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The optical properties of 9 MeV electron irradiated GaSe crystals

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***Abstract* — Two absorption bands in transparency region in high-energy electron irradiated GaSe crystals have been experimentally found. The optical transmission spectra of the crystals are studied in order to elucidate the origin and energy positions of related defect states. The measurements of optical transmission spectra temperature dependencies, radiation defect annealing and analysis of the optical spectra within existing theoretical models were performed.**

Keywords — radiation defects; gallium selenide; electron irradiation; transmission spectra; deep levels

I. Introduction

Gallium selenide is one of the widely used nonlinear optical crystals [1-5]. A number of studies were devoted to influence of doping and irradiation on the properties of GaSe crystals [1, 6, 7]. In the present work we performed 9 MeV electron irradiation of GaSe crystals. After irradiation two absorption bands in GaSe transparency region appeared which were not reported in previous works. We performed a number of optical measurements including low-temperature ones and test the applicability of the existing simplified models for description of our results.

II. Experimental Details and Model Approaches

The electron irradiation was done at nuclear reactor of Karpov Institute of Physical Chemistry (Obninsk, Russia) with fluences Φ up to 10^{18} cm^{-2}. As far as neutron irradiation is concerned, our GaSe samples became radioactive after neutron irradiation and were not available for measurements.

The optical spectra were measured using USB 4000+ spectrometer (Ocean Optics, USA) in spectral range 350-1050 nm. The low-temperature measurements were done using a closed cycle cryostat CCS-300S/204-HT (Janis, USA).

The annealing of radiation defects was performed by 10 minits exposition on the heater in vacuum chamber at temperatures up to 400 ^{0}C.

There are few analytic formulas describing spectral depenencies of photoionization cross section σ of deep defect states in semiconductors.

For “energy band–deep level” transitions the formula deduced by Lucovsky can be used [8]:

$$\sigma(\hbar\omega) = \frac{1}{n}\left(\frac{E_{eff}}{E_0}\right)^2 \frac{16\pi e^2\hbar}{3m^* c} \frac{E_A^{1/2}(\hbar\omega - E_A)^{3/2}}{(\hbar\omega)^3}, \qquad (1)$$

where n is refractive index, E_{eff}/E_0 – effective field ratio, E_A – defect ionization energy, m* – effective mass.

Basically, this formula was used for semiconductors with introduced impurities and gave satisfactory description of experimental results when optical transition energies were lower than half-band-gap. For crystals with radiation defects this approach was also utilized for electron irradiated $ZnGeP_2$ crystals [9]. In our case optical transition energies exceeded half-band-gap energy and transitions “deep level–energy band” could be supposed. We have adopted the Lucovsky formula and used the following expression to fit our experimental data:

$$\alpha(\hbar\omega) = A_1\frac{(\hbar\omega - E_{A1})^{1/2}}{(\hbar\omega)^3} + A_2\frac{(\hbar\omega - E_{A2})^{1/2}}{(\hbar\omega)^3}. \qquad (2)$$

Here α is absorption coefficient.

As was mentioned above the revealed in our work spectral features were not observed before in irradiated GaSe, but similar spectra were reported for GaS crystals irradiated with neutrons [10].The authors of [10] supposed formation of Frenkel pairs as result of nuclear reactions and the spectral width of the absorption bands was explained by influence of Coulomb interaction between ionized vacancies and interstitial atoms:

$$\hbar\omega = E_g - E_A + \frac{e^2}{\varepsilon R}, \qquad (3)$$

where E_g - band gap energy, R – distance between defect centers, ε - dielectric susceptibility.

III. Results

Two absorption bands in GaSe transparency region appeared in the irradiated crystals and their intensities definitely increase with increasing fluence (Fig. 1).

Low-temperature measurements of the optical transmission were done to move the Fermi level, which is about 0.3 eV above the top of the valence band in our GaSe crystals, and observe changes in the spectral features. It is seen that with

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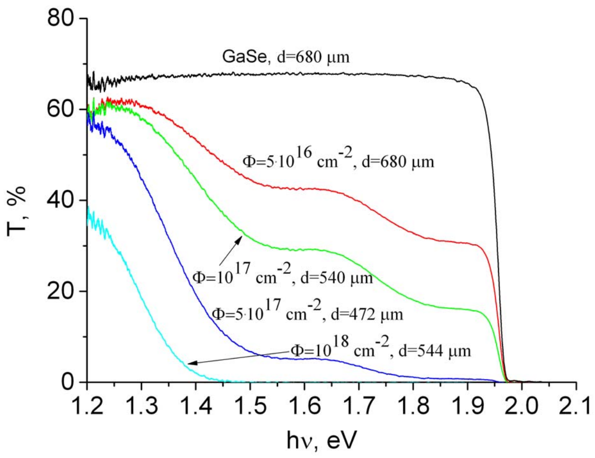

Fig. 1. Room temperature transparency spectra of as-grown and electron irradiated GaSe crystals. Thicknesses of the samples are shown on the plot.

decreasing temperature the lower energy absorption band become less intensive and shifts to the higher energies while the higher energy absorption band become more intensive and shifts to the lower energies (Fig. 2).

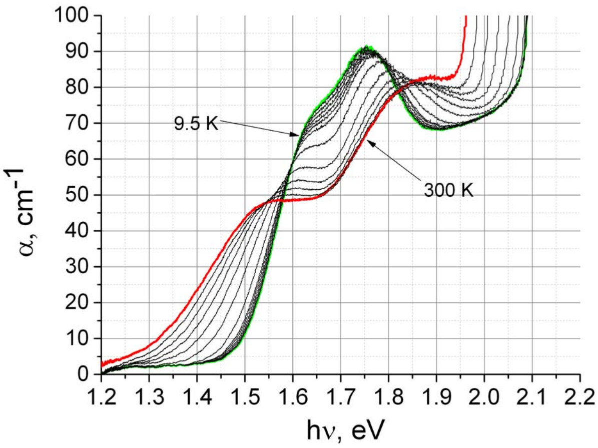

Fig. 2. Temperature dependence of absorption spectrum of GaSe crystal irradiated with fluence 10^{18} cm^{-2}.

The results of approximation of the room temperature optical transmission spectrum of GaSe irradiated with fluence 10^{18} cm^{-2} by expression (2) are presented in Fig. 3. It is seen that it is possible to reproduce the basic features of the experimental curve and to get reasonable defect center energy positions. On the other hand it is more difficult to reproduce low temperature spectra with expression (2).

If during the electron irradiation Frenkel pairs are formed it is possible to use the relation (3) to get the broadness of the radiation defect induced absorption bands. In GaSe the distance between a Ga atom and its nearest possible interstitial position is 2.488 Å and the distance to the second nearest interstitial is 4.51 Å. For selenium atom the nearest interstitial position is between the layers and is located at 2.694 Å, the second nearest interstitial is at 4.627 Å. This gives values of the last term in (3) of 0.7 and 0.4 eV for Ga and 0.65 and 0.39 eV for Se. The full spectral width of absorption band at room temperature (Fig. 1) is about 0.7 eV.

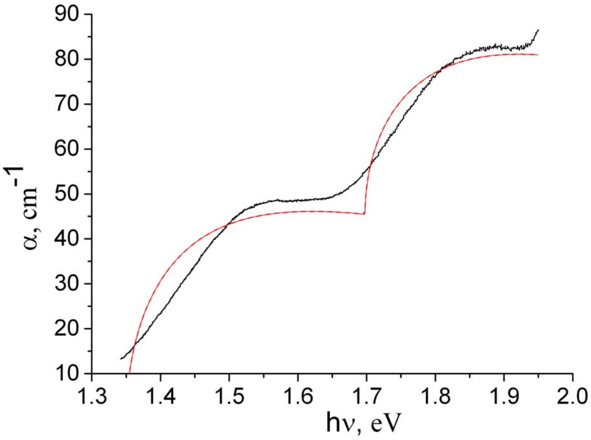

Fig. 3. Absorption spectrum of GaSe crystal irradiated with fluence 10^{18} cm^{-2} (T=294 K). Experimental (black) and theoretical (red) curves are drawn. The numerical fitting parameters of expression (2) are A_1=377.59 cm^{-1}eV$^{5/2}$, E_{A1}=1.35 eV, A_2=613.1 cm^{-1}eV$^{5/2}$, E_{A2}=1.7 eV.

As it is seen on Fig. 4. the observed radiation defects in GaSe are readily annealed. Also the crystals are definitely retain its crystal structure without any sign of amorphization.

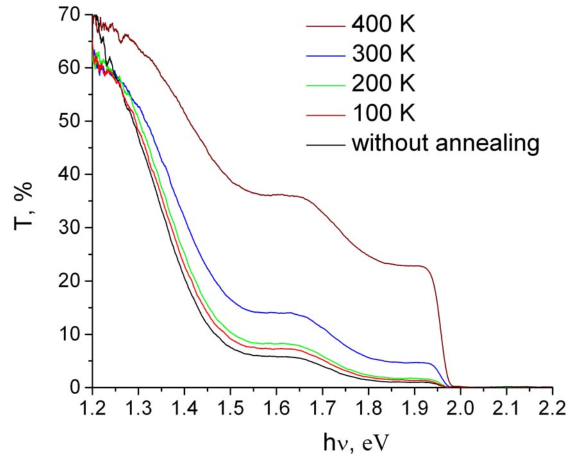

Fig. 4. Transmission spectra of GaSe crystal irradiated with fluence 10^{18} cm^{-2} after annealing at 100, 200, 300 and 400 ^{0}C.

It should be pointed out that in [10] the formation of "steps" on transmission spectra in GaS was connected with nuclear reactions under neutron irradiation. In our experiments the observed spectral features are very similar and nuclear reactions are not expected under the performed electron irradiation.

IV. Coclusion

It can be concluded that the simplified approaches used in literature do not explicitly describe the experimental data obtained in the present study for electron irradiated GaSe. It is reasonable to suppose that more complex defects are formed leading to formation of energy band in the forbidden gap. On the other hand the induced defects are annealed at relatively low temperatures that is possible for point defects like Frenkel pairs.

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