PHOTOVOLTAIC EFFECT IN MONOCRYSTALS CuGaSe₂

I. KITAY OGLU, A.G. BAGIROV

Institute of Physics Azerbaijan NationalAcademy of Sciences H.Javid av, 33, Baku, 370143

At the temperature 77 K the photovoltaic current of the short-circuit is observed in monocrystals CuGaSe₂ in the region of wavelengths (400-1200). At the increase of the light intensity from 1 to 6.7 lux the negative peak reduces in the dependence $J_{s,c} \sim f(\lambda)$ and changes the sign. At further rise of the light intensity the spectrum form has the initial view. Depths of the impurity levels disposition (0.4 eV and 0.6 eV) were valued.

Triple semiconductors of $\hat{A}^{I} B^{III} C_{2}^{VI}$ type are perspective materials for the creation on their base of high-effective transformers of the solar energy, photoreceivers of the high efficiency. The interest to the compound CuGaSe₂ is caused by the perspective of its use as the nonlinear transformers. The stimulated radiation is observed in CuGaSe₂ [1].

Results of the research of the short-circuit current dependence on the wave length in monocrystals $CuGaSe_2$ with the purpose of the opportunities clarification of its use as photocells of the high efficiency are shown in the present paper. Monocrystals $CuGaSe_2$ are crystallized in the chalcopyrite structure (the spatial group D_{2d}^{12}).

The compound $CuGaSe_2$ was obtained by the melting of initial components, taken in the stechiometric ratio.

The synthesis of the semicrystalline product was carried out in evacuated quartz ampoules up to 10^4 mm. mc.

Monocrystals were grown by the method of the chemical transport reactions. The crystalline iodine was used as a conveyer. Lattice parameters (a=5.607, n=10.99, n/a=1.960) were determined in the consequence of the roentgenography research. Obtained monocrystals had the specific resistance $r=10^2 \div 10^7$ Ohm cm and r-type conductivity.

Contacts from Jn and Jn-Ga eutectics were applied on samples for the measurement of the short-circuit current from the wavelength. Samples were illuminated by the monochromator SPM -2.

Samples were connected to the device B7-30 at measurements of the short-circuit current. Measurements were carried out at the temperature of the liquid nitrogen on samples with the specific resistance from $\mathbf{r}=10^2$ Ohm ñm. to 10^7 Ohm ñm.Samples may be divided into 2 groups. In the first group of samples (low-resistance), the sign inversion of the short-circuit current is observed in the dependence of the short-circuit current on the wavelength $J_{s.c.} -\mathcal{A}(\mathbf{I})$. In the second group of samples (high-resistance), the sign inversion of the short-circuit current is not observed.

The typical spectral dependence of the short-circuit current on the wavelength for low-resistance samples is presented on fig.1. It is seen on figure, that the dependence of the short-circuit current on the wave length has a complicated nature. In the range of wavelengths I=625-825 nm the short-circuit current changes the polarity. In the range of wavelengths $500\div900$ nm the diffusion photo e.m.f. exceeds the surface-barrier photo e.m.f. [2].

At first, at illumination the photodiffusion flow is directed from the illuminated side to back rear side and the positive peak $J_{s,c}>0$ is observed.

At the increase of the light intensity the reduction of the positive peak rise and inversion $J_{s.c}<0$ are observed. The latter fact is in agreement with results [2,3]. At the increase of

the light intensity from 1 to 6.7 lux the growth of the negative peak reduces and changes the sign. At further increase of the light intensity the value of the short-circuit current $J_{s.c}$ does not depend on the wavelenght (fig.2).



Fig 1. The inversion of the short-circuit current spectrum of monocrystals CuGaSe₂ after the irradiation by the light.



Fig.2. The dependence of the short-circuit current at the light intensity from 0,1 to 6,7 lux in the region of the fundamental absorption edge.

The negative peak is observed in the region of the fundamental absorption edge and has the fine structure A (720.7 nm) and B (736.7 nm)-fig.1. The mechanism of the PVE creation may be described by two methods:

I - By the charges division because of electrons and holes diffusion at the presence of the concentration gradient,

II – By the charges division because of spatial heterogeneities in samples [4].



Fig.3. The spectral dependence of the short-circuit current photovoltage in monocrystals $CuGaSe_2$ after the preliminary irradiation by the laser (I=0,63 mkm)

In low-resistance samples $CuGaSe_2$ (partially compensated crystals) Fermi level is placed between the valent band and acceptor level, the semiconductor reveals the p-type conductivity with the acceptor concentration N_A - N_D . At the increase of the light intensity in consequence of the

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free holes capture the compensation of the initial conductivity occurs on levels of radiation donors. Fermi level shifts in the direction of the forbidden band middle, the sample resistance increases (the conductivity reduces). This process is profitable in the energy respect, especially for wide-band semiconductors, as, for example, monocrystals CuGaSe₂.

The peak A (720.7 nm), observed in spectra, has the exciton nature [4,5]-fig.1. Obviously, the independence of the short-circuit current on the wavelength in the range 600-900 nm is connected with the compensation of acceptor levels by donor levels and the appearance of impurity bands. At further increase of the impurity centers concentration (at the expense of the compensation) the impurity band expands and mixes with the valent band, that is why the short-circuit current reduces (fig.2).

The PVE saturation is observed at the irradiation by the laser light (fig.3). The influence of the preliminary exposure time by the laser light on the PVE spectrum was investigated. Depths of the two levels disposition (0.4 eV and 0.6 eV) were valued from the part of the PVE spectrum saturation.

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