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Optical spectra and energy band structure of single crystalline $CuGaS_2$ and $CuInS_2$

S Levcenko[1], N N Syrbu[2], V E Tezlevan[1], E Arushanov[1,3], S Doka-Yamigno[3], Th Schedel-Niedrig[3,4] and M Ch Lux-Steiner[3]

[1] Institute of Applied Physics, Academy of Sciences of Moldova, Chisinau, MD 2028, Moldova
[2] Technical University of Moldova, Chisinau, MD-2004, Moldova
[3] Hahn-Meitner Institut GmbH, Glienicker Straße 100, D-14109 Berlin, Germany

E-mail: schedel-niedrig@hmi.de

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Abstract

The reflection spectroscopy of chalcopyrite $CuGaS_2$ and $CuInS_2$ single crystals has been applied for light polarized perpendicular ($E \perp c$) and parallel ($E \parallel c$) to the optical axis in the photon energy range between 1.5 and 6 eV at 77 K. By using the Kramers–Kronig relations, the spectral dependences of the real ε_1 and imaginary ε_2 components of the complex dielectric function $\varepsilon(E) = \varepsilon_1(E) + i\varepsilon_2(E)$ have been calculated for the investigated materials. As a result, the energy band structure of $CuGaS_2$ and $CuInS_2$ at photon energies higher than the fundamental band gap is derived from the analysis of the structures observed in $\varepsilon(\omega)$ spectra. Additionally, the spectral dependences of the complex refractive index, extinction coefficient and absorption coefficient s of $CuGaS_2$ and $CuInS_2$ single crystals are determined in the 1.5–6 eV photon energy range.

1. Introduction

The $CuGaS_2$ (CGS) and $CuInS_2$ (CIS) I–III–VI2 semiconducting compounds crystallize in the chalcopyrite structure belonging to the space group $I\bar{4}2d$-D_{2d}^{12}. Materials of this group have been intensively investigated in the past and are currently used in optoelectronics devices [1, 2]. The energy band structure of these compounds has been calculated as a ternary analog of zinc-blende type semiconductors [3–7]. Transmission, photoluminescence, reflectivity and Raman spectra of $CuGaS_2$ and $CuInS_2$ have also been studied [8–23] previously. An exciton spectrum [15, 24] and emission of biexcitons [21], a resonant Raman scattering of exciton polaritons [17] and an interference of exciton additional waves, as well as a spatial dispersion of exciton polaritons [18, 19], were observed. The energy band structure of $CuGaS_2$ and $CuInS_2$ at

[4] Author to whom any correspondence should be addressed.

photon energies higher than the fundamental band gap has not been well studied [10, 22–24] up to now. The available data sets have been obtained on the basis of ellipsometric investigations on polished samples [22] or, alternatively, by using reflectivity [10, 23, 24] performed on as-grown samples under non-polarized light conditions [24]. It is worth mentioning that the Kramers–Kronig relation for an analysis of the data has not been used up to now and that the observed electronic transitions are currently interpreted only at the points T, Γ and N of the Brillouin zones (BZ) [10, 23, 24] according to theoretical calculations [3, 4].

Recently, the values of the interband energetic distances have been shown at the BZ points T, Γ and N of the calculated band structure of CGS by Laksari *et al* [7]. Additionally, Ahuya *et al* [5] have published a theoretical band structure of CGS along various symmetry directions including not only the T, Γ, N points but also the Z, X and P points of the BZ. This band structure is similar to the published theoretical band structure of Jaffe and Zunger [3, 4], but is calculated along various symmetry directions, which open additional opportunities in the interpretation and localization of the observed electronic transitions.

Reflectivity as well as ellipsometry studies combined with calculations of the optical constants by using the Kramers–Kronig relations are widely used for a determination of the complex dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + \mathrm{i}\varepsilon_2(\omega)$ [25, 26]. The structures observed in the $\varepsilon(\omega)$ spectra are attributed to interband critical points (CPs) which are related to regions of the band structure with a huge or a singular point electronic density of states. An accurate knowledge of the dielectric function over a wide range of wavelengths is indispensable for many applications.

In this paper we present reflectivity spectra measured at 77 K and obtained from the mirror-like natural surfaces of as-grown $CuGaS_2$ and $CuInS_2$ single crystals measured in the polarization $E \perp c$ and $E \parallel c$ in the photon energy range of 1.5–6 eV. By using the Kramers–Kronig relations the spectral dependences of the real ε_1 and imaginary ε_2 component of the complex dielectric function ε for $CuGaS_2$ and $CuInS_2$ were calculated. As a result the structure found in the dielectric function was analyzed and related to the electronic band structure of $CuGaS_2$ and $CuInS_2$. The spectral dependences of the complex refractive index, extinction coefficient and absorption coefficient were also determined in the 1.5–6 eV photon energy range.

2. Experimental details

$CuGaS_2$ and $CuInS_2$ crystals in the form of 1 mm thick platelets with surfaces of (0.5×1.5) cm^2 or prisms with $(8 \times 8 \times 4)$ mm^3 sizes were grown from the gas phase in closed quartz ampoules. The reflectivity is measured at 77 K using a Specord M-40 two-beam spectrometer from a (110) surface containing the c [001] axis. The samples were mounted on the cold finger of a vacuum cryostat.

3. Results

3.1. Optical constants

The $CuGaS_2$ and $CuInS_2$ single crystals show well pronounced structures of the reflectivity spectra in the range of $E > E_g$ at 77 K as presented in figure 1. Up to nine peaks are observed in polarization $E \parallel c$ and $E \perp c$. The structure of the reflectivity spectra is richer than that earlier reported [10, 22–24]. By taking into consideration the detected amplitude of the reflection coefficient, it is possible to define a phase of the reflected beam.