

PREPARATION AND PROPERTIES OF PHOTSENSITIVE Cu₃In₅S₉ THIN FILMS

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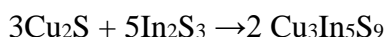
Highly photosensitive thin films of the Cu₃In₅S₉ compound were obtained by the method of instantaneous thermal evaporation of a substance in vacuum. Impurity photoconductivity and an impurity absorption band with a maximum at 1,15 eV were detected. It is assumed that the high concentration of impurity electronic states is due to the presence in the films of a high concentration of cation and anion vacancies in the structure of the crystal lattice.

Keywords: Cu₃In₅S₉, thin film, photoconductivity, absorption, vacancies, defective crystal

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INTRODUCTION

The scientific literature provides data on the existence in the Cu-In-S ternary system of ternary semiconductor phases CuInS₂, CuIn₁₁S₁₇, CuIn₅S₈, Cu₃In₂S₆ and Cu₃In₅S₉, which have relatively close melting temperatures and a narrow region of homogeneity in the phase diagram [1]. Studies of the physical properties of these phases have shown their features that are of practical interest in the fields of photonics, optics, optoelectronics and photocatalysis [2-6]. The production of Cu-In-S thin films by spray pyrolysis [7] showed that the composition of the deposited thin film predominantly corresponds to the chemical formula Cu₃In₅S₉. The semiconductor compound Cu₃In₅S₉ is formed in a quasi-binary system according to the reaction formula



Crystals of the In₂S₃ compound are defective crystals and, depending on temperature, have α -, β - and γ -phase states. The crystal structure refers to a spinel structure in which cation vacancies are randomly arranged in octahedral or octahedral and tetrahedral positions. The CuIn₅S₈ compound also crystallizes in a spinel structure and has 25% vacancy in the cation sublattice and is classified as a defect crystal.

It was shown in [8] that the compound Cu₃In₅Te₉, isostructural to Cu₃In₅S₉, also has 11.6% vacancies in the cation sublattice of the crystal structure. The Cu₃In₅S₉ compound crystallizes in a monoclinic structure with cell parameters $a = 0,660$ nm, $b = 0,691$ nm and $c = 0,812$ nm and $\beta = 890$ [8]. Cu₃In₅S₉ single crystals are brittle and easily break off mechanically along the crystallographic c axis, forming a mirror-smooth surface.

PREPARATION AND EXPERIMENTAL PROCEDURE

The Cu₃In₅S₉ compound was synthesized in an evacuated quartz ampoule with a conical end, by direct melting of individual components taken in stoichiometric ratios. The synthesis of a charge with a total weight of 20 g was carried out in a horizontal position of the ampoule. Therefore, the substance was evenly distributed along the length of the ampoule and had a homogeneous large-block composition. Thin films of Cu₃In₅S₉ were obtained by thermal evaporation of a grain of crystal dust in a vacuum chamber. The synthesized substance was crushed into dust particles with an average size of 100 mkm and poured into a hopper equipped with a special device capable of controlled delivery of the substance into a glass ceramic crucible. After filling, the chamber was pumped out to 10⁻⁵ mm Hg. Art. and the crucible was heated to 1240°C. Dust particles entering the crucible instantly evaporated without contacting the walls of the crucible. High-quality glass-ceramic was used as a substrate.

The photoconductivity of thin films was measured in a stationary mode by irradiating the sample with light from a halogen lamp. A diffraction monochromator with double dispersion was used as a monochromator. Photoluminescence of thin films was studied under the influence of second harmonic radiation (532 nm) of a pulsed Nd:YAG laser. The duration and power of the light pulse were 12 ns and 0,4 MW, respectively.

EXPERIMENTAL RESULTS AND DISCUSSIONS

Thin films of Cu₃In₅S₉ obtained by the above method had high photosensitivity. The ratio of the dark resistance of the film to the resistance illuminated with white light of 200 Lux of a sample with a thickness of 0,5 mm was $\geq 10^2$ times.

In Figure 1 shows the photocurrent spectra of a Cu₃In₅S₉ thin film at temperatures of 100 K (1) and 300K (2), calculated per unit photon. Photocurrent

spectrums cover a fairly wide range of radiation energies (0,9...3,3 eV). Taking into account the data from [8], the long-wavelength edge of the spectrum in the range of 0,9...1,5 eV is formed by impurity photoconductivity, since the band gap of the $\text{Cu}_3\text{In}_5\text{S}_9$ crystal is 1,62 eV at 15 K. The maximum photosensitivity of thin films is achieved at about 2 eV

photon energy. With an increase in temperature from 100 K to 300 K, the maximum of the spectrum increases almost 3 times. Considering that the spectra of a thin film covers a significant part of the solar radiation spectrum on the Earth's surface, we can recommend $\text{Cu}_3\text{In}_5\text{S}_9$ films as the active substance of a solar cell.

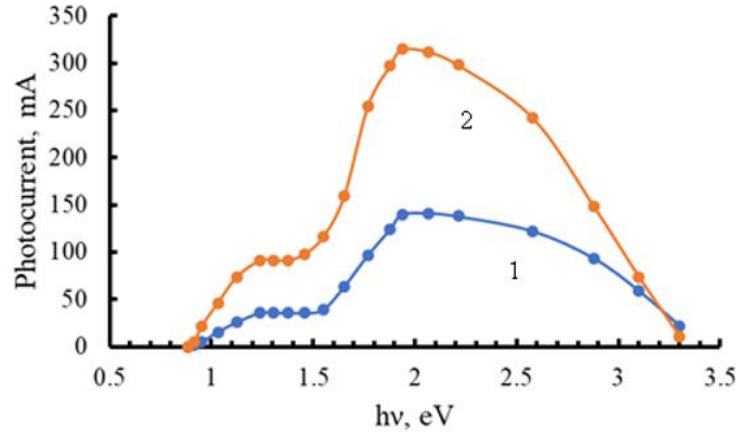


Fig. 1. Photocurrent spectra of a $\text{Cu}_3\text{In}_5\text{S}_9$ thin film at temperatures of 100 K (1) and 300 K (2).

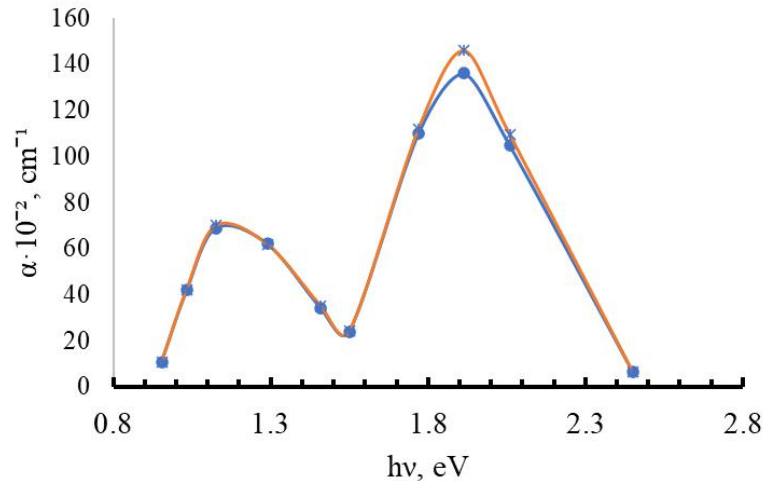


Fig. 2. $\text{Cu}_3\text{In}_5\text{S}_9$ spectra of the absorption coefficient of the thin layer.

The absorption coefficient spectra of $\text{Cu}_3\text{In}_5\text{S}_9$ thin films are in agreement with the photocurrent spectrum (Fig. 2). Impurity absorption in the absorption coefficient spectrum of a thin film is expressed as an absorption band with a maximum of 1,15 eV. The value of the impurity absorption maximum is approximately two times lower than the intrinsic absorption maximum. This means that in a thin film of $\text{Cu}_3\text{In}_5\text{S}_9$ there is a huge concentration of impurity states caused by cation and anion vacancies of the crystal lattice.

As a result of various studies, donor levels with burial depths $E_{D1}=0,017\text{eV}$, $E_{D2}=0,28\text{eV}$, $E_{D3}=0,76\text{eV}$

and an acceptor level with activation energy $E_A=0,16\text{eV}$ were identified in $\text{Cu}_3\text{In}_5\text{S}_9$ crystals. Therefore energy

$$\Delta E = E_g - (E_{D2} + E_A) = 1,18 \text{ eV} \quad (1)$$

It turns out that it is close to the maximum of impurity absorption and therefore it can be assumed that in the crystal there is a large concentration of donor and acceptor impurity states, which determine the impurity absorption.

The impurity absorption coefficient is expressed by the formula [10]:

$$K = \frac{256\pi e^2 \hbar |P_{vc}|^2 E_v^{\frac{1}{2}}}{Rcm^2 \hbar \omega (m_c E_D)^{3/2}} \sum_v \frac{m_p^{\frac{3}{2}}}{[1 + (m_v E_v / m_c E_D)]} (N_D - n_D) \quad (2)$$

where, $(N_D - n_D)$ is the concentration of free electronic states at donor levels, R is the reflection index, P_{vc} is the matrix element of the momentum operator, $E_v = \hbar\omega - E_D - E_g$ is the kinetic energy of the electron in the valence band. As can be seen in (2), the absorption coefficient linearly depends on the concentration of free

electronic states at donor levels. The comparable values of the impurity and intrinsic absorption coefficients indicate the presence of a high concentration of donor and acceptor electronic states, caused by cationic and anionic vacancies of the crystal lattice.

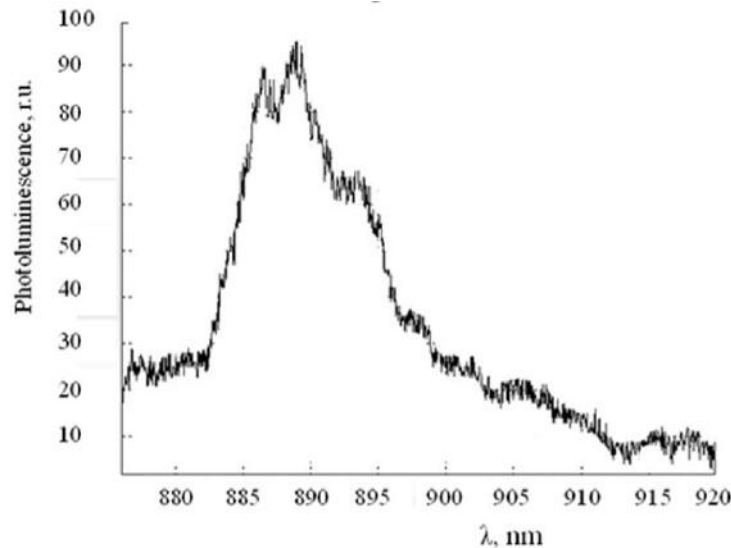


Fig. 3. Photoluminescence spectrum of a $\text{Cu}_3\text{In}_5\text{S}_9$ thin film excited by a laser pulse.

The photoluminescence spectrum of a $\text{Cu}_3\text{In}_5\text{S}_9$ thin film at 300 K is shown in Fig. 3. The spectrum covers the region of impurity absorption, and the maximum emission is observed at 1,39 eV. Apparently,

in the recombination of nonequilibrium electrons excited by laser radiation, the main role will be played by the depleted donor level with a depth of $E_{D2} = 0,28\text{eV}$.

- [1] *Vasyl Tomashik*. Cu–In–S (Copper–Indium–Sulfur). Non-Ferrous Metal Systems. Springer-Verlag Berlin, Heidelberg, 2006; V11C1(1): p. 300-318
- [2] *Alice D. P. Leach, Janet E. Macdonald*. J. Phys. Chem. Lett. 2016, 7, 3, pp. 572–583
- [3] *Shigeru Ikeda, Takayuki Nakamura, Sun Min Lee, Tetsuro Yagi, Takashi Harada, Tsutomu Minegishi, Michio Matsumura*. Chemistry-Europe, ChemSusChem, 2011, Volume 4, Issue 2, pp. 262-268.
- [4] *Shuming Liu, Lijuan Chen, Tingting Liu, Sheng Cai, Xiaoxiao Zou, Jingwen Jiang, Zhiyuan Mei, Zhihui Gao, Hong Guo*. Chemical Engineering Journal, Volume 424, 2021, p. 130325.
- [5] *Gary Hodes, Tina Engelhard, John A. Turner, David Cahen*. Solar Energy Materials, (1985), Volume 12, Issue 3, Pages 211-219.
- [6] *Rongfeng Guan, Xiaoxue Wang, Qian Sun*. J. Nanomaterials. Nanomaterials for Solar Energy Harvesting and Storage, Volume 2015, doi.org/10.1155/2015/579489/
- [7] *Seigo Ito, Toshihiro Ryo*. Advances in Materials Science and Engineering. Volume 2012, Article ID 136092, 6 pages. doi:10.1155/2012/136092
- [8] *Min Li, Yafen Xia, Yong Luo, Yaqiong Zhong, Jiaolin Cui*. J. Physical Chemistry Chemical Physics, v. 22, Issue 13, 2020, pp. 6993-7003
- [9] *N.M. Gasanly*. Optik, Volume 127, Issue 12, 2016, Pages 5148-5151.
- [10] *B.K. Ridley*. Quantum Processes in Semiconductors. U.S.A. Oxford University Press, 1993, p. 394.

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