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Optical constants of $\text{Cu}_2\text{ZnGeS}_4$ bulk crystals

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The dielectric functions of $\text{Cu}_2\text{ZnGeS}_4$ bulk crystals grown by the Bridgman method were measured over the energy range 1.4 to 4.7 eV at room temperature using variable angle spectroscopic ellipsometry. The observed structures in the dielectric functions were adjusted using the Adachi's model and attributed to interband transitions E_0 , E_{1A} , and E_{1B} at $\Gamma:(000)$, $N(A):2\pi/a(0.5\ 0.5\ 0.5)$, and $T(Z):2\pi/a(0\ 0\ 0.5)$ points of the first Brillouin zone, respectively. The model parameters (threshold energy, strength, and broadening) have been determined using the simulated annealing algorithm. The decrease in the first gap, E_0 , has been attributed to a higher Ge-S hybridization. The spectral dependence of the complex refractive index, the absorption coefficient, and the normal-incidence reflectivity were also derived. © 2010 American Institute of Physics. [doi:10.1063/1.3500439]

I. INTRODUCTION

In the past few years, many studies for finding new materials based on the adamantine multinary compounds have been initiated. These compounds can be designed by various combinations of elements in the vicinity of the group IV element, among them, the $\text{I}_2\text{-II-IV-VI}_4$ family has recently received special attention for their potential applications in photovoltaics and optoelectronics.¹⁻⁵ For instance, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) films possess promising characteristic optical properties: a band gap energy of about 1.5 eV and large absorption coefficient in the order of 10^4 cm^{-1} . CZTS-based thin film solar cells of efficiency over 6.7% have been fabricated. More recently a nonvacuum, slurry-based coating method and particle-based deposition, enabled the fabrication of $\text{Cu}_2\text{ZnSn}(\text{Se},\text{S})_4$ devices with over 9.6% efficiency.⁶ Those results suggest that the CZTS-based solar cells are promising candidates for the next generation of solar cells.³ The obtained results increase the interest in other members of the $\text{I}_2\text{-II-IV-VI}_4$ family too, including $\text{Cu}_2\text{ZnGeS}_4$ which could be considered as possible wide gap material for photovoltaic applications.

The $\text{Cu}_2\text{ZnGeS}_4$ crystals crystallize in the tetragonal stannite-type structure (space group $I\bar{4}2m$) (Refs. 5 and 7) or in the orthorhombic structure (space group $Pmn2_1$).⁷ Concerning the physical properties of these semiconducting compounds, it should be noted that they have been scarcely investigated. Only infrared transmission⁸ and electrical resistivity^{2,8} have been reported. Very recently, the structural and electronic properties of $\text{Cu}_2\text{ZnGeS}_4$ have been studied using first-principles calculations.⁹ However, the optical properties and in particular optical constants of $\text{Cu}_2\text{ZnGeS}_4$ have not been investigated yet. This, in spite of the fact that the structures in the optical spectra are directly related to the

band structure of the material itself. The aim of this work is to determine experimentally the optical constants of $\text{Cu}_2\text{ZnGeS}_4$ bulk crystals using spectroscopic ellipsometry (SE) and to characterize the corresponding main electronic interband transitions by fitting the obtained values using the Adachi's model. The model values obtained for the energy thresholds have been compared with those obtained from first-principle calculations. In addition, since the knowledge of the refractive index as well as the absorption coefficient of the material is important for the design and development of optoelectronic devices, the corresponding values are also listed for future reference.

II. EXPERIMENTAL DETAILS

$\text{Cu}_2\text{ZnGeS}_4$ crystals were grown by the modified Bridgman method. The energy dispersive x-ray microanalysis (EDAX) was used to measure the composition of the sample. The results of such analysis have been gathered in Table I. All samples show good stoichiometric composition of Cu ($\sim 25\%$) and S ($\sim 50\%$) while the ratio of Ge/Zn varies from 0.92 to 1.19. The structure of ingots was checked by x-ray powder diffraction. All of them showed polycrystalline phases and presented two structures: the dominant one is stannite-type and the other is orthorhombic (space group $Pmn2_1$).

The optical measurements were carried out with a variable angle spectroscopic ellipsometer at room temperature in

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

$\text{Cu}_2\text{ZnGeS}_4$	Cu (at. %)	Zn (at. %)	Ge (at. %)	S (at. %)	Ge/Zn	Cu/2Ge
G1	25.3	12.8	11.7	50.2	0.92	1.08
G2	25.8	11.3	12.5	50.4	1.11	1.03
G3	26.3	10.5	12.5	50.7	1.19	1.05

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the photon energy range from 1.4 to 4.7 eV at every 0.025 eV, at two incidence angles Φ , 60° and 70° to ensure a consistent and accurate determination of the dielectric function of the compounds. All the studied samples show an isotropic behavior probably due to a random orientation of the crystallites with sizes smaller than the wavelengths of the measurements, even though the measured dielectric function of the anisotropic $\text{Cu}_2\text{ZnGeS}_4$ represents the contributions both of ordinary and extraordinary components of the dielectric tensor. Special attention was paid to the preparation of good quality “pure” surface as it was proposed by Alborno *et al.*¹⁰ to minimize non desired effects such as normal and microscopic roughness. In these conditions the real and imaginary parts of the dielectric function $\varepsilon(E)=\varepsilon_1(E)+i\varepsilon_2(E)$ can be obtained for a homogeneous and isotropic substrate from the equation of two-phase (substrate-ambient) model

$$\varepsilon = \sin^2 \Phi \left[1 + \tan^2 \Phi \left(\frac{1-\rho}{1+\rho} \right)^2 \right], \quad (1)$$

where Φ is the incidence angle of the photon beam and ρ is the complex reflectance ratio of the Fresnel coefficients.¹⁰

III. THEORETICAL MODEL

The Adachi's model for the dielectric function (MDF) describes features of the complex dielectric function $\varepsilon(E)$ of crystalline materials by electronic transitions between bands in the neighborhood of critical points (CPs) assuming parabolic bands. The MDF, successfully applied to model the dielectric function and the optical constants of zinc-blende III-V semiconductors^{11,12} and I-III-VI₂ chalcopyrite compounds^{13–15} has been applied in our SE data analysis. Hence, the complex dielectric function of $\text{Cu}_2\text{ZnGeS}_4$ was described as for I-III-VI₂ materials by the sum of three terms [Eq. (2)] corresponding, respectively, to the one-electron contributions at the E_0 and $E_{1\beta}$ CPs, where $\beta=A,B$ refers to different energy transitions after the main one, and an additional constant $\varepsilon_{1\infty}$,

$$\varepsilon(E) = \varepsilon_0(E) + \varepsilon_1(E) + \varepsilon_{1\infty}. \quad (2)$$

The first term, $\varepsilon_0(E)$, corresponding to the fundamental gap, E_0 , is assigned to the three-dimensional (3D) M_0 CP

$$\varepsilon_0(E) = A E_0^{-3/2} \chi_0^{-2} (2 - (1 + \chi_0)^{1/2} - (1 - \chi_0)^{1/2}), \quad (3)$$

with $\chi_0 = (E + i\Gamma)/E_0$, where A and Γ are the strength and the damping energy of the E_0 gap, respectively.

The second term, corresponding to the higher CPs $E_{1\beta}$ ($\beta=A,B$), is assigned to the two-dimensional (2D) M_0 CPs and is given by

$$\varepsilon_1(E) = - \sum_{\beta=A,B} B_{1\beta} \chi_{1\beta}^{-2} \ln(1 - \chi_{1\beta}^2), \quad (4)$$

with $\chi_{1\beta} = (E + i\Gamma_{1\beta})/E_{1\beta}$, where $B_{1\beta}$ and $\Gamma_{1\beta}$ are the strength and damping constants of the $E_{1\beta}$ transitions, respectively.

The inclusion of an additional term, $\varepsilon_{1\infty}$, in the $\varepsilon(E)$ expression improves the fit of experimental data.^{11–16} This term contains the contributions of higher lying interband transitions. The $\varepsilon_{1\infty}$ parameter may take a second order poly-

FIG. 1. Experimental spectral dependence of dielectric function $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$. The panel (a) shows the $\varepsilon(E)$ function with CPs labeled for G1, G2, and G3 samples and the panel (b) shows the comparison between experimental (squares) and numerically calculated (solid lines) using the MDF model and the SA algorithm for G3 sample.

nomial dependence of the photon energy¹⁶ or may even be constant^{11–15} in the studied spectral range. In our calculations this parameter has been taken as constant.

The unknown parameters of the optical transitions entering in Eqs. (2)–(4) were adjusted using the simulated annealing (SA) algorithm¹⁷ to obtain the best fit to the experimental $\varepsilon(E)$ spectra through the minimization of the following objective function:¹⁴

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

where N is the number of photon energies at which $\varepsilon(\omega)$ was measured, 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 the complex dielectric function at E_i point.

IV. RESULTS AND DISCUSSIONS

Figure 1(a) shows the dielectric functions of $\text{Cu}_2\text{ZnGeS}_4$ for G1, G2, and G3 samples. In the low energy region $E < 2.5$ eV, the $\varepsilon(E)$ functions of G1 and G2 samples show a remarkable coincidence, while the $\varepsilon(E)$ function of G3 sample is shifted 0.1 eV toward low energies, and in the $\varepsilon_1(E)$ spectrum an additional structure appears near 1.8 eV. In the intermediate energy region, from 2.5 to 3.3 eV, the $\varepsilon(E)$ function shows a similar behavior for all samples although there are small differences in the absolute values. In the high energy region, from 3.3 eV up to 4.7 eV, some differences in the $\varepsilon(E)$ can be observed. The maximum of the $\varepsilon_1(E)$ function and the value of inflection point toward a

TABLE II. Model parameter values.

Samples	Parameters										Error	
	E_0 (eV)	Γ_0 (eV)	A (eV ^{1.5})	E_{1A} (eV)	Γ_{1A} (eV)	B_{1A}	E_{1B} (eV)	Γ_{1B} (eV)	B_{1B}	$\varepsilon_{1\infty}$	ε_1 (%)	ε_2 (%)
G1	2.28	0.27	40.0	2.88	0.11	0.38	4.34	0.46	2.87	0.49	1.6	2.1
G2	2.25	0.22	35.0	2.87	0.15	0.57	4.28	0.49	2.98	0.47	1.7	1.5
G3	2.13	0.21	26.6	2.85	0.17	0.71	4.03	0.53	3.04	0.76	1.8	1.6

positive slope for the $\varepsilon_2(E)$ function are shifted to low energies as the Ge/Zn ratio increases from G1 to G3 samples (Table I).

The spectra exhibit several CP structures E_0 , E_{1A} , and E_{1B} labeled in Fig. 1(a). In the region between 1.7 and 2.4 eV the energy thresholds of the fundamental absorption edge $E_0=E_g$ are broad and a sharp onset is not observed. The origin of this broadening effect is probably due the presence of impurities or a secondary phase that provides additional scattering effects. Taking into account that the additional structure near 1.8 eV was not observed in $\varepsilon_2(E)$ spectrum of the G3 sample and that the accuracy of the measured ε_2 values is not high in the low absorption region, we have described the line shapes of the $\varepsilon(E)$ spectra by Eq. (3) for all the studied samples. A second E_{1A} and a third E_{1B} energy thresholds appear in the intermediate and high energy regions, respectively. The Adachi's model [Eqs. (3) and (4)] was applied to calculate the dielectric function of the studied crystals. The resulting analytical lines from the fits of the experimental data in Fig. 1(b) have been obtained considering CPs of the 3D-type [Eq. (3)] in the E_0 region and of the 2D-type [Eq. (4)] in the E_1 region. The model parameters A, B, E_0 , E_{1A} , E_{1B} , and Γ of the interband transitions were calculated using the global optimization routine (SA algorithm) which enables to obtain a good fit without providing good initial estimations. The values of these parameters are given in Table II. The results of such calculation are displayed in Fig. 1(b), where the solid squares represent our experimental data and the continuous lines show the best fit. It can be seen that a good agreement between calculated and experimental data has been obtained. As an indication of the accuracy with respect to the experimental values, the relative errors have also been calculated and they lie in the 1.6%–1.8% and 1.5%–2.1% ranges for the real and the imaginary parts of the $\varepsilon(E)$, respectively, for the studied materials (Table II). In the next paragraphs we will discuss separately the first gap, E_0 , and the other two energy thresholds, E_{1A} and E_{1B} .

The obtained values for the threshold energy E_0 are 2.28, 2.25, and 2.13 eV for the samples G1, G2, and G3, respectively (Table II). Following Chen *et al.*,⁹ the theoretically calculated direct band gaps for $\text{Cu}_2\text{ZnGeS}_4$ kesterite and stannite-type are 2.27 and 2.06 eV, respectively. The determined band gap values for our samples are in good agreement with the theoretically deduced gaps for the kesterite structure, with a deviation lower than 6%. This permits to assign E_0 to an electronic transition at the $\Gamma:(000)$ point, thus corresponding to a direct transition from the valence band maximum to the conduction band minimum (CBM).⁹

However it is interesting to analyze the decrease in the band gap values as a function of the Ge content in our samples. Indeed, comparing Tables I and II, the E_0 value decreases when the Ge/Zn ratio increases. After Ref. 9, the CBM state is localized mainly on the Ge–S bond while the VMB state is localized mainly on the Cu–S bond. A Ge-richer sample implies a higher Ge–S hybridization, which induces a lower antibonding level in the CBM, and hence a reduction in the band gap.

The second E_{1A} and third E_{1B} energy thresholds appear respectively in the regions below 2.9 and 4.4 eV, which can, respectively, be attributed to transitions at the high CPs $N(A):2\pi/a(0.5 \ 0.5 \ 0.5)$ and $T(Z):2\pi/a(0 \ 0 \ 0.5)$ of the first Brillouin zone, since the values deduced from Fig. 5 of Ref. 9 are 2.9 eV and 4.1 eV for these transitions, respectively. The calculated values of strength and damping constants of E_{1B} transitions are close to each other, while the energy of the transition diminishes as the Ge/Zn ratio increases.

Our model does not take into account the contribution of an indirect transition to $\varepsilon(E)$ since such mechanism is expressed by a second order process in the perturbation and hence the reported value, 2.04 eV, by Yao *et al.*⁸ for the indirect band gap of $\text{Cu}_2\text{ZnGeS}_4$ cannot be compared with our values. On the other hand, from Fig. 5 of Ref. 9, only the calculated bands for the primitive modified CuAu with space group $P42m$ present a possible indirect optical gap of around 1.9 eV, while the kesterite and stannite-type band models show only direct transitions.

The optical constant values that are of interest for the design of optoelectronic devices, namely, the complex refractive index $n^*=n+ik$, the normal-incidence reflectivity R , and the absorption coefficient α , can be readily computed from well known equations.¹⁵ The experimental spectral dependences of n and k , as well as the calculated ones using the Adachi's model and the SA algorithm, are presented in Fig. 2 for the studied samples. Figure 3(a) shows the spectral dependence of α and R for the three samples and Fig. 3(b) shows the comparison between experimental and theoretically calculated α and R using the Adachi's model and the SA algorithm for G3 sample. A good agreement is observed for all the samples. Similar to $\varepsilon(E)$, the $n^*(E)$, $\alpha(E)$, and $R(E)$ spectra reveal several structures at E_0 , E_{1A} , and E_{1B} CPs. In Table III the values of n and k for the most stoichiometric sample G2 are listed.

It should also be noted that the plot of $(ah\nu)^2$ against $(h\nu)$ (Fig. 4) shows a linear dependence around the E_0 energy threshold observed in the $\varepsilon(E)$ spectra, whose extrapo-

FIG. 2. Experimental spectral dependence of the real refractive index n and extinction coefficient k . The left panel (a) shows n and k for G1, G2, and G3 samples and the right (b) shows comparison between experimental and theoretically calculated n and k using the Adachi's model and the SA algorithm for G3 sample.

lations yield values of 2.24, 2.23, and 2.16 eV for G1, G2, and G3 samples, respectively, thus confirming the presence of direct allowed transitions at these energies, as well as the band gap values associated and deduced before.

V. CONCLUSIONS

We have studied the optical properties of $\text{Cu}_2\text{ZnGeS}_4$ polycrystalline bulk samples by the SE technique. Optical

FIG. 3. Experimental spectral dependence of absorption coefficient α and normal-incidence reflectivity R . The left panel (a) shows α and R for G1, G2, G3 and samples and the right (b) shows comparison between experimental and theoretically calculated α and R using the Adachi's model and the SA algorithm for G3 sample.

TABLE III. Refraction index of the $\text{Cu}_2\text{ZnGeS}_4$, G2 sample. Reported only values every 0.1 eV.

Energy (eV)	n	k
1.4	2.65	0.07
1.5	2.68	0.07
1.6	2.71	0.08
1.7	2.75	0.09
1.8	2.79	0.10
1.9	2.83	0.12
2.0	2.87	0.14
2.1	2.92	0.17
2.2	2.97	0.21
2.3	3.01	0.29
2.4	3.02	0.37
2.5	3.02	0.43
2.6	3.02	0.48
2.7	3.03	0.53
2.8	3.03	0.60
2.9	3.02	0.67
3.0	2.99	0.74
3.1	2.95	0.79
3.2	2.91	0.83
3.3	2.86	0.85
3.4	2.82	0.87
3.5	2.80	0.87
3.6	2.80	0.86
3.7	2.81	0.88
3.8	2.83	0.91
3.9	2.85	0.95
4.0	2.85	1.01
4.1	2.85	1.06
4.2	2.85	1.12
4.3	2.83	1.20
4.4	2.81	1.27
4.5	2.76	1.35
4.6	2.70	1.40
4.7	2.66	1.43

constants such as the complex refractive index, absorption coefficients and normal-incidence reflectivity as well as the dielectric function have been determined. The measured spectra reveal structures at the E_0 , E_{1A} , and E_{1B} CPs assigned to interband transitions. The spectral dependence of the real and imaginary parts of the complex dielectric function for

FIG. 4. Plot of $(\alpha h\nu)^2$ as a function of the photon energy ($h\nu$) for G1 and G3 samples.

$\text{Cu}_2\text{ZnGeS}_4$ crystals have been modeled in the 1.4–4.7 eV photon energy range using the Adachi's model and the global optimization routine (SA algorithm). A good agreement with the experimental data has been obtained and the model parameters (strength, threshold and energy broadening) have been calculated. A redshift in the E_0 , E_{1A} , and E_{1B} transitions with increasing Ge/Zn ratio was observed. The first gap, E_0 , has been assigned to an electronic transition at $\Gamma:(000)$ point as a direct gap, and the decrease in its value with Ge/Zn value has been attributed to a higher Ge–S hybridization. The second E_{1A} and third E_{1B} energy thresholds have been attributed to transitions at the high CPs $N(A):2\pi/a(0.5 \ 0.5 \ 0.5)$ and $T(Z):2\pi/a(0 \ 0 \ 0.5)$ of the first Brillouin zone.

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- ¹H. Hahn and H. Schulze, *Naturwiss.* **52**, 426 (1965).
- ²D. M. Schleich and A. Wold, *Mater. Res. Bull.* **12**, 111 (1977).
- ³H. Katagiri, K. Jimbo, S. Yamada, T. Kamimura, W. S. Maw, T. Fukano, T. Ito, and T. Motohiro, *Appl. Phys. Express* **1**, 041201 (2008).
- ⁴S. Schorr, G. Wagner, M. Tovar, and D. Sheptyakov, *Mater. Res. Soc. Symp. Proc.* **1012**, Y03 (2007).
- ⁵O. V. Parasyuk, L. V. Piskach, Y. E. Romanyuk, I. D. Oleksyuk, V. I. Zarembo, and V. I. Pekhnyo, *J. Alloys Compd.* **397**, 85 (2005).
- ⁶T. Todorov, K. B. Reuter, and D. B. Mitzi, *Adv. Mater. (Weinheim, Ger.)* **22**, E156 (2010).
- ⁷K. Doverspike, K. Dwight, and A. Wold, *Chem. Mater.* **2**, 194 (1990).
- ⁸G.-Q. Yao, H.-S. Shen, E. D. Honig, R. Kershaw, K. Dwight, and A. Wold, *Solid State Ionics* **24**, 249 (1987).
- ⁹S. Chen, X. G. Gong, A. Walsh, and S.-H. Wei, *Phys. Rev. B* **79**, 165211 (2009).
- ¹⁰J. G. Albornoz, R. Serna, and M. Leon, *J. Appl. Phys.* **97**, 103515 (2005).
- ¹¹S. Adachi and T. Taguchi, *Phys. Rev. B* **43**, 9569 (1991).
- ¹²S. Adachi, *J. Appl. Phys.* **68**, 1192 (1990).
- ¹³T. Kawashima, S. Adachi, H. Miyake, and K. Sugiyama, *J. Appl. Phys.* **84**, 5202 (1998).
- ¹⁴A. B. Djurisić and E. H. Li, *Appl. Phys. A: Mater. Sci. Process.* **73**, 189 (2001).
- ¹⁵M. León, R. Serna, S. Levchenko, A. Nateprov, A. Nicorici, J. M. Merino, and E. Arushanov, *J. Appl. Phys.* **101**, 013524 (2007).
- ¹⁶C. C. Kim, J. W. Garland, H. Abad, and P. M. Raccah, *Phys. Rev. B* **45**, 11749 (1992).
- ¹⁷A. Corana, M. Marchesi, C. Martini, and S. Ridella, *ACM Trans. Math. Softw.* **13**, 262 (1987).