A_{0\alpha} = \frac{4}{3} \left(\frac{3}{2\mu_{0\alpha}} \right)^{3/2} P_{0\alpha}^2,$$

$\mu_{0\alpha}$ is the combined density-of-states mass, $P_{0\alpha}^2$ is the squared momentum-matrix element, and Γ is the damping energy of the $E_{0\alpha}$ gap.

$$\varepsilon_1(E) = - \sum_{\beta=A,B} B_{1\beta} \chi_{1\beta}^{-2} \ln(1 - \chi_{1\beta}^2), \quad (3)$$

where

$$\chi_{1\beta} = \frac{E + i\Gamma_{1\beta}}{E_{1\beta}},$$

with $B_{1\beta}$ and $\Gamma_{1\beta}$ the strengths and damping constants of the $E_{1\beta}$ transitions, respectively.

Following Djuricic and Li,¹¹ the damping constant Γ is replaced in the model for E_{1A} transition by frequency dependent damping constant Γ' with the energy dependent expression,^{13,14}

$$\Gamma'(E) = \Gamma \exp \left[-\alpha \left(\frac{E - E_g}{\Gamma} \right)^2 \right], \quad (4)$$

where α and Γ are the adjustable model parameters, while E_g is the energy of the CP at which transition occurs. The replacement gives a better agreement between the calculated and experimental data.¹¹

To obtain the model parameters, the simulated annealing (SA) algorithm has been used,^{11,15} and hence they are obtained through the minimization of the following objective function:

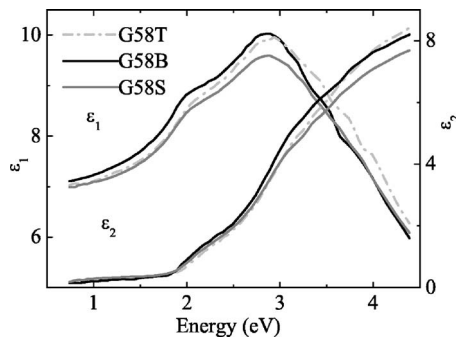


FIG. 1. Real (ε_1) and imaginary (ε_2) parts of the dielectric function vs energy for G58T, G58B, and G58S samples.

$$F = \sum_{i=1}^N \left(\left| \frac{\varepsilon_1(\omega_i)}{\varepsilon_1^{\text{expt}}(\omega_i)} - 1 \right| + \left| \frac{\varepsilon_2(\omega_i)}{\varepsilon_2^{\text{expt}}(\omega_i)} - 1 \right| \right)^2, \quad (5)$$

where the summation is performed over the range of available experimental points and $\varepsilon_1^{\text{expt}}(\omega_i)$, $\varepsilon_1(\omega_i)$ and $\varepsilon_2^{\text{expt}}(\omega_i)$, $\varepsilon_2(\omega_i)$ are the experimental and calculated values of the real and imaginary parts of complex dielectric function at point ω_i , respectively. As a result, good agreement with experimental data of III-V materials is obtained.⁹⁻¹¹

IV. RESULTS AND DISCUSSIONS

The optical functions of the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the pseudodielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ for G58T, G58B, and G58S samples are given in Fig. 1. The measured spectra exhibited several structures at the CP's. Adachi's model dielectric function is applied to model the dielectric function as well as the optical constants of G58 crystals.

Figure 2 shows the real and imaginary parts of the dielectric function of G58S sample as a function of energy. The solid triangles represent the experimental data and the solid line corresponds to the calculated dielectric function using Adachi's model. Good agreement between our calculations and the experimental data is observed for the nearly stoichiometric G58S sample (Fig. 2) as well as for the G58T and G58B ones with some deviation from stoichiometry. As an indication of accuracy with respect to experimental values,

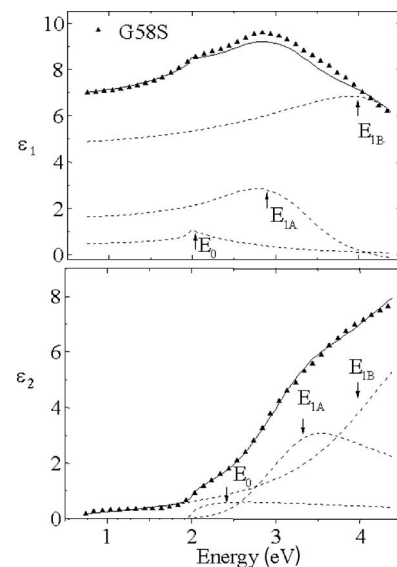


FIG. 2. Real (ε_1) and imaginary (ε_2) parts of the dielectric function vs energy for G58S samples. The solid lines represent fits of these data to the sum of Eqs. (2) and (3). The fit determined CP parameters are listed in Table II. Individual contributions to $\varepsilon(E)$ of the E_0 , E_{1A} , and E_{1B} gaps are also shown by the dashed lines.

TABLE II. Calculated model parameter values using the stimulated annealing algorithm.

Parameter	Samples					
	G58B		G58T		G58S	
A (eV ^{1.5})	6.20		5.59		5.16	
E_0 (eV)	1.92		2.02		1.98	
Γ (eV)	0.01		0.01		0	
B_{1A} (eV)	1.93		1.64		1.58	
E_{1A} (eV)	2.93		2.96		2.95	
Γ_{1A} (eV)	0.33		0.32		0.35	
α	0.21		0.25		0.29	
B_{1B} (eV)	4.54		4.84		4.93	
E_{1B} (eV)	4.18		4.12		4.23	
Γ_{1B} (eV)	0.72		0.71		0.88	
Error	ϵ_1	ϵ_2	ϵ_1	ϵ_2	ϵ_1	ϵ_2
	2.3%	4.4%	2.1%	6.6%	2.5%	7.7%

the relative errors have been calculated, laying in the 2%–2.5% and 7%–8% ranges, respectively, for the real and imaginary parts of the dielectric functions for the studied compounds (Table II). The model parameters A , B , E_g (E_0 , E_1), and Γ calculated using the SA algorithm are given in Table II. The values of E_0 , $E_1(A)$, and $E_1(B)$ are in good agreement with those⁷ determined by fitting the numerically obtained second-derivative spectra $d^2\varepsilon(\omega)/d\omega^2$ of the experimental $\varepsilon(\omega)$ data. The lowest value of E , observed in the region below 2 eV, corresponds to the fundamental energy gap value, $E_0=E_g$, well distinguished for each studied sample (Fig. 1). Second, $E_1(A)$, and third, $E_1(B)$, energy thresholds appear in the region between 2 and 5 eV.

Since band structure calculations are not available for CuGa₅Se₈, those for CuInSe₂ (CIS) and CuGaSe₂ (CGS) have been used for the identification of the observed energy values. It is well established that the main transitions contributing to $\varepsilon(E)$ for Cu(In,Ga)Se₂ occur at the Brillouin zone (BZ) center (fundamental gap at Γ) and BZ edge points N and T (predominant upper transitions).¹⁶ The energy threshold of the fundamental absorption edge $E_0=E_g$, well identified in the spectra of studied compounds, can be related to an electronic transition at the Γ point. Our values of E_g , at room temperature, 1.92–2.02 eV (Table II), are in a reasonable agreement with those^{4,5} previously determined using optical absorption spectroscopy. Variation in the reported values of the band gap can be attributed to the compositional changes of the OVC materials. The chalcopyrites and OVC's exhibit unusually high tolerance to deviations in stoichiometry. In fact, CuInSe₂ shows band gap values ranging from 0.94 to 1.04 eV. In the region of 2.5–4.6 eV, two transitions for G58, named as $E_1(A)$ and $E_1(B)$, have been observed. We assume that they can be attributed to transitions at the N point in the BZ following Refs. 17 and 18 where ellipsometric data on CIS and CGS have been analyzed. The measured energy separation between these two transitions corresponds to the crystal-field splitting of the valence band at the N point. The crystal-field splitting at the N point is about

1.2 eV, close to that (1.25 eV) estimated for CuGa₃Se₅.⁷ A value of 0.8 eV was reported for CGS and CIS crystals.^{9,16,19}

Recently, the effect of Cu deficiency on the optical functions of CIS [(4CuInSe₂)_x(CuIn₅Se₈)_{1-x}] and CuIn_{1-x}Ga_xS₂ thin films has been reported and discussed.^{17,18,20} Several authors found a reduction in the absorption strength in the spectral region of 1–3 eV for Cu-poor CuInSe₂ that was explained in terms of the density of the Cu 3d states in the valence band.¹⁸ Cu-poor CIS samples showed higher band gap values that can be caused by a lattice constant decrease due to reduced p - d hybridization, with a lattice deformation due to Cu deficiency.²⁰

According to the theoretical calculations of Jaffe and Zunger,²¹ verified by x-ray photoelectron spectroscopy,^{22,23} the upper valence band of Cu-III-VI₂ chalcopyrites is formed exclusively by p - d hybridization of Cu 3d and VI 4p atomic levels, whereas the group-III cations are not involved: the different structures of the Cu 3d density of states (DOS) are almost insensitive to substitutions of the group-III cations (In and Ga). The existence of Cu d character in the upper valence band has a significant consequence for the optical band gaps in these compounds.²¹ The $\Gamma_{15}(d)$ -like combinations of the d orbitals interact with the $\Gamma_{15}(p)$ -like combinations of the anion p orbitals ($\Gamma_{4v}^{(7)} + \Gamma_{5v}^{(2)}$) at the valence-band maximum (VBM). The strength of this interaction depends inversely on the energy separation between the Cu d orbitals and the anion p orbitals. This repulsive interaction pushes the higher energy component [$\Gamma_{15}(d)$ -like] to higher energies, thereby reducing the band gap relative to systems with more tightly bound d orbitals. This p - d repulsion accounts for about half of the observed reduction in the band gaps of the Cu-III-VI₂ compounds relative to their II-VI binary analogs. As one replaces Cu by Ag, Zn, or Cd, this d - p atomic energy gap increased rapidly, leading to a reduction in d - p hybridization and to the predominance of sp bonding.²¹

In the case of Cu-poor CIS, the p - d repulsion is expected to be smaller than that of stoichiometric CIS. The effect of the decrease in this repulsive interaction would lead to a lowering of the VBM as well as a minor lowering of the conduction-band minimum.²⁴

Our results show an increase of the band gap (E_0 and E_{1A}) for the Cu-poorest sample, G58T (Table II). The E_0 and E_{1A} values are higher than that for the nearly stoichiometric sample (G58S) and the Cu-rich samples (G58B) (Table II). Following Han *et al.*,^{17,18,20} it could be explained by the reduction of the p - d interaction, assuming that there is no change in the crystal structure and we can consider that Cu-poor G58 is a chalcopyrite with Cu deficiency.

Theoretical calculations of the electronic band structure and DOS of CuInSe₂ and CuIn₅Se₈ show a reduction of the DOS within 3–4 eV of the VBM.^{24–26} A reduction in the density of the Cu 3d state near the VBM due to Cu deficiency results in a decrease in the amplitude of the absorption coefficient α of CIS.¹⁸

Comparing the absorption coefficient spectra α [calculated using Eq. (8) given below] of nearly stoichiometric and Cu deficient CuGa₅Se₈, it can be seen (Fig. 3) that the latter

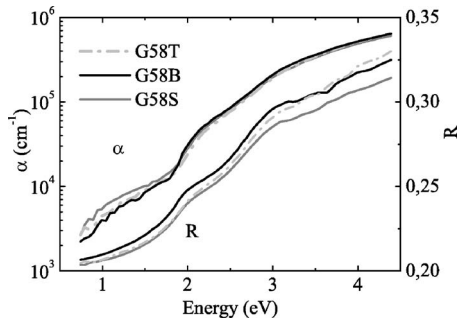


FIG. 3. Comparison of absorption coefficient (α) and normal-incidence reflectivity (R) between stoichiometric G58S (7.15 at. % Cu), Cu-poor G58T (6.29 at. % Cu), and Cu-rich (8.73 at. % Cu) G58B samples.

shows a depression of the absorption coefficient in the spectral region of 1–3 eV, which is in agreement with that observed in $(4\text{CuInSe}_2)_y(\text{CuIn}_5\text{Se}_8)_{1-y}$ films.¹⁸

The optical parameters of interest can be computed readily, namely, the complex refractive index n^* , the normal-incidence reflectivity R , and the absorption coefficient α ,

$$n^* = n + ik = (\varepsilon_1 + i\varepsilon_2)^{1/2}, \quad (6)$$

$$R = [(n-1)^2 + k^2] / [(n+1)^2 + k^2], \quad (7)$$

$$\alpha = 4\pi k / \lambda, \quad (8)$$

where λ is the wavelength of light in vacuum.

The experimental spectral dependences of n , k , R , and α as well as the calculated ones using Adachi's model and the SA algorithm are presented in Fig. 4 only for the nearly stoichiometric G58S sample. The two other samples show similar dependences and good agreement is observed for all studied samples. The obtained values of the interband CP parameters (strength, threshold energy, and broadening) are given in Table II. All these optical spectra are found to reveal

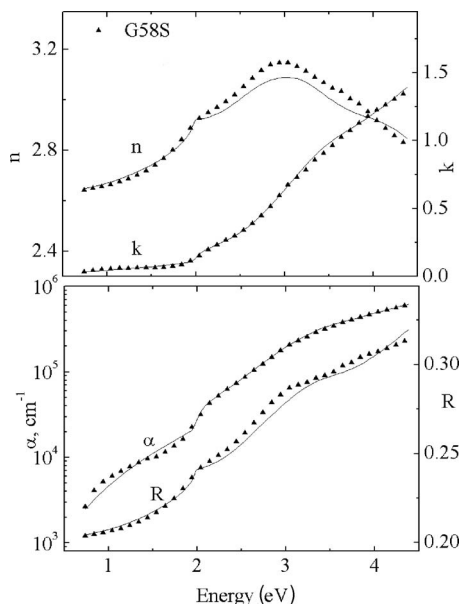


FIG. 4. Spectral dependence of the real refractive index (n) and the extinction coefficient (k) for absorption coefficient (α) and normal-incidence reflectivity (R) for G58S sample.

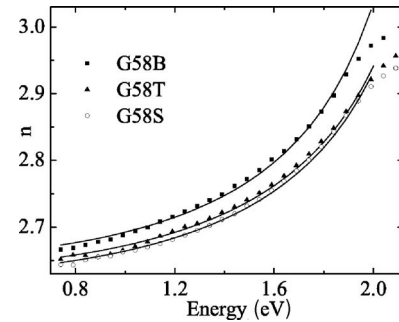


FIG. 5. (n) vs photon energy for G58T, G58B, and G58S samples. The solid line shows the calculated result of Eq. (9).

distinct structures at each CP (Fig. 4). The samples studied show an absorption tail below the fundamental gap edge. The tail results from defects and grain boundaries in polycrystalline material.¹⁶

The experimental n data are analyzed using a simple theoretical model, namely, the first-order Sellmeier equation,¹²

$$n^2(\lambda) = A + \frac{\lambda^2}{\lambda^2 - B}, \quad (9)$$

where A and B are the fitting parameters. The solid line in Fig. 5 shows the fitted result of Eq. (9) to the experimental data. Values of the fitting parameters A and B are 5.96, 0.241; 5.91, 0.241; and 6.04, 0.263 for G58 T, G58 S, and G58B, respectively. As $\lambda \rightarrow \infty$, the electronic contribution to the dielectric function approaches a limiting value ε_∞ , the high-frequency dielectric constant. The value of ε_∞ which is equal to $\varepsilon_\infty = n^2(\lambda \rightarrow \infty) = A + 1$ is about 7 for CuGa_5Se_8 . The reported values for CuInSe_2 and CuGaSe_2 are ranged between 6–6.9 and 4.2–5.1, respectively, and that for CuGa_3Se_5 is $\varepsilon_\infty = 7.2$.^{12,27}

V. CONCLUSIONS

The spectral dependence of the real $\varepsilon_1(\omega)$ and imaginary $\varepsilon_2(\omega)$ parts of the pseudodielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ as well as of the refractive index, extinction coefficient, absorption coefficient, and normal-incidence reflectivity of CuGa_5Se_8 ordered vacancy compound crystals are modeled in the 0.8–4.4 eV photon energy range using a modification of Adachi's model of optical properties of semiconductors and SA algorithm. Good agreement with experimental data is obtained, and the model parameters (strength, threshold energy, and broadening) are determined. It is found that Cu-poor CuGa_5Se_8 samples show an increase in band gap due to a reduction in the p - d interaction. The results presented offer a valuable set of optical-constant data for CuGa_5Se_8 that can be useful for the design of solar cells based on these compounds.

ACKNOWLEDGMENTS

We would like to thank Dr. N. Allsop for useful discussion. Financial support from INTAS program (Project No. 03-51-6314) and from Spanish government MEC project

ENE 2004-07446-C02-01/ALT/ and MAT2003-01490 is acknowledged.

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