I. INTRODUCTION

Chalcopyrite-type semiconductor compounds are superior materials for thin film photovoltaic cells. Laboratory and bulk samples6–10 have been reported so far.2,3 Samples* of this work are to model the optical constants of Cu2In4Se7 and CuGa3Se5 crystals and CuGa3Se5 crystals have been reported.12 The main aim of this work is to model the optical constants of Cu2In4Se7 and CuGa3Se5.

CuInSe2 and CuGaSe3 have been grown by the Bridgman (B) method. Compositional measurements were carried out by energy dispersive x-ray microanalysis (EDAX). Samples used for the optical study show some deviation from stoichiometry (Table I). Experimental details concerning the structural analysis and SE measurements are given in Ref. 12.

II. THEORETICAL MODEL

Two different methods are usually used to analyze in detail the observed structures of the dielectric function, namely, fitting the numerically differentiated experimental spectrum to analytical line shapes11,13 and modeling of measured ε(E) spectra, using interband transitions models.14–16 In our paper main attention is paid to the latter. The former has been used for our compounds in Ref. 12 and the obtained values of the transition energies will be presented to compare the results of both methods.

TABLE I. Data on compositional measurements of samples studied carried out by EDAX.

<table>
<thead>
<tr>
<th>Samples*</th>
<th>Cu (at. %)</th>
<th>In (or Ga) (at. %)</th>
<th>Se (at. %)</th>
<th>In/Cu (or Ga/Cu)</th>
<th>Se/Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuInSe2 (B247/B)</td>
<td>16.6</td>
<td>31.1</td>
<td>52.3</td>
<td>1.9</td>
<td>3.1</td>
</tr>
<tr>
<td>CuGaSe2 (G35/B)</td>
<td>13.1</td>
<td>34.55</td>
<td>52.35</td>
<td>2.6</td>
<td>4.0</td>
</tr>
<tr>
<td>CuGaSe2 (G35B/B)</td>
<td>12.7</td>
<td>35.08</td>
<td>52.22</td>
<td>2.8</td>
<td>4.1</td>
</tr>
</tbody>
</table>

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Adachi’s model dielectric function has been successfully applied to model the dielectric function as well as the optical constants of III-V and I-II-VI$_2$ compounds.$^{14-16}$ The complex dielectric function as a function of energy $E=\hbar \omega$ is described by the sum of terms corresponding to one-electron contributions at critical points $E_{0\alpha} (\alpha=A, B, C)$ and $E_{1\beta} (\beta = A, B)$, $\varepsilon_0(E)$ and $\varepsilon_1(E)$, and an additive constant $a$,

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

The $E_{0\alpha}$ ($\alpha=A, B,$ and $C$) gaps in chalcopyrite crystals were assigned to the three-dimensional (3D) $M_0$ critical point. Assuming that the valence and conduction bands are parabolic and using the Kramers-Kronig transformation, the contribution of these gaps to $\varepsilon_0(E)$ can be written as

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

with

$$A_{0\alpha} = (4/3)(3/2 \mu_{0\alpha})^{3/2} p_{0\alpha}^2,$$

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

$$\chi_{0\alpha} = (E + i\Gamma)/E_{0\alpha}.$$

In Eq. (2) $\mu_{0\alpha}$ is the combined density-of-states mass, $p_{0\alpha}^2$ is the squared momentum-matrix element, and $\Gamma$ is the damping energy of the $E_{0\alpha}$ gap. It is worth mentioning that normally, one should calculate the separate contributions from $E_{0\alpha}$ ($\alpha=A, B,$ and $C$) critical points according to Eq. (2), but in our case, splitting among these critical points is not observed, and $E_{0\alpha}$ has been treated as a single degenerate one. Contributions of the two-dimensional (2D) $M_0$ critical points $E_{1\beta}$ are given by Adachi’s model,$^{15}$

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

with

$$\chi_{1\beta} = (E + i\Gamma_{1\beta})/E_{1\beta}, \quad (3)$$

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

Djurisic et al.$^{17}$ have proposed the acceptance-probability-controlled simulated annealing (APCSA) algorithm to obtain the model parameters. It is known that all fitting routines based on classical optimization algorithms, such as Levenberg-Marquardt or simplex algorithms, require initial parameter values close to the final ones to provide a meaningful solution and it is usually hard to provide good initial values for adjustable parameters of the model. Therefore, to determine accurately the model parameters, one should employ a global optimization routine, such as a simulated annealing algorithm employed in Ref. 17. Djurisic and Li$^{16}$ have modeled the optical constants of hexagonal GaN, InN, and AlN using Adachi’s model and obtained good agreement with experimental data. Model parameters are determined using the APCS algorithm through minimizing the following objective function:

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

where the summation is performed over the available experimental points and $\varepsilon_1^{\text{expt}}(E_i)$, $\varepsilon_1(E_i)$, $\varepsilon_2^{\text{expt}}(E_i)$, and $\varepsilon_2(E_i)$ are, respectively, the experimental and calculated values of the real and imaginary parts of complex dielectric function at point $E_i$.

### III. RESULTS AND DISCUSSIONS

The real $\varepsilon_1(E)$ and imaginary parts $\varepsilon_2(E)$ of the pseudodielectric function $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$ for Cu$_2$In$_4$Se$_7$ and CuGa$_3$Se$_5$ crystals are shown in Figs. (1a) and (1b). The structures observed in the $\varepsilon(E)$ spectra are attributed to interband critical points (CP’s), related to regions of the band structure with large or singular point electronic density of states.

We have applied Adachi’s model and APCS algorithm to our SE data analysis. Figures (1a) and (1b) show the real and imaginary parts of the dielectric functions of I247/B, G35/B, and G35T/B as a function of the energy. The solid circles represent our experimental data, while the solid lines show the dielectric function calculated using Adachi’s model. Excellent agreement between our calculations and experimental data can be observed. As an indication of accuracy with respect to experimental values, the relative errors have been calculated. These values are, respectively, about 0.9%-1.5% and 3.2%-4.1% for the real and imaginary parts of complex dielectric function for Cu$_2$In$_4$Se$_7$ and CuGa$_3$Se$_5$ crystals.

The model parameters $A$, $B$, $E_0$, $E_{1\alpha}$, and $\Gamma$ calculated using APCS algorithm are given in Table II. The values of $E_0$, $E_{1\alpha}$, and $E_{1\beta}$ are in a good agreement with those obtained from an analysis of the numerically derived $d^2 \varepsilon(E)/d\omega^2$ (Table II). The lowest value of $E_{0\alpha}$, observed in the region below 2 eV of CuIn$_3$Se$_5$, corresponds to its fundamental energy gap $E_0$=$E_g$. A second $E_1(A)$ and third energy thresholds $E_{1\beta}$ appear in the region between 2 and 4.5 eV. The fit-determined $E_0$ and $E_1$ values, together with their related strength and broadening parameters, are listed in Table II. The resulting analytical lines from the fits of the experimental data in Figs. 1(a) and 1(b) have been obtained considering CP’s of the three-dimensional-type 3D in the $E_g$ region and of the type 2D in the $E_1$ region. It is worth mentioning that reasonable agreement can be achieved between experimental data and calculated curves.
TABLE II. Model parameter values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>G35B/B</th>
<th>G35T/B</th>
<th>I247/B</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$ (eV)</td>
<td>7.71</td>
<td>7.9</td>
<td>5.15</td>
</tr>
<tr>
<td>$E_0$ (eV)</td>
<td>1.85 (1.88)</td>
<td>1.86 (1.88)</td>
<td>1.125 (1.15)</td>
</tr>
<tr>
<td>$\Gamma$ (eV)</td>
<td>0.057</td>
<td>0.049</td>
<td>0.03</td>
</tr>
<tr>
<td>$B_{1A}$</td>
<td>2.33</td>
<td>2.42</td>
<td>2.38</td>
</tr>
<tr>
<td>$E_{1A}$ (eV)</td>
<td>2.89 (2.87)</td>
<td>2.9 (2.94)</td>
<td>2.55 (2.60)</td>
</tr>
<tr>
<td>$\Gamma_{1A}$ (eV)</td>
<td>0.31</td>
<td>0.305</td>
<td>0.31</td>
</tr>
<tr>
<td>$B_{1B}$</td>
<td>3.59</td>
<td>3.31</td>
<td>3.28</td>
</tr>
<tr>
<td>$E_{1B}$ (eV)</td>
<td>4.14 (3.97)</td>
<td>4.12 (3.94)</td>
<td>4.01</td>
</tr>
<tr>
<td>$\Gamma_{1B}$ (eV)</td>
<td>0.75</td>
<td>0.61</td>
<td>0.73</td>
</tr>
<tr>
<td>$a$</td>
<td>0.54</td>
<td>0.72</td>
<td>0.88</td>
</tr>
</tbody>
</table>

Error \[ e_1 \quad e_2 \quad e_1 \quad e_2 \quad e_1 \quad e_2 \]

Values of $E_0$ and $E_1$ calculated by fitting the numerically differentiated experimental spectrum to analytical line shapes are in brackets.

Band structure calculation needed to perform identifications of the observed energy transitions is not available for Cu$_2$In$_4$Se$_7$ and CuGa$_3$Se$_5$. Identifications of the observed energy have been done taking into account the CuInSe$_2$ and CuGa$_2$Se$_5$ band structure calculations. As it has been established for such compounds, the main transitions contributing to $\varepsilon(E)$ occur at the Brillouin zone (BZ) center (fundamental gap at $\Gamma$) and at the $N$ and $T$ points in the BZ edge (predominant upper transitions). The energy threshold of the fundamental absorption edge $E_0=\varepsilon_1$ corresponds to direct transition from the valence band maximum to the conduction band minimum at the center of the BZ ($\Gamma$ point). Our obtained values of $E_0$=1.125 for I247 and 1.85 eV for and G35 at room temperature (Table II) are in a reasonable agreement with those obtained from the optical measurements. The variation in the reported values of the band gap of OVC can be attributed to the compositional change. The chalcopyrites and OVCs usually exhibit high tolerance to deviations in stoichiometry. In fact, CuInSe$_2$ shows band gap values ranging from 0.94 to 1.04 eV. In the region of 2.5–4.6 eV two transitions for I247 and G35 named as $E_1(A)$ and $E_1(B)$ have been observed. They can be attributed to transitions at the $N$ point in the BZ following Refs. 18 and 19, where ellipsometric data on CuInSe$_2$ and CuGa$_2$Se$_5$ were analyzed. The energy separation between these two transitions corresponds to the crystal-field splitting of the valence band at the $N$ point. The differences in energy $E_1(A)=E_1(B)$ are about 1.25 and 1.45 eV for G35 and I247, respectively. The value of about 0.8 eV was reported for CuInSe$_2$ and CuGa$_2$Se$_5$ crystals.

Optical parameters, namely, the complex refractive index $n=i\alpha+i\kappa$, normal-incidence reflectivity $R$ and the absorption coefficient $\alpha$, can be obtained from the present study in the form of practical functions, since they are directly related to the complex dielectric function $\varepsilon(E)=\varepsilon_1(E)+i\varepsilon_2(E)$. The real refractive index $n$ and extinction coefficient $\kappa$ are given by:

\begin{align}
\alpha(E) &= \frac{4\pi}{\lambda} k(E),
\end{align}

\begin{align}
R(E) &= \left[ \frac{n(E)-1}{n(E)+1} \right]^2 + k(E)^2
\end{align}
effect has been observed in CuInSe₂ and GaAs indicates that the characteristic structures of dielectric function of CuGa₃Se₅ crystals slowly vanish as the concentration of gallium increases.

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

\[ n^2(\lambda) = A + \frac{\lambda^2}{\lambda^2 - B}, \]  

where A and B are the fitting parameters. The solid line in Fig. 4 shows the fitted result of Eq. (9) to the experimental data. Values of the fitting parameters A, B, are equal to 6.6, 6.23, 0.285 for CuIn₅Se₇ and CuGa₅Se₅, respectively. As \( \lambda \to \infty \), the electronic contribution to the dielectric function approaches a limiting value \( \varepsilon_{\infty} \), the high-frequency dielectric constant. The value of \( \varepsilon_{\infty} \) which is equal to \( \varepsilon_{\infty} = n^2 (\lambda \to \infty) = A + 1 \) is about 7.6 and 7.2 for CuIn₅Se₇ and CuGa₅Se₅, respectively. The \( \varepsilon_{\infty} \) values reported for CuInSe₂ and CuGaSe₂ are about 6–6.9 and 4.2–5.1, respectively.

Therefore, the \( \varepsilon_{\infty} \) values for Cu(In/Ga)Se₂ OVC are higher than those for the Cu(In/Ga)Se₂ chalcopyrites. This is especially for the case of the Ga-based compound.

We have analyzed the SE data for CuIn₅Se₇ and CuGa₅Se₅, Zhang et al. reported the existence of ordered defect compounds CuM₃Se₈, CuM₃Se₉, Cu₂M₃Se₁₂, and CuM₃Se₉ with \( M = \text{In or Ga} \). The EDAX data in Table I suggest that the present G35 crystals may also be CuGa₃Se₁₂. We concluded that the Ga-based compound is CuGa₃Se₅ taking into account both the EDAX data and the structural data and the \( E_g \) data. No possibility to compare our data with CuGa₃Se₁₂. Neither the structural nor the \( E_g \) data are available at present for CuGa₃Se₁₂.

IV. CONCLUSIONS

Spectral dependence of the real part \( \varepsilon_1(E) \) and imaginary part \( \varepsilon_2(E) \) of the pseudodielectric function \( \varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E) \) as well as of the complex refractive index, extinction coefficient, absorption coefficient, and normal-incidence reflectivity of CuIn₅Se₇ and CuGa₅Se₅ crystals are modeled in the 0.8–4.4 eV photon energy range using Adachi’s model of optical properties of semiconductors and APCSA algorithm. For the studied compounds, no previous attempts were made to model the experimental data. The excellent agreement with experimental data is obtained over the entire range of photon energy. Model parameters (strength, threshold energy, and broadening) are determined using the APCSA method. The values of the lowest direct gap (\( E_0 \)) and higher energy CP’s are in a good agreement with those obtained from the numerically differentiated experimental spectra of \( \varepsilon(E) \). The present results offer a valuable set of data for CuIn₅Se₇ and CuGa₅Se₅ that can be useful for the design of solar cells based on these compounds.

ACKNOWLEDGMENTS

Financial supports from INTAS program (Project 03-51-6314), Comunidad de Madrid (Project FOTOFLEX S-0505/ENE/0123), and from Spanish government MEC (Projects ENE 2004-07446-C02-1 and MAT2003-01490) are acknowledged. One of the authors (S.L.) would like to thank the World Federation of Scientists for financial support.

REFERENCES


FIG. 4. n vs photon energy for CuIn₅Se₇ and CuGa₅Se₅ crystals. The solid line shows the calculated result of Eq. (9).