Structural investigation of CuIn$_5$Se$_8$ single crystals by optical second harmonic generation, ellipsometry, and photoluminescence

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CuIn$_5$Se$_8$ bulk single crystals were characterized using ellipsometry, photoluminescence (PL), and optical second harmonic generation (SHG). The refractive $n(E)$ and absorption $k(E)$ indices as functions of photon energy $E$ are determined. The structure of the PL spectrum suggests the presence of the Cu-rich nonstoichiometric phases at the natural surfaces of the CuIn$_5$Se$_8$ sample. The best fit of the experimental SHG data is achieved by assuming that CuIn$_5$Se$_8$ belongs to the 42$m$ symmetry group. This result is in contradiction with x-ray analysis (62$m$ group), which testifies to the difference in surface and bulk structure. © 2006 American Institute of Physics.

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Cu–In–Se selenides with Cu vacancies and a surplus of In atoms, such as CuIn$_5$Se$_8$ and CuIn$_5$Se$_9$, together with the basic compound CuInSe$_2$, are of great interest as prospective materials for fabrication of relatively cheap thin-film high efficiency solar cells. But until now the crystal structure of materials for fabrication of relatively cheap thin-film high efficiency solar cells. But until now the crystal structure of CuIn$_5$Se$_8$ films have been prepared by different deposition processes. A stable film with hexagonal structure was obtained via the reaction of Cu+Se and In+Se layers, whereas a metastable film with tetragonal structure was deposited by an alternative process using CuInSe$_2$ and In$_2$Se$_3$ layers.

In this letter we report results on optical second harmonic generation (SHG) as well as photoluminescence (PL) investigations of the as-grown CuIn$_5$Se$_8$ single crystals. X-ray analysis of the crystal structure as well as ellipsometric measurements were performed and their results are used in the theoretical analysis of the experimental SHG characteristics.

Bulk CuIn$_5$Se$_8$ single crystals were grown by gas transport reaction method using iodine as transport agent. The samples were optically homogeneous with a platelike shape and mirrorlike natural faces, which were used directly for SHG, ellipsometric, PL, and x-ray measurements.

Structural characterization of samples was carried out with the Laue method, perpendicular to the plane of the platelike sample. A perfect ternary symmetry was observed, revealing the presence of a ternary axis perpendicular to the platelike sample, and three planes of symmetry $m$. An optical activity of our samples was checked at room temperature in two different areas of 0.5 and 6 mm$^2$ using solid state pulsed lasers at 1.6, 1.2, and 1.0 μm. The lack of optical activity demonstrated that point group does not have an inversion symmetry. This fact and the symmetry elements present in the Lauegram are characteristic of the hexagonal point group 62$m$. The principal axis $c$ (i.e., [0001]) of this group is oriented normal to the plate.

The ellipsometric measurements and data analysis were performed with a variable angle spectroscopic ellipsometer (J. A. Woollam Co., Inc.). The obtained refractive $n(E)$ and absorption $k(E)$ indices as functions of photon energy $E$ are presented in Fig. 1. The experimental values of $n(E)$ and $k(E)$ were used for the theoretical evaluation of the sample structure by fitting the calculated SHG dependences to the experimental ones.

The PL of the CuIn$_5$Se$_8$ single crystals was excited by an Ar$^+ laser at 514 nm and detected using a cooled (77 K) Ge detector. All spectra were corrected for the characteristics of

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the experimental optical system. PL spectra taken at two temperatures (4 and 197 K) are shown in Fig. 2. From the analysis of the spectral shapes by means of their deconvolution in Gaussian bands at least three elementary components can be revealed. At low temperatures these bands are centered at \( E_1 = 1.07 \), \( E_2 = 1.0 \), and \( E_3 = 0.90 \) eV [Fig. 2(a)]. As the temperature increases the relative intensity of the first spectral band diminishes. At \( T > 150 \) K its contribution becomes negligible and the PL spectra are dominated by components \( E_2 \) and \( E_3 \) with maxima located at 0.97 and 0.85 eV, respectively [\( T = 200 \) K, Fig. 2(b)].

The peak energies of the three spectral components are considerably smaller than the band gap value of CuIn\(_5\)Se\(_8\) [\( E_g = 1.23-1.27 \) eV, 10 K (Ref. 9)]. The relatively large bandwidth of these components (0.1–0.15 eV) and their temperature dependences are typical for the free-to-bond (via deep centers) radiative recombination mechanism\(^{10}\) under the conditions of a strong electron-phonon interaction.\(^{11}\) The \( E_2 \) peak (determining the position of the integral PL spectrum maximum at low temperatures) is located at the same energy as the PL maximum of the CuIn\(_5\)Se\(_8\) single crystals investigated in Ref. 10 whereas the \( E_1 \) energy corresponds to the PL maximum position observed by the same authors for CuIn\(_5\)Se\(_8\). The long wavelength component \( E_3 \) is centered practically at the same energy and has the same shape like the PL broad band observed for CuIn\(_3\)Se\(_5\) polycrystalline samples.\(^{12}\) These data suggest that the optically excited surface layer of the CuIn\(_5\)Se\(_8\) sample, where the radiative recombination takes place, contains phases with a surplus of Cu atoms in comparison with the stoichiometric composition 1:5:8.

Because of the strong absorption of UV light in the CuIn\(_5\)Se\(_8\) sample, the investigation of its structure by SHG was performed in reflection. The as-grown natural face of the crystal was used as “reflecting” plane. Ti:sapphire laser radiation (fundamental wavelength \( \lambda_n = 780 \) nm, pulse width 100 fs) was focused onto a spot of about 100 \( \mu \)m in diameter at 45° incidence. The SH radiation at \( \lambda_{2n} = 390 \) nm was detected by means of a photomultiplier and a standard photon counting system. Polarization of the fundamental wave (\( p \)-in or \( s \)-in) was varied by rotating a Berek compensator; the polarization of the SH waves (\( p \)-out or \( s \)-out) was chosen by Glan prisms. The SH intensity as a function of the sample azimuthal rotation angle \( \varphi \) was measured for \( p \)-in, \( p \)-out, \( p \)-in, \( s \)-out, \( s \)-in, \( p \)-out, and \( s \)-in, \( s \)-out polarization geometries. The experimental dependencies are shown in Fig. 3.

The measured SHG dependences were used for the determination of the crystal structure and the identification of crystallographic indices of the reflecting plane. For these purposes, the theoretical model describing SHG in a medium with strong absorption was developed. Indices of reflection and absorption at both fundamental and second harmonic wavelengths were considered as isotropic. However, the anisotropy of the nonlinear susceptibilities tensor was taken into account. The model allows us to vary the orientation of the reflecting plane with respect to the crystallographic axes of the crystal. Several adjustable parameters such as the comp...
ponents of the nonlinear susceptibility tensor (depending on the crystal symmetry) were included in the model and were determined by means of fitting the calculated dependencies $I_{2\omega}(\varphi)$ to the measured ones. Some parameters used in the model were taken as fixed, including the values for the refractive ($n_{\omega}=2.832$, $n_{2\omega}=2.641$) and absorptive ($k_{\omega}=0.536$, $k_{2\omega}=1.315$) indices, that were obtained from the ellipsometry data. The model provides the numerical simulation of all four measured dependencies $I_{2\omega}(\varphi)$ of the SHG. It should be noted that we have tested the model on a number of results published earlier by us, as well as by others. The model successfully reproduced the SHG intensity as a function of azimuthal angle for CuGaS$_2$ (112) bulk single crystals, as well as for bulk GaAs (Ref. 7) for CuIn$_5$Se$_8$ and in several papers to describe the experimental data are presented in Fig. 3. Our calculations were taken as fixed, including the values for the reflecting plane, and not for 6m reflecting plane, and not for 6

In this work for CuIn$_3$Se$_5$ the fitting procedure was performed for two symmetry groups: (i) the hexagonal group 62m obtained from our x-ray measurements with (0001) as reflecting plane, and (ii) the tetragonal group 42m, proposed in Ref. 7 for CuIn$_5$Se$_8$ and in several papers to describe the CuIn$_3$Se$_5$ structure.

The calculated dependencies $I_{2\omega}(\varphi)$ for 42m and the experimental data are presented in Fig. 3. Our calculations show that the best fit is achieved for the 42m group with the (112) reflecting plane, and not for 62m group obtained from x-ray analysis.

The fact that the SHG results lead to a different symmetry group is most likely related to the following: for the strongly absorbing CuIn$_3$Se$_5$ the SHG is mainly generated by the thin surface layer of this composition.1–4 This may indicate a surplus of Cu atoms at the final stage of the crystal growth process or is due to surface segregation. As an additional confirmation that the CuIn$_3$Se$_5$ PL spectrum obtained in Ref. 10 To clarify this result further investigations are necessary.

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