IR-SPECTROSCOPY AND AFM-MICROSCOPY OF THE SURFACE OF GAMMA-IRRADIATED GaS AND GaS:Yb LAYERED SINGLE CRYSTALS

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For the first time, information on the surface relief of the layered GaS and doped GaS:Yb single crystals subjected to gamma-irradiation was obtained using atomic force microscopy (AFM) and Fourier-transform infrared spectroscopy (FTIR). It was found that GaS is characterized by a non-uniform distribution of irregularities with different heights and periodicities, and when doping crystals with Yb atoms, the distribution of irregularities becomes more orderly, the height and periodicity of irregularities decreases. In the FTIR spectra, changes in the reflection coefficients of the surface of GaS and GaS:Yb single crystals are observed as a function of the gamma-irradiation dose (Φ_γ = 30…200 krad), and on the basis of spectroscopic and microscopic changes, it was found that doped single crystals are the most radiation-resistant.

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INTRODUCTION

Layered A^3B^6 semiconductors, in particular, gallium sulfide single crystals (GaS) are promising materials for radiation detectors of various types. On the basis of these single crystals, radiation detectors of gamma-quanta operating at room temperature [1–5] are fabricated. The increased interest in these compounds is due to the anisotropy of their crystalline structure, which allows obtaining perfect faces with a sufficiently low density of surface states, which is important for obtaining high quality heterojunctions.

One of the effective methods for changing the surface of layered gallium sulfide single crystals is to irradiate it with γ-quanta [2–6]. The depth of penetration of gamma-quanta is comparable to the value of the inverse light absorption coefficient (~ 10^2 nm), which leads to the desorption of gases from the surface and recharging the surface active centers. This factor is decisive in many processes occurring near the surface of the crystal. Therefore, studying the effect of external influences, including gamma-radiation, on the edge photoconductivity (FC) of a defective semiconductor, one can establish the role of surface heterogeneity and roughness during its formation [4]. The most informative methods for studying the surface of semiconductors are the methods of FTIR and AFM [7, 8].

Based on these considerations, the present work presents the results of AFM and FTIR studies of changes in the surface relief of gamma-irradiated layered GaS and GaS:Yb single crystals.

EXPERIMENTAL TECHNIQUE

Single crystals of p-GaS were grown by the method of directional solidification of the melt (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 resistivity of the samples obtained along and perpendicular to the C axis at room temperature was $3\cdot10^7$ and $2\cdot10^9$ Ω·cm, respectively. Doping of Yb was carried out in the process of crystal growth, and the concentration of Yb in crystals was $N_{Yb} \sim 10^{18}$ cm^{-3}. Indium, which was smelted on the surface of gallium sulfide at a temperature of 150 °C, was used as the ohmic contacts. Microstructural and X-ray phase analyzes showed that the obtained crystals were homogeneous and did not contain crystalline inclusions [2, 3].

The Fourier transform infrared reflection spectra of the samples were recorded on a Varian 3600 FTIR 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°.

Microscopic studies of the surface relief of the initial gamma-irradiated GaS and GaS:Yb samples were carried out with an AFM. For this purpose, two-dimensional (2D) and three-dimensional (3D) surface AFM images were obtained, as well as histograms (distribution curves of surface images on the size of irregularities) in the horizontal and vertical directions. Samples were irradiated with gamma-quanta from a ^{60}Co source at room temperature with a dose rate $d\Phi_\gamma/dt$ = 15.66 rad/s. The samples were irradiated with doses of 30, 50, 100, 140, and 200 krad [6, 9].

RESULTS AND ITS DISCUSSION

IR reflection spectra in the region of lattice oscillations of the initial (1) and irradiated doses of Φ_γ = 140 (2) and 200 krad (3) of GaS and GaS:Yb single crystals are shown in Fig. 1. As seen from Fig. 1,a (curve 1), in the reflection spectra transverse ν_{TO} = 315.3 cm^{-1} and longitudinal ν_{LO} = 365.6 cm^{-1} oscillations, which converge to classical dispersive analysis, are observed in the original GaS. Gamma-irradiation of GaS samples with doses of 140 and 200 krad slightly changes (distorts) the lattice reflection spectra (curves 2 and 3). With an increase in the gamma-irradiation dose, the value of the reflection coefficient decreases, and the region of residual rays deepens. The observed feature in the band of residual GaS rays that appears in the irradiated samples can presumably be explained by a change in the surface state under the action of gamma-radiation and the formation of quasi-phonons, which lie in the region of residual rays [10].

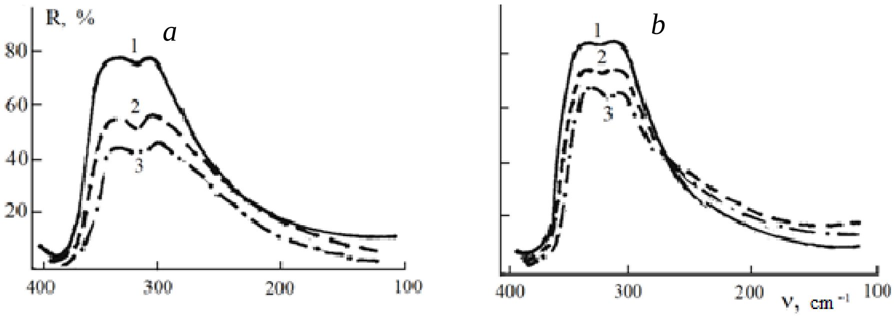

Fig. 1. FTIR spectra of the original, non-irradiated (1), and irradiated with doses of $\Phi_\gamma = 140$ *(2) and 200 krad (3) of GaS (a) and GaS:Yb (b) single crystals*

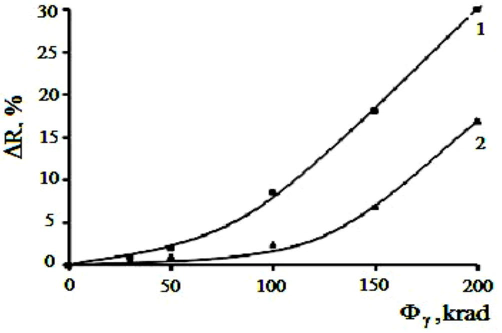

Fig. 2. Changes of the values of the difference of the reflection coefficient (ΔR) depending on the absorbed dose of gamma-irradiation for GaS (1) and GaS:Yb (2) single crystals

Fig. 1,b shows the reflection spectra of the initial (curve 1) and irradiated doses of 140 and 200 krad (curves 2 and 3) of the GaS:Yb samples. As can be seen from Fig. 1,b, the doping of gallium sulfide with ytterbium actually does not affect the values of the frequencies of longitudinal and transverse oscillations. However, the surface state improves and is accompanied by an increase in the reflection coefficient (albedo) by $R \sim 5…8\%$. Gamma-irradiation of GaS:Yb samples with doses of 140 and 200 krad leads to a deterioration of the surface state, since R values with increasing absorbed radiation dose are decreasing. Fig. 2 presents the changes in the values of the difference of the reflection coefficient $\Delta R = R_0 - R$ (where R_0 and R are the reflection coefficients of the original and gamma-irradiated samples, respectively) depending on the absorbed gamma-irradiation dose for the GaS (curve 1) and GaS:Yb samples (curve 2). A comparative analysis of these dependencies reveals the following:

1. Both dependencies are close to a parabolic law.
2. The growth rate of the difference ΔR determined in the linear regions of dependences in the case of gamma-irradiated GaS samples is ~ 1.5 times higher than the growth rate of the ΔR value in the case of gamma -irradiated GaS:Yb samples.
3. The sharp increse in the difference ΔR occur for GaS samples with an absorbed dose of $\Phi_\gamma \geq 50$ krad, and for GaS:Yb samples at $\Phi_\gamma \geq 140$ krad.

The observed features of the curves of ΔR versus Φ_γ for GaS and GaS:Yb samples show that the gallium sulfide surface is more sensitive to gamma-ray effects than gallium sulfide surface doped with ytterbium. In this case, the effect of gamma-quanta causes the heterogeneity and roughness of the surface and, consequently, leads to its deterioration in these layered single crystals.

The obtained results are in good agreement with the results of [5], according to which, GaS and GaS:Yb single crystals with values of $\Phi_\gamma \leq 140$ krad are radiation-resistant, and above these values of absorbed doses, respectively, are not radiation-resistant.

Changes in the surface relief of layered GaS and GaS:Yb single crystals caused by gamma-quanta were also traced by the microscopic (AFM) method. As an example, Fig. 3 shows three-dimensional (3d) images of the surface of the original (see Fig. 3,a,b) and gamma-irradiated with 140 krad (see Fig. 3,c,d) samples of GaS and GaS:Yb, respectively. Comparison of the surfaces of the initial single crystals shows that if the surface of gallium sulfide is characterized by the presence of sub-roughness and heterogeneity, the introduction of ytterbium impurity into the GaS structure leads to a smoothing and uniformity of its surface. In this case, the depth of irregularities in the case of GaS:Yb decreases by a factor of ~ 5 (from 8 to 40 nm) compared to GaS.

Irradiation of GaS and GaS:Yb single crystals with a dose of 140 krad is accompanied by a change in the surface state of these samples. After irradiation with gamma-rays with a dose of 140 krad, the surface state of GaS deteriorates significantly, while minor changes occur on the GaS:Yb surface. Annealing the samples at a temperature of $t = 100$ °C for 1 hour partially restores the surface of the irradiated samples. It should be noted that the analysis of 3D images of surfaces of γ-irradiated GaS and GaS:Yb samples with doses of 30, 50, 100, 140, and 200 krad allows us to conclude that the boundary values of the dose of surface changes are 50 and 140 krad, respectively.

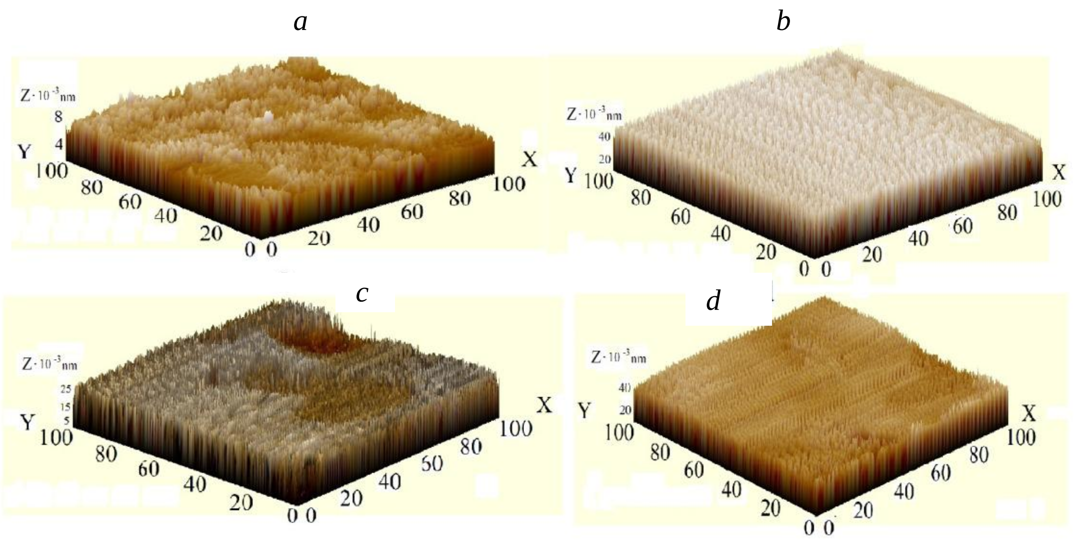

Fig. 3. Three-dimensional images of the surface of the original (a, b) and γ-irradiated dose with of 140 krad (c, d) of GaS (a, c) and GaS:Yb(b, d) single crystals

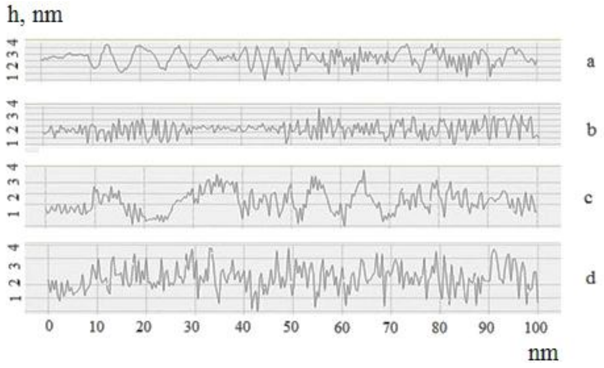

Fig. 4. Histograms of 2d images of the initial (a, b) and γ-irradiated doses of 140 krad (c, d) of GaS single crystals in horizontal (a, c) and vertical (b, d) directions

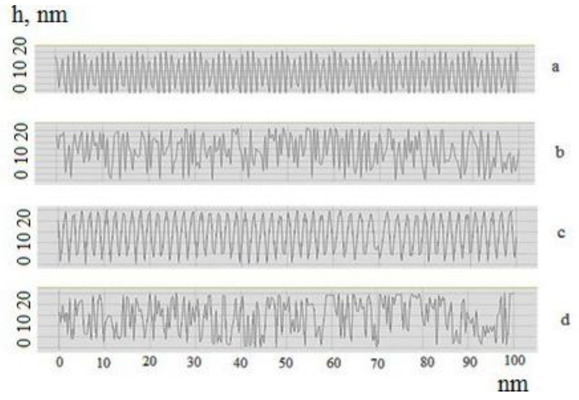

Fig. 5. Histograms of 2d images of the initial (a, b) and γ-irradiated dose of 140 krad (c, d) GaS:Yb single crystals in the horizontal (a, c) and vertical (b, d) directions

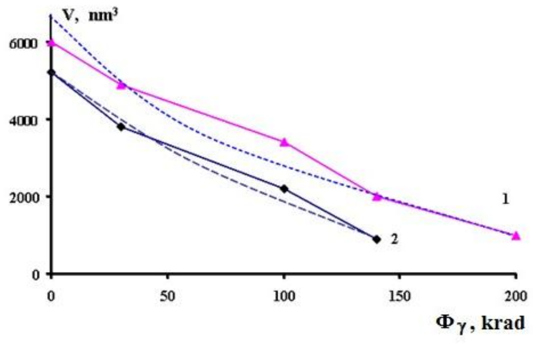

Fig. 6. Dose dependences of the free volume of irregularities in GaS (1) and GaS:Yb (2) single crystals. (Dashed lines show exponential approximating (regression) dependences)

Figs. 4 and 5 show the histograms of 2D images (curves of the distribution of surface images by the size of irregularities) in the horizontal and vertical directions of the selected section (100×100 nm). As can be seen from the histograms, the GaS single crystal is characterized by an uneven distribution of irregularities, both in the horizontal and in the vertical directions with different heights of ~ 30…40 nm and a frequency of ~ 16 nm (see Fig. 4,a,b). GaS:Yb single crystal histograms show a uniform distribution of irregularities in both horizontal and vertical directions with the same height of ~ 25 nm and a frequency of ~ 13 nm (see Fig. 5,a and b). Irradiation with a dose of 140 krad of these samples leads to a strong (see Fig. 4,c,d) and minor (see Fig. 5,c,d) changes in histograms for GaS and GaS:Yb, respectively.

Considering the sub-roughness profile in the framework of multifractal analysis, we can assume that it has the invariance property when the same unit free volume (straight cone of height h and diameter d) is continuously repeated over the entire area [8, 9].

The dose dependence of a single free volume of irregularities (a single average volume of a relief-forming cone), which is shown in Fig. 6, was studied. The dependence is exponential: $V=A\cdot e^{kx}$ (V is a single average volume of a relief-forming cone, A is a single crystal constant, k is an absorption coefficient, x is the irradiation dose). As can be seen from Fig. 6, with an increase in the gamma-irradiation dose to 140 krad, the value of a single average volume of the relief-forming cone V decreases by ~ 2.5…5 times (from 6000 and 5500 to 2500 and 1000 nm^3) for GaS and GaS:Yb, respectively.

CONCLUSIONS

The surface relief of undoped GaS and doped GaS:Yb single crystals subjected to gamma-irradiation was studied by AFM and FTIR. It was found that GaS is characterized by an uneven distribution of irregularities with different heights ~ 30…40 nm and a frequency of ~ 16 nm subjected to gamma-irradiation. When doping crystals with Yb atoms, the distribution of irregularities becomes more orderly, the height is ~ 25 nm, and the periodicity of ~ 13 nm irregularities decrease. In the FTIR spectra, changes in the reflection coefficients of the surface of GaS and GaS:Yb single crystals are observed as a function of the gamma-irradiation dose (Φ_γ = 30…200 krad), and on the basis of these changes, it was found that doped single crystals are the most radiation-resistant.

The use of a single average volume of a relief-forming cone was introduced as a characteristic of the development of the surface of layered crystals. Regression dependencies of the effect of the degree of irradiation on a single average volume of the relief-forming cone are proposed, expressed in the exponential form $V = A\cdot e^{kx}$. The dependence was established between the distribution profile of a single free volume of irregularities (a single average volume of a relief-forming cone), obtained by AFM and the radiation resistance of layered GaS:Yb single crystals.

In order to explain the experimental facts established by us, we propose the following physical model of the processes occurring during the accumulation of clusters of defects consisting of V_{Ga} and Ga_i in the form of a cone in grown crystals. When pure and impurity GaS single crystals are irradiated with $E \approx 1.2$ MeV and a low dose of 30…200 krad, apparently due to radiation-stimulated annealing of defects, the clusters of defects decompose, releasing V_{Ga} (of which the cluster of defects consists) and Ga_i which is located on the periphery of the defect clusters. In this regard, the volume of the periphery of the relief-forming cone decreases with increasing radiation dose and, as a result, the smoothing of defects on the surface of crystals occurs [11]. Thus, the dose adjustment of defects and the rate of change of free volume depending on the dose of radiation determines the radiation resistance of materials and does depend on the initial state of their surfaces.

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ИК-СПЕКТРОСКОПИЯ И АСМ-МИКРОСКОПИЯ ПОВЕРХНОСТИ ГАММА-ОБЛУЧЕННЫХ СЛОИСТЫХ МОНОКРИСТАЛЛОВ GaS И GaS:Yb

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Впервые методами атомно-силовой микроскопии (АСМ) и ИК-фурье-спектроскопии получена информация о рельефе поверхности нелегированных GaS и легированных монокристаллов GaS:Yb, подвергнутых гамма-облучению. Установлено, что для монокристаллов GaS характерно неравномерное распределение неровностей с различной высотой и периодичностью, а при легировании кристаллов атомами Yb распределение неровностей упорядочится, их высота и периодичность уменьшатся. В ИК-фурье-спектрах наблюдаются изменения коэффициентов отражения поверхности монокристаллов GaS и GaS:Yb в зависимости от дозы гамма-облучения (Φ_γ = 30…200 крад), и на основе этих изменений установлено, что легированные монокристаллы являются более радиационно стойкими.

ІК-СПЕКТРОСКОПІЯ І АСМ-МІКРОСКОПІЯ ПОВЕРХНІ ГАММА-ОПРОМІНЕНИХ ШАРУВАТИХ МОНОКРИСТАЛІВ GaS І GaS:Yb

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Вперше методами атомно-силової мікроскопії (АСМ) і ІК-фур'є-спектроскопії отримано інформацію про рельєф поверхні нелегованих GaS і легованих монокристалів GaS:Yb, підданих гамма-опроміненню. Встановлено, що для монокристалів GaS характерний нерівномірний розподіл нерівностей з різною висотою і періодичністю, а при легуванні кристалів атомами Yb розподіл нерівностей упорядкується, їх висота і періодичність зменшаться. В ІК-фур’є-спектрах спостерігаються зміни коефіцієнтів відбиття поверхні монокристалів GaS і GaS:Yb в залежності від дози гамма-опромінення ($\Phi\gamma$ = 30...200 крад), і на основі цих змін встановлено, що леговані монокристали є більш радіаційно стійкими.