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ABSTRACT

of the dissertation for the degree of Doctor of Science

FEATURES OF NON-EQUILIBRIUM ELECTRONIC PROCESSES IN THIN FILMS AND NANOSTRUCTURES OF COMPOUNDS BASED ON A^{I}, B^{III} AND C^{VI}

Speciality: 2220.01 – Semiconductor physics

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Applicant: **Rovshan Mamed Mamedov**

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The dissertation work was carried out at the Department of "Semiconductor Physics" of Baku State University.

Scientific Consultants: Doctor of Physical and Mathematical Sciences, Professor
Vagif Museib Salmanov

Doctor of Physical Sciences, Professor
Ali Hasan Huseynov

Official opponents: Corresponding Member of ANAS, Doctor of Physical and Mathematical Sciences, Professor
Oktay Abil Samedov

Doctor of Physical and Mathematical Sciences, Associate Professor
Talat Rzagulu Mehdiyev

Doctor of Physical and Mathematical Sciences, Professor
Karim Rahim Allahverdiyev,

Doctor of Physical Sciences, Professor
Adil Polad Abdullayev

Dissertation council ED 1.14 of Supreme Attestation Commission under the President of the Republic of Azerbaijan operating on the basis of the Institute of Physics of the Ministry of Science and Education of the Republic of Azerbaijan.

Chairman of the Dissertation Council: Academician
Arif Mamed Hashimov

Scientific Secretary of the Dissertation Council: Doctor of Physical Science, Associate Professor
Rafiga Zabil Mehdiyeva

Chairman of the Scientific seminar: Doctor of Physical and Mathematical Sciences, professor
Huseyn Behbud Ibrahimov

GENERAL CHARACTERISTIC OF THE WORK

The relevance of the work and the state of the art. The rapid development of laser physics and semiconductor technology poses new challenges for researchers in the search for new semiconductor materials that meet the growing needs of quantum electronics, nonlinear optics and, in general, semiconductor electronics.[1] Semiconductor materials are characterized by a wide range of changes in physical parameters, a large set of values of the width of the forbidden zone, various types of conductivity, easily changeable concentrations of free current carriers, etc. All this allows the effective use of semiconductors for the detection and study of fundamentally new physical phenomena, and also indicates the prospects for using semiconductor materials to create modern devices and instruments on their basis. [2]

Among the main directions of fundamental developments in laser physics, one can single out studies of the interaction of intense radiation with matter. In the problem of the interaction of laser radiation with a solid, of particular interest is the question of studying the phenomena occurring in semiconductor crystals excited by ultra-high light fluxes. In semiconductors with a very high polarizability, nonlinear effects are expressed especially strongly. The use of lasers allows us to study several new aspects of the behavior of nonequilibrium current carriers in semiconductors. In particular, due to the high power of modern quantum generators, it is possible to create exceptionally high densities of nonequilibrium current carriers. The study of nonequilibrium phenomena in perfect crystals at such high carrier concentrations represents a completely new area of semiconductor physics. These studies are especially interesting because they make it possible to study a number of subtle effects caused by the interaction between charge carriers, and, in particular, collective effects in a system of high-density excitons.

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[1] Басов, Н.Г. Проблемы квантовой электроники // Природа, – 1990, – №10, – с.28-35.

[2] Алферов Ж.И. История и будущее полупроводниковых гетероструктур // Физика и техника полупроводников, – 1998, – 32(1), – с. 3-18.

As shown by our theoretical and experimental studies, the semiconductor compounds AI, BIII and CVI fully meet these requirements. Due to the layered structure with pronounced anisotropy, high polarizability, optical homogeneity, natural mirror surfaces, strong and broadband absorption of light in a wide frequency range, the presence of exciton absorption with a sufficiently high binding energy, the possession of a band gap width corresponding to the generation frequency of modern lasers, a variety of nonlinearity mechanisms and the availability of a proven technology for obtaining thin films and nanostructures on their basis, these compounds are in demand in various fields of optoelectronics. Studies of nonlinear optical, nonequilibrium electronic processes and quantum-dimensional phenomena in little-studied, and at the same time promising layered semiconductors of the AI, BIII and CVI type, open up great prospects for designing new devices with a wide range of functional capabilities on their basis.

The dissertation aimed to obtain crystals, thin films and nanostructures of semiconductor compounds A^{I}, B^{III} and C^{VI}, conduct a structural analysis, study the features of nonlinear optical and nonequilibrium electronic phenomena and identify the possibility of using this class of semiconductors as materials and elements of optoelectronics.

To achieve this the specified purpose, the following tasks were set:

1. To obtain optically homogeneous single crystals, thin films and nanostructures of A^{I}, B^{III} and C^{VI} semiconductor compounds by the Bridgman, discrete evaporation and chemical deposition methods.

2. To study the internal structure and structure of the obtained thin films and nanoparticles using X-ray diffraction analysis (XRD), atomic force microscope (AFM), energy dispersive X-ray spectroscopy (EDAX) and scanning electron microscope (SEM).

3. To study the features of electrical, optical, photoelectric and luminescent phenomena under high laser excitation intensities.

4. To detect and study nonlinear optical phenomena in thin films and nanoparticles of A^{I}, B^{III} and C^{VI} semiconductor compounds under the action of laser radiation.

5. To study the features of nonequilibrium electronic phenomena in thin films and nanoparticles of semiconductor compounds A^{I}, B^{III} and C^{VI} at high densities of electron-hole pairs generated by laser radiation.

6. To identify the possibility of practical application of A^{I}, B^{III} and C^{VI} crystals in quantum electronics and nonlinear optics.

Methods and objects of research. The tasks set in the work were solved based on experimental and theoretical studies. In this case, modern methods of laser spectroscopy were used, such as pump-probe spectroscopy, nonlinear interference, beam distortion, delay time measurement method, time of flight measurement method, non-stationary photoconductivity study method, non-stationary digital system method containing a storage oscilloscope and a computer system (Board Master 800 ABI 8).

The following radiation sources were used: gas – continuous helium-neon (He-Ne) and pulsed nitrogen (N_2) lasers, solid-state – picosecond yttrium-aluminum-garnet ($YAG:Nd^{+3}$) and nanosecond ruby lasers, a pulsed liquid dye laser with a tunable wavelength, as well as a collimated light source.

During the work, complex studies were carried out, including analytical processing of electrical, optical, photoelectric and luminescent characteristics of materials and structures using modern optical devices, such as a double-dispersion monochromator (spectral resolution ~ 0.024 nm at a wavelength of 600 nm), a storage oscilloscope, special detectors for laser radiation, an electronograph, X-ray structural analysis, etc.

The objects of the research were single crystals, thin films and nanoparticles of A^{I}, B^{III} and C^{VI} compounds (GaSe, GaS, InSe, $AgIn_5S_8$, $Cu_3In_5Se_9$, $Cu_3Ga_5S_9$,), solid solutions $GaSe_{1-x}S_x$, Schottky barriers In_2O_3–InSe–Pt, heterojunctions n-InSe/p-GaSe, $InSe/GaSe_{1-x}S_x$. This choice of object was determined, first of all, by the features of the crystal structure of these materials – layering with sharply expressed anisotropy, transparency in a wide frequency range and the existence of a developed technology for obtaining perfect crystals. On the other hand, the choice of the object of the research was significantly influenced by the ratio between the width of the forbidden band of the studied class of semiconductors and the energy of radiation quanta of

powerful light sources.

The scientific novelty of this work is as follows:

−Nonlinear absorption in layered A3B6 semiconductor crystals was experimentally detected at high laser excitation intensities;

−Bleaching was detected in the exciton resonance region in GaSe crystals at high optical excitation levels;

−The nonlinear absorption coefficient and refractive index were determined in GaSe thin films;

−The band filling effect was detected in GaSe thin films at high optical excitation levels;

−Thermal nonlinearity was detected in InSe under laser excitation;

− Two-photon photoconductivity was detected in Cu3Ga5S9 crystals under laser excitation;

− Two-photon and three-photon absorption were experimentally observed in GaS thin films;

− Photoluminescence features and nanosecond relaxation of photocurrent were detected in CuIn5S8 crystals at a high optical excitation level;

−photoluminescence was observed in GaS-GaSe heterostructures under two- and three-photon excitation by laser light;

−the anisotropy of the mobility of nonequilibrium current carriers was determined by measuring the photoconductivity in GaSe crystals at high excitation intensities;

− the occurrence of drift capacitance in 2D InSe crystals was detected;

− ultrafast photocurrents were detected in a thin-layer InSe structure under laser excitation;

−a new method for obtaining an n-p structure based on InSe and AgIn5S8 thin films was developed;

−a laser ablation method for obtaining InSe and GaSe thin films was proposed;

−Schottky barriers based on In2O3 -InSe-Pt compounds with a high conversion efficiency were created;

−photoelectric converters based on ZnO-Cu InS2 heterostructures were created;

−a new method for changing the intensity of laser radiation was

proposed.

− **Theoretical and practical significance of the tesearch.**

−the nonlinear absorption detected in InSe, GaSe and $Cu_3Ga_5S_9$ crystals indicates the potential for using these crystals as materials and elements of quantum electronics;

− the effect of 2- and 3-photon photoluminescence detected in GaS-GaSe heterostructures can serve as the main method for studying multilayer semiconductor epitaxial heterostructures.

− the effect of filling the bands with nonequilibrium carriers at high levels of optical excitation observed in GaSe makes it possible to create a semiconductor laser based on these crystals;

−ultrafast photocurrents and intense radiation in the near IR region of the spectrum detected at room temperature show the potential for using the thin-layer InSe structure for high-speed electronics and photonics technology.

−optical filters for laser radiation created based on GaSe and InSe crystals make it possible to change the radiation intensity of various lasers by more than two orders of magnitude and can be effectively used as a cutoff filter for high-power laser radiation;

− developed, based on compounds (In_2O_3-InSe-Pt) Schottky barriers allow them to be used as a photovoltaic converter of solar energy;−discovered inversion of the conductivity type in thin films of $AgIn_5S_8$ and InSe, can be used to create semiconductor p-n structures.

The main provisions submitted for defense:

−mechanisms of nonlinear absorption in layered crystals of GaSe, InSe and $Cu_3Ga_5S_9$ at high levels of optical excitation;

− mechanism of occurrence of two-photon and three-photon absorption in thin films of GaS and GaSe under the action of laser radiation;

− physical basis and principle of operation of a semiconductor laser based on GaSe crystals;

−the reason for the peculiarity of photoconductivity of anisotropic GaSe crystals at high excitation intensities;

− mechanisms of occurrence of photoluminescence and nanosecond relaxation of photocurrent in $CuIn_5S_8$ crystals at a high level of optical excitation;

−mechanism of occurrence of the quantum-size effect in InSe nanoparticles;

−mechanism of formation of p-n junction in thin films of $AgIn_5S_8$ and InSe under laser excitation.

−the operating principle of optical filters based on GaSe and InSe crystals for laser radiation in the visible and near infrared spectral regions;

−the operating principle of laser detectors based on GaSe and InSe crystals;

−the mechanisms of formation of Schottky barriers (In_2O_3-InSe-Pt) and heterostructures (InSe/$GaSe_{1-x}S_x$) by methods of landing on an optical contact and laser radiation.

Publications. The topic of the dissertation is reflected in 87 works. The number of published articles on the dissertation is 87. Of these, 29 were published in journals included in the Scientific Citation Index: «Оптика и спектроскопия», «Известия ВУЗов, Томск», «Журнал физической химии», «Журнал технической физики», «Российские нанотехнологии». It is also worth mentioning the articles published in journals International Journal of Current Research (USA), Nanosystems: Physics, chemistry, mathematic; Chalcogenide Letters, Journal of Materials and Applications, Modern Physics Letters B.

Approbation and application. he main materials of the dissertation were presented and discussed at the following conferences, meetings, symposia and seminars: Republican Scientific Conference «Современные проблемы физики» (Баку, 2007); International conference «Conf. Proce. of 6th Inter. Conf. on Tech. and Phys. Prob. of Pow. Eng. (ICTPE) » (Тегеран, Иран, 2010), International conference «Бярпаолунан енержи мянбяляриндя истифадя олунан проб. вя перспектив.» (Баку, 2012), Аграрные науки XXI века. Актуальные исследования и перспективы (Санкт-Петербург, Россия), "İnternational Conference Modern Trends in Physics" Beynəlxalq elmi konfransı (Bakı 2017, 2019), Ümummilli lider Heydər Əliyevin anadan olmasının 94-cü ildönümünə həsr olunmuş "Müasir təbiət elmlərinin aktual problemləri Beynəlxalq Elmi Konfrans" (Gəncə 2017, 2018, 2019, 2020, 2021, 2022), ADİU,

“Respublikamızda qida və tekstil saneyesinin inkişafı perspektivləri və qarşıda duran vəzifələr”, Magistrantların və Gənc tədqiqatçıların “Fizika və astronomiya problemləri” Beynəlxalq Elmi Konfransı (Bakı 2018), Tətbiqi fizika və energetikanın aktual məsələləri Beynəlxalq Elmi Konfransın(Sumqayıt 2018), Актуальные проблемы пищевой и легкой промышленности (Gəncə, GTU0, «Tətbiqi fizika və energetikanın aktual məsələləri II Beynəlxalq elmi konfrans» (SDU, 2020), “Beynəlxalq Elmi Konfrans «Актуальные вопросы прикладной физики и энергетики» (СГУ), International scientific and technical conference on micro and nanotechnology in electronics (Нальчик, Россия 2019, 2021), nd were also discussed at seminars of the Department of Semiconductor Physics.

Structure and scope of the dissertation:

The dissertation consists of 368289 signs (427331 characters including references); introduction 12699 signs, six chapters; Chapter I 68609 signs, Chapter II 96581 signs, Chapter III 32107 signs, Chapter IV 26911 signs, Chapter V 64776 signs, Chapter VI 56942 signs, conclusions 4618 signs, list of abbreviations and symbols 781 signs and list of references and 422 titles, 194 figures, 5 tables. The list of published works related to the content of the dissertation is given at the end of the abstract.

BASİC CONTENT OF THE WORK

The introduction substantiates the relevance of the chosen topic, defines the goal and, accordingly, the tasks to be solved. The scientific novelty, practical value and main provisions submitted for defense are presented. A summary of the dissertation work is given.

The first chapter is devoted to the experimental study of the electrical, optical, photoelectric and luminescent properties of ternary chalcogenides A^{I}, B^{III} and C^{VI} under the influence of conventional (classical) light sources.

Progress in the field of technical use of semiconductor devices poses new challenges for researchers related to the search for new semiconductor materials. At present, intensive work is being carried out

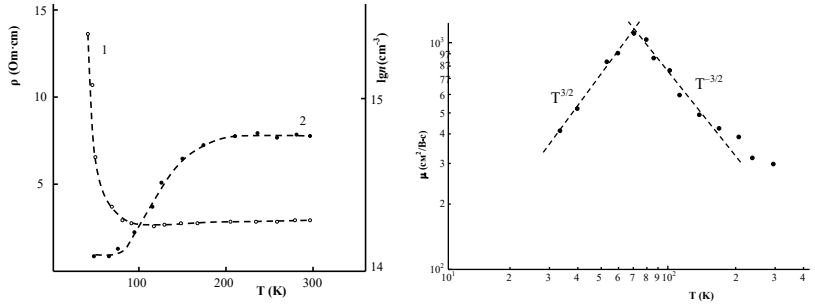
to study complex chemical compounds with semiconductor properties. Such compounds may include chemical compounds based on elements and groups of the periodic table. Ternary chalcogenide compounds are attracting increasing interest because they have a complex of extremely important properties and are widely used in various fields of new technology. Comprehensive studies of the physical properties and the development of standard technology for synthesis, growing single crystals and obtaining thin films of each of these compounds make it possible to fully reveal their practical significance and prospects for implementation in the production of electronic devices.

The studied crystals of A^{I}, B^{III} and C^{VI} were obtained by slow cooling of the melt at a constant temperature gradient. In the process of synthesis and growth of single crystals, methods were used that exclude the possibility of formation of a vacancy of a volatile component in a high concentration. The temperature dependences of the electrical conductivity, concentration and mobility of current carriers in InSe crystals were experimentally studied. The studied InSe single crystals were grown by the Bridgman-Stockbarger method. When studying the absorption spectra, an automated monochromator with double dispersion M833 (spectral resolution ~0.024 nm at a wavelength of 600 nm) with computer control and a detector recording radiation in the wavelength range of 350-2000 nm was used. Measurements were carried out in the temperature range of 4.2-300 K for two directions, parallel and perpendicular to the optical axis "c".

The band gap in InSe, determined from the dependence $\alpha^2 \sim f(h\nu)$, was found to be $E_g = 1.32$ eV. Based on Hall measurements, the main electrical parameters, Hall constant (R), specific resistance (ρ), current carrier concentration (n), mobility (μ), and conductivity type of InSe thin films in the direction parallel and perpendicular to the optical axis "c" were determined. It should be noted that the mobility is quite large (~9000 $cm^2/V \cdot sec$), which is a very important parameter for the manufacture of high-speed laser radiation detectors.

The temperature dependences of the specific resistance and carrier concentration in a wide temperature range from 4.2 K to 300 K are shown in Fig. 1,a. As follows from the figure, the specific resistance in the temperature range of 100 – 300 K remains practically constant,

and the electron concentration increases with increasing temperature.



a **b**

Fig. 1. a-Dependences of specific resistance (1) and concentration (2) on temperature of InSe thin films, b- dependence of InSe mobility on temperature.

From the ρ(T) dependence in the range of 20–100 K, the activation energy of the impurity level was determined to be 48 meV. In the dependence of the InSe mobility on temperature, there are mainly two trends in the change in mobility (Fig. 1, b). First, up to 77 K, an increase in mobility is observed, and then, starting from this value, it decreases. The change in the Hall mobility of current carriers with temperature obeys the laws $\mu \sim T^{3/2}$ (< 77 K) and $\mu \sim T^{-3/2}$ (> 77 K), which corresponds to the scattering of carriers on impurity ions and acoustic vibrations of the lattice.

This chapter also presents the results of studies of cathodoluminescence (CL), photoluminescence and photo-conductivity in single crystals of compounds $AgIn_5S_8$, $Cu_3In_5Se_9$ and $Cu_3Ga_5S_9$.

Based on the obtained data, a donor level with a depth of 0.260 eV and an acceptor level at a height of 0.167 eV from the maximum of the valence band were revealed in the forbidden zone of single crystal $AgIn_5S_8$ $\left(\Delta E_g = 1{,}71 \text{ эВ, при } 300 \text{ K}\right)$. The electron transition with an energy of 2.06 eV detected from the photoconductivity spectrum is a transition of electrons from the valence band to the higher one by 0.32 eV from the bottom of the conductivity band to the subband. The presence of this subband is confirmed by studying the temperature dependence of mobility and thermo-e.m.f. in $AgIn_5S_8$.

The photoluminescence spectra of $Cu_3In_5Se_9$ were studied at temperatures of 160 and 210 K. Comparison of the emission spectra at low temperatures with those at room temperature shows that the emission band at about 1.5 eV disappears with decreasing temperature. Considering that the energy is significantly greater than the band gap of $Cu_3In_5Se_9$ (1.06 eV at 300 K), it can be assumed that at low temperatures free excitons pass into a localized state due to the enhancement of Auger recombination of electrons excited by laser radiation (2.3 eV) in the conduction band. Then the equidistant bends in the emission band spectrum in the high-energy region can be attributed to phonon repetition.

In the photoluminescence spectrum of $Cu_3Ga_5S_9$ at 200 K, a radiation line appears, associated with radiative recombinations of nonequilibrium charges localized at impurity levels and at levels caused by intrinsic defects of the crystal lattice. Since $Cu_3Ga_5S_9$ crystals have n-type conductivity, and the band gap at 300 K is 2.15 eV, it can be assumed that electrons of donor levels and holes of the valence band, as well as holes of acceptor levels, participate in radiative recombination. The entire spectrum can be divided into two main radiation bands with a maximum of about 1 and 1.45 eV. These bands are caused either by recombination of donor-acceptor pairs or by recombination of the impurity level - valence band type.

Single crystals of compound $Cu_3Ga_5S_9$ are insensitive to light at room temperature. However, when samples are heated, their photoconductivity increases so much that it is entirely possible to recommend using this material as a photodetector operating in the wavelength range of 0.5-0.8 μm.

When the crystal is excited by quanta with an energy of 2.1 eV, a sharp increase in the photocurrent is observed above 485 K, caused by an increase in the absorption coefficient with temperature. It is known that large values of the absorption coefficient contribute to the occurrence of radiative processes in semiconductors. Therefore, we analyzed the recombination processes using the approximation of the lux-ampere characteristic (LAC). On the LAC, in the region of 300 ÷

400 K, the slope of the dependence $lg\, i_\phi \sim lg\, I$ at high intensities becomes less than ½, and at low illumination, the slope changes with temperature (dependencies $i_\phi(T) = const$ were recorded in those parts of the LAC where the recombination is quadratic). Thus, it can be considered that the recombination of nonequilibrium charge carriers in single crystals $Cu_3Ga_5S_9$ is characterized by interband transitions.

To determine the parameters of local levels, the thermally stimulated conductivity of samples $Cu_3Ga_5S_9$ was investigated. Two maxima are observed in the spectrum. At the same heating rate, the maxima of the thermally stimulated current (TSC) do not shift depending on the duration of preliminary illumination of the sample. Therefore, the sticking levels are slow.

The second chapter of the dissertation is devoted to the study of nonlinear optical phenomena in layered A^I, B^{III} and C^{VI} crystals under the action of laser radiation.

In InSe crystals, nonlinear absorption at high excitation intensities was studied theoretically and experimentally. In our experiments, a picosecond YAG:ND^{+3} laser generating light pulses with a duration of 25 ps, operating in the mode-locked mode, was used as a light source. After amplification, the light pulse was split into two: the first, converted in the KDP crystal into a light pulse with a doubled frequency ($\hbar\omega_H = 2{,}34эВ$), served as an excitation source, the second was converted into a light pulse with a wide spectral distribution when passing a cell with heavy water (0.75÷1.5) μm. The crystals were excited by an intense light pulse with an energy of $\hbar\omega = 2{,}34$ eV (the second harmonic of the neodymium laser) and the absorption spectra were recorded using a probe pulse. The time delay between the probe light pulse and the pump pulse was achieved by changing the path length of the pump pulse. The spectral distribution of the probe pulse that passed through the InSe sample was studied using a DFS-12 double monochromator.

Fig. 2a shows the dependence of the transmittance of InSe single crystals at T=77 K on the radiation intensity when the crystals are excited by light with a quantum energy of *hv*=1.327 eV. This energy

corresponds to the resonant exciton absorption of InSe. As can be seen from the figure, nonlinear absorption is observed in the exciton resonance region and the sample becomes bleached at the specified radiation frequency at high excitation levels.[3] A more detailed study of the bleaching and the dynamics of nonlinear absorption of light in the exciton resonance region was carried out at T=4.2 K.

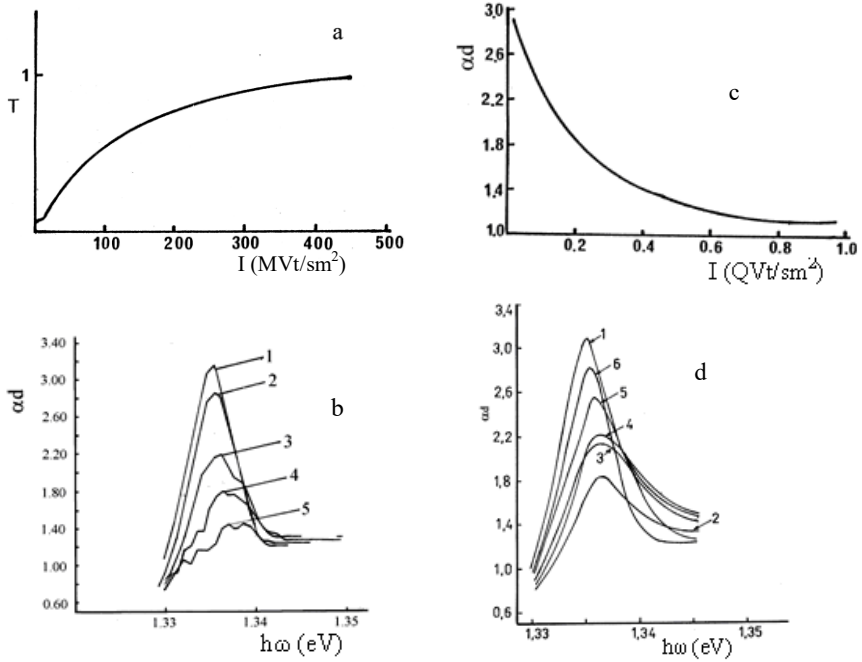


Fig. 2. a) Dependence of the transmittance on the excitation intensity, b) Absorption spectra of InSe at different excitation intensities, c) Dependence of the optical density of InSe on the excitation intensity, d) Absorption spectra of InSe at different time delays between the pump pulse and the probe pulse.

Fig. 2b shows the spectral dependences of the optical density of an InSe single crystal (there is zero time delay between the pump and

[3] Кязым-заде, А.Г. Оптические нелинейности в кристаллах GaSe и InSe при лазерном возбуждении / В.М.Салманов, А.Г.Гусейнов, Р.М.Мамедов [и др.] // Оптика и спектроскопия, – Санкт.- Петербург, – 2014,– № 4(116), – с.130-133.

probe pulses). As can be seen from the figure, the exciton peak decreases and broadens with increasing pump power. The optical density of the studied crystals decreases approximately threefold with increasing excitation power to 0.8 GW/cm^2 (Fig. 2c). Fig. 2d shows the absorption spectra of InSe at different time delays between the pump and probe pulses. Broadening of the spectral line and a shift of the exciton absorption maximum to the region of high energies relative to the unexcited state are observed. In our opinion, the experimentally observed nonlinear absorption of light and its time evolution in the region of exciton resonance in layered InSe crystals can be explained by the process of exciton screening by the plasma of nonequilibrium carriers generated by laser light (Mott transition).

$$n_{Mott} = \frac{\pi}{3}\left(\frac{1{,}46}{4a_{ex}}\frac{m_0}{m_e + m_h}\right)^3 \qquad (1)$$

Estimates show that the critical concentration required for the Mott transition in InSe is $n_{Mott} = 2{,}5 \cdot 10^{16} см^{-3}$. The density of nonequilibrium carriers created by a laser with an intensity of $I_0 = 1.5 \times 10^{25}$ photons/cm^2·s and a duration of $\Delta t = 3 \times 10^{-9}$ s is $\Delta n = \alpha I_0 \Delta t = 4.5 \times 10^{19}$ cm^{-3} (where $\alpha \approx 10^3$ cm^{-3} is the absorption coefficient at the edge of intrinsic absorption). It is evident that the values of the nonequilibrium carrier concentration obtained by us exceed the exciton density required for the Mott transition by three orders of magnitude. On the other hand, the mechanism of screening of the Coulomb interaction by free carriers in InSe is also supported by the determination of the screening length using the formula:

$$L = \hbar / 2(\pi/3)^{1/6} N^{-1/6} \frac{\varepsilon^{1/2}}{em^{*1/2}} \qquad (2)$$

where ε – is the permittivity of the crystal, m∗ – is the effective mass, N – is the concentration of generated carriers.

The screening length calculated using formula (2) turned out to be equal to L ~ 10 A^0, which is much smaller than the exciton radius (~ 37 A^0) in InSe.

The nonlinear absorption coefficient and refractive index in GaSe under laser excitation have been experimentally investigated. It

is known that the physical properties of semiconductors depend to a great extent on the influence of external factors: pressure, temperature, electric field, doping, etc. These and other factors affect the absorption band edge in different ways. Under all-round compression of the crystal, provided by the so-called hydrostatic pressure, the distance between its atoms decreases. But the decrease in the interatomic distance causes an increase in the width of the forbidden zone. With an increase in temperature, the lattice expands and the oscillations of the atoms relative to the equilibrium positions increase. Except some semiconductors (CuCl, PbS,…), an increase in temperature leads to a decrease in the width of the forbidden zone.

The electric field leads to an effective broadening of all levels and a low-energy shift of the absorption edge (Franz-Keldysh effect). The red shift of the absorption edge leads to an increase in optical absorption at energies lower than the band gap. In a degenerate (heavily doped) semiconductor, the absorption edge is at much higher energies than in the intrinsic material (Burstein-Moss effect). The explanation for this effect is that, due to the sufficiently low density of states in the conduction band, a relatively small number of electrons can fill this band, which will affect the absorption edge. In other words, many states near the bottom of the conduction band are already filled and therefore cannot accept electrons optically excited from the valence band.

We have shown that, along with the above-mentioned external influences (pressure, temperature, electric field, doping, etc.), intense laser radiation can also significantly affect the absorption band edge, which will lead to a change in the optical parameters of the substance, the absorption coefficient and the refractive index.

Currently, various experimental methods are used to measure nonlinear optical parameters of semiconductors: pump-probe spectroscopy, optical interferometry, four-wave mixing, three-wave mixing, nonlinear transmission measurement, beam-distortion technique, referred to as a z-scan, and Moire deflectometery.

Two light sources were used in the experiment. The second harmonic of the Nd:YAG laser (λ=532 nm with a repetition rate of 10 Hz, a maximum power of 12 MW/cm^2 and a duration of ~ 10 ns) was

used as an excitation source. A halogen lamp served as the second light source to measure the transmission of the samples excited by laser radiation.

The absorption spectra of GaSe at low (~ 0.1 MW/cm^2, curve 1) and high (~ 5 MW/cm^2, curve 2) excitation intensities are shown in Fig. 3,a. As can be seen from the figure, at high excitation levels the edge of the band shifts toward lower energies (red shift).

The change in the absorption spectrum is shown in Fig. 3,b. The shift in the absorption spectrum toward lower energies leads to a change in the refractive index. From the Kramers-Kronig relation, the change in the refractive index at a photon energy of $\hbar\omega$ can be determined as:

$$\Delta n(\hbar\omega) = \frac{hc}{\pi}\int_0^\infty \frac{\Delta\alpha(\hbar\omega')}{(\hbar\omega')^2 - (\hbar\omega)^2} d(\hbar\omega') \qquad (3)$$

Using equation (3) to calculate the change in refractive index associated with the change in absorption in Fig. 3.b, we obtain the result shown in Fig. 3.c. As can be seen from the figure, in this case the induced change in refractive index is negative below the band edge and positive on the high-energy side.

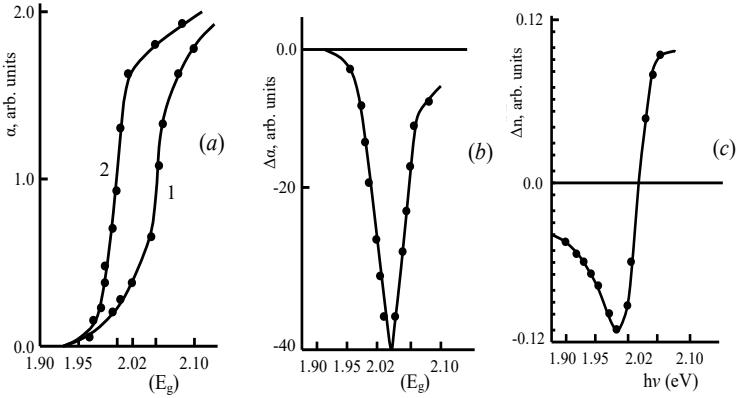


Fig. 3. Optical nonlinearity in GaSe. (a) Absorption spectra at the edge of the absorption band at low (curve 1) and high (curve 2) excitation intensities. (b) Change in the absorption coefficient. (c) Change in the refractive index.

In our opinion, the observation of nonlinear absorption in GaSe crystals is due to nonradiative recombination of nonequilibrium electron-hole pairs generated by laser light.

Indeed, when a semiconductor is excited by powerful laser radiation, electron-hole pairs are formed, the concentration of which can reach ~ 10^{18}-10^{19} cm^3. The recombination of these carriers occurs mainly through two channels, radiative or nonradiative. In semiconductors with conventional band gap values (1-2 eV), the intensity of radiative recombination is insignificant.

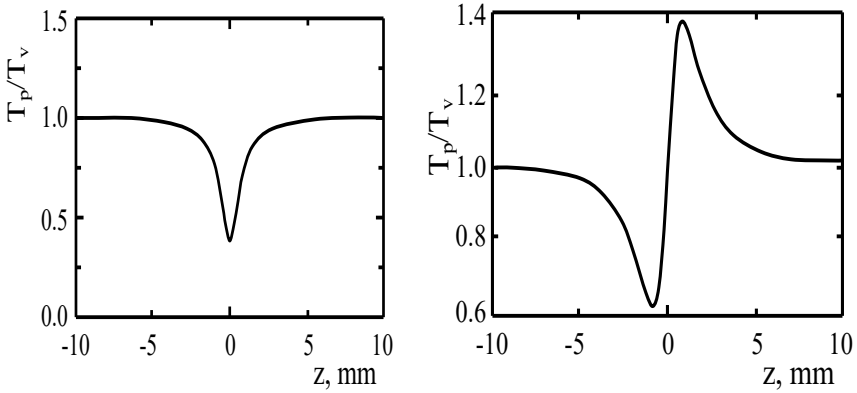
During radiative recombination, photons are emitted, the energy of which corresponds to band-to-band, exciton or impurity transitions. In the case of nonradiative recombination, electron-hole pairs transfer their energy to the crystal due to phonon radiation, which corresponds to lattice heating. In the experiment, nonradiative recombination is observed in the overwhelming majority of cases. Typically, in semiconductor crystals, heating the sample reduces the band gap with a corresponding red shift relative to the edge of the absorption band. As a result of the effect of laser heating, the absorption coefficient and refractive index of the substance change.

A more detailed study of the nonlinear parameters of GaSe was carried out using the z-scan method. A Rhodamine 6G liquid dye laser with N_2 laser pumping at the laser output was used as an excitation source. The wavelength tuning region was (594-643) nm, with a repetition rate of 20 Hz, a maximum power of 10 MW/cm^2 and a pulse duration of ~3 ns. The z-scan method used in the work, first introduced by Sheikh-Bakh, is well known and is used to study the nonlinear properties of optical materials. The method allows one to determine the magnitude and sign of the nonlinear refractive index, as well as the two-photon absorption coefficient.

This method is based on the use of the self-focusing effect of a converging Gaussian beam in a sample with nonlinear optical properties. The method for determining nonlinear constants consists of moving the sample along the optical axis near the focus of the lens used to form the converging Gaussian beam and measuring the radiation power passing through the sample. The open-aperture z-scan method is used to measure the nonlinear absorption coefficient. When

moving the sample along the z-axis with a transition through the focus, the dependence of the total transmission intensity can be measured as a function of the sample position. The closed-aperture z-scan method is used to estimate the nonlinear refractive index. Since the spot size in the detector plane changes due to the self-focusing effect, placing a finite aperture diaphragm in front of the detector ensures measurement of the nonlinear refractive index. The laser beam is directed towards the sample after passing through a narrow focusing lens L. The amount of light transmitted through the sample is detected by detector D2 through the final aperture, while the incident laser intensity is determined by detector D1. No additional lens is used after the sample, so that the far-field profile of the transmitted intensity can be measured by detector D2. The position of the sample relative to the focal plane of the lens is varied and the laser transmission intensity is measured at each position. The transmitted intensity through the aperture as a function of the position z is related to the nonlinear refractive index.

Figure 4a shows the dependence of transmission as a function of the sample position relative to the lens focus (z-scan with open aperture).



a ***b***

Fig. 4. Transmission as a function of sample position relative to the lens focus: (a) z-scan with open aperture, (b) z-scan with closed aperture.

As can be seen from the figure, this dependence is symmetrical concerning the lens focus (z=0 mm), where the minimum transmission is observed. T_V is the sample transmission at low incident radiation intensity (in the absence of nonlinear effects), T_P is the sample transmission at high incident radiation intensity.[4] The characteristic shape of the transmission function for z-scan with a closed aperture is shown in Fig. 4b. In the case when a sample with a positive nonlinear refractive index is located far from the lens focus, the intensity of the radiation passing through the sample is small and, since the sample thickness is small, the transmission changes insignificantly with movement. As soon as the sample approaches the focus, the intensity in the beam becomes sufficient for self-focusing in the sample. The location of the peak and trough of the transmittance in the z-scan experiment allows one to determine the sign of the nonlinearity. The magnitude of the index change can be obtained by analyzing the z-scan transmittance. The magnitude of the nonlinear change in the index $\Delta n(\omega)$ (the value on the axis at the focus, z = 0) leads to a change in phase:

$$\Delta\Phi_0 = (2\pi / \lambda)\Delta n(\omega) L_{eff}, \qquad (4)$$

where $L_{eff} = (1 - \exp(-\alpha l)/\alpha$ – is the effective length of the sample, λ – is the laser wavelength.

The phase change and hence the refractive index change are obtained from the measured value ΔT_{PV}, which is defined as the difference between the peak and valley transmittances, $\Delta T_{pv} = T_p - T_v$. Since $\Delta T_{pv} \approx 0.45(\Delta\Phi)$, the nonlinear refractive index $\Delta n(\omega)$ can be represented in the following form:

$$\Delta n(\omega) = \frac{\Delta T_{PV} \cdot \lambda \cdot \alpha}{0.405 \cdot 2\pi(1 - \exp(-\alpha l)}, \qquad (5)$$

[4] Кязымзаде, А.Г. Нелинейные коэффициент поглощения и показатель преломления в GaSe при лазерном возбуждении / В.М.Салманов, А.Г.Гусейнов, Р.М.Мамедов [и др.] // BDU xəbərlər, – 2019, – №4, – с. 1-10.

where λ=620 nm – is the wavelength of laser radiation, α≈10^3 cm^{-1} – is the absorption coefficient of GaSe at the edge of the absorption band, *l*=100 μm – is the thickness of the samples used.

Estimates show that in the case of excitation of GaSe crystals by laser radiation with a maximum power of W~10 MW/cm^2, the change in the nonlinear refractive index is Δn(ω)≈0.12. At low excitation intensities of W~0.5 MW/cm^2, the change in the nonlinear refractive index is only Δn(ω)≈0.069.

The next section of this chapter is devoted to the study of the band filling effect in GaSe thin films at high optical excitation levels. It is known that in semiconductors at high optical excitation levels a large number of electron-hole pairs are generated. Electrons and holes, as fermions, obey the Pauli principle: at each energy level of the band, which is determined by the wave vector k, there can be no more than two electrons with oppositely directed spins. The occupied state is no longer available as a final state in the process of optical absorption. Due to the principle of energy minimization, carriers in the quasi-equilibrium state occupy accessible states from the bottom of the band, so that the energetically lowest states are occupied first. This leads to the filling of the states near the bottom of the conduction band with electrons, and in the upper part of the valence band with holes. In this way, the band filling leads to a bleaching of the absorption band edge and its shift to the high-energy region of the spectrum.

As experimental results have shown, the concentration of nonequilibrium carriers created by a laser with an intensity of ~ 4.5×10^{19} cm^{-3} is sufficient to shift the edge of the absorption band to the high-energy region of the spectrum. Knowing the concentration of nonequilibrium carriers generated by laser radiation, one can determine the height of the filling zones ΔE

$$\Delta n = \frac{8\pi}{3h^3}(2m_e\Delta E)^{3/2} \qquad (6)$$

Using the effective mass values for GaSe ($m_h = 0{,}5m_0$) and

knowing the concentration of nonequilibrium carriers ($\Delta n = 4{,}5 \times 10^{19}$ cm^{-3}), we can determine ΔE using equation (6).

We have discovered the phenomenon of thermal nonlinearity in thin InSe films under laser excitation. As the experimental results show, with an increase in the excitation intensity, the transmission value decreases and the spectra shift toward longer waves.

The decrease in the width of the forbidden band of InSe with temperature can be described by the following empirical relationship

$$E_g(T) = 1250\, meV - \frac{0.58T^2}{T + 226\, K}\frac{meV}{K} \qquad (7)$$

Indeed, estimates using formula (7) show that heating an InSe crystal with laser radiation to 50-60 ^{0}C can lead to a shift in the absorption edge to the long-wave region of ~ 10 meV. Thus, the presented experimental results show that a simple method can be used to detect and study the thermal nonlinearity of the optical parameters of InSe thin films under laser excitation, which helps to distinguish thermally induced nonlinearities from optical nonlinearities of electronic origin.

The luminescence and photoconductivity features of layered crystals $Cu_3In_5S_9$ under the action of laser radiation were experimentally investigated. Fig. 5 shows the photoluminescence spectra of crystals $Cu_3In_5S_9$ at different radiation intensities. The crystals were excited by the 2nd harmonic of the Nd:YAG laser ($h\nu = 2.34$ eV). As can be seen from the figure, the photoluminescence spectra at T=300 K cover the wavelength range of 700-950 nm.[5]

[5] Гусейнов, А.Г. Особенности люминесценции и фотопроводимости слоистых кристаллов $Cu_3In_5S_9$ под действием лазерного излучения / А.Г.Кязым-заде, В.М.Салманов, Р.М.Мамедов [и др.] Оптика и Спектроскопия, – 2016, – 121(6), – с. 966-969.

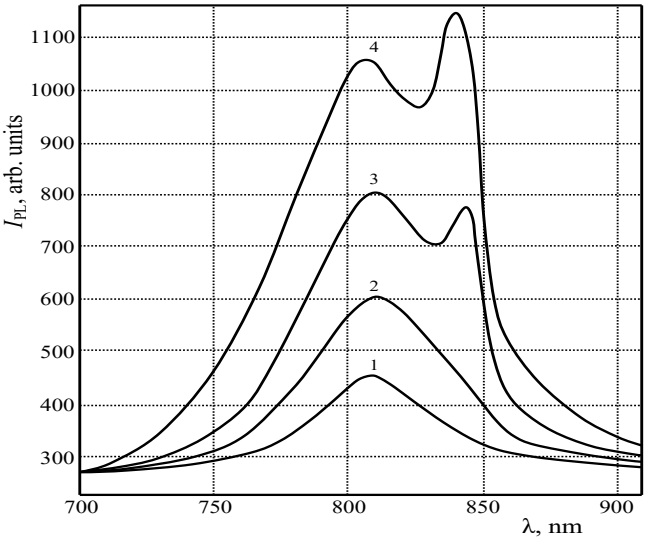


Fig. 5. Photoluminescence spectra of crystals at different excitation intensities I (kW/cm^2·sec.): 1- $5\cdot10^{23}$, 2- $3\cdot10^{24}$, 3- $5\cdot10^{25}$, 4-$2\cdot10^{26}$.

In our opinion, the observed luminescence bands can be caused by the presence of $Cu_3In_5S_9$ in the forbidden zone of crystals, the level of intrinsic defects created by anion and cation vacancies in the crystal lattice.

From the temperature dependence of the electrical conductivity of the Cu3In5S9 crystal in the range of 110-350 K, the activation energies of two donor levels were determined: 0.28 and 0.76 eV. At low temperatures, shallow donor levels are partially in a depleted state. Therefore, at low temperatures, electrons excited by light, passing from the valence zone to local donor levels, create photoconductivity of the crystal. The photocurrent in the energy range of 0.9-1.5 eV is due to donor and acceptor levels formed by anion-cation vacancies of the crystal lattice.

The third chapter of the dissertation is devoted to the experimental study of the processes of two-photon and three-photon absorption in layered semiconductors A^I, B^{III} and C^{VI}. Two-photon photoconductivity was experimentally studied and the absorption coefficient was determined in ternary semiconductor compounds

$Cu_3Ga_5Se_9$ under the action of laser radiation.

The registration of photocurrent and laser radiation pulses was carried out using a technique that allows recording single nanosecond pulses on the screen of a storage oscilloscope (Tektronix TDS-1002B).

As the experimental results showed, the dependence of the amplitude value of the nonequilibrium photoconductivity ($\Delta\sigma$) on the intensity of laser light (I_0) during excitation of $Cu^3Ga^5Se^9$ crystals by the second harmonic of the YAG:Nd^{+3} laser is linear (Fig. 6, curve 1).

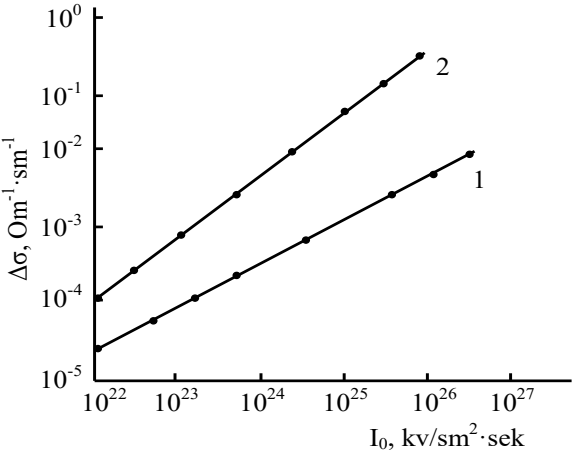


Fig. 6. Dependence of photocurrent on the intensity of laser light I_0: 1-excitation by the second harmonic of laser light with energy $\hbar\omega = 2{,}34$ эВ , 2-excitation by laser light with energy $\hbar\omega = 1{,}17$ эВ .

In the case of excitation of crystals by light, the quantum energy ($\hbar\omega = 1{,}17$ eV) of which is less than the width of the forbidden band of the crystal (E_g ~ 1.74 eV), a quadratic dependence is observed, $\Delta\sigma \sim I_0^2$ (curve 2).

The relaxation curves of the nonequilibrium photoconductivity are shown in Fig. 7,a,b,c. As can be seen from the figure, the relaxation time at relatively low excitation intensities is $\tau \sim 10^{-4}$ sec. With an increase in the excitation intensity, the relaxation time

decreases. The dependence of τ on I_0 is shown in Fig. 7,d. A change in the intensity from $2\cdot10^{25}$ quan/cm^2·sec to $2\cdot10^{26}$ quan/cm^2·sec leads to a decrease in τ by approximately three times. The decrease in the lifetime can be due to an increase in the concentration of nonequilibrium carriers generated by laser radiation. Estimates show that at an excitation intensity of $I_0=2\cdot10^{26}$ quan/cm^2·sec, the concentration of nonequilibrium carriers reaches a value of $\Delta n\sim10^{18}$ cm^{-3}.

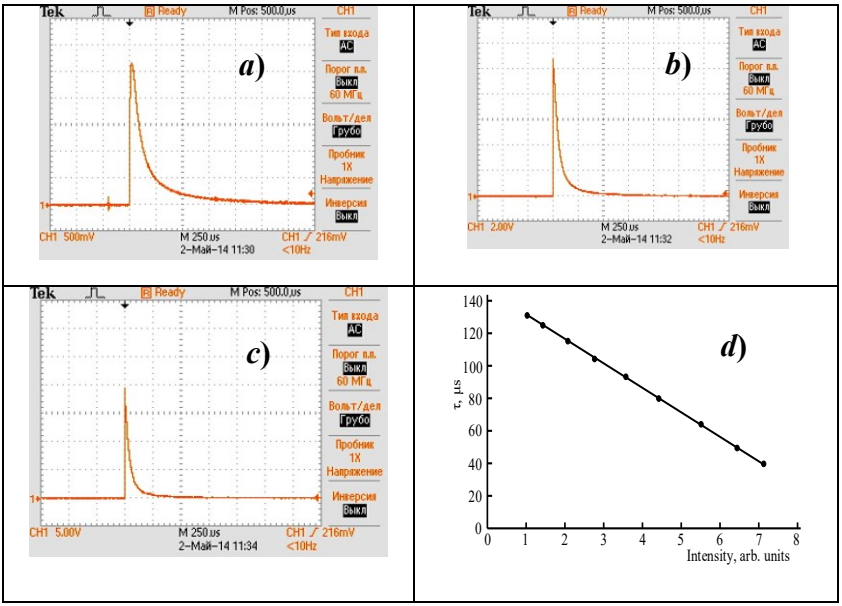


Fig. 7. Relaxation curves of nonequilibrium photoconductivity of $Cu_3Ga_5Se_9$ crystals. I_0, quan/cm^2·sec; 1 - $2\cdot10^{23}$, 2 - $1\cdot10^{24}$, 3 - $6\cdot10^{25}$.

The mechanism that results in the emergence of nonequilibrium carriers in the zone can be established by the type of dependence of $\Delta\sigma$ on I_0. Since the duration of the laser pulse Δt is less than the characteristic lifetime of the carrier in the zone τ (Δt<τ), the value of the specific photoconductivity will be determined only by the generation rate and the following expression is valid:

$$\Delta\sigma_{уд.} = e\mu k\beta I_0 \Delta t \qquad (8)$$

where e is the electron charge, μ is the carrier mobility, k is the absorption coefficient, β is the quantum yield, I_0 is the light intensity, Δt is the duration of the exciting light pulse.

In the case of single-photon absorption, the absorption coefficient k does not depend on the light intensity, then the specific photoconductivity will be proportional to the incident light intensity $\Delta\sigma_{уд} \sim I_0$. With multiphoton absorption, the light absorption coefficient $k^n \sim I_0^{n-1}$. With two-photon absorption, the absorption coefficient is proportional to the intensity $k^{(2)} \sim I_0$. Therefore, the dependence of the photoconductivity on the exciting light intensity with two-photon excitation is quadratic $\Delta\sigma_{уд} \sim \kappa^{(2)}(I_0) I_0 \sim I_0^2$. Thus, the detection of a quadratic dependence in the photoconductivity (or concentration, since $\Delta\sigma = e\Delta n\mu$) of nonequilibrium carriers on the exciting light intensity indicates the implementation of two-photon photoconductivity in semiconductor crystals.

Indeed, as our experimental results show with single-photon excitation of $Cu_3Ga_5Se_9$ crystals by the second harmonic of a neodymium laser $(\hbar\omega > E_g)$, when the transition of carriers from the valence band to the conduction band occurs, the LAC of photoconductivity becomes linear (Fig. 6, curve 1). With two-photon excitation of $(\hbar\omega < E_g)$, a quadratic dependence of Δσ on I_0 is observed (Fig. 6, curve 2).

Fig. 8 shows the dependence of the two-photon absorption coefficient on the excitation intensity. As can be seen from the figure, the dependence of $k^{(2)}$ on I_0 is linear up to high light intensities. The two-photon absorption coefficient $k^{(2)}$ was found to be equal to $7 \cdot 10^{-3}$ cm^{-1} at a light intensity of $I_0 = 1 \cdot 10^{25}$ quan/cm^2·sec.

The value of the two-photon absorption coefficient determined from the experimental study of photoconductivity was compared with theoretical values. The theoretical value of the two-photon absorption coefficient is determined by the formula:

$$k^{(2)} = \frac{64\pi e^4 M^{\frac{1}{2}} E_g \left(2\hbar\omega - E_g\right)^{\frac{3}{2}} f_{cv}}{3\varepsilon c^2 (2\hbar\omega)^4 m_0} \cdot I_0, \qquad (9)$$

where E_g is the band gap of the semiconductor, I_0 is the intensity of the incident light, ε is the permittivity of the substance, $\hbar\omega$ is the energy of the incident quantum, M is the reduced effective mass, and f_{cv} is the oscillator strength.

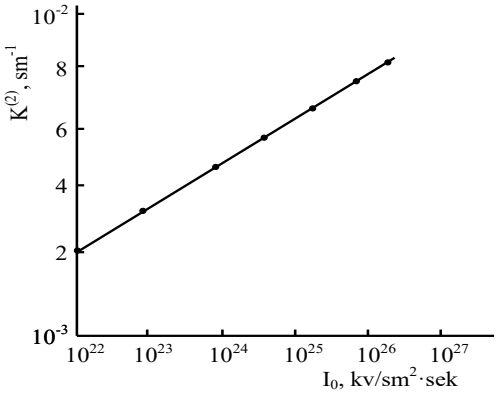


Fig. 8. Dependence of the two-photon absorption coefficient on the light intensity.

The calculated value of the two-photon absorption coefficient $k^{(2)}$ based on formula (9), taking into account the corresponding parameters of the $Cu_3Ga_5Se_9$ crystals ($E_g = 1{,}74$ эВ, $m_n = 0{,}15m_0$, $m_p = 0{,}04m_0, \varepsilon = 4{,}1$), gives the value $k^{(2)}=3\cdot10^{-3}$ cm^{-1} at a light intensity of $1\cdot10^{25}$ quan/$cm^2\cdot$sec. As can be seen, this value is in good agreement with the experimentally found value of $k^{(2)}$.

In conclusion, let us dwell on the naturally arising question of whether the observed transitions under the action of light with $\hbar\omega < E_g$ are a consequence of two-step excitation. In this connection, it should be noted that if two-step transitions were to dominate in our case, then the dependence of the absorption coefficient on the light

intensity, found from the photoconductivity measurement, could not remain linear in the entire investigated range of incident light intensities, since at high excitation levels the filling of impurity centers should begin to have an effect and the two-step absorption coefficient should experience saturation. In the experiment, as can be seen from the data presented, the situation is the opposite.

As mentioned above, depending on the exciting laser radiation parameter and the physical parameters of the substance under study, various methods for studying multiphoton absorption can be used: direct measurement of optical absorption, photoluminescence, and nonequilibrium photoconductivity. In our opinion, the radiative recombination method and layered gallium sulfide (GaS) crystals are the most suitable combination for the experimental study of multiphoton processes.

Gallium sulfide has a band gap of 2.53 eV at T = 300 K, so the light of the 2nd harmonic of the Nd:YAG laser ($\hbar\omega$ = 2.34 eV) should lead to two-photon absorption, and the light of the 1st harmonic ($\hbar\omega$ = 1.17 eV) should lead to three-photon absorption.

In the luminescence spectra of GaS crystals with two-photon excitation by the second harmonic of a Nd:YAG laser ($\hbar\omega$=2.34 eV), two maxima with wavelengths of 415 nm and 490 nm are observed. The weak high-energy emission line with the energy $\hbar\omega$=3.00 eV is apparently due to direct optical transitions. The intense emission line with the energy $\hbar\omega$=2.53 eV is associated with indirect transitions at the fundamental absorption edge. This is also evidenced by the data we obtained from the absorption spectrum of GaS. The dependence of the luminescence intensity on the excitation intensity with two-quantum excitation has a character in the form $I_{\text{lum}} = I_{\text{las}}^{2.5}$.

The intensity of the emission lines associated with the indirect optical transition is one order of magnitude higher than the intensity of the emission lines associated with the direct optical transition. In our opinion, this is due to the self-absorption process, which is often encountered in semiconductors with indirect forbidden bands. It is possible to excite electrons in both valleys, thus obtaining direct and indirect radiative recombination. Even though the electrons will quickly relax to the lowest energies, i.e., to the indirect valley, and

despite the strong absorption of high-energy photons in direct transitions, some fraction of high-energy radiation can be detected in very thin samples, especially with laser excitation. Observation of direct transitions under such unfavorable conditions is possible only because of the relatively high probability for direct transitions.

With three-quantum excitation of GaS crystals, characteristic radiation with a maximum of ~ 490 nm is observed. However, the radiation intensity is much weaker than with two-quantum excitation. The dependence of the luminescence intensity on the excitation intensity with three-quantum excitation has a character in the form of $I_{\text{lum}} = I_{\text{las}}^{3.4}$. Thus, the appearance of radiation characteristic of GaS and the course of the dependence of luminescence on the excitation intensity indicate the presence of a three-photon absorption process.

The ratio of the two-quantum absorption coefficient (K_2) to the three-quantum absorption coefficient (K_3) was determined. For this purpose, the light intensities of the first (I_1) and second (I_2) harmonics of the Nd:YAG laser, which lead to the same radiation, were measured. Considering that the carrier generation rates are equal to $K_2I_2 = K_3I_1$, for the intensity $I_1 = 10$ MW/cm^2 the ratio (K_2/K_3) turned out to be of the order of 10^4. This value can be compared with the theoretical value of the ratio (K_2/K_3) theory. If we use the results of calculations according to the perturbation theory in the second order for K_2 and in the third order for K_3, we have:

$$(K_2/K_3)_{\text{reop.}}=0.1\,\frac{\mu n\hbar^2\omega_1^4 c}{\pi e^2(3\hbar\omega_1-\Delta)I_1}\left(\frac{\omega_1}{\omega_2}\right)^5 \qquad (10)$$

where $\mu = \dfrac{m_e m_n}{m_e + m_n}$, $n -$ is the refractive index, Δ is the band gap, ω_1 and ω_2 are the frequencies of the 1st and 2nd harmonics of the Nd:YAG laser, respectively, and I_1 is the light intensity at ω_1.

For I_1=10 MW/cm^2 this ratio is equal to $3\cdot10^4$, which agrees well with the experimental estimate. The estimates show that in the three-photon absorption process the concentration of nonequilibrium carriers generated by laser radiation reaches a value of ~ $5\cdot10^{12}$ cm^{-3}.

The next section of the dissertation is devoted to the study of photoluminescence of the GaS-GaSe heterostructure under two- and

three-photon excitation by laser radiation.

The absorption spectrum of GaS crystals at 300 K covers wavelengths from 400 to 1100 nm (Fig. 9,a). Starting from a wavelength of 600 nm, a noticeable increase in absorption is observed towards shorter wavelengths. Considering that GaS is a semiconductor with an indirect band gap, the band gap width of the studied samples was determined from the dependence $\alpha^{1/2} \sim f(h\nu)$, which turned out to be equal to Eg=2.53 eV (Fig. 9,b). Similar studies conducted with thin GaSe films showed that the band gap width is Eg=2.02 eV (Fig. 10).

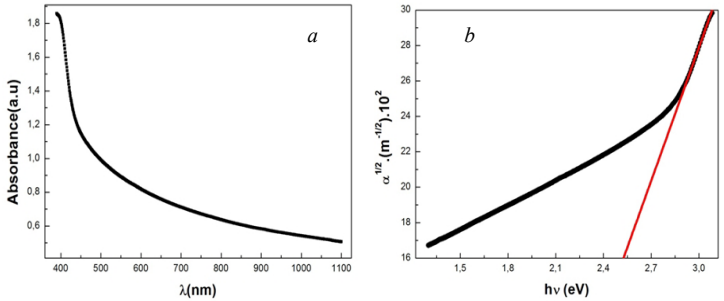


Fig. 9. a-absorption spectrum of GaS, b-dependence of $\alpha^{1/2} \sim f(h\nu)$.

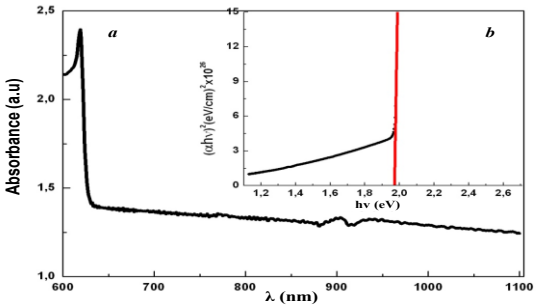


Fig.10. a-absorption spectrum of GaSe, b-dependence of $\alpha^{2} \sim f(h\nu)$.

Comparison of the absorption spectra of GaSe with the luminescence spectra suggests that the recombination radiation detected in GaSe under single-photon excitation with a maximum of

λ=607 nm is due to the band-to-band edge radiation, while the radiation with a maximum of λ=760 nm is associated with deep impurity levels. It should be noted that the intense emission line with a wavelength of 490 nm (ħω=2.53 eV) is associated with indirect transitions at the fundamental absorption edge. This is also evidenced by the data we obtained from the absorption spectrum of GaS. The weak high-energy emission line with an energy of ħω=3.00 eV is due to direct optical transitions.

Figure 11 shows the emission spectra of the GaS-GaSe heterostructure excited by the second harmonic of the Nd:YAG laser (ħω=2.34 eV). As can be seen from the figure, four maxima with wavelengths of 415 nm, 490 nm, 607 nm and 760 nm are observed in the luminescence spectra of the GaS-GaSe heterostructure. Since the laser radiation energy is less than the GaS band gap ($\hbar\omega<E_g$), it can be argued that the emission lines with maxima at 415 nm and 490 nm are due to two-photon excitation. The longest-wavelength maxima at 607 nm and 760 nm are due to single-photon excitation, since the laser radiation energy is greater than the GaS band gap ($\hbar\omega>E_g$).

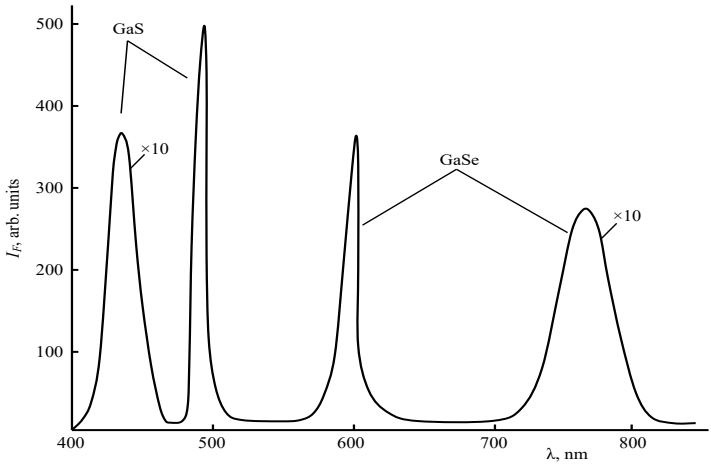


Fig.11. Emission spectrum of the GaS-GaSe heterostructure excited by the second harmonic of a Nd:YAG laser (ħω=2.34 eV).

As can be seen from Fig. 11, the intensity of the emission lines

in GaS associated with indirect optical transitions is one order of magnitude higher than the intensity of the emission lines associated with direct optical transitions. In our opinion, this is due to the self-absorption process, which is often encountered in semiconductors with indirect forbidden zones.[6]

With three-photon excitation of GaS by the first harmonic of a Nd:YAG laser, with a quantum energy of ħω=1.17 eV, only characteristic emission with a maximum of λ=490 nm is observed. It is not surprising that with 2- and 3-photon excitation, the same emission line with a maximum of λ=490 nm is observed. This is because if the process of generation of nonequilibrium carriers depends only on the frequency and intensity of laser radiation, then further processes of carrier motion and recombination in most cases are practically independent of the radiation by which these carriers were released.

It is known that the probability of a single-photon process is proportional to the first power of the laser radiation intensity

$$W^{(1)} = \sigma^{(1)}(\omega)I \qquad (11)$$

where $\sigma^{(1)}(\omega)$ is the effective cross-section, I is the intensity of the laser radiation.

Unlike single-photon processes, the probability of multiphoton processes depends on the radiation intensity nonlinearly (power law)

$$W^{(k)} = \sigma^{(k)}(\omega)I^{(k)} \qquad (12)$$

where k is the number of photons participating in the multiphoton process.

Therefore, the luminescence intensity with three-photon excitation should be much lower than with two-photon, which is

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[6] Салманов, В.М. Фотолюминесценция гетероструктур GaS-GaSe при двух и трехфотонном возбуждении лазерным излучением / А.Г.Гусейнов, Р.М.Мамедов [и др.] // Известия ВУЗ-ов, Физика, Томск, – 2022, – 65(9), – с. 54-59.

observed in the experiment. In addition, the half-width of the emission line with three-photon absorption is 2 times greater than with two-photon and is 60 nm. The dependence of the luminescence intensity on the excitation intensity is of the $I_{\text{lum}} = I_{\text{las}}^3$.

Thus, the appearance of luminescence upon excitation by laser light with a quantum energy of ħω=1.17 eV, 3 times smaller than the band gap of the substance under study, and the dependence of luminescence on the excitation intensity indicate the presence of a three-photon absorption process in GaS. The emission line with a maximum of λ=607 nm, arising during two-photon excitation in GaSe is identical to that detected during single-photon excitation. However, the emission intensity is much weaker than during single-photon excitation. The dependence of the luminescence intensity on the excitation intensity is the same as during two-photon excitation of GaS, and is quadratic. According to the data of the work, by measuring the concentration of carriers created during two-photon excitation, it can be estimated that at laser light intensities of I_1=10 MW/cm^2, the three-quantum absorption process creates $5 \cdot 10^{12}$ cm^{-3} carriers.

The fourth chapter of the dissertation examines nonequilibrium electronic processes occurring in semiconductor compounds A^{I}, B^{III} and C^{VI} under laser excitation.

Due to the specific layered structure, GaSe crystals have a strong anisotropy of mobility caused by the presence of an energy barrier in the direction perpendicular to the layers (axis $\vec{c}$). This property of the crystal is usually studied using electrical measurements. This method is often unsuitable due to the high resistance of the compounds under consideration and does not allow one to determine the nature of the barriers. Optical and luminescent methods are also unacceptable, since the presence of layers does not allow one to carry out optical measurements along the layers, and the nature of individual emission lines observed in the photoluminescence spectra cannot always be unambiguously interpreted. A method for studying the photoconductivity of layered crystals at high levels of optical excitation allows one to eliminate such disadvantages. In this case, the configuration of the contacts allows one to direct the external

electric field applied to the sample along and across the layers. On the other hand, using a high level of optical excitation, when a high concentration of electron-hole pairs is generated, allows one to control the barrier height by light doping up to the degeneracy of the semiconductors.

We have investigated the photoconductivity features of GaSe at high optical excitation levels. The studied GaSe single crystals were grown by the Bridgman method and had p-type conductivity. Current contacts had different locations on the surface of a rectangular sample, which allow measuring the photoconductivity in the longitudinal ($\vec{E} // \vec{c}$) and transverse ($\vec{E} \perp \vec{c}$) directions relative to the $\vec{c}$ axis. The specific resistance of the samples varied in the range of 10^3-10^5 Ohm·cm. The mobility and concentration of carriers determined by Hall measurements were equal to 20 $cm^2/V \cdot s$ and $1 \cdot 10^{13} \div 4 \cdot 10^{14}$ cm^{-3}, respectively. GaSe crystals were irradiated with pulses of a liquid laser (active medium - rhodamine 6G), which was pumped by a nitrogen laser. The range of wavelength tuning of the laser radiation (594 ÷ 643) nm completely covered the fundamental edge of the GaSe absorption band (E_g = 2.02 eV at T = 300 K). The pulse power was 120 kW with a duration of 3 ns, and the pulse repetition frequency was 20 Hz. The intensity of laser radiation was varied using calibrated neutral filters.

The lux-ampere characteristics of photoconductivity (LAC), taken at different excitation wavelengths corresponding to the photoconductivity maxima, are shown in Figure 12. Curves a and b correspond to the case when the applied electric field is directed perpendicularly and parallel to the $\vec{c}$ axis. As can be seen from the figure, in case $\vec{E} \perp \vec{c}$ (curve a), a linear dependence of the photocurrent $\Delta\sigma$ on the excitation intensity *I* is observed, and in case $\vec{E} // \vec{c}$ (curve b), in a certain range of intensities, a stronger dependence $E\Delta\sigma \sim I^{2.5}$ occurs, where $\Delta\sigma$ is the value of photoconductivity, *I* is the intensity of the incident light.

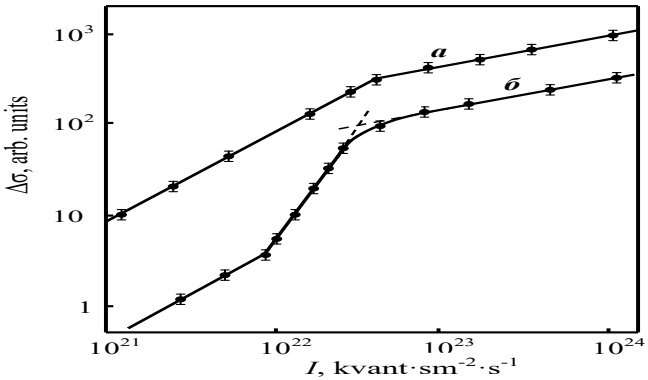

Fig. 12. Dependence of the photoconductivity of GaSe crystals on the intensity of laser radiation with a wavelength of λ1 = 620 nm ($\vec{E} \perp \vec{c}$, curve a), λ2 = 630 nm ($\vec{E} // \vec{c}$, curve b).

The lux-ampere characteristic of photoconductivity can be explained by the influence of the energy barrier on the mobility of nonequilibrium carriers. Indeed, in the presence of a barrier, the photocurrent is determined by those carriers that are activated at the height of the equilibrium barrier ΔE_0. With an increase in the excitation level, the concentration of nonequilibrium carriers Δn grows and upon reaching a certain concentration Δn determined by the condition $\Delta n \approx N_c$ (N_c is the effective density of states), degeneration of the semiconductor begins due to light doping. With a further increase in the excitation level, a shift occurs within the Fermi quasi-level bands, which in turn reduces the height of the interlayer barrier ΔE. In this case, photoconductivity can be described as:

$$\Delta\sigma(I) = e\mu_0 \Delta n(I) \exp(-\frac{\Delta E(I)}{kT} = e\mu_0 \Delta n(I) \exp(-\frac{\Delta E_0 - \xi_n(I)}{kT}, \quad (13)$$

where μ_0 is the mobility in the absence of a barrier, ξ_n is the quasi-Fermi level, measured from the bottom of the conduction band.

Calculations show that in the specified region the LAC is well described by formula (13). Since the length of this region is

determined by condition $0 \le \xi_n \le \Delta E_0$, the LAC of photoconductivity allows one to determine the equilibrium barrier height ΔE_0 by the formula:

$$\Delta E_0 = kT ln\left[\frac{\Delta\sigma_2}{\Delta\sigma_1}\left(\frac{I_1}{I_2}\right)^{\alpha}\right], \qquad (14)$$

where $\Delta\sigma_1$ and $\Delta\sigma_2$ are the photoconductivity values, respectively, at intensities I_1 and I_2, α is the index of the dependence $\Delta n \sim I\alpha$, which is equal to unity in the case of $t_{imp} < p\ \tau$ ($t_{imp.}$ is the pulse duration, τ is the carrier lifetime). Estimates have shown that $\Delta E_0 \approx 50$ meV. Since these barriers are not removed by screening nonequilibrium carriers up to degeneracy ($\Delta n \sim 10^{18}$ cm^{-3}), it can be assumed that they are not associated with a non-uniform distribution of impurities or defects. In particular, they can be caused by a consequence of the disorder of the arrangement of layers relative to each other, which occurs in layered materials.

We have already noted that the observed features in the transmission and luminescence spectra of GaSe and InSe crystals can be explained by the interaction of excitons at high excitation intensities and screening of the Coulomb interaction by free carriers generated by laser light. Of particular interest is the detection of exciton interaction in the study of photoconductivity of nonequilibrium current carriers. The generation of high concentrations of nonequilibrium carriers by laser excitation should also affect the exciton photoconductivity of the crystals studied.

Figure 13a shows the photoconductivity spectra ($\Delta\sigma$) of GaSe crystals at different excitation intensities (I_0). At low pump powers, the well-known exciton photoconductivity with a maximum at a photon energy of $\hbar\omega \approx 2.00$ eV is observed. With increasing pump power, the concentration of nonequilibrium carriers increases, which leads to an increase in photoconductivity in the exciton region (curve 2). A further increase in excitation intensity leads to broadening and disappearance of the exciton peak (curves 3 and 4), but the photoconductivity beyond the fundamental absorption edge increases sharply.

Figure 13b shows an oscillogram of the photocurrent pulse upon

excitation of GaSe crystals by the 2nd harmonic of Nd:YAG laser radiation. As can be seen from the figure, two recombination channels are observed: fast τ_1=1.7 μs and slow τ_2=20 ms. The fast recombination channel is associated with the recombination of free excitons, and the slow section is probably due to an impurity center.

In our opinion, the observed features in the transmission and luminescence spectra of GaSe crystals can be explained by the interaction of excitons at high excitation intensities and screening of the Coulomb interaction by free carriers generated by laser light. Indeed, during resonant excitation of GaSe crystals by laser light, electrons and holes are bound into excitons. Subsequently, with an increase in the excitation intensity, the exciton density increases, and when it reaches a certain critical value (Mott transition), interaction between excitons occurs, which leads to the decay of excitons and the formation of free electron-hole pairs.

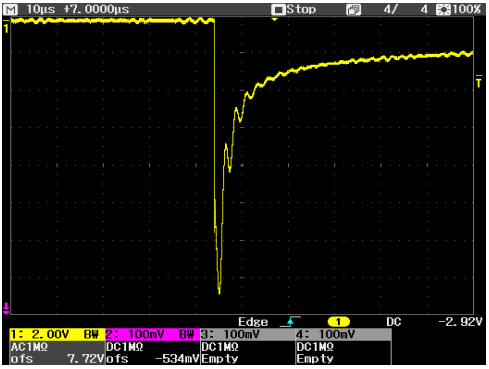

Fig. 13. a- Photoconductivity spectra of GaSe crystals at different excitation intensities, MW/cm^2: 1-0.46, 2-2.28, 3-6.14, 4-12; b- Oscillogram of the photocurrent pulse during excitation of GaSe crystals by the 2nd harmonic of the Nd:YAG laser.

In this work we have experimentally studied the absorption of IR light by free carriers created by laser radiation in InSe crystals. A pulsed Nd:YAG laser was used to excite nonequilibrium carriers. The light of a 400 W quartz halogen incandescent lamp passed through a silicon filter was used as a source of infrared radiation to study the

absorption on free carriers. Light with wavelengths λ=(1.2-2.5) μm passed through the sample and filters cutting edge and laser radiation, was focused on a fast germanium photodiode. Due to the absorption of light by nonequilibrium electrons and holes, pulse modulation of the probing IR light occurred and the relaxation of this pulse reflected the extinction of carriers in the crystal over time. The photocurrent relaxation curves were observed on the screen of a storage oscilloscope (TektronixTDS – 2012C). The broadband amplification path made it possible to observe pulses of both polarities with fronts from 0.15 to 20 μs without distortion.

Fig. 14a shows the dependence of the IR light modulation signal (ΔM) on the excitation intensity of laser light (*I*).

As can be seen from the figure, a linear signal with subsequent saturation is observed. The change in the intensity of the probing IR light transmitted through the sample ΔM(t) (the magnitude of the modulation signal) can be written as follows:

$$\Delta M(t) = M_{max}\left[1 - exp(-\sigma_{n+p}\int_0^d \Delta n(x,t)dx)\right] \qquad (15)$$

where σ_{n+p} is the total value of the cross-section of light absorption by nonequilibrium electrons and holes, M_{max} is the value of the modulation signal at a high excitation level, $\Delta n(x,t)$ is the concentration of nonequilibrium pairs at a depth x from the sample surface.

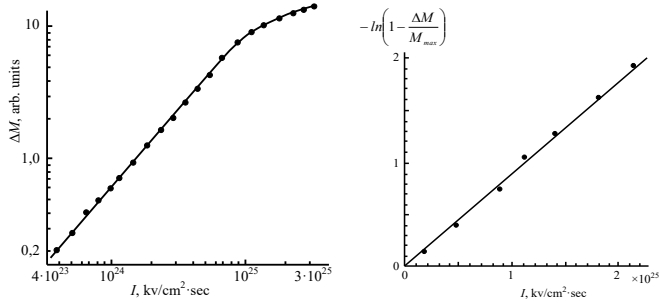

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Fig.14. (a) Dependence of the absorption modulation signal in InSe on

the excitation intensity I; (b) Dependence of $ln(1-\frac{\Delta M}{M_{max}})$ on the excitation intensity I.

To determine the cross-section of light absorption by nonequilibrium carriers σ_{n+p}, the pulse amplitude ΔM(t) was changed. The dependence of $ln(1-\frac{\Delta M}{M_{max}})$ on the excitation intensity *I* is shown in Fig. 14, b. The cross-section of absorption of probing light by nonequilibrium carriers $\sigma_{n+p} = 2{,}4 \cdot 10^{-18}$ cm^2 was determined from the slope of this dependence.

Estimates of the concentration values showed that at high excitation intensities, the concentration of nonequilibrium carriers reaches a value of ~ $6 \cdot 10^{19}$ cm^{-3} (R~0.3; I≈10^{25} quantum/cm^{2}s; t_u = 10 ns; α=$2 \cdot 10^3$ cm^{-1}. This value is several orders of magnitude higher than the concentration of equilibrium carriers and the concentration of impurity levels in InSe. Therefore, at a high level of optical excitation, the predominant type of recombination of nonequilibrium electrons in indium selenide is bipolar interband recombination. This paper presents the results of a study of the drift capacitance in 2D InSe crystals. A 1.3 μm thick InSe film was irradiated with a 12 ns laser pulse with a wavelength of 535 nm. As a result, an equal number of nonequilibrium electrons and holes were generated. High-mobility electrons quickly leave the film drain. After the illumination ceases, some of the nonequilibrium electrons in the middle of the film holes recombine with electrons and a high-resistance region of neutral atoms is formed.

Thus, after the termination of optical excitation, along with the usual relaxation of the photocurrent caused by the recombination of nonequilibrium charge carriers, the drift capacitance formed by the region of charged positive ions in the near-anode region of the film and cathode electrons is also discharged.

Therefore, the relaxation process can be considered as a dissipative flow of the relaxation type and the Maxwell-Cattaneo

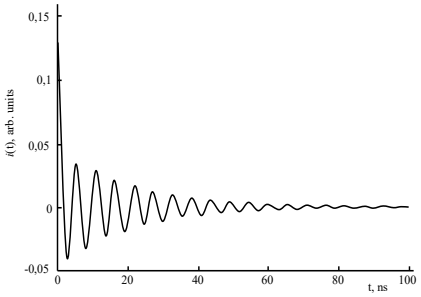
equation can be applied to it:

$$j+\tau\frac{dj}{dt}=-\sigma\nabla\varphi, \qquad (16)$$

where j is the current density, τ is the photocurrent relaxation time, is the film conductivity, and $\varphi=\frac{q}{C}$ is the potential drift capacity. The kinetics of the photocurrent can be written as:

$$i=Ae^{-\frac{t}{\tau}}-A'e^{-\delta t}\cos\omega t, \qquad (17)$$

where, $A=\frac{\upsilon q_0}{\ell}$, $A'=\frac{q'_0\sigma S}{C\ell}$. When choosing the values of the constant A = 0.08; A' = 0.05; τ = 0.5 ns; $\delta=0{,}05$ ns-1 and $\omega=20$ ns-1, the dependence $i(t)$, calculated according to formula (17), has the form shown in Fig. 15,a.



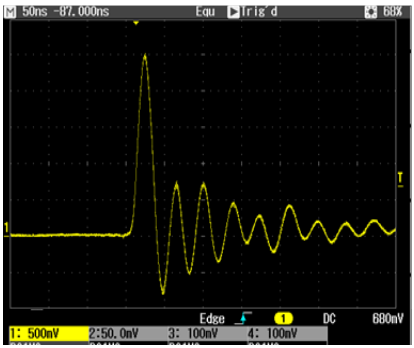


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Fig. 15. a-Calculated dependence of current on time using the Maxwell-Cattaneo equation. b- Experimental time dependence of relaxation current in ultrathin InSe films under the influence of pulsed laser radiation.

The kinetics of photocurrent in ultrathin InSe films under the action of pulsed laser radiation with a duration of 12 ns is shown in

Fig. 15, b. Comparing the calculated and experimental dependences of the relaxation current on time, we observe their good agreement. Thus, equation (17) can be used for mathematical modeling of the relaxation of current pulses in ultrathin two-dimensional crystals of the indium selenide type. In this case, we mean the need to take into account the properties of indium selenide. As noted above, the mobility of electrons in InSe nanolayers is many times greater than the mobility of holes. This feature is necessary for the appearance of drift capacitance in two-dimensional crystals.

The fifth chapter presents the experimental results of obtaining nanostructures based on GaSe and InSe crystals, analysis of the structure and studies of their electrical, optical, photoelectric and luminescent properties. Studies of quantum-size phenomena in poorly studied, and at the same time promising layered semiconductors of the A^3B^6 type, open up great prospects for designing new devices with a wide range of functional capabilities on their basis.

GaSe nanoparticles were obtained by chemical deposition (M-CBD). In this case, an important role is played by the manufacture of substrates, preparation of compositions and the process of obtaining itself. We chose glass and GaSe crystals as substrates. GaSe crystals were grown by the Bridgman method. The dimensions of the crystalline substrates were $10\times6\times0.5$ mm^3.

Thin GaSe films on a glass substrate were grown by hydrochemical deposition from a solution containing sodium selenosulfate (Na_2SeSO_3) and gallium chloride ($GaCl_3$). The initial raw materials were high-purity substances: Se, Ga, Na_2SO_3 and HCl. Initially, the compounds Na_2SeSO_3 and $GaCl_3$ were synthesized by the following reactions:

$$\begin{aligned} &Na_2SO_3 + Se \rightarrow Na_2SeSO_3, \\ &Ga + 3HCl \leftrightarrow GaCl_2 + \frac{3}{2}H_2, \end{aligned} \qquad (18)$$

then, aqueous solutions of sodium selenosulfate and gallium chloride were prepared in the ratio required to form GaSe, with a composition corresponding to the stoichiometric composition. In this solution, the

substrates were kept for one to ten minutes. Then, the growth of GaSe compound nanoparticles was carried out according to the following sequence: four containers with liquids were used. The first contained a gallium chloride solution, the second distilled water, the third a sodium selenosulfate solution, and the fourth, also distilled water. The substrates were kept in these containers successively for 20 seconds, 10 seconds, 15 seconds, and 10 seconds, respectively. This process was repeated 30 times in a row.

The internal structure and structure of the obtained samples were studied using X-ray diffraction (XRD), atomic force microscopy (AFM), energy dispersive X-ray spectroscopy (EDAX), and scanning electron microscopy (SEM). X-ray diffraction analysis showed that the nanoparticles belong to the β -modification of GaSe (a=3.75A^0, c=15.94A^0) with a hexagonal structure. The space symmetry group is D_{6h}^4.

Based on the X-ray diffraction patterns, the sizes of the obtained nanoparticles were calculated using the Debye-Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (19)$$

where D is the size of the nanoparticles, k = 0.9 is the line shape factor, β = 0.1355 is the full width at half maximum (FWHM), λ is the wavelength of the X-ray radiation, λ = 1.54 A^0, θ is the Bragg angle, cosθ = 0.99.

Estimates show that the sizes of GaSe nanoparticles are in the range of 4÷20 nm.

Images obtained using SEM show that the obtained substances consist of spherical nanocrystals with sizes of (7-20) nm, which are collected in a polydisperse form. The EDAX method showed that the ratio of gallium to selenium is Ga:Se=1:1, indicating that the composition of the substance is in a stoichiometric ratio (Fig. 16).

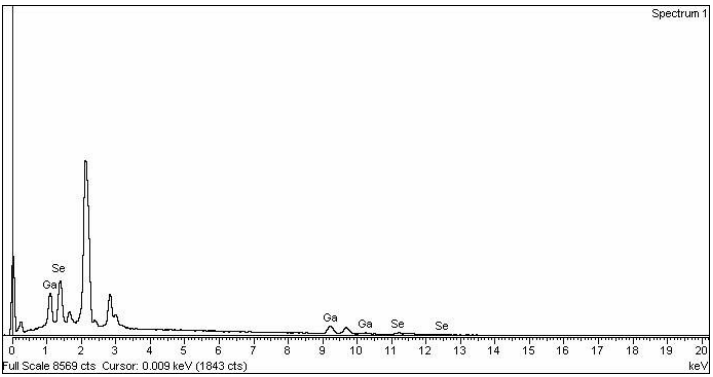

Fig.16. EDAX images of GaSe nanoparticles.

Fig. 17 (a) shows the absorption spectrum of GaSe nanoparticles on a glass substrate. Based on the spectral dependence, the width of the forbidden zone of the nanoparticles and the activation energies of the impurity levels located in the forbidden zone were determined. As can be seen from the figure, the absorption in the short-wave region corresponds to an energy of 3.69 eV. In our opinion, this value is equal to the width of the forbidden zone of the studied GaSe nanoparticles. In this case, the width of the forbidden zone of the nanoparticles turns out to be much larger than E_g for GaSe crystals. The values of Eg found by us for GaSe crystals turned out to be equal to E_g=1.98 eV.

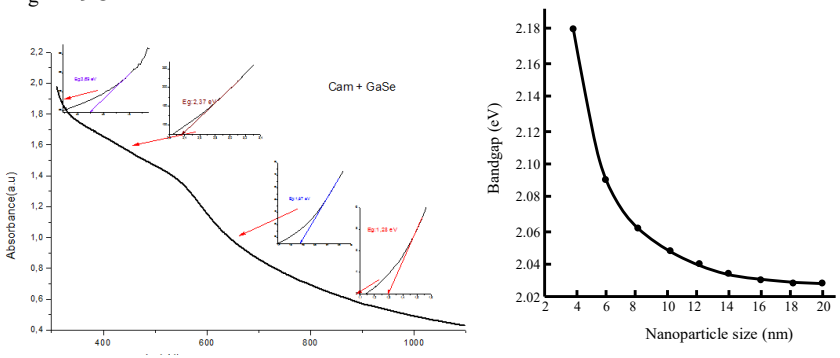

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Fig. 17. Absorption spectrum of GaSe nanoparticles on a glass substrate (a), Dependence of the GaSe band gap on the size of the nanoparticles (b).

It should be noted that the increase in the width of the forbidden zone of nanoparticles compared to a massive crystal is a characteristic feature of semiconductor nanoparticles. It is known that the width of the forbidden zone of nanoparticles depends on the width of the forbidden zone of the crystal (E_g), the reduced mass of the crystal under study (m_r) and the size of the nanoparticles (a):

$$E_{g(nano)} = E_{g(crystal)} + \frac{\hbar^2 \pi^2}{2 m_r a^2} \qquad (20)$$

Our assessments, taking into account the GaSe parameters, show that the calculated values of the width of the forbidden bands of the nanoparticles are in satisfactory agreement with the value found based on the absorption spectrum.

The peaks of 2.37 eV, 1.87 eV and 1.28 eV observed in the absorption spectrum of GaSe nanoparticles are apparently due to electron transitions from the capture centers located in the forbidden band to the conduction band, respectively.

Since GaSe has p-type conductivity, these localized centers act as acceptor levels and the dark conductivity is due to thermal activation of holes from these centers to the valence band. The distances of these levels from the valence band are $\Delta E_p = 2.41$ eV, 1.82 eV, 1.32 eV and 0.32 eV, respectively.

Fig. 17, b shows the dependence of the band gap of GaSe nanoparticles on the size of the nanoparticles. As can be seen from the figure, the quantum-size effect begins to significantly affect the band gap when the size of the nanoparticles becomes less than 10 nm.

This chapter also discusses the electrical and optical properties of InSe nanoparticles. InSe nanoparticles were also obtained by chemical deposition (M-CBD - chemical bath deposition method).

Fig. 18, a shows AFM images of InSe nanoparticles on a glass substrate. As can be seen from the figures, a homogeneous distribution of particles is not observed in the presented figures.

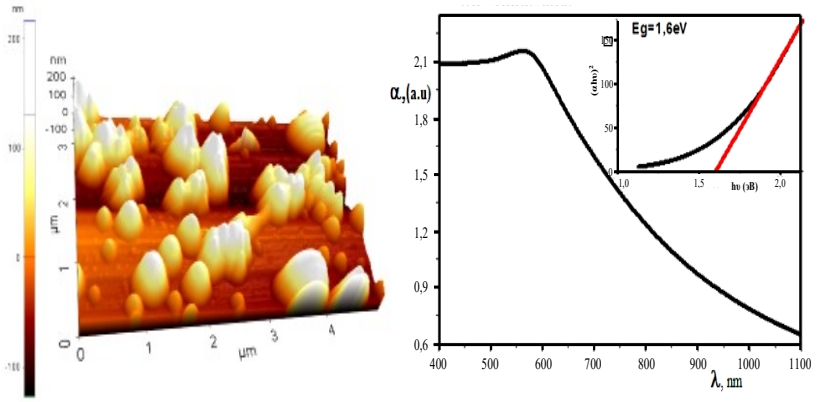

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Fig. 18. a-AFM images of InSe nanoparticles on a glass substrate, b-Absorption spectrum of InSe nanoparticles on a glass substrate.

Fig. 18b shows the absorption spectrum of InSe nanoparticles on a glass substrate. Based on the spectral dependence, the band gap width of InSe nanoparticles was determined. Considering that InSe is a direct-gap semiconductor, the band gap width of InSe nanoparticles was determined from the $\alpha^2 \sim f(h\nu)$ dependence, which turned out to be equal to 1.6 eV. This value of the band gap width of nanoparticles turns out to be much larger than E_g for InSe crystals ($E_g \sim 1.23$ eV).

The sixth chapter is devoted to the practical application of A^I, B^{III} and C^{VI} compounds. Our theoretical and experimental studies of nonlinear optical and nonequilibrium electronic processes in A^I, B^{III} and C^{VI} semiconductor compounds under laser excitation revealed several possibilities for using this class of substances in nonlinear optics and quantum electronics. The results obtained can be used in laser technology, laser ablation of solids, inversion of semiconductor conductivity, the effect of laser radiation on the structure of nanoparticles, solar energy converters based on nanostructures, optical laser light filters, high-speed nanosecond laser radiation detectors, a new method for producing ultrathin films, etc. All these studies were carried out using various gas, solid-state, liquid lasers and using modern methods for studying optical absorption, photoconductivity and luminescence using two-photon spectroscopy,

light distortion, etc.

One of the effective methods of controlling the properties of semiconductors is the method of laser processing, the use of which allows, depending on the relationship between the quantum energy $\hbar\omega$, the intensity of laser radiation I and the width of the forbidden zone E_g, to transform its surface $(\hbar\omega > E_g)$ or volume $(\hbar\omega < E_g)$ properties. The interactions of powerful laser radiation with various substances have various characters, which at present have not received an exhaustive explanation.

As the experimental results show, when n-InSe thin films are excited by a pulsed Nd:YAG laser with a wavelength of λ=1064 nm and a power of ~6 MW/cm^2, a change in the conductivity type is observed (Fig. 19). The section of the sample, which had n-type conductivity before laser irradiation, has p-type conductivity after irradiation. At the same time, a change is also observed in the current-voltage characteristic (CVC) of the studied samples. If before laser irradiation the CVC had a symmetrical linear characteristic, then after laser irradiation the CVC has a diode characteristic, the rectification coefficient at 2 V is ~$2\cdot10^2$. The mechanism of current flow through the p-n junction is of a recombination nature. Illumination of the samples with incandescent lamp light greatly enriches the region of the space charge of the p-n junction.

Analysis of the structure of InSe thin films showed that the composition of the film is uniform over the entire area of the film.

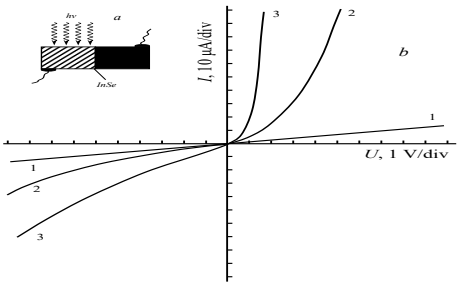
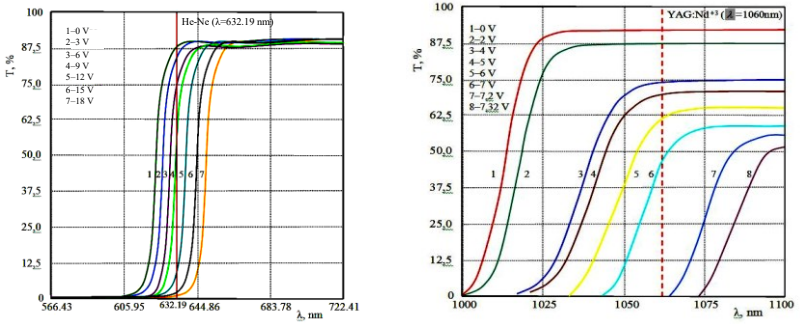


Fig. 19. Volt-ampere characteristics of InSe thin films before (1) and after (2) laser irradiation, (3) - current-voltage characteristics under illumination.

In our opinion, the inversion of the conductivity type in InSe thin films under the action of laser radiation can be caused by a local change in the dynamics of the behavior of crystal lattice defects due to heating, or as a result of light absorption in structural inhomogeneities.

The effect of the electric field and laser radiation on the absorption and luminescence spectra of GaSe and InSe thin films was also considered. Fig. 20,a shows the transmission spectra of GaSe at different values of the electric field applied to the sample. When a field is applied to the sample in the direction parallel to the optical axis $\vec{c}$, a shift of the absorption band edge to the long-wavelength region of the spectrum is observed. With an increase in the field strength to 20 V/cm, the shift of the absorption band edge is 50 nm. A similar shift in InSe samples with an applied electric field of 7.3 V/cm is 88 nm (20,b). The dependence of the magnitude of the absorption band edge shift ($\Delta\lambda$) on the applied electric field (E) for GaSe and InSe has a power-law character $\Delta\lambda \sim E^n$, where n= 2.1¸ 2.5.

Fig. 20 also shows the emission spectrum lines of the He-Ne laser (a) and Nd:YAG laser (b), respectively. As can be seen from the figures, when the absorption band edge in the GaSe and InSe thin films is shifted, the transmission spectra intersect the spectral line of the lasers, therefore, it is possible to control the intensity of the He-Ne laser and Nd:YAG laser radiation passing through the GaSe and InSe thin films, respectively, from the maximum permissible value down to zero, by changing the intensity of the corresponding field applied to the crystals.



a ***b***

Fig. 20. Transmission spectra of GaSe (a) and InSe (b) at different

values of the electric field applied to the sample.

The most probable mechanism for explaining the experimental results, in our opinion, may be associated with the Joule heat caused by the electric field and subsequent amplification of crystal lattice vibrations, leading to a shift of the absorption band edge. Estimates show that in a GaSe sample with a resistivity of ~10^3 Ohm×cm, under the action of an electric field of up to 85 V/cm, Joule heat of ≈1.9 W/cm^2 is released. This value is sufficient to heat the sample by 45-500 C. In InSe samples with a resistivity of ~10^2 Ohm×cm, under the action of an electric field of 50 V/cm, Joule heat of ~11.6 W/cm^2 is released, which heats the sample to 245 ^{0}C. The dependence of the shift value at ΔT=40 K on the resistance (R) of samples cut from different ingots also testifies in favor of the thermal mechanism of the absorption band edge shift (Dl). With decreasing resistance of the samples, the magnitude of the shift of the absorption band edge increases. Thus, the electrical heating of the samples stimulated by an external electric field leads to a shift of the absorption band edge to the long-wave region of the spectrum.

We have discovered, for the first time in InSe, ultrafast photocurrents at room temperature under the action of a Nd:YAG laser (Fig. 21, a). As can be seen from the figure, photocurrent generation continues during the action of the laser pulse, the rise and fall of the photosignal does not exceed 15 nanoseconds. The dark current is 6×10^{-6} A at an applied external voltage of ~1 V. The sensitivity of the sample was equal to 0.25 μA/μV at an incident radiation wavelength of λ=1060 nm. The dependence of the photocurrent on the applied voltage in the intensity range (1.42÷12) MW/cm^2 is linear, up to 25 V.

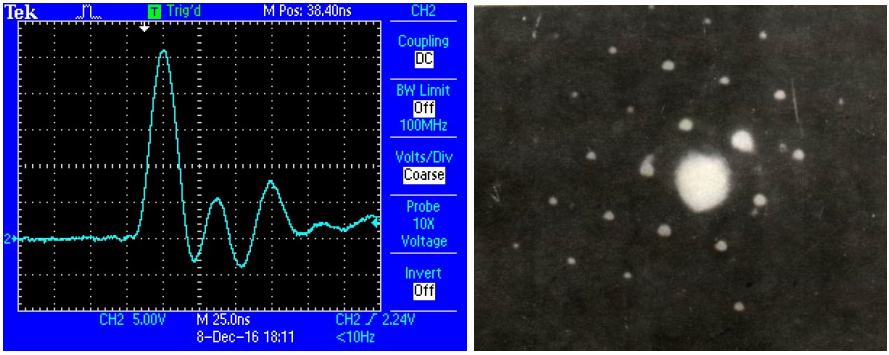


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Fig. 21. a-Oscillogram of photocurrent in InSe at excitation intensity of ~6 MW/cm^2, b-Electron diffraction patterns from InSe films deposited on a NaCl cleavage at ~300 ^{0}C after irradiation with a Nd:YAG laser.

In our opinion, the reason for the occurrence of ultrafast photocurrent generation is the presence of two types of centers in the forbidden zone of InSe crystals: sensing "r"-centers and fast "S"-type. The presence of r-centers in the forbidden zone of n–InSe at a distance of $E_{vr} \approx 0.25$ eV from the valence zone allows electrons to be transferred from r-centers to the conduction zone under the action of laser radiation with an energy of $\hbar\omega = 1{,}17$ eV. Electrons excited to the c-zone will recombine through S-centers, which causes the fast component of the photocurrent.

In conclusion, we note that the ultrafast photocurrents and intense radiation in the near IR region of the spectrum that we discovered at room temperature demonstrate the potential for using the InSe thin-layer structure for high-speed electronics and photonics technology.

In the dissertation, InSe thin films were obtained by pulsed laser irradiation. A ruby laser operating in the Q-switching mode was used as a radiation source. The particles evaporated under the action of laser radiation were placed on NaCl substrates at a temperature of 300 ^{0}C. Electron diffraction patterns of InSe thin films obtained under the action of laser radiation show good agreement between the parameters

of the obtained thin films and the initial material (Fig. 21, b).

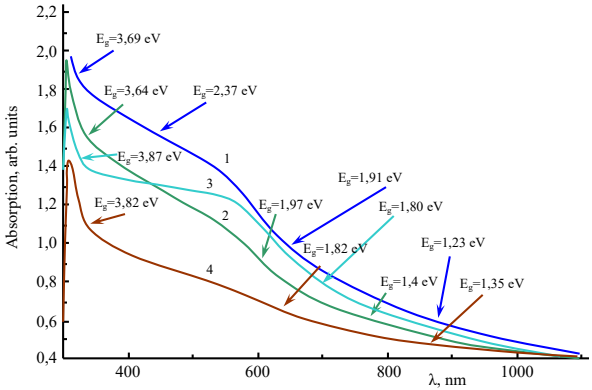

Fig.22. Optical absorption spectra of nanoparticles $GaSe\langle Dy, Er, Nd\rangle$ on a glass substrate: 1 – $GaSe$; 2 – $GaSe\langle Er\rangle$; 3 – $GaSe\langle Nd\rangle$; 4 – $GaSe\langle Dy\rangle$.

GaSe nanoparticles doped with rare earth elements Nd, Er and Dy were obtained using the SILAR method. Fig. 22 shows the optical absorption spectra of GaSe<Dy, Er, Nd> nanoparticles. As can be seen from the figure, in addition to the main absorption edge (~600 nm), the absorption spectrum of GaSe nanoparticles extends into the short-wave region up to ~330 nm.

Comparison of the absorption spectrum of GaSe nanoparticles with its energy diagram suggests that in addition to the transition centered in the Brillouin zone at the main absorption edge $\Gamma_2^- \rightarrow \Gamma_3^-$ in the short-wave region of the spectrum, there is also a $M_2^- \rightarrow M_1^+$ transition (~3.69 eV). In our opinion, the features observed in the absorption spectrum of GaSe<Dy,Er,Nd> nanoparticles are associated with electron transitions created by rare earth elements Dy, Er, Nd in the GaSe crystal lattice.

The luminescence spectrum of GaSe nanoparticles differs sharply from the luminescence spectrum observed in its crystals (Fig. 23). If the luminescence spectrum of GaSe crystals is mainly associated with exciton transitions present at the absorption edge and

impurity transitions in the long-wave region, then the luminescence spectrum of GaSe nanoparticles has a fine structure: there are two main maxima in the visible region and a number of weak maxima. The same pattern is observed in the luminescence spectra of GaSe<Dy,Er,Nd> nanoparticles (Table 1).

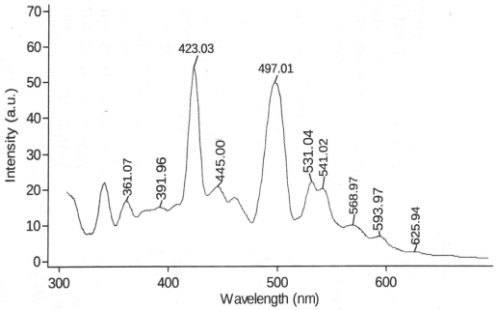

Fig.23. Luminescence spectrum of GaSe nanoparticles on a glass substrate.

Table 1

Electronic transitions observed in GaSe nanoparticles doped with rare earth elements Dy, Er, Nd

GaSe $\lambda(nm)$	*GaSe (Er)* $\lambda(nm)$	*GaSe (Nd)* $\lambda(nm)$	*GaSe (Dy)* $\lambda(nm)$
361.07	362.00	361.07	361.07
391.96	393.03	391.06	423.03
423.03	423.03	423.03	445.00
445.00	446.06	446.06	461.06
497.01	461.96	498.95	495.97
531.04	498.95	531.04	531.04
541.02	531.04	541.02	541.02
568.97	541.02	570.00	566.02
593.07	568.97	592.05	593.97
625.04	592.94		625.94
			658.98

We have proposed a new method for obtaining an ultra-thin film of indium selenide. Using the method of thermal evaporation of indium selenide in a vacuum and deposition of vapor on the surface of the liquid, ultra-thin films of InSe were obtained. The method is based on the process of thermal evaporation of the InSe compound and deposition of vapor on the free surface of the liquid in a vacuum.

Evaporation of polycrystalline indium selenide crushed to a size of 10-20 μm was carried out in a glass-graphite crucible preheated to a temperature exceeding the melting point of InSe by 20±3 K. Crushed InSe dust particles were fed into the crucible by a special device that allowed controlling the amount of the fed mass. The substrate, located at a height of 15 cm from the crucible, is a multilayer structure. The upper layer is glass, 0.5 mm below there is a metal grid filled with liquid. Due to wettability with the grid, the thick liquid almost uniformly covers the lower side of the grid. The temperature of the liquid was controlled by thin thermocouples attached to the metal grid. Oil was used as a liquid, which is chemically neutral to InSe vapors and has a low vapor pressure in a vacuum. After deposition of InSe vapor on the liquid surface, the multilayer substrate is turned upside down and the grid with the formed indium selenide film is separated from the liquid.

The remaining liquid was removed by holding the grids with the InSe thin film in vacuum at 415 K for one hour. The grid material was a copper-zinc alloy thread with a diameter of 200 μm. The compositional analysis of the substance deposited on the metal grid and its morphological structure were studied using a scanning electron microscope. It should be noted that when the electron beam hits the InSe film on the grid window, the film is destroyed. Therefore, we have not yet been able to carry out a structural analysis of the free film. However, the film is ideally homogeneous, individual components of indium selenide are uniformly distributed over the entire area of the film. Numerous estimates of the film thickness showed that it is ~1.8 μm. The mass ratio of indium and selenium in the thin film was determined from the EDAX spectrum. The ratio of the atomic masses of indium and selenium coincides well with the ratio of the percentage masses of the thin film components presented

in the right corner of the histogram. Therefore, it can be verified that the composition of the obtained thin film corresponds to the stoichiometric formula of InSe.

The features of photoconductivity and luminescence of CdS thin films and $Cd_{1-x}Zn_xS$ solid solutions obtained by chemical pulverization with subsequent pyrolysis under laser excitation were experimentally investigated. Pulsed liquid (473 – 547) nm and nitrogen (337 nm) lasers were used as radiation sources. The photoconductivity and photoluminescence spectra of $Cd_{1-x}Zn_xS$ thin films were experimentally investigated depending on the composition x at different excitation intensities and the relaxation curves of nonequilibrium photoconductivity. It was shown that the observed features in the photoconductivity and photoluminescence spectra of $Cd_{1-x}Zn_xS$ thin films are due to direct band-to-band transitions. At high intensities of optical excitation in CdS thin films, light amplification is observed.

We have fabricated multilayer Si-$ZnO-CuInSe_2$-ZnO heterostructures on the surface of monocrystalline silicon substrates using vacuum deposition. The volt-ampere, volt-capacitive and spectral distributions of heterojunctions in the $p-CuInSe_2-n-ZnO$ transition region have been investigated. The parameters of the heterojunctions have been estimated and it has been shown that the heterojunctions can be used as solar energy converters.

CONCLUSION

1. Optically homogeneous single crystals, thin films and nanostructures of binary and ternary compounds based on the elements A^{I}, B^{III} and C^{VI} were obtained by the Bridgman method, flash thermal evaporation in vacuum and electrochemical deposition, respectively. Structural and elemental analyses of the obtained thin films and nanoparticles were carried out using X-ray diffraction (XRD), atomic force microscope (AFM), energy dispersive X-ray spectroscopy (EDAX) and scanning electron microscope (SEM).
2. The nonlinear absorption in InSe crystals in the exciton resonance

region, detected at high levels of optical excitation, is due to the screening of the Coulomb interaction by free carriers and the exciton-exciton interaction. The density of electron-hole pairs generated by laser light in InSe (~ $3x10^{19}$ cm^{-3}) significantly exceeds the density required for the Mott transition in these crystals (~ $2.5x10^{16}$ cm^{-3}).

3. The change in the refractive index in thin GaSe films at high optical excitation intensities and the observed shift of the absorption band edge to the low-energy region of the spectrum are associated with nonradiative recombination of nonequilibrium electron-hole pairs generated by laser light.

4. Filling of energy bands at high levels of optical excitation of GaSe leads to the bleaching of the absorption band edge, with its simultaneous shift to the high-energy region of the spectrum. The observed effect of filling of bands allows to create a semiconductor laser based on thin GaSe films.

5. At high intensities of laser excitation of InSe crystals, the effect of thermal nonlinearity occurs, as a result of which the refractive index changes and the medium behaves as a collecting or diverging lens. It is shown that thermal nonlinearity has a long response time, determined by the time required to cool the crystal. This slow response helps to distinguish thermally induced nonlinearities from optical nonlinearities of electronic origin.

6. The emission bands revealed in the photoluminescence spectra of $Cu_3In_5S_9$ crystals under laser excitation are due to the presence of levels in the forbidden zone of the crystal, caused by vacancies in the nodes of the anion and cation sublattice.

7. Two- and three-photon absorption was detected in GaS and $Cu_3Ga_5Se_9$ crystals at high optical excitation intensities. The two-photon absorption coefficient in GaS was found to be equal to $7 \cdot 10^{-3}$ cm^{-1} at a light intensity of $I_0=1 \cdot 10^{25}$ quan/$cm^2 \cdot$sec. The ratio of the two-photon absorption coefficient to the three-photon absorption coefficient in $Cu_3Ga_5Se_9$ was found to be of the order of 10^4.

8. A new method for determining the composition and energy parameters of epitaxial semiconductor layers with a graded-gap structure is proposed using GaS-GaSe as an example. With two- and three-photon excitation of the GaS-GaSe heterostructure by laser

radiation, the composition, the value of the forbidden zone, the thickness of the layers, the concentration of deep and shallow impurities that determine the nature of recombination processes and, consequently, the efficiency of the structures being implemented are determined from the interpretation of the photoluminescence spectra.

9. A method for determining the effective cross-section of light absorption by nonequilibrium charge carriers in InSe generated by laser light, $\sigma_{n+p} = 2{,}4 \cdot 10^{-18}$ cm^2, is proposed. The presence of a rapid decline in the pulse relaxation curve allows InSe crystals to be proposed as a detector for recording short laser pulses operating in the IR region of the spectrum.

10. The ultrafast photocurrents detected in the thin-layer structure of InSe under laser excitation are due to the presence of a fast recombination channel with a large capture cross-section in this substance.

11. Laser radiation attenuators have been manufactured that are capable of reducing the radiation intensity of various lasers (He-Ne, YAG:Nd^{+3}, liquid lasers) by more than two orders of magnitude, and can also be used as cutoff light filters. The physical basis of laser radiation attenuators operating in the visible and near infrared spectral regions is associated with the effect of shifting the edge of the absorption band of GaSe and InSe crystals under the influence of an electric field.

12. Thin InSe films were obtained using ruby pulsed laser irradiation. Electron diffraction patterns of thin InSe films obtained under the influence of laser radiation show good agreement between the parameters of the obtained thin films and the initial material. It is shown that the inversion of the conductivity type in thin InSe and $AgIn_5S_8$ films under the influence of laser radiation can be caused either by a local change in the dynamics of the behavior of crystal lattice defects due to heating, or as a result of light absorption in structural inhomogeneities.

13. For the first time, a technology for growing ultra-thin InSe films by thermal evaporation and vapor deposition on the surface of the liquid phase has been developed. The composition and thickness of the resulting films have been determined using EDAX and SEM

methods.

14. The occurrence of drift capacitance in 2D thin InSe films has been detected. It has been shown that after optical excitation of the film by a light pulse with a duration of tens of nanoseconds, along with the usual relaxation of the photocurrent caused by the recombination of nonequilibrium charge carriers, a discharge of the drift capacitance occurs. Therefore, the relaxation process can be considered as a dissipative flow of the relaxation type and the Maxwell-Cattaneo equations can be applied to it

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