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SPECTRAL PHOTORESISTIVE FIELD EFFECT IN γ -IRRADIATED LAYERED CRYSTALS GaS AND GaS <Yb>

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Abstract: The effect of the surface electric field on the edge photoconductivity in undoped and ytterbium-doped ($N_{Yb} \sim 10^{18} \text{ cm}^{-3}$) layered GaS crystals at $T = 77 \text{ K}$ and irradiated with γ rays was investigated. It was found that the photoconductivity of layered crystals in the region of the absorption edge caused by the charge exchange of surface levels is formed as a result of electric smoothing of the potential fluctuations of the surface energy bands. The degree of smoothing of the surface bending of the zones depends on the dose of γ -irradiation, the concentration of impurity atoms, and also on the magnitude and direction of the transverse electric field.

Key words: edge photoconductivity, electric field, irradiation, gamma quanta, layered semiconductors, exciton, near-surface centers

1. Introduction

Layered semiconductors of the type $A^{III}B^{VI}$, in particular, gallium monosulfide, have high photosensitivity in the IR and UV spectral regions and exhibit high radiation resistance to radiation [1-8]. Interest in these compounds is caused by the peculiarity of the crystal structure associated with anisotropy and leading to the manifestation of a number of interesting properties. In particular, the anisotropic structure of gallium monosulfide [9] makes it possible to obtain sufficiently perfect faces with a sufficiently low density of surface states, which is important for achieving high-quality heterojunctions.

The large value of the absorption coefficient in the maxima of the exciton lines of $A^{III}B^{VI}$ type compounds ($\sim 10^5 \text{ cm}^{-1}$) leads to the fact that the state of the surface and near-surface region (presence of impurities and defects on the surface, high electric fields) should have a significant effect on photoconductivity processes (PP) involving excitons [10–11]. The optical and photoelectric properties of layered $A^{III}B^{VI}$ semiconductors were studied in detail in [3, 4, 12]. It is shown that the shift of the fundamental absorption edge in strong fields is due to the decay of excitons. In [7], the contribution to the PP of the dissociation of electron-hole pairs was investigated. It was found that during the formation of the PP near the edge of the main absorption band, the ionization of excitons trapped by deep traps and their subsequent ionization contributes. Along with the above effects, such phenomena as volume and surface effects, ionization of surface centers, as well as changes in carrier mobility in an electric field can influence the formation of the spectra of the phase transitions of layered crystals.

An effective method of changing the state of a surface was its bombardment with γ -quanta [13]. The depth of penetration of γ -quanta is comparable to the magnitude of the return light absorption coefficient ($\sim 10^2 \text{ nm}$) and leads to the desorption of gases from the surface and the reloading of the surface and near-surface centers. This factor is decisive in many processes occurring near the surface of the crystal. Therefore, by studying the influence of external influences, including the electric field, on the edge phase transition of a defective semiconductor, one can establish the role of surface inhomogeneity in the formation of photoconductivity.

This paper presents the results of a study of the influence of a strong surface electric field on the edge photoconductivity in undoped and ytterbium-doped ($N_{Yb} \sim 10^{18} \text{ cm}^{-3}$) layered GaS crystals at $T = 77 \text{ K}$ irradiated with γ - rays.

2. Experimental technique

Single crystals of p-GaS were grown by the method of directional melt crystallization (a vertical version of the Bridgman method). When growing GaS, an excess of sulfur (1.5%) was used to determine the possibility of filling vacancies with sulfur atoms. The specific resistance of the obtained samples along and perpendicular to the axis of the spire at room temperature was $2 \cdot 10^9$ and $3 \cdot 10^7 \text{ Ohm}\cdot\text{cm}$, respectively. The doping of Yb was carried out in the process of crystal growth, and the concentration of Yb in crystals was $N_{Yb} \sim 10^{18} \text{ cm}^{-3}$. To create ohmic contacts, indium was used as a material, which was smelted on the surface of gallium sulfide at a temperature of 150°C . The samples were irradiated with γ -quanta on a Co^{60} installation at 300K . The irradiation crystals were cooled with liquid nitrogen vapor, and their temperature did not rise above 290K .

The spectra of the PP samples of single-crystal p-GaS plates $50\text{--}100 \mu\text{m}$ thick were measured in different cells at different electric fields. The voltage applied to the samples from the direct current source was $\sim 100 \text{ V}$, the electric field was directed to $E_n \parallel c$, c -where is the crystal axis.

The PP spectra were measured in the wavelength range of $0.4\text{--}0.6 \mu\text{m}$ when the samples were illuminated with monochromatic radiation in the constant electric field mode. The spectra of the PP were recorded using an electrometric amplifier of the type B7-30. A halogen lamp was used as a light source using a monochromator of the type MS3504i with a resolution of $2.6 \text{ nm} / \text{mm}$. All spectra were normalized relative to the number of incident photons. To determine the role of the surface electric field in the formation of the edge spectra of phase transitions of crystals, the technique described in [14] was used. A sample with the above thickness was placed between the capacitor plates. The field potential (U_n) in the cell was varied by changing the voltage from the power source (Keithley-248/E). The direction of the electric field between the plates was changed by changing the polarity of the electrical contacts in the cell. Photoexcitation was carried out with focused radiation from a low-power halogen lamp on the side of the capacitor control plate, which is a semitransparent layer of SnO_2 . The electric field applied to the sample surface (U_n) varied in the range of $10^2\text{--}10^5 \text{ V/cm}$. Microstructural and X-ray phase analyzes showed that the obtained crystals were homogeneous and did not contain crystalline inclusions [13].

3. Results and its discussion

The spectral dependences of the edge photoconductivity of the obtained p-GaS crystals, depending on the magnitude and direction of the electric field at the field electrode U_n ($U_n < 0$, $U_n > 0$, $U_n = 0$, $T = 77 \text{ K}$), are shown in Fig. 1. It can be seen from the figure that the high-energy maximum of the phase transition $h\nu_{\text{max}} = 2.52 \text{ eV}$ in the spectra of the phase transition of a GaS crystal lies in the region of the exponential portion of the fundamental absorption edge and, therefore, is due to its own zone-to-band transitions. According to [15], the energy of interband transitions a maximum of PP. Then from presented on fig. 1 (curve 1) of the results, it follows that the band gap of crystalline GaS corresponds to $E_g = 2.52 \text{ eV}$ ($T = 77 \text{ K}$). Consequently, in the general form of the PP spectrum, it can be noted that the application of an electric field in different directions leads to a transformation of the PP spectra. Since at $U_n > 0$, the photosensitivity in the region of the fundamental absorption edge increases, and at $U_n < 0$ it decreases, which is associated

with a change in the magnitude and sign of the surface bending of zones, depending on the direction of the applied electric field. In addition, the observed additional maximum in the spectrum at $h\nu = 3.0$ eV (Fig. 1, curve 3) is absent at $U_n < 0$, and this may be due to the formation of spatial heterogeneity of the near-surface electric field [16].

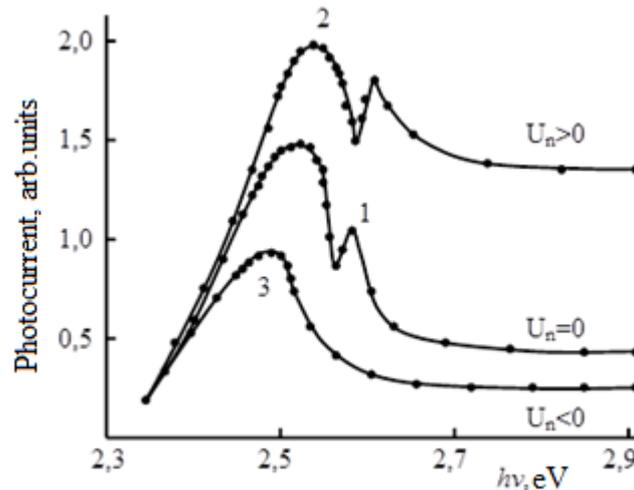


Fig. 1. The spectral distribution of the photoconductivity of a layered GaS crystal at different values of the electric field strength on the cell plate ($T = 77$ K): 1 - $U_n = 0$; 2- $U_n > 0$; 3- $U_n < 0$

Characteristic changes in the PP spectra upon the application of an external electric field are also observed in γ -rays in irradiated samples (Fig. 2). As can be seen from the figure, in the irradiated samples with γ -quanta, the dose $\Phi_\gamma < 50$ krad, when applying an electric field $U_n > 0$ on the control plate of the photosensitivity cell in the region of the absorption edge (Figure 2, curve 2) increases by approximately 30-40%, relatively unirradiated sample (curve 1). It should be noted that further irradiation ($\Phi_\gamma > 50$ krad) reduces the GaS PP over the entire spectral region studied. The intensity of the additional maximum at 2.62 eV decreases with an increase in the radiation dose and disappears at a dose of 200 krad (Fig. 1, curves 1,2,3). This is due to the appearance of a large number of recombination centers with a large cross-section for the capture of electrons.

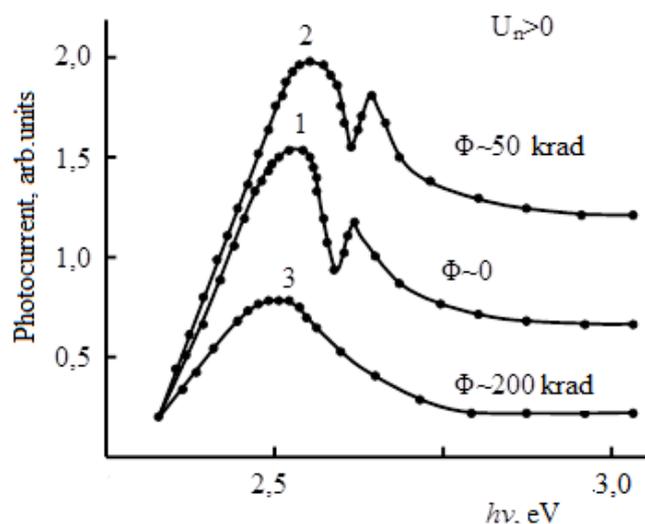


Fig. 2. The spectral distribution of the photoconductivity of a layered GaS crystal irradiated with γ -quanta at doses ($U_n > 0$; $T = 77$ K): 1 - $\Phi = 0$; 2- 50 krad; 3- 200 krad

In fig. 3 shows the PP spectra of the irradiated GaS samples when the electric field $U_n < 0$ is applied to the control plate of the cell. Note that in all the source crystals studied, the maximum of the phase transition is observed near the fundamental absorption edge at $\lambda_{\max} = 490\text{nm}$. $U_n < 0$ on the control plate of the cell leads to a decrease in the PP over the entire spectral range under study. When irradiated with γ -quanta with a dose of $\Phi_\gamma = 50$ krad, the position of the own maximum in the spectra of the phase transition and the shape of the spectrum remains the same as in the case of $U_n > 0$, but the value of the photocurrent decreases slightly (curve 2). Further, with irradiation, the photosensitivity of the samples decreases, which is caused by an increase in the concentration of recombination centers in the studied samples, which are chalcogenide vacancies (curve 3).

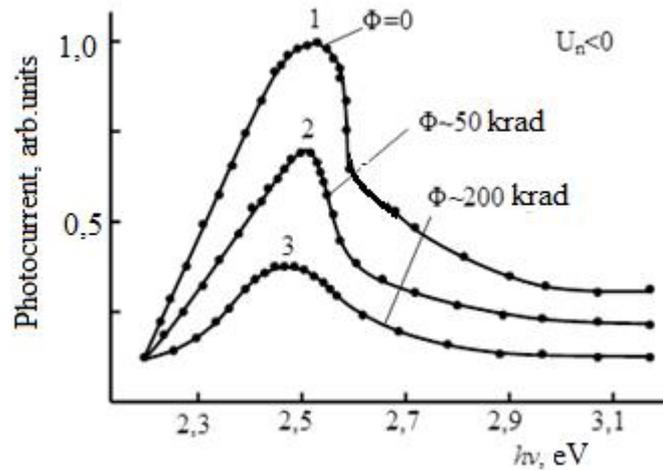


Fig. 3. The spectral distribution of the photoconductivity of a layered GaS crystal irradiated with γ -quanta at doses ($U_n < 0$; $T = 77$ K): 1- $\Phi = 0$; 2- 50 krad; 3- 200 krad

In fig. 4 shows the dose dependence of the PP signal in the region of the absorption edge at different values of the voltage on the cell plate. As can be seen from the figure, the photosensitivity of the samples when the electric field is applied is $U_n < 0$, decreases exponentially (curve 2) with increasing radiation dose, and at $U_n > 0$ increases (curve 1). The detected non-monotonic dependence of the PP signal as a function of the magnitude and direction of the electric field at the field electrode U_n , suggests its connection with the actual spectrum of surface states of layered GaS.

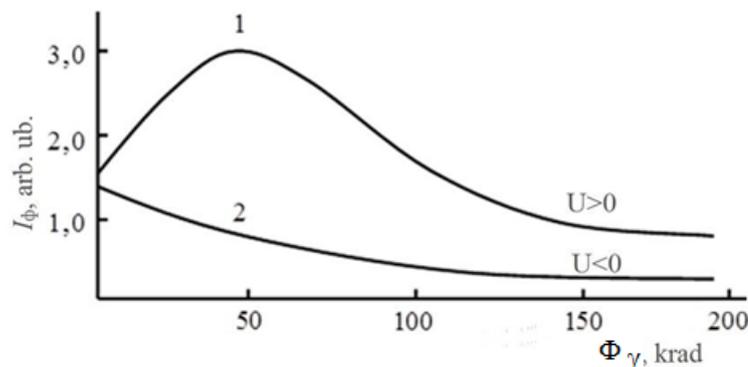


Fig. 4. Relative change in the photoconductivity of a layered GaS crystal as a function of the γ -gamma radiation dose at various values of the electric field strength on the cell plate ($T = 77$ K).

Figures 5 and 6 show the spectra of the phase transitions of the GaS <Yb> samples before and after irradiation when an electric field is applied to the control plate of the cell (100 K). As can be seen from the figure, in p-GaS <Yb> photosensitivity in the region of the absorption edge when $U_n > 0$ increases, and when $U_n < 0$ it decreases slightly, which is due to the restructuring of charged defects under the action of an electric field [5,8,9,12]. When p-GaS <Yb> is irradiated with γ -quanta, characteristic changes in the PP spectra are superimposed an external electric field is also unobserved. It follows from the figure that in p-GaS <Yb> samples, when irradiated with γ -quanta with a dose of 50 krad, the position of its maximum in the PP spectra and the shape of the spectrum remains the same as in the case before irradiation of crystals, but with $U_n > 0$, the photocurrent increases (curve 1). Further, with increasing irradiation, the photocurrent of the samples decreases slightly in the region of fundamental absorption, which is caused by an increase in the concentration of recombination centers (curve 2).

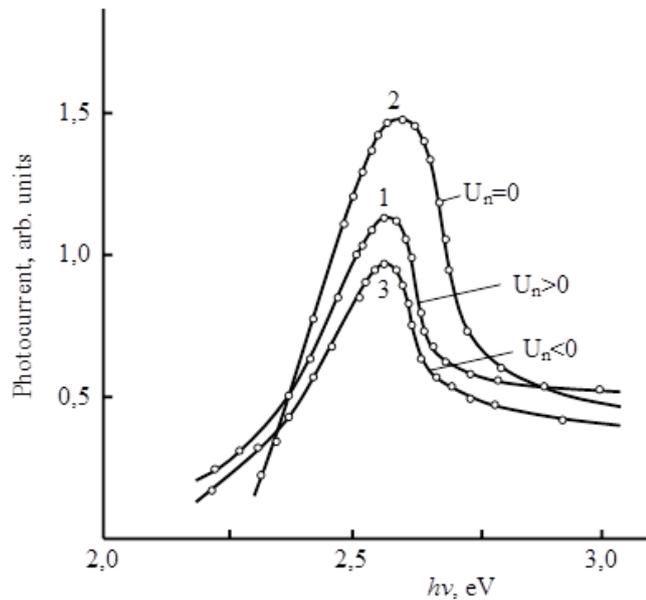


Fig. 5. The spectral distribution of the photoconductivity of a layered GaS (Yb) crystal at various values of the electric field strength on the cell plate ($T = 77$ K).

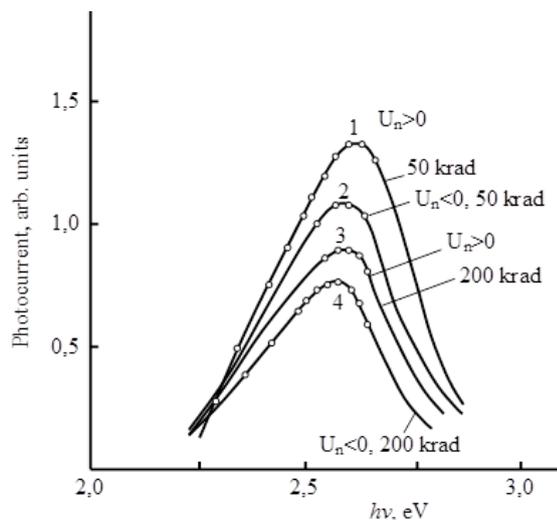


Fig. 6. The spectral distribution of the photoconductivity of a GaS (Yb) crystal at different doses of radiation and the values of the electric field strength on the cell plate ($T = 77$ K).

Thus, the experimental analysis of the phase transitions of layered GaS crystals shows that the presence of various inhomogeneities on the crystal surface and the potential relief associated with them significantly affect their phase transitions in the region of the absorption edge. It is known [17] that in real layered A^{III}B^{VI} type crystals there are intrinsic (vacancies in lattice sites and interstitial atoms, uncontrolled impurities) point defects ($\sim 10^{17} \text{ cm}^{-3}$), as well as their complexes with each other, which form localized electronic states on the surface crystal. According to [14], the effect of inhomogeneous surface potential on the form of the PP spectra is related to the dependence of the surface recombination rate of photocarriers on the surface bending of the energy zones of the material. Similar results were obtained for bulk CdS samples. The decisive role of the inhomogeneous surface electric field in the formation of the fine structure of the PP spectra due to excitons is shown. In our case, the phase transitions of layered crystals are due to the charge exchange of surface states or the presence of charged inclusions on the surface. Indeed, it can be seen from the results obtained that the presence of two types of defects in the initial and doped GaS crystals causes the appearance of stresses in the crystal lattice, which leads to the transformation of the PP spectra in the region of the edge absorption edge measured at $T = 77\text{K}$. It can be seen from the spectra that the high-energy maximum at $h\nu \sim 2.52 \text{ eV}$ is located in the exponential part of the absorption edge and is caused by the band-to-band transition of electrons. Note that the imposition of an external transverse electric field, depending on the direction of the voltage on the field electrode, leads to a change in the magnitude of the phase transition in the region of the absorption edge. In other words, the energy position of the maximum of the phase transition in the spectra does not change, also when doping and irradiating with γ -quanta of the crystal. Note that the photocurrent depends on how the surface of the crystal is treated and is determined by the rate of surface recombination of charge carriers. The observed increase in the photocurrent at $U_n > 0$ and the decrease in the photocurrent at $U_n < 0$ in the region of the absorption edge may be due to the presence of recombination potential barriers [17], which are controlled by recombination of charge photon stars. The reason for the emergence of potential barriers is the existence on the surface of charged inhomogeneous inclusions consisting of a vacancy of cations and anions. It is assumed that when an external electric field is applied, the surface bending of the energy bands at the interface of the crystal-defect matrix changes, changing the rate of surface recombination [18-21]. Studies have shown that an increase in the phase transition in the region of the absorption edge, when exposed to an electric field - $U_n > 0$, is due to electrical smoothing of the potential bending at the boundary of the crystal surface areas. The decrease in the pressure factor, when exposed to an electric field, is due to an increase in the potential barrier between surface inclusions, which consists of gallium vacancies and impurity atoms. Studies have shown that when irradiated with γ -quanta in GaS crystals, donor-type defects are formed [6, 7], which compensate for the initial acceptor centers. This leads to the enhancement of the process of smoothing the bending of zones on the surface when an external electric field is applied $U_n > 0$. As the surface electric field increases, it increases, while the photosensitivity in the region of the absorption edge increases. With this in mind, it can be assumed that in layered crystals, including GaS, there are non-uniformly distributed local deformation fields of compression and tension stresses, which significantly change the spectrum of deep electronic states in the band gap and, as a result, significantly change the overall appearance of the PP spectrum.

4. Conclusion

The results obtained lead to the conclusion that the main factor determining the edge phase transition of layered p-GaS crystals is the local inhomogeneous electric field of the surface electric

charge. Indeed, in layered crystals, characterized, according to [17], and by our data, which have surface bending of zones, the electric field on the surface of the crystal changes with the magnitude and direction of the transverse electric field strength. By changing the magnitude and sign of the transverse field, one can control the photosensitivity of a layered crystal in the region of the absorption edge at low temperatures.

The effect of such states on the PP spectra can be controlled by doping and irradiating a layered crystal. It has been established that the degree of compensation in these materials can be controlled by using γ -quanta, which generates point defects over the entire surface. This assumption is confirmed by the experimental results obtained.

Thus, the influence of an external electric field on the phase transition in the initial and doped GaS <Yb> crystals is associated with a change in the rate of charge carrier supply to the recombination centers and a change in the bending of the energy bands on the crystal surface crystal, the main factor is the surface electric field arising due to the localization of charge carriers in surface electronic states.

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СПЕКТРАЛЬНЫЙ ФОТОРЕЗИСТИВНЫЙ ЭФФЕКТ ПОЛЯ В γ -ОБЛУЧЕННЫХ СЛОИСТЫХ КРИСТАЛЛАХ GaS И GaS <Yb>

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Резюме: Исследовано влияние поверхностного электрического поля на краевую фотопроводимость в нелегированных и легированных иттербием ($N_{Yb} \sim 10^{18} \text{ см}^{-3}$) слоистых кристаллах GaS при $T=77\text{K}$, облученных γ - квантами. Обнаружено, что фотопроводимость слоистых кристаллов в области края поглощения, обусловленной перезарядкой поверхностных уровней, формируется в результате электрического сглаживания флуктуации потенциала поверхностных энергетических зон. Степень сглаживания поверхностного изгиба зон зависит от дозы γ -облучения, концентрации атомов примеси, а также от величины и направления поперечного электрического поля.

Ключевые слова: краевая фотопроводимость, электрическое поле, облучение, гамма-кванты, слоистые полупроводники, экситон, приповерхностные центры

γ -KVANTLARLA ŞÜALANDIRILMIŞ GaS VƏ GaS <Yb> KRİSTALLARINDA FOTOREZİSTİV SAHƏ EFFEKTİ

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Xülasə: Aşqarlanmamış və itterbi ilə aşqarlanmış ($N_{Yb} \sim 10^{18} \text{ см}^{-3}$) laylı GaS kristallarında $T=77 \text{ K}$ temperaturunda udulma zolağında fotokeçiriciliyə səth elektrik sahəsinin təsiri araşdırılmışdır. Müəyyən edilmişdir ki, səth energetik zonanın potensialının fluktasiyası nəticəsində səth səviyyələrinin yüklənməsi səbəbindən udulma zolağında laylı kristallarda udulma zolağında fotokeçiricilik yaranır. Səth zonasının əyilmə dərəcəsi şüalanma dozəsindən, tətbiq edilən sahənin qiymət və istiqamətindən asılıdır.

Açar sözlər: kənar fototeçiricilik, elektrik sahəsi, şüalanma, qamma-kvantalar, laylı yarımkəçiricilər, eksiton, yaxın səthlər