ELECTRICAL PROPERTIES OF CuInSe$_2$ CRYSTALS OBTAINED BY GAS TRANSPORT METHOD

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The ternary compounds of I-III-VI$_2$ group and their solid solutions recently became one of the most promising materials for the fabrication of high efficiency solar cells [1-3]. The unique physical properties and relatively low cost of the material allow to use CuIn(Ga)Se$_2$ thin films in the low cost large area photo-converters with the efficiency reaching 17% [4]. The further increase of the photo-converters efficiency is stipulated by the fabrication of the epitaxial CuIn(Ga)Se$_2$ layers with the minimum concentration of the native lattice defects.

The results of the charge carriers concentration, mobility and electrical conductivity temperature dependence studies in CuInSe$_2$ crystals and thin layers in the temperature range of 77 – 380 are brought in the given paper.

CuInSe$_2$ single crystals were obtained by the transport chemical reactions method. The iodine as a transport agent and the synthesized compound as an initial transported material were used. The CuInSe$_2$ crystals growth was carried out]n two-section furnace. The ampoule with the synthesized material was horizontally introduced into the furnace so that its part containing the synthesized material was situated in the high temperature (780°C) region of the furnace and the other part in the lower temperature region (720°C). The transport reaction between the synthesized substance and iodine leading to the crystal growth occurs at the above named stable temperatures. The growing material transport rate was of 22-34 mg/hr. As a result a high quality single crystals in the form of the plates with the dimensions of 6 x 10 x 1 mm^3 were grown

By using the obtained crystals as a source CuInSe$_2$ thin layers were fabricated by "flash" evaporation method. The evaporator temperature was 1100–1250°C and the substrate temperature was varied in the temperature range 250–500C. The layers deposition rate was 0.1–0.4 μm/min depending on substrate temperature. CuInSe$_2$ layers had the thickness of 0,2–3 μm.

The main electrical parameters at 80K and 300 K of the investigated CuInSe$_2$ single crystal and layers are given in Table. All investigated crystals and layers have p–type of conductivity.

The charge carriers concentration temperature dependence in CuInSe$_2$ crystals is brought in Fig.1. The charge carriers concentration increase by three orders of magnitude with the temperature increase is observed in the whole temperature range of the investigation. One should notice that the

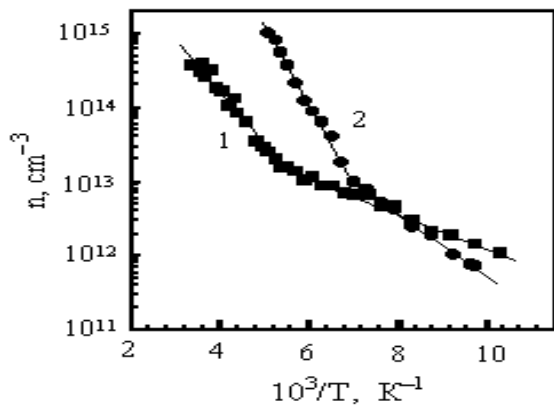| №	n, cm^{-3}		σ, (Ω·cm)$^{-1}$		μ, cm^2/V·s		ΔE, eV
	80 K	300K	80 K	300 K	80K	300K	
CIS1 (crystal)	$1 \cdot 10^{12}$	$7.5 \cdot 10^{14}$	$7 \cdot 10^{-6}$	$1.5 \cdot 10^{-4}$	34	1.2	0.08 0.22
CIS2 (crystal)	$6 \cdot 10^{11}$	$6 \cdot 10^{15}$	$1 \cdot 10^{-5}$	$3.4 \cdot 10^{-4}$	104	0.35	0.15 0.3
CISS1 (layer)	$4 \cdot 10^{14}$	$6 \cdot 10^{17}$	$2.5 \cdot 10^{-3}$	$1.5 \cdot 10^{-1}$	32	2.3	0.1 0.2
CISS3 (layer)			$2.5 \cdot 10^{-2}$	$8.5 \cdot 10^{-2}$			

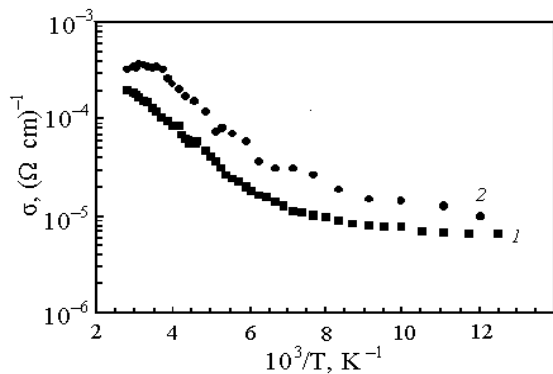*Fig.1.   Concentration   temperature dependence*

Fig.2. Conductivity temperature dependence   for CuInSe$_2$ crystals

temperature dependencies have two different slopes which is different for different crystals. So, if in the temperature range of 80-140K the concentration dependence on temperature is more weak and the dependences slope differ significantly, then in the higher temperature range the n(1000/T) dependence slope increases and became less observable. By taking into account that the studied temperature range is related to the impurity conductivity region the impurity activation energy was determined from ln(nT$^{-3/4}$)=f(1000/T) dependence which was of 0,08eV and 0,15eV for the low temperature region and of 0,22eV and 0,30eV for the high temperature region. The electrical conductivity temperature dependence for the both samples is analogous (Fig.2). So, up to the temperatures of ≈160K the conductivity practically does not depend on temperature and at higher temperatures the conductivity increase became significant and is determined by the impurity activation energy of ≈0,2eV. It is well known that in p- CuInSe$_2$ crystals conductivity the impurity levels of cation vacancies and inter-knots halogen atoms play the predominant role.
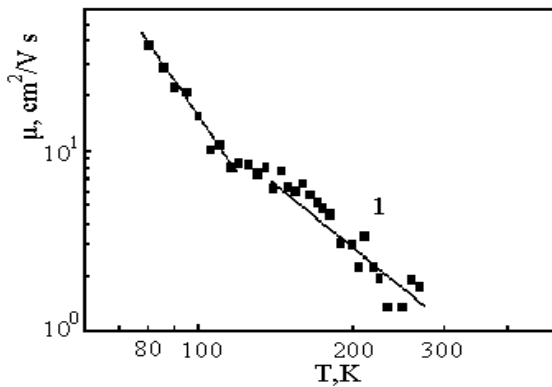
Fig.3. Mobility temperature dependence for CuInSe$_2$ crystals

The comparison of the obtained results with the data from paper [5] shows that in the studied crystals two types of the native defects are possible: a) vacancies in the copper sub-lattice with the activation energy of ~ 0,07eV; and b) the vacancies in the indium sub-lattice with the activation energy of ~ 0,22eV. From the measurements of the Hall coefficient and electrical conductivity the charge carriers mobility was calculated. The charge carriers mobility temperature dependence is given in Fig.3. One can see that the mobility decreases with the temperature increase in the whole temperature range of investigation. Two slopes of dependence were observed which correspond to a power dependence of the charge carriers mobility on temperature of $\mu \sim T\alpha$ type. The α index of this dependence has the value of $\alpha_1 \approx -2,4$ in the low temperature region and of $\alpha_2 \approx -2,6$ in the high temperature region. One can suppose that the charge carriers mobility temperature dependence in the studied samples show the influence of charge carriers scattering on the lattice thermal oscillations and to the presence of a high concentration of the dislocations in CuInSe$_2$ crystals.

The CuInSe$_2$ crystals photoconductivity spectral dependencies at 300K are given in Fig.4. The curve 1 corresponds to the starting crystal and curve 2 corresponds to the photo-conductivity spectral dependence of the same crystal after its annealing in vacuum at 250ºC. In the both cases the photosensitivity covers the wavelength range from 0,7μm to 1,4μm. For the starting crystal the photosensitivity is rather low up to the wavelength of ~1,2 μm and a narrow maximum at ~ 1,28 μm which corresponds to the CuInSe$_2$ band gap with the account of its temperature shift. For the annealed sample the photo-sensitivity increase is observed , which indicates to the decrease of the amount of the surface states as a result of the annealing. At the same time the photosensitivity maximum is shifting to the lower wavelength region ($\lambda \approx 1,24$ μm).

The comparison of the CuInSe$_2$ crystals and thin layers main parameters (Table 1) had shown that the charge carriers concentration in the layers is by 2-3 orders of magnitude comparable to the same in the crystals. Accordingly this leads to the conductivity increase. The CuInSe$_2$ layers photoconductivity is rather low, which indicates to a high concentration of the native defects in the studied layers.
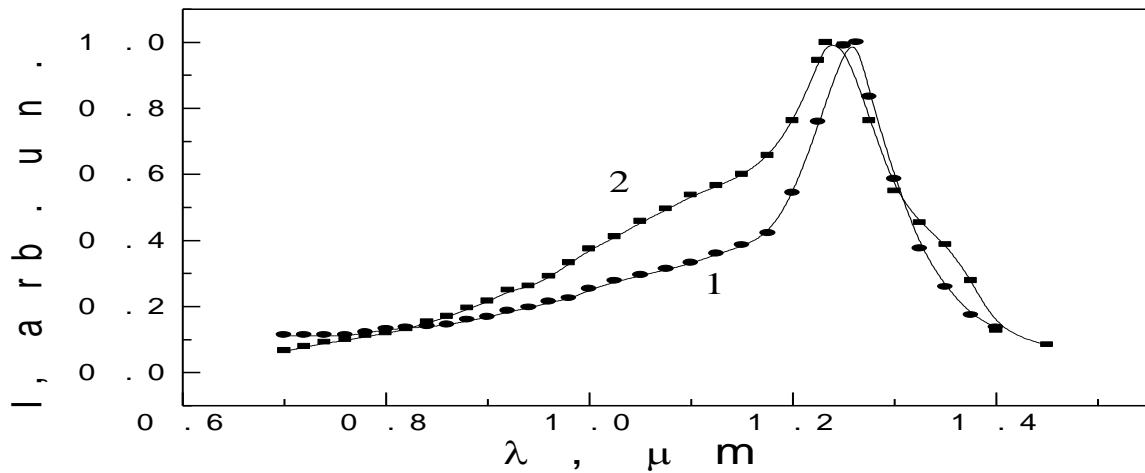
Fig. 4. Photoconductivity spectra of CuInSe$_2$ crystals:
1 – starting crystal: 2 – after annealing.

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