Effect of Laser Annealing on the Dynamics of Defects in the Crystal Lattice of the Cu₃Ga₅Se₉ Single Crystal

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I. INTRODUCTION
The interaction of high-power laser radiation with semiconductor is complex process [1-2]. This process becomes even more complicated if the semiconductor material is a binary or ternary chemical compound. This can be seen from the example of the Cu₃Ga₅Se₉ single crystal. Some elements of the crystalline structure of this compound are determined in [3]. They are very different from those binary analog or binary chalcogenide [5]. However, processes of synthesis and growth of single crystals of the binary and ternary chalcogenide, compatible in one technological cycle for creating the various multilayer structures. Functionality of these structures is based on the features of the physical properties of each of the semiconductor layer. The luminescent properties studied in [4] may include to such features. The work [6] shows that the Cu₃Ga₅Se₉ crystals have a number of physical properties of practical interest. In particular, it has been shown that in a wide range of temperatures (200 ÷ 450 K) photosensitivity increases steadily with the increase of temperature, and the region of the photosensitivity cover the 1.35 ÷ 1.9 eV electromagnetic radiation energy. At high level of optical excitation, the recombination of non-equilibrium charge carriers occurs mainly through fast recombination levels caused by the cation vacancies in the crystal lattice [7]. It is shown that Cu₃Ga₅Se₉ is of interest as a material for the production of the energy converter of the concentrated electromagnetic radiation into electrical energy.

II. EXPERIMENTAL PROCEDURE
Cu₃Ga₅Se₉ compounds synthesized by the direct fusion of the elements in the amount, corresponding to the stoichiometric ratio of the formula, and by adding certain mass of easily volatile component to generate the vapor pressure in the empty volume of the ampoule. Synthesis and growth of single crystals is carried out in evacuated quartz ampoules. The single crystals were grown by slow cooling of the liquid melt at constant temperature gradient in the horizontal position of the ampoule. The resulting ingots were homogeneous in composition and properties throughout the length. The specific conductivity of the samples at 300 K was ≃ 3 · 10⁶ Ω⁻¹·cm⁻¹.

Single-crystalline samples over the entire surface were exposed to laser annealing at 600 K by laser radiation with a wavelength of 535 nm and an average power of 4 W at a pulse repetition frequency of 8.2 kHz.

III. EXPERIMENTAL RESULTS AND DISCUSSION
Measure of the temperature dependence of the electrical conductivity of Cu₃Ga₅Se₉ single crystals showed that the electrical conductivity is caused by the activation of electrons from the donor level with a depth of 0.12 eV from the bottom of the conduction band over the wide temperature range (77 ÷ 450 K). After repeated cooling up to 75 K and subsequent heating of the crystal up to 800 K, the rate of the dependence of electrical conductivity on temperature was not changed. However, under the laser annealing during 15 ÷ 30 minutes in vacuum at the temperature of 600 K its conductivity is reduced to about 4 order and a crystal transforms to new stable state. The crystal becomes more photosensitive, and the relaxation time of the photocurrent is dramatically reduced.

Figure 1 shows typical spectra of the photocurrent of as grown Cu₃Ga₅Se₉ crystals at temperatures 195 (1) 325 (2) and 360 K (3). According to the analysis of the spectra, the photoconductivity of the crystal is caused by electron transitions from the valence band to levels with energy of 1.62 and 1.74 eV. The first transition corresponds to the transition of electrons from the valence band to partially devastated donor level with the depth of 120 meV, created by selenium vacancies (anion) in the crystal lattice. The second transition occurs between the valence band and the conduction band, i.e. the minimum width of the forbidden band of the
crystal is equal to 1.74 eV. It is found that under the thermal annealing of samples in selenium vapor, low-energy band of about 1.62 eV occurs on the absorption spectra and photoconductivity is abruptly quenched.

Fig. 1. Photoconductivity spectra of Cu₅Ga₃Se₉ single crystals at different temperatures, T, K: 1 - 195, 2 - 325, 3 - 352.

The temperature dependence of the photocurrent of Cu₅Ga₃Se₉ single crystal has a complex nature (Fig. 2, curve 1) and tends to increase the photocurrent with the increase of the temperature from 200 to 400 K. However, in the samples, subject to laser annealing, this dependence is simplified (curve 2). In the range of 250 ÷ 400 K responsible for the activation of the photocconductivity is a mechanism that explains the increase in the lifetime of non-equilibrium charge carriers due to the thermal filling of the activation level.

Fig. 2. Temperature dependences of the photocurrent for Cu₅Ga₃Se₉ crystals before (1) and after (1') of the laser annealing.

After laser annealing photosensitivity of the samples increased by 10⁷ times. Figure 3 shows the photocurrent spectra of Cu₅Ga₃Se₉ crystal subjected to laser annealing at 600 K for 15 minutes. Comparing the curves in Fig. 3, presented the spectra at 360 K before and after the laser annealing, it is seen that after the laser annealing in the crystal activated photoconductivity due to electron transition to the height of 1.54 eV.

Fig. 3. Photoconductivity spectra of Cu₅Ga₃Se₉ single crystals subjected to laser-annealing. T, K: 1' - 256, 2' - 289, 3' - 360.

The kinetics of the laser annealing after a certain dose of radiation intensity within five minutes, we consider watching kinetics of the photocurrent after each annealing procedure under the action of a Π-shaped monochromatic radiation of the incandescent lamp (λ = 720 nm). Fig. 4 and 5 show the kinetics of the photocurrent after each stage of laser annealing. Curve 1 shows the kinetics of the photocurrent newly obtained sample. Other curves (2, 3, 4) illustrate the kinetics of the photocurrent as increasing of the annealing dose. At low intensities of the laser irradiation (curves 2, 3, 4) steady-state level of the photocurrent occurs after filling the trapping levels. With a further increase in the intensity of the laser radiation, on the curves (5 - 8) appear fast recombination centers.

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subjected to laser annealing at high levels of excitation, LAC passes to quasi-saturation. The observed dependence is not standard, and can be explained as follows. Taking into account that in the band gap of the investigated crystals exists deep recombination levels with a concentration $N_r$ (1.1 eV) and with the degree of filling with holes $\eta = \frac{p_r^0}{N_r}$, hence under the action of light the transitions of type 1 and 2 (Fig. 6, c) are possible. At low light intensities $\Delta p < p_r^0$ and $\Delta p \approx \Delta n$, it can be assumed that the degree of filling of the levels as a result of transitions 2, does not change. In this case, the photoconductivity is determined by transitions 1 and LAC has linear character, i.e. $\tau = \frac{1}{\gamma p_r^0} \approx \text{const}$.

However at relatively high intensities, when $\Delta p \approx p_r$, the degree of levels filling $\eta$ increases with increasing of light intensity. Since the probability of transitions of 4 type depends both on the electron density at these levels and the concentration of non-equilibrium holes in the valence band, the recombination of electrons at the levels is quadratic in nature. Thus, $n_r = (N_r - p_r) \sim I^{0.5}$, $p_r \sim I^{0.5}$ and $\eta_n = \frac{1}{\gamma p_r} \sim I^{0.5}$.

Consequently, the LAC of the photoconductivity is of the form $\Delta \sigma_{ph} \sim I^{1.5}$, which is consistent with experimental
results. As the number of recombination centers that have created in the crystal with a laser annealing is finite, at high levels of optical excitation all levels are excited and on the LAC quasi-saturation is observed. It should be noted that the considered case, in a manner similar to two-photon excitation. However at that, the role of virtual levels acts real levels, thereby increasing the probability of transition. As a result increases the lifetime of non-equilibrium charge carriers with increasing of optical excitation level or temperature.

IV. CONCLUSION

Like the CuGaSe$_2$, CuGa$_5$Se$_8$ and Cu$_2$In$_4$Se$_9$ crystals [9-15] anion vacancy (V$_{Se}$) creates in Cu$_5$Ga$_3$Se$_9$ a donor level, and cation vacancies (V$_{Cu}$ and V$_{Ga}$) - acceptor levels. The depths of these levels in CuGaSe$_2$ differ from the corresponding levels depths in Cu$_5$Ga$_3$Se$_9$. Acceptor level due to V$_{Ga}$ plays the role of the activator of the photocurrent in the temperature range 200 ÷ 350 K. The degree of filling of activating centers depends not only on temperature but also on the concentration of selenium vacancies, which creates a donor level at a depth of 120 meV from the conduction band minimum. As a result of irradiation of Cu$_5$Ga$_3$Se$_9$ crystals with high-power laser radiation, to confirm the result of [4], the ionized atoms of copper and gallium move to selenium vacancies, so that the compensation of the donor occurs and forms a new electron-hole pair on the cation-anion vacancies. As a result of reducing the capture cross-section of the recombination centers, electrical conductivity, due to donor level decreases, and the photosensitivity of the sample increases.

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