Structural investigation of CuIn_5Se_8 single crystals by optical second harmonic generation, ellipsometry, and photoluminescence

L. Kulyuk, V. Mirovitskii, E. Arushanov, and V. Tezlevan

Institute of Applied Physics, ASM, Academic Str. 5, Kishinau MD-2028, Moldova

M. Leon

Departamento de Fisica Aplicada C-XII, Universidad Autonoma de Madrid, 28049 Madrid, Spain

E. Mishina^{a)} and N. Sherstyuk

Moscow State Institute of Radioengineering, Electronics and Automation, Prosp. Vernadskogo 78, 119454 Moscow, Russia

T. Dumouchel and E. Fortin

Department of Physics, University of Ottawa, Ontario K1N 6N5, Canada

Th. Rasing

Institute for Molecules and Materials, Radboud University Nijmegen, Toernooiveld 1, 6525 ED, The Netherlands

(Received 13 April 2006; accepted 30 August 2006; published online 13 October 2006)

CuIn_5Se_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_5Se_8 sample. The best fit of the experimental SHG data is achieved by assuming that CuIn_5Se_8 belongs to the $\bar{4}2m$ symmetry group. This result is in contradiction with x-ray analysis ($\bar{6}2m$ group), which testifies to the difference in surface and bulk structure. © 2006 American Institute of Physics.

[DOI: [10.1063/1.2362578](https://doi.org/10.1063/1.2362578)]

Cu–In–Se selenides with Cu vacancies and a surplus of In atoms, such as CuIn_3Se_5 and CuIn_5Se_8 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 this family of materials has been under discussion. Several different structures of both CuIn_3Se_5 and CuIn_5Se_8 were observed experimentally^{1–4} and a few alternative structural models (such as “defect P chalcopyrite” and “vacancy ordered compound”⁵) have been proposed to explain these contradictions. First-principles calculations demonstrated that the total energies of all these models are extremely close: the difference between them not exceeding 4 meV/atom.⁶ This explains why the long-period ordering of defects/vacancies cannot be determined experimentally without ambiguity. The structure of CuIn_3Se_5 depends considerably on the crystal growth conditions and annealing history. Thus, one can manipulate the actual structure of these crystals using differences in fabrication. In Ref. 7 both hexagonal and tetragonal CuIn_5Se_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_2Se_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_5Se_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_5Se_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 mm² 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 Lauegram⁸ are characteristic of the hexagonal point group $\bar{6}2m$. 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_5Se_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

^{a)}Electronic mail: mishina_elena57@mail.ru

FIG. 1. (Color online) Refraction and absorption indices of CuIn_5Se_8 single crystal.

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 [$T\approx 200$ K, Fig. 2(b)].

The peak energies of the three spectral components are considerably smaller than the band gap value of CuIn_5Se_8 [$E_g=1.23\text{--}1.27$ 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 mechanism¹⁰ under the

FIG. 2. (Color online) PL spectra of CuIn_5Se_8 single crystal at 4 K (a) and 197 K (b) (dashed lines—the deconvoluted Gaussian bands).

FIG. 3. (Color online) Measured SH intensities for CuIn_5Se_8 and theoretical curves calculated for $42m$ group symmetry and (112) reflecting plane for different polarization combinations.

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_5Se_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_3Se_5 . 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 $\text{CuIn}_2\text{Se}_{3.5}$ polycrystalline samples.¹² These data suggest that the optically excited surface layer of the CuIn_5Se_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_5Se_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 $\lambda_\omega=780$ nm, pulse width 100 fs) was focused onto a spot of about 100 μm in diameter at 45° incidence. The SH radiation at $\lambda_{2\omega}=390$ 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 SHG waves (p -out or s -out) was chosen by Glan prisms. The SH intensity as a function of the sample azimuthal rotation angle φ was measured for p -in, p -out, p -in, s -out, s -in, p -out, and s -in, s -out polarization geometries. The experimental dependences 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 com-

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,^{13,14} as well as for bulk GaAs (Ref. 15) and ZnO films.^{16,17}

In this work for CuIn_5Se_8 the fitting procedure was performed for two symmetry groups: (i) the hexagonal group $\bar{6}2m$ obtained from our x-ray measurements with (0001) as reflecting plane, and (ii) the tetragonal group $\bar{4}2m$, proposed in Ref. 7 for CuIn_5Se_8 and in several papers to describe the CuIn_3Se_5 structure.

The calculated dependencies $I_{2\omega}(\varphi)$ for $\bar{4}2m$ and the experimental data are presented in Fig. 3. Our calculations show that the best fit is achieved for the $\bar{4}2m$ group with the (112) reflecting plane, and not for $\bar{6}2m$ 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_5Se_8 the SHG is mainly generated by a very thin surface layer. The thickness of this layer can be estimated by $d \propto \lambda_{2\omega}/(4\pi k_{2\omega})$ and for our sample it is equal to 24 nm. This is less than 0.1% of the sample thickness which accounts for the difference in point groups obtained. The bulk of the sample has the hexagonal symmetry as probed by x rays, which correspond to the stoichiometric composition 1:5:8. On the contrary, a few dozen atomic layers at the surface have evidently a stoichiometry that is more closely to 1:3:5, as the tetragonal structure is observed for 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

thin surface layer is close to the composition 1:3:5, one can mention the coincidence between the positions of the E_1 PL spectral component revealed in this work and of the CuIn_3Se_5 PL spectrum obtained in Ref. 10. To clarify this result further investigations are necessary.

Financial support from the INTAS program (Project No. 03-51-6314) is acknowledged. Three of the authors (L.K., E.M., and N.S.) gratefully acknowledge the hospitality of the Institute for Molecules and Materials during their stay in Nijmegen.

- ¹L. S. Palatnik and E. J. Rogacheva, Dokl. Akad. Nauk SSSR **174**, 80 (1967) [Sov. Phys. Dokl. **12**, 502 (1967)].
- ²T. Hanada, A. Yamana, Y. Nakamura, O. Nittono, and T. Wada, Jpn. J. Appl. Phys., Part 2 **36**, L1494 (1997).
- ³W. Hönl, G. Kühn, and U.-C. Boehnke, Cryst. Res. Technol. **23**, 1347 (1988).
- ⁴B. H. Tseng and C. A. Wert, J. Appl. Phys. **65**, 2254 (1989).
- ⁵S. B. Zhang, Su-Huai Wei, Alex Zunger, and H. Katayama-Yoshida, Phys. Rev. B **57**, 9642 (1998).
- ⁶C.-H. Chang, Su-Huai Wei, J. W. Johnson, S. B. Zhang, N. Leyarovska, Grant Bunker, and T. J. Anderson, Phys. Rev. B **68**, 054108 (2003).
- ⁷N. Kohara, S. Nishiwaki, T. Negami, and T. Wada, Jpn. J. Appl. Phys., Part 1 **39**, 6316 (2000).
- ⁸M. León, R. Fernández-Ruiz, V. Tezlevan, and E. Arushanov, Moldavian J. Phys. Sci. **3-4**, 299 (2004).
- ⁹C. Rincon, S. M. Wasim, G. Marin, R. Marquez, L. Nieves, G. Sanchez Perez, and E. Medina, J. Appl. Phys. **90**, 4423 (2001); S. Levchenko, N. N. Syrbu, E. Arushanov, V. Tezlevan, R. Fernández-Ruiz, J. M. Merino, and M. León, *ibid.* **99**, 073513 (2006).
- ¹⁰R. Bacewicz, J. Filipowicz, and A. Wolska, Inst. Phys. Conf. Ser. **152**, 507 (1997).
- ¹¹D. V. Lang, in *DX Centers in III-V in Deep Centers in Semiconductors: A State of the Art Approach*, 2nd ed., edited by S. T. Panteleides (Gordon and Breach, New York, 1992), p. 591-601.
- ¹²S. Mahanty, J. M. Merino, R. Diaz, F. Rueda, J. L. Martin de Vidales, and M. León, Inst. Phys. Conf. Ser. **152**, 499 (1997).
- ¹³K. Tanaka and H. Uchiki, Opt. Commun. **193**, 313 (2001).
- ¹⁴J. H. Schon, E. Arushanov, L. L. Kulyuk, A. Micu, D. Shaban, V. Tezlevan, N. Fabre, and E. Bucher, J. Appl. Phys. **84**, 1274 (1998).
- ¹⁵J. Ducuing and N. Bloembergen, Phys. Rev. Lett. **10**, 474 (1963).
- ¹⁶H. Cao, J. Y. Wu, H. C. Ong, J. Y. Dai, and R. P. H. Chang, Appl. Phys. Lett. **73**, 572 (1998).
- ¹⁷G. Buinitskaya, L. Kulyuk, V. Mirovitskii, E. Rusu, E. Mishina, and N. Sherstyuk, Superlattices Microstruct. **39**, 83 (2006).