# RADIATION MODIFICATION OF THE STRUCTURE OF LAYER CRYSTALS OF SULFIDE GALLIUM

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The radiation modification of the structure of a layered GaS crystal by the Fourier-IR and Raman spectroscopy methods in the absorbed dose ($\Phi_\gamma$ = 30…200 krad) of gamma-irradiation was studied. It was established that at irradiation doses of $\Phi_\gamma \leq 50$ krad a half-width and intensities Raman lines and IR adsorption bands the characterizing the layer oscillations does not change, which is due to the stability of the crystal lattice. At absorbed doses of $\Phi_\gamma \geq 50$ krad, changes in these parameters are observed, which lead to a change in the degree of structural disorder and, consequently, of the radiation structural modification of the layered crystal. Fourier-IR reflection spectra revealed that gamma-irradiation at doses of $\Phi_\gamma \geq 50$ krad leads to a deterioration of the surface state of gallium sulphide.

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## INTRODUCTION

GaS single crystals have a typical layered structure, have a pronounced structural anisotropy and are of theoretical and experimental interest in the fields of optoelectronics and radiation materials science [1–7]. It is known that for layered semiconductors, the presence, in addition to intrinsic lattice defects and uncontrolled impurities, is characteristic [1]. They can enter both natural layers and interlayer spaces. When these compounds are irradiated, radiation defects are also formed in the interlayer spaces, where they can interact with impurities. In addition, the use of layered materials as a buffer material to reconcile the difference in the lattice constants necessitates research into the effect of anisotropic mechanical stresses on the electronic spectra and structural parameters of a crystal. Taking into account these data, it can be assumed that the accumulation of radiation defects in layers and interlayers leads to a violation of the periodicity of the structure and interaction of interlayer and intra-layer regions.

The analysis of literature data shows that the structure and electronic spectrum of layered semiconductors modified by impurities and radiation are poorly studied and require further investigation. Therefore, studies of radiation effects in layered semiconductors, in particular GaS, are promising from a practical point of view for predicting the durability of materials under the influence of ionizing radiation.

In this paper we present the results of experimental studies of the structural modification in layered GaS crystals under the action of gamma-quanta obtained by the Fourier-Raman spectroscopy method. The effect of gamma-irradiation on the surface states of gallium sulphide on the Fourier-IR reflection spectra is also considered.

## TECHNIQUE OF EXPERIMENTS

Single crystals of GaS were grown by the Bridgman method. During the cultivation an excess of sulfur (1.5%) was used to determine the possibility of filling vacancies with sulfur atoms. The resistivity of the samples obtained along and perpendicular to the C axis at room temperature was $2\cdot10^8$ and $3\cdot10^6$ Ω·cm, respectively. On the basis of X-ray analysis it was established that the grown single crystals of GaS have a β-modification, and the lattice parameters are $a$ = 3.755Å and $c$ = 23.92 Å.

The vibrational spectra of GaS were investigated by Fourier-Raman spectroscopy. The Fourier-Raman spectra were obtained with the Raman U1000 micro Raman spectrometer with the Nikon Eclipse LV150 optical microscope at room temperature. The LCS-DTL-317 laser with radiation at a wavelength of λ ~ 532 nm was used as an excitation source. Raman spectra were obtained on a spectrometer in the frequency range ν = 10…500 $cm^{-1}$. Fourier IR spectra of the samples were recorded on a FTIR Varian 3600 spectrometer in the frequency range ν = 400…100 $cm^{-1}$ at room temperature. The reflection spectra were obtained at an angle of incidence φ = $15^0$. The samples were irradiated with γ quanta from a $^{60}Co$ source at room temperature with a dose rate of $\Phi_\gamma$ = 15.66 rad/s. At the same time, the absorbed dose was $\Phi_\gamma$ = 30…200 krad [8].

## RESULTS AND ITS DISCUSSION

In Fig. 1 shows the Fourier-Raman spectra of a p-GaS single crystal at room temperature. It is seen that in the Raman spectra for monocrystals of GaS five-line lines are observed at frequencies of 23.2; 75; 188.4; 294.2, and 360.2 $cm^{-1}$, the assignment of which is shown in the Tabl. 1, and they coincide with the results given in [6, 7].

Analysis of the spectra obtained shows that the low-frequency lines (23.2 and 75 $cm^{-1}$) corresponding to the modes $E^2_{g2}$ and $E^1_{g1}$ are caused by oscillations between the layers, where the coupling is carried out with the help of a weak Van der Waals force, and they show a single-mode nature. The remaining modes for oscillations of the type $E^2_{g1}$, $E^1_{g2}$, and $A^1_{g2}$, correspond to the lines 188.4; 294.2, and 360.2 $cm^{-1}$ can be associated with the redistribution of vacancies created both by sulfur atoms and by gallium atoms in the crystal layers [10].

The energy levels in GaS semiconductors for the vacancies of the anion, cation, and for anion and cation substitution were calculated in [11].

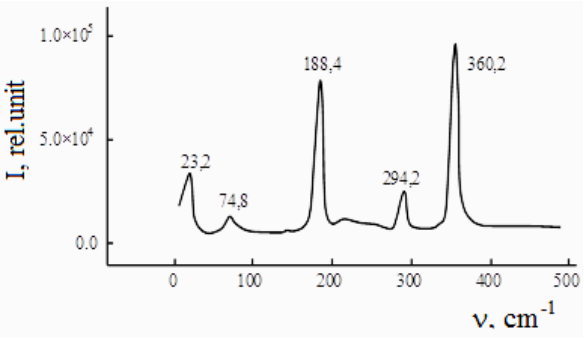


*Fig. 1. Fourier-Raman spectra of a layered GaS crystal*

Table 1

| Wave type at 300 K | Literary data ν, $cm^{-1}$ | The data of this work ν, $cm^{-1}$ |
|---|---|---|
| $E^2_{2g}$ | 23 | 23.2 |
| $E^1_{1g}$ | 75 | 74.8 |
| $A^1_{1g}$ | 189 | 188.4 |
| $E^1_{2g}$ | 295 | 294.2 |
| $A^2_{1g}$ | 360 | 360.2 |

Anionic and cation vacancies in these semiconductors lead to energy levels in the forbidden band within the valence band, and also to levels in the allowed band inside the valence band. According to the calculated data, in GaS crystals for a cation vacancy, the energy levels of local defects relative to the top of the valence band in the forbidden band are 0.2; 0.4, and 0.6 eV, for an anion vacancy of 0.1 and 0.5 eV.

When irradiating single crystals of GaS with γ-quanta with a dose of $\Phi_\gamma = 30…200$ krad, Raman spectra undergo changes in the spectral characteristics (intensities and half-widths) of the 188.4, 294.2, and 360.2 $cm^{-1}$ lines, as well as 23.2 and 74.8 $cm^{-1}$. Fig. 2 shows the variation of the Raman lines of the interlayer vibration $E^2_{g1}$ at ν = 23.2 $cm^{-1}$ and within the layer vibration $A^1_{1g}$ at ν = 188.4 $cm^{-1}$, depending on the absorbed dose of γ-irradiation. With an increase in the absorbed dose to $\Phi_\gamma = 200$ krad, these lines are transformed, which is accompanied by a change in their spectral characteristics (I and $\nu_{1/2}$).

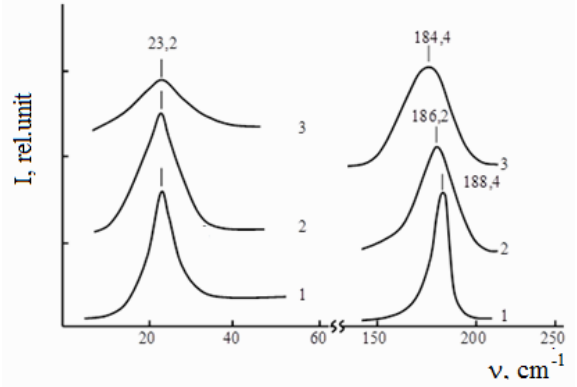


*Fig. 2. Fourier-Raman spectra of the unirradiated (1) and γ-irradiated layered GaS crystal; $\Phi_\gamma$ = 100 (2) and 200 krad (3)*

As an example, Fig. 3,a shows the Raman half-width curves of the interlayer $A^1_{1g}$ lines at ν = 188.4 $cm^{-1}$ (curve 1) and inside the layer $E^2_{g1}$ at 23.2 $cm^{-1}$ oscillations (curve 2) of the GaS crystal from the dose of gamma-irradiation, respectively. From Fig. 2 shown that the half-widths of the lines vary insignificantly in the region of the absorbed dose $\Phi_\gamma \leq 50$ krad, and then in the region of high absorption dose ($\Phi_\gamma = 50…200$ krad) the dependence is linear, but the rate of change of the line half-width increases. In this case, the half-width of the $\nu_{1/2}$ line of the $E^2_{g1}$ vibration irradiated with a dose of $\Phi_\gamma = 200$ krad GaS increases by a factor of ~ 2.3 (from 12 to 28 $cm^{-1}$). Raman spectra analysis shows that inhomogeneous line broadening and unequal rates of increase of $\nu_{1/2}$ with radiation dose are associated with an increase in the mechanical tension in the interlayers and layers of the crystal with the accumulation of radiation defects.

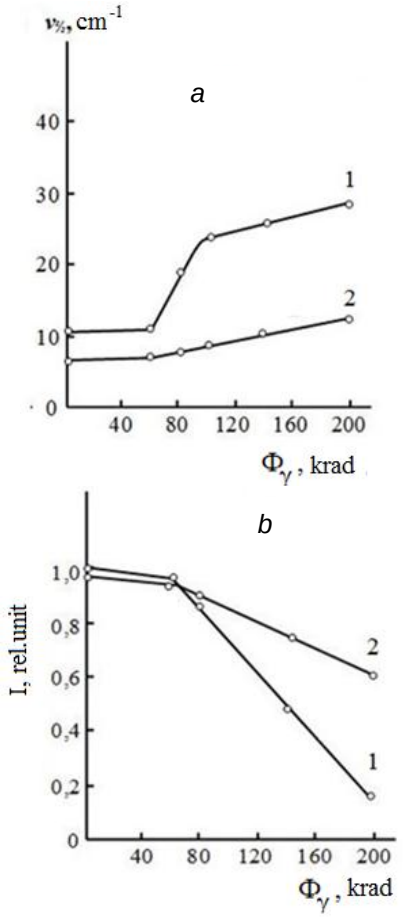


*Fig. 3. Dose dependences of half-width (a) and intensity (b) Ramanlines of the interlayer $A^1_{1g}$ (1) and inside the layered $E^2_{2g}$ (2) oscillations of the GaS crystal*

In Fig. 3,b shows the dependence of the line intensity of the interlayer and layer oscillations $E^2_{g1}$ and $A^1_{1g}$ of the crystal on the dose of γ-irradiation. It can be seen from the figure that the intensity of the lines decreases insignificantly when γ-quanta are irradiated with a dose of $\Phi_\gamma = 50$ krad, and the intensity decreases strongly at high doses ($\Phi_\gamma \geq 50$ krad), which is caused by an increase in the interaction of radiation defects with structural defects. At the same time, the intensity of the interlayer oscillation decreases with increasing the absorbed dose (curve 1) by a factor of ~ 2.5 as compared with the intensity within the layer oscillations. It can be seen from the spectra that the

accumulation of radiation defects in layers occurs faster than in interlayers. The nature of the changes in the intensities of the bands and half-widths of the spectra with irradiation shows that in the high-dose region (above $\Phi_\gamma \geq 50$ krad) as a result of the interaction of radiation defects created by γ-quanta with lattice defects, the initial periodicity of the structure of layered crystals undergoes changes that promote a more intense propagation of phonons along axis of symmetry. The obtained spectral data are in good agreement with the results of the dependence of the formation of radiation defects on the dose of gamma-irradiation [9]. According to [9], in this dependence, a linear region in which the concentration of radiation defects increases by a factor of ~ 6 (N from $1 \cdot 10^{15}$ to $6 \cdot 10^{15}$ $cm^{-3}$) is observed in the region of the absorbed dose $\Phi_\gamma = 50 \ldots 200$ krad.

To study the defect states in semiconductors, it is of interest to study the conditions of threshold formation. In [11], threshold energy and displacement energy for layered $A^{III}B^{VI}$ semiconductors were also calculated. The energy of displacement of the $E_d$ atoms from the crystal lattice sites is an important quantity determining the rate of radiation damage of the crystals. The energy of displacement is usually called the smallest amount of energy that must be transferred to one of the atoms of the lattice of the crystal, so that it finds itself in the nearest interstitial position (Tabl. 2).

Table 2

| Semicon-ductor | Bond | Sublimation energy, eV | The displacedatom | Displacement energy, eV | Threshold energy, eV |
|---|---|---|---|---|---|
| GaS | Ga – S | 3.225 | S | 18.36 | 221.912 |
| | | | Ga | 12.11 | 299.653 |
| | Ga – Ga | 3.139 | Ga | 11.94 | 296.175 |
| | S – S | 2.15 | S | 15.13 | 188.036 |

We have also studied the effects of gamma-irradiation on the near-surface states of gallium sulphidemonocrystals. To this end, in the field of lattice vibrations, the IR spectra of the reflection of the initial (1) and irradiated doses of $\Phi_\gamma = 100$ (2) and 200 krad (3) of GaS samples were obtained (Fig. 4). As can be seen from the figure, in the reflection spectra of the original GaS, transverse $\nu_{TO} = 315.3$ $cm^{-1}$ and longitudinal $\nu_{LO} = 365.6$ $cm^{-1}$ oscillations are observed, which converge to the classical dispersion analysis. The gamma-irradiation of GaS samples with doses of 100 and 200 krad slightly alters (distorts) the spectra of lattice reflection. With an increase in the dose of γ-irradiation, the value of the reflection coefficient decreases by a factor of ~ 1.6 ($R$ decreases from 78 to 50%), and the region of the residual rays also deepens. The observed singularity in the band of residual GaS rays appearing in irradiated samples can be presumably explained with the modification of the surface state under the action of gamma-radiation and the formation of quasiphonons that lie in the region of the residual rays [10].

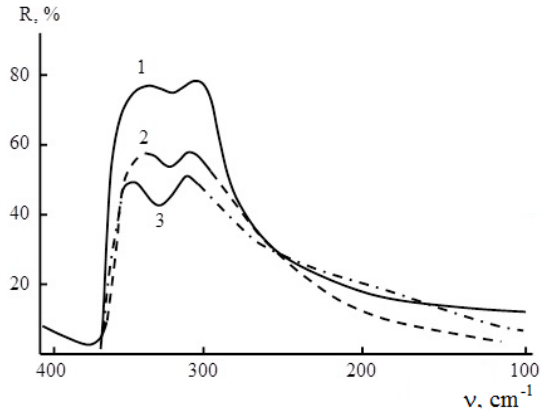


*Fig. 4. Fourier-IR spectra of the reflection of the initial (1) and γ-irradiated doses of 100 (2) and 200 krad (2) samples of GaS obtained at room temperature*

To identify the nature of the observed Raman lines of layered crystals, we use the data of [6, 7, 12, 13], taking into account the selection rules. It is known that layered crystals are formed from layers containing four atomic planes. Inside the layers, the bond has an ion-covalent character, and the interlayer interaction is predominantly due to Van der Waals forces with a small addition of Coulomb forces. The anions and cations are located in planes perpendicular to the crystalline C axis in the S-Ga-Ga-S sequence. The arrangement of atoms inside the layer corresponds to the space group $D_{(sh)}^1$ [3–6]. It was predicted in [1, 11–13] that the presence of a large number of packing defects (~ $10^{17}$ $cm^{-3}$) in layered crystals, as well as the formation of complex radiation defects under the influence of radiation in layers, can lead to a violation of the periodicity of the structure and changes in the interlayer and inside layered interactions. From our results it follows that the Raman intensity and half-widths of the lines and IR absorption bands in the spectra of the layered GaS (Figs. 1–3) irradiated with gamma-quanta by doses of $\Phi_\gamma \leq 50$ krad slightly change, which shows a partial restoration of the periodicity of the structure with radiation defects. When γ-quanta are irradiated with a dose of up to $\Phi_\gamma \geq 50$ krad, intensity decreases and the half-width increases, which is caused by an increase in the interlayer space tension. A similar result was observed in [12], where the spectra of the Raman resonance spectrum in layered GaSe under pressure were investigated. It is shown that the character of the change in line intensities with pressure is associated with the formation of local regions with residual stress in the volume of the crystal. Taking into account these data, it can be assumed that the growth of radiation defects with increasing radiation dose leads to an increase in the intensity in the interlayer space, as a result of which the crystal deforms. The degree of violation of the periodicity of the structure depends on the concentration of radiation defects in the interlayer

regions of the crystal and in the crystal in the region of the residual stress.

An analysis of the available data on the band structure of crystals, such as GaS [6, 7] allows us to consider the model of the motion of electronic bands in layered crystals with a pressure that takes into account not the deformation of the unit cell as a whole, but the variation inside the layer and interlayer distances separately. The difference between the interatomic distances inside the layers and between the layers reflects the anisotropy of the binding forces in layered crystals. This is evidenced by the values of the elastic constants characterizing the elastic properties of layered crystals [7, 14, 15]. Analysis of the data on the temperature behavior of the elastic constants of graphite obtained in. [7] also makes it possible to notice a tendency for a more rapid change in the interlayer elastic constants as compared to the inside layers. In view of this circumstance, it is established that in the course of the reconstruction of the defects both the phonon and the electronic subsystem of the crystal change.

## CONCLUSION

In the present work, the radiation modification of the structure of a layered GaS crystal by the Fourier-Raman spectroscopy method in the region of the absorbed dose of gamma-irradiation was studied ($\Phi_\gamma$ = 30…200 krad). It has been established that the Raman lines characterizing the inter- and intralayer vibrations at irradiation doses $\Phi_\gamma \leq 50$ krad are unchanged, due to the stability of the crystal lattice and indicate the radiation resistance. At absorbed doses of $\Phi_\gamma \geq 50$ krad, changes in these spectral parameters are observed, which are caused by a change in the degree of structural disorder with irradiation of the layered crystal and indicate its radiation structural modification. According to the IR reflection spectra in the field of lattice vibrations, gamma-irradiation of gallium sulphidemonocrystals at absorbed doses of $\Phi_\gamma \geq 50$ krad leads to a deterioration in the near-surface state of GaS samples.

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## РАДИАЦИОННАЯ МОДИФИКАЦИЯ СТРУКТУРЫ СЛОИСТЫХ КРИСТАЛЛОВ СУЛЬФИДА ГАЛЛИЯ

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Исследована радиационная модификация структуры слоистого кристалла GaS методом фурье-раман-спектроскопии в области поглощенной дозы гамма-облучения ($\Phi_\gamma$ = 30…200 крад). Установлено, что при дозах облучении $\Phi_\gamma \leq 50$ крад полуширина и интенсивности раман-линий, характеризующие слоевые колебания, не изменяются, что связано со стабильностью кристаллической решетки. При поглощенных дозах $\Phi_\gamma \geq 50$ крад наблюдаются изменения этих параметров, что вызвано изменением степени структурного беспорядка и, следовательно, радиационной структурной модификацией слоистого кристалла. По фурье-ИК-спектрам отражения выявлено, что гамма-облучение при дозах $\Phi_\gamma \geq 50$ крад приводит к ухудшению поверхностного состояния сульфида галлия.

## РАДІАЦІЙНА МОДИФІКАЦІЯ СТРУКТУРИ ШАРУВАТИХ КРИСТАЛІВ СУЛЬФІДУ ГАЛІЮ

***Р.С. Мадатов, М.М. Гаджиєва, Ф.Г. Асадов, З.І. Асадова***

Досліджена радіаційна модифікація структури шаруватого кристала GaS методом фур'є-раман-спектроскопії в області поглиненої дози гамма-опромінення ($\Phi_\gamma$ = 30...200 крад). Встановлено, що при дозах опроміненні $\Phi_\gamma \leq 50$ крад напівширина і інтенсивності раман-ліній, що характеризують шарові коливання, не змінюються, що пов'язано зі стабільністю кристалічної решітки. При поглинених дозах $\Phi_\gamma \geq 50$ крад спостерігаються зміни цих параметрів, що викликано зміною ступеня структурного безладу і, отже, радіаційною структурною модифікацією шаруватого кристала. За фур'є-ІЧ-спектрами відображення виявлено, що гамма-опромінення при дозах $\Phi_\gamma \geq 50$ крад призводить до погіршення поверхневого стану сульфіду галію.