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INFLUENCE Of γ-IRRADIATION on OPTICAL PROPERTIES Of GaSe CRYSTALS

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ABSTRACT

Performed in this work are low-temperature (T = 4.5K) investigations of exciton photoluminescence spectra in layered GaSe crystals both non-doped and doped with Zn and Sn in concentrations < 0.01 wt. %. The crystals were irradiated with γ-quanta of the energy within the range 0 to 34 MeV with the doses up to 10^{14} γ/cm^2. It has been shown that irradiation with the above doses results in improvement of quality in non-doped GaSe crystals: there disappears the "thin structure" of the emission line inherent to free excitons related with stacking fault defects of crystalline layers, observed is ordering the sets of bound exciton lines related with deep acceptors. As a consequence, there observed is an essential increase in the parameter S_0 – integrated intensity of radiative recombination of free and bound excitons.

Analogous changes related with healing of defects in GaSe crystalline lattice are observed after doping with Zn impurity. Irradiation of these crystals with γ-quanta causes increasing S_0, too. By contrast, doping with Sn impurity results in a sharp drop of S_0 that begins to grow after irradiation with γ-quanta.

Key words: GaSe, layered crystals, γ-quanta, semiconductor sensors

INTRODUCTION

GaSe layered crystals are related to A^3B^6 binary compounds. Due to sharp anisotropy of their chemical bonds – strong ion-covalent ones inside layers and weak van-der-Waals between layers – GaSe crystals can be easily intercalated both with atoms and molecules, which makes them to be promising materials for hydrogen energetics [1, 2], accumulators of electric energy [3], and heterostructures with high photosensitivity based on them can be applied in solar cells [4-6].

At the same time, it seems interesting to investigate influence of γ-irradiation on optical properties of these crystals with the aim to use them as components of sensors for ionizing radiation.

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EXPERIMENTAL METHODS AND SAMPLE MANUFACTURING

GaSe single crystals, both pure and intentionally doped with impurities, were grown using the Bridgmann method. The concentration of Zn and Sn impurities in charge did not exceed 0.01 wt. %.

To study the irradiation influence on optical properties, we chipped the plates with the thickness 3 to 5 mm from GaSe ingots and then cut the samples with dimensions 5x5 mm^2 from these plates.

Prepared by this way semiconductor samples was irradiated with γ-quanta in the electron accelerator providing the electron energy 35 MeV and average beam current close to 250 mA. The electron beam was converted into bremsstrahlung on tantalum target. The samples were placed at the angle 90^0 relative to the incident electron beam. Irradiation was carried out with γ-quanta possessing energies within the range 0 to 34 MeV. The spectrum of γ-quanta from a thick tantalum converter was calculated using the program "GEANT". Duration of exposure was chosen in such a manner that could provide the necessary fluence of γ-quanta within the interval 10^{11} to 10^{15} γ/cm^2.

Quality of reference and irradiated crystals, the amount of impurities in them as well as their distribution in crystals were checked using the optical transmission microscope Carl Zeiss Primo Star 5 providing the 1000-fold magnification and electron scanning microscope Zeiss EVO 50 XVP with INCA ENERGY 450 detector.

Measurements of photoluminescence (PL) spectra were made using 0.6-m monochromator МДР-23 with the grating 1200 lines/mm. The spectral width of the slit did not exceed 0.25 meV during experiments. Investigations of PL spectra at $T = 4.5$K were made using the helium cryostat A-255 designed in the Institute of Physics, NAS of Ukraine. It is equipped with the system UTRECS K-43 allowing to control the sample temperature within the range 4.2 to 350K with the accuracy 0.1K. Excitation of PL spectra was made using a current-wave semiconductor laser with the wavelength 532 nm and stable power 80 mW. Photomultipler tube ФЕУ-79 served as a radiation detector.

RESULTS AND DISCUSSION

Fig. 1a shows electron-microscopic image of GaSe crystal surface, when the crystal does not contain any intentionally introduced impurity. These crystals are characterized by the presence of spherical formations with the size 100 to 500 nm. As shown in [2], these formations are inclusions of the amorphous phase inherent to red monoclinic β-Se precipitating in the course of growth into interlayer space of GaSe. These inclusions can be easily eliminated in the following annealing of crystals placed into an evacuated ampoule for 2 to 3 hours at $T = 400$ ^{0}C. There, residual selenium escapes from the crystal and is deposited on ampoule walls, and the inclusions observed in the electron microscope disappear.

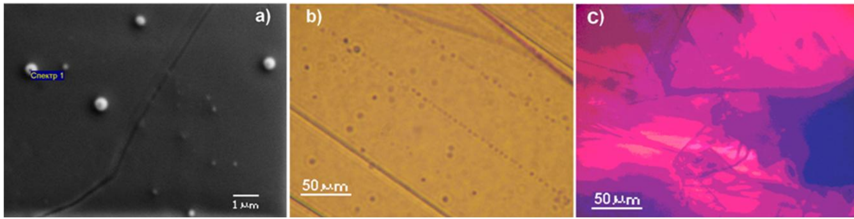

Fig. 1 – a) SEM image of undoped GaSe crystal sample obtained at 10000-fold magnification on Zeiss EVO 50 XVP scanned electron microscope, b) and c) image of GaSe crystal doped with 0.01 wt.% Zn and 0.2 wt.% Zn obtained on transmission optical microscope Carl Zeiss Primo Star 5 at 1000-fold magnification.

The investigations performed in this work using the INCA ENERGY 450 detector with energy dispersion showed that Zn and Sn impurities are inhomogeneously distributed in GaSe crystals even at low concentrations (0.01 wt. %).

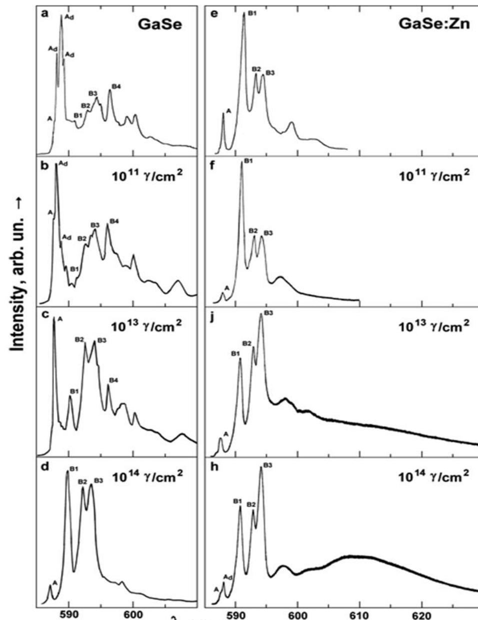

Fig.2. PL spectra of the non-irradiated (a) and irradiated with γ-quanta of the doses 10^{11}, 10^{13} and 10^{14} γ/cm² (b – d) GaSe crystals at T = 4.5K. (e – h) – PL spectra of the GaSe crystal doped Zn (0.01 wt. %) obtained in the same experimental conditions

They are mainly accumulated in the vicinity of dislocations (*Fig. 1b*) generated by the very impurities in the growing process. When their concentration exceeds 0.1 wt. % (see *Fig. 1c*), the inhomogeneous distribution can be observed even in the optical microscope Primo Star 5.

Scanning the sample surface with an electron beam using the step 1 – 20 μm showed that the actual local concentration even at low its values 0.01wt. % can differ by 5 to 10 times in various parts of the crystal, while irradiation of the crystals with γ-quanta up to the doses 10^{14} γ/cm² does not result in any redistribution of impurities and does not influence on quality of studied crystal surfaces.

Depicted in *Fig. 2* are the PL spectra of non-doped and doped with Zn (0.01 wt. %) GaSe crystals obtained at T = 4.5K for the cases of crystals non-irradiated and radiated up to the doses 10^{14} γ/cm². Low-

temperature emission spectra of non-doped GaSe crystals are well studied [7]. They are characterized (see *Fig. 2a* and *Table 1*) by the presence of the “thin structure” inherent to A-line of free exciton emission as well as a wide set of B1 to B4 emission lines related to bound excitons. Besides, there is a band at 610 nm attributed to point defects.

The presence of the “thin structure” inherent to free excitons in GaSe is, as a rule [8, 9], related with stacking fault defects of crystal layers, and availability of bound excitons – with various point defects inside these layers.

As it is seen from *Fig. 2*, γ-irradiation of non-doped crystals up to the doses 10^{11} γ/cm^2 does not result in essential changes of the spectrum. The following increase in the irradiation dose up to 10^{13} γ/cm^2 results in the fact that there vanishing are: the “thin structure” of the line for free exciton (Ad-lines) as well as the group of lines for bound excitons. For the doses 10^{14} γ/cm^2, the emission spectrum consists of A- and B1- to B4-lines of free and bound excitons.

Besides, *Table 1* and the insert in *Fig. 3c* show that with increasing the irradiation dose in non-doped GaSe crystals one can observe the three-fold increase in the parameter S_0, where S_0 is the integrated intensity of radiative recombination (PL) of free and bound excitons reduced to the initial (non-irradiated and non-doped) GaSe crystal.

Table 1

Crystal; irradiation doses, γ/cm^2	Wave length of emission line maximum, nm					S_0
	A, Ad	B1	B2	B3	B4	
GaSe	587.8, 588.1, 588.6, 589.3	590.9	592.6	594.1	596.5	1
10^{11}	587.8, 588.1, 588.9, 589.3	590.9	592.6	594.1	596.6	1.3
10^{13}	587.8	590.2	592.6	594.0	596.3	2
10^{14}	587.4	590.0	592.4	593.5	597.4	3.1
GaSe:0.01Zn	587.8	591.2	593.0	594.2	598.6	1.5
10^{11}	588.0	591.0	593.0	594.2	597.1	1.2
10^{13}	587.7	590.8	593.0	594.2	598.1	1.6
10^{14}	587.7, 588.2	591.0	592.9	594.4	597.8	2.8
GaSe:0.01Sn	587.2	591.7	-	594.2	596.7	0.05
10^{11}	587.2	591.7	-	594.2	596.7	0.04
10^{13}	587.6	591.4	593.3	595.7		0.06
10^{14}	5876	591.2	593.0	595.5		0.12

This transformation of the spectrum for the non-doped GaSe crystal as well as increase of S_0 indicate improved quality of the crystalline structure in the process of γ-quantum "annealing", as a consequence of reduced amount both of point defects and the layer packing ones. In its turn, it leads to reduced decay (scattering) of free excitons by lattice defects and increased their lifetime, which causes growth of the integrated intensity of exciton radiative recombination.

Analogous changes related with a lowered amount of emission lines for excitons related with lattice defects were observed earlier after isothermal annealing of GaSe crystals [10], however, as shown in [11], multiple irradiation of these crystals with power laser pulses at the wavelengths lower than the forbidden gap width results in essential extinction of the PL spectrum.

As a rule, GaSe crystals possess *p*-type conduction. Due to various growth technologies, there present are deep acceptor levels located 80 to 150 meV above the valence band [12, 13]. Therefore, in accord with [14], doping the Ga^{++} vacancies [8] with low concentrations of iron group impurities being in the 2+ charge state results in healing of point defects in the crystalline structure of GaSe.

Indeed, as seen from *Fig. 2e*, doping with the Zn impurity possessing the concentration 0.01 wt. % also results in healing of point and packing defects in crystalline layers – there remain only lines for free exciton and those bound with deep acceptors. In this case, the spectrum of non-irradiated GaSe:0.01Zn crystals (*Fig. 2e*) becomes practically identical with that of non-doped GaSe crystal irradiated with high doses of γ-quanta (*Fig. 2d*), and the integrated radiation intensity S_0 becomes even a little higher than that in non-doped non-irradiated GaSe. Like to the case of non-doped crystals, increasing the γ-irradiation dose for the crystals GaSe:0.01Zn results in growth of the parameter S_0. Thereof, one can conclude that doping the GaSe crystals with Zn impurity in low concentrations and γ-irradiation of non-doped GaSe crystals lead to healing of point defects in the crystalline lattice and ordering the crystal layers.

Indeed, Zn impurity (possessing two valence electrons), when substituting Ga^{++} vacancies in crystalline layers, could recover covalent bonds between Ga and Se atoms, which essentially improve crystal quality. However, contrary to two-valence Zn, the Ga atom belonging to the third group in Periodic Table possesses three valence electrons that form in GaSe hybrid *s-p* bond with Se. Here, two electrons form covalent bonds with three Se atoms, which complete 4*p*-shells of Se atoms, and the residual electron being bound with the electron of the neighbor Ga atom completes their *s*-shells.

As a consequence, Zn impurity cannot heal the acceptor caused by absence of Ga atom in the layer. It only partially heals the crystal layer by binding some part of residual Se present in the interlayer space, and retains the Ga^{+} vacancy (acceptor). When the irradiation dose increase, there arises a point

defect center, which causes appearance of the intense PL band around 610 nm. At the doses close to 10^{14} γ/cm^2, the integrated intensity of this band becomes comparable with the radiation intensity of free and bound excitons (*Fig. 2h*).

In relation with the mentioned above, it seems also interesting to study the influence of doping the GaSe crystals with fourth-group impurities on PL spectra and their stability in the course of γ-irradiation. As this impurity, we chose Sn atoms that have four valence electrons and posses ability of the hybrid chemical *s-p* bonding. When substituting Ga vacancies, this impurity is able to recover covalent bonds both with Ga atoms inside the layer and with Se atoms precipitating into the interlayer space.

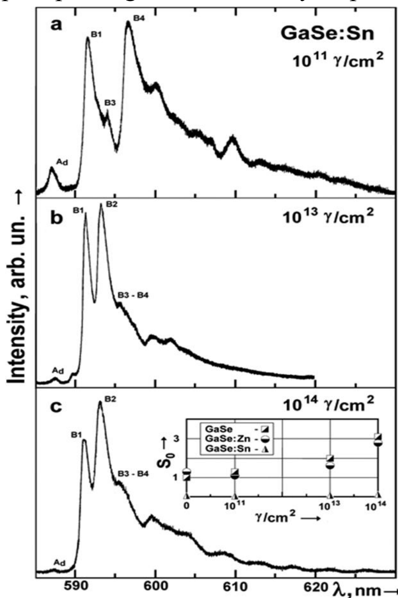

Fig. 3. PL spectra of GaSe:0.01Sn crystals (γ-irradiated with the doses 10^{11}; 10^{13} and 10^{14} γ/cm^2) measured at $T = 4.5$K (a - c). In the insert: dependence of the parameter S_0 on the irradiation dose for the crystals GaSe, GaSe:0.01Zn and GaSe:0.01Sn under the same temperature conditions

In this case, Sn impurity has one excess electron that may create a deep donor level in the forbidden gap. Perhaps, just these levels located 350 – 400 meV below the conduction band bottom were observed in [8, 15].

It should be noted that the grown GaSe:0.01Sn crystals as well as studied by us GaSe crystals both Zn-doped and non-doped possess mirror chipped surfaces. However, contrary to Zn-doped and non-doped crystals, their integrated radiation intensity S_0 at $T = 4.5$K (see Table 1) was about 5% of a pure GaSe crystal. PL spectra of these crystal are not changed with increasing γ-irradiation doses up to 10^{11} γ/cm^2; one can clearly observe PL emission within the range typical for free and bound excitons (see *Fig. 3a*). But as it can be seen in the insert to *Fig. 3c* and in Table 1, S_0 parameter begins to grow with next increasing the γ-irradiation dose, while the structure of emission spectrum tends to be closer to that of Zn-doped and non-doped GaSe crystals.

This sharp decrease of the parameter S_0 when doping GaSe crystals with Sn needs special further investigation. Perhaps, this impurity creates centers (defects) that are able to efficiently quench secondary radiation due to radiationless recombination of excitons on them. To confirm this assumption our

preliminary investigations of conductivity have shown that GaSe:0.001Sn are low-resistant instead to high-resistant pure GaSe.

CONCLUSIONS

It has been shown that γ-irradiation with the doses up to 10^{14} γ/cm^2 results in improvement of quality in non-doped GaSe crystals: there disappears the "thin structure" of the emission line inherent to free excitons related with stacking fault defects in crystalline layers, observed is ordering the sets of bound exciton lines related with deep acceptors. As a consequence, there observed is an essential increase in the parameter S_0 – integrated intensity of radiative recombination of free and bound excitons.

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