Journal of Radiation Researches, vol.11, No.2, 2024, Baku
Current transport characteristics in gamma-irradiated GaS(Yb) layered single crystals
pp. 22–28

PACS: 71.23.Cq

CURRENT TRANSPORT CHARACTERISTICS IN GAMMA-IRRADIATED GaS(Yb) LAYERED SINGLE CRYSTALS

R.S. Madatov[1,2], T.B. Tagiev[1], M.A. Mammadov[1], R.M. Mamishova[1,3], A.Sh. Khaligzadeh[1]

[1]*Institute of Radiation Problems, MSE AR*
[2]*National Aviation Academy,*
[3]*Azerbaijan University of Architecture and Construction, MSE AR*
msrahim@mail.ru, aydankhaligzade@gmail.com

Abstract: The electrical and photoelectrical properties of GaS<Yb>0.1at% single crystals irradiated with γ-quanta at doses up to $D \leq 50$ krad were studied. It was found that γ-irradiation involves both donor- and acceptor-type defects, in which the gallium vacancy is dominant. It was found that the increase in electrical conductivity of the irradiated crystal at low temperatures is due to the formation of a complex involving an ytterbium atom (~ 0.039 eV). In contrast, the quenching of the electrical conductivity in the 200 ÷ 250K range is attributed to the formation of a deep donor level with an activation energy of ~ 1.48 eV. It was established that, with increasing radiation dose, the depth of quenching decreases and the quenching temperature shifts toward higher values.

Keywords: concentration, alloy, acceptor, donor, dose, photoelectric.

1. Introduction

The role and significance of the interaction processes of impurities and defects in controlling the properties of semiconductor materials are especially critical in complex semiconductor compounds, which include, in particular, compounds of the $A^{III}B^{VI}$ group [1–5]. Possessing unique photoelectric, radiation and electro-optical characteristics [6–10], compounds of this group have not yet found widespread application in modern optoelectronic devices due to the limited research and the complexity of controlling impurity–defect interactions within them. The study of the physico-chemical regularities governing the restructuring of structural defects and impurity-defect interactions in single crystals of $A^{III}B^{VI}$ compounds, as well as the establishment of interrelations between these processes, remains a relevant research objective.

In this paper, we present the results of studies on the electrical and photoelectric properties of GaS(Yb) single crystals irradiated with γ-quanta, aiming to determine the effect of the interaction between structural and radiation-induced defects on the electrical and photoelectric behaviour of layered GaS(Yb).

This work aimed to study the effect of irradiation on the structural properties of layered GaS(Yb) (x = 0.01 at.%).

2. Experimental part

GaS <Yb> (0.1%) single crystals were grown using directional Bridgman–Stockbarger crystallisation. Yb doping was introduced during the growth of the single crystal. The obtained crystals exhibited p-type conductivity, with a resistivity of 10^9 Ω·cm at room temperature. Ohmic contacts were formed using indium, which was fused to the surface of gallium sulphide at a temperature of 150 °C. Samples were irradiated with γ-quanta using a Co^{60} apparatus at 300 K. The crystals were cooled with pairs of liquid nitrogen during irradiation, and their temperature did not exceed 290 K. The measurement technique for the electrical and photoelectric characteristics of the samples is described in [11]. To measure the current in the samples, we used an apparatus consisting of a universal voltmeter–electrometer V7-30, a microvolt–ampere meter F-136, and a monochromator MS3504i, operating in the temperature range T = 110–300 K and the wavelength range λ = 380–800 nm.

3. Discussion of Experimental Section and Conclusions

The temperature dependence of the electrical conductivity of undoped and Yb-doped (0.1 at%) GaS single crystals, both before and after γ-ray irradiation, is shown in Fig. 1. As seen from the figure, the electrical conductivity of the undoped GaS crystal (Fig. 1, curve 1), is almost independent of temperature in the range T = 130–230 K, while in the higher temperature region (T > 230 K), it increases with temperature. In this case, the activation energy values for conductivity, determined from the slope of the high-temperature branch of the σ (1/T) curve, are ~ 1.807 eV, while from the low-temperature part of the σ (1/T) curve, they are ~ 0.015 eV. For the doped GaS(Yb) sample (Fig. 1, curve 2), a linear section with a slope of ~ 0.049 eV is observed on the curve of the electrical conductivity versus temperature. The variation of σ (1/T) in the range from 100 to 300 K shows that in the doped samples, the carrier concentration decreases in the low-temperature range of 100–210 K, while it increases in the 210–300 K range compared to the initial samples. A sharp increase in the conductivity in σ (T) at temperatures above ~ 210 K can be explained by the onset of hopping conductivity, which is observed in samples with a high defect content [15].

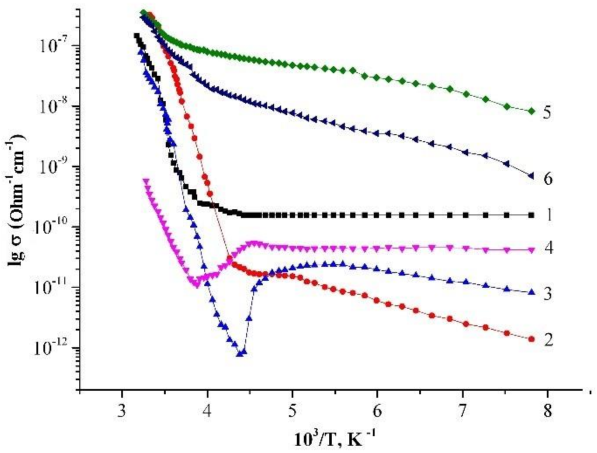

Fig. 1. Temperature dependence of electrical conductivity in GaS and GaS<Yb>0,1at% monocrystals
1 – GaS; 2 – GaS<Yb>0,1at%; 3 – GaS<Yb>0,1at%, $D_γ$ = 20 krad; 4 – GaS<Yb>0,1at%, $D_γ$ = 50 krad; 5 – GaS<Yb>0,1at%,E = 2.59 eV; 6 – GaS<Yb>0,1at%, E = 2.3 eV.

From Fig. 1, curves 1 and 2, it can be inferred that deep levels with an ionization energy of ~ 1.80 and ~ 1.72 eV exist in the forbidden band of the investigated initial and doped GaS crystals, respectively. As seen in Fig. 1, curves 1 and 2, the increase in conductivity at T > 200 K in GaS <Yb>0.1 at% crystals is associated with the formation of an acceptor-type level. It can be assumed that Yb atom impurities in GaS form two levels, both an acceptor (Ea ~ 1.72 eV) and a donor (Ed ~, 049 eV), with significantly different concentrations. As seen in Fig. 1, curve 3, after irradiation with gamma quanta, in doped GaS <Yb>, a decrease in conductivity is observed in the temperature range of 220–300 K, while an increase in conductivity occurs at low temperatures (100–200 K). As seen in the figure, for the doped samples before and after irradiation (curves 2 and 3), two rectilinear sections corresponding to levels associated with the presence of Yb (~ 0.049 and ~ 0.039 eV) are observed on the curves. This indicates that when GaS <Yb> crystals are irradiated, an additional level is introduced with the participation of ytterbium. However, it should be noted that the behaviour of the electrical conductivity curves in irradiated GaS <Yb> samples (curve 3, D = 20krad) in the temperature range (200–270 K) differs from that of the non-irradiated samples. As seen in curves 3 and 4, in the 200–270 K range, the irradiated GaS <Yb> samples exhibit a quenching of conductivity. With increasing irradiation dose, the depth of quenching decreases, and the quenching band shifts to the higher temperature side. It was found that after irradiation of the GaS <Yb>(0.1 at%) crystal with $D\gamma = 20$ and 50 krad (Fig. 1, curves 3 and 4), the value of the activation energy of the impurity conductivity changes with increasing irradiation dose, from 0.049 (curve 2) to 0.016 eV (curve 4), respectively. It can be observed that in the high-temperature region ($T > 200 \div 230$ K), the electrical conductivity of the samples increases with increasing irradiation dose. The calculated activation energy for the irradiated samples varies from 1.72 (curve 2) to 1.36 eV (curve 4), which is attributed to the generation of additional intrinsic charged radiation defects and changes in their distribution within the crystal structures.

To clarify the role and behaviour of radiation defects and ytterbium atoms in layered GaS crystals, the effect of illumination ($h\nu = 2.59$ and 2.3 eV) on the electrical conductivity of the samples was studied. As seen in Fig. 1, curves 5 and 6, when the samples are illuminated with monochromatic light, the levels become filled, weakening the dependence of the current on temperature.

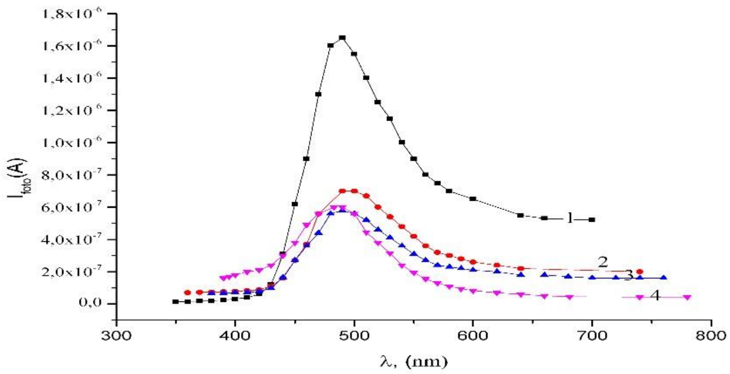

Fig.2. Photoconductivity spectra for GaS and GaS<Yb>0,1at% monocrystals at room temperature (T = 300 K).
1 – GaS; 2 – GaS<Yb>0,1at%; 3 – GaS<Yb>0,1at%, $D_\gamma = 20$ krad; 4 – GaS<Yb>0,1at%, $D_\gamma = 50$ krad.

The spectral distributions of photoconductivity at room temperature for GaS and GaS<Yb>0.1 at.% crystals, both before and after irradiation with gamma- quanta, are shown in Fig. 2. The maximum of photoconductivity is observed near the fundamental absorption edge at $\lambda_{max} = 490$ nm (curve 1) in the initially studied crystals. The photoconductivity at $\lambda = 490$ nm decreases (curve 2) in crystals doped with ytterbium. After irradiation of the GaS <Yb> at.0.1% crystal, the photoconductivity decreases, and while the maximum wavelength remains unchanged, the photoconductivity in the impurity region at $\lambda = 740$ nm decreases by approximately 5 times after irradiation with a dose of $D_\gamma = 50$ krad.

Spectral photoconductivity curves for undoped and yttrium-doped sulphide gallium crystals were also recorded at T = 110 K after γ-irradiation with different doses (D_γ = 20 krad, D_γ = 50 krad, Fig. 3).

As seen in Fig. 3, the photosensitivity of doped GaS<Yb> crystals in the studied wavelength range (λ = 380÷800 nm) is nearly an order of magnitude higher than that of the undoped crystals. Thus, the doping of layered GaS crystals with ytterbium leads to an increase in dark resistivity and the emergence of high photosensitivity in the spectra at low temperatures. It is observed that when the samples are irradiated with gamma rays at a dose of D_γ = 20 krad, the position of the intrinsic maximum in the photoconductivity spectra and the shape of the spectrum remain unchanged compared to the pre- irradiation state of the crystals; however, the photocurrent slightly decreases (at λ_{max} = 490 nm).

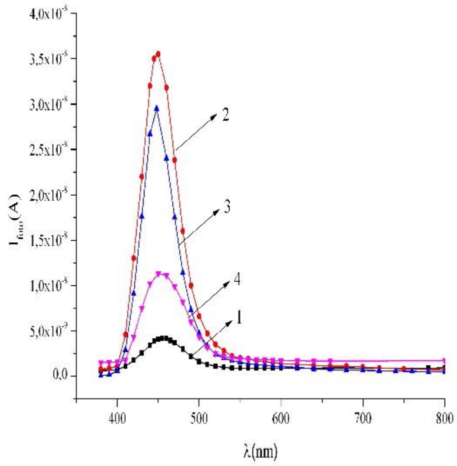

Fig. 3. Photoconductivity spectra of GaS and GaS<Yb>0,1at% monocrystals at a temperature of T = 110 K 1 – GaS; 2 – GaS<Yb>0,1at%; 3 – GaS<Yb>0,1at%, D_γ = 20 krad; 4 – GaS<Yb>0,1at%, D_γ = 50 krad.

However, the magnitude of impurity photoconductivity at wavelengths λ > 700 nm decreases significantly compared to that in non-irradiated crystals, which is attributed to an increased concentration of interstitial gallium atoms. With increasing irradiation dose (up to 50 krad), both a slight decrease in photocurrent in the fundamental absorption region (λ_{max} = 490 nm) and an increase in wavelengths λ > 700 nm are observed. Further, irradiation leads to a decrease in photosensitivity, which is attributed to an increased concentration of recombination centers - chalcogen vacancies- in the investigated samples.

As is known [5, 6, 12], layered crystals, particularly GaS, are composed of layers containing four atomic planes arranged in an S-Ga-Ga-S sequence. Each metal is tetrahedrally surrounded by three chalcogen atoms and one metal atom, forming a metal-metal bond. The metal atoms in the structure exhibit a coordination number of 4, forming sp^3-tetrahedral coordination involving s^2p^4 electrons. The sulphide atom exhibits a pyramidal coordination with a coordination number of 3, involving its p^3 and main s^2p^4 electrons. The metal-metal bond, along with the compensation of excess electrons, contributes to the formation of semiconductor band structures. The orientation of the bonds in the metal atoms imparts a predominantly covalent character to the chemical bonding in these compounds. The negative charge on the metal and the positive charge on the chalcogen are reduced by the contribution of the overall bond in these compounds. Between the layers, the mutual action is due primarily to forces of the van der Waals type, with a minor addition of Coulomb forces.

Upon alloying the studied single crystals of gallium sulphide, ytterbium ions, due to the relatively small difference in radii between them and the atoms of the metallic component (gallium), can occupy both the natural layers (by replacing the Ga vacancies or occupying interstices) and interlayer space. As a result, firstly, the number of vacancy-type structural defects decreases because the anion atoms, by accepting ytterbium electrons, reduce the hole concentration; and secondly, the ytterbium atoms occupying vacancies in different layers form covalent bonds between neighbouring layers, which are stronger than the Van der Waals bonds. This results in the healing of structural defects, which causes a decrease in the electrical conductivity of the crystals (Fig. 1, curve 2). The increase in electrical conductivity of GaS (Yb) at $T > 200$ K is attributed to the creation of a deep level by ytterbium. The electrical conductivity of the crystals increases at low temperatures (100–200 K) and decreases sharply in the 200–250 K region (Fig. 1, curve 3) when the crystals are irradiated with small doses (30 krad). The observed feature in the $\sigma(1/T)$ dependence can be related to the existence of acceptor levels at 0.037 eV and donor levels at 1.48 eV, which result from the formation with participation of initial defects and impurities. An interesting reduction in the depth of the dark current is observed between 200−250 K, accompanied by a shift of the minimum to the high-temperature side. This may be caused by a decrease in the concentration of the donor centres due to the dissociation of the complex involving an impurity atom and a cation vacancy.

It should be taken into account [6, 7, 13, 14] that irradiation of GaS crystals with γ-quanta mainly leads to simple point defects. These defects accumulate with increasing irradiation and redistribute a significant fraction of the recombination current flow of non-equilibrium carriers. The interstitial gallium atoms are responsible for the photoconductivity in the impurity region in the samples. Gamma irradiation of GaS <Yb> 0.1 at.% leads to a decrease in photosensitivity in the spectral region at $\lambda = 740$ nm (Fig. 2, curve 4). It can be assumed that similar changes will be characteristic of GaS. This indicates a decrease in the concentration of the gallium vacancy, apparently due to its interaction with Yb atoms. It should be noted that irradiation of undoped GaS single crystals leads to an increase in impurity photoconductivity due to an increase in the concentration of gallium vacancies. According to the results of the study, it can be concluded that ytterbium atoms in GaS replace gallium atoms, forming a shallow donor level. In this case, partial compensation of acceptor levels occurs, leading to a decrease in the dark concentration of free holes. Therefore, at $T = 110$ K , the photosensitivity of the doped and irradiated samples increases in the intrinsic region of the spectrum, while in the impurity region of the spectrum, it decreases at low doses and then increases with a further dose escalation (Fig. 3, curves 2.3 and 4). As seen in Fig. 2, at $T = 300$ K, the photoconductivity of GaS <Yb> samples decreases across the entire spectral range with increasing irradiation. This behaviour of the photoconductivity spectra is attributed to the restructuring of structural defects [5, 8, 9, 15] and the impurity-defect interactions induced by irradiation [16, 17] in single crystals of $A^{III}B^{VI}$ compounds. This circumstance enables the development of materials with predetermined properties and positions gallium sulphide as a promising material for a wide range of electronic and optoelectronic device applications.

Thus, the obtained experimental results can be explained in the framework of the model proposed in [1, 5, 13].

According to this model, gamma-ray irradiation of GaS <Yb> crystals introduces both donor- and acceptor-type defects. Assuming that the concentrations of simple defects in the metal and chalcogen sublattices are equal, the dominant role is played by acceptor-type defects (such as metal vacancies and interstitial chalcogen atoms). With increasing γ-irradiation doses in GaS and GaS (Yb) samples, no inversion of conductivity type is observed, indicating a high concentration of structural defects. These defects are intrinsic structural defects by character and nature. The electrical and photoelectric properties of these crystals are mainly determined by their electroactive point defects, whose concentration and the energy positions of the corresponding levels are influenced by technological operations.

References

1. R.S. Madatov, A.I. Najafov, T.B. Tagiev, A.R. Mobili, Effect of gamma irradiation on the electrical conductivity of the layered compound GaS, *Inorg. Mater.*, Vol. 44, 2008, pp. 100–103, https://doi.org/10.1134/S0020168508020039
2. R.S. Madatov, T.B. Tagiyev, A.I. Najafov, I.F. Gabulov, Sh.P. Shekili, Optical and photoelectrical properties of lamellar gallium sulfide single crystals irradiated by γ-quanta, *Semicond. Phys. Quantum Electron. Optoelectron.*, Vol. 9, No. 2, 2006, pp. 8–11, https://doi.org/10.15407/spqeo9.02.008
3. M. Caraman, V. Chiricenco, L. Leontie, I.I. Rusu, Photoelectrical properties of layered GaS single crystals and related structures, *Mater. Res. Bull.*, Vol. 43, 2008, pp. 3195–3201, https://doi.org/10.1016/j.materresbull.2008.04.014
4. V. Zólyomi, N.D. Drummond, V.I. Fal'ko, Band structure and optical transitions in atomic layers of hexagonal gallium chalcogenides, *Phys. Rev. B*, Vol. 87, 2013, p. 195403, https://doi.org/10.1103/PhysRevB.87.195403
5. H. Kamimura, K. Nakao, Band structure of the semiconducting layer compounds, *J. Phys. Soc. Jpn.*, Vol. 21, 1966, pp. 27–31, Avvailable at: PDF
6. A.I. Najafov, O.Z. Alekperov, *Neorg. Mater.*, 1991, pp. 2432–2433.
7. H. Ertap, T. Baydar, M. Yüksek, M. Karabulut, Structural and optical properties of gallium sulfide thin film, *Turk. J. Phys.*, Vol. 40, No. 3, 2016, pp. 297–303, https://doi.org/10.3906/fiz-1604-14
8. R.H. Williams, J.V. McCanny, R.B. Murray, L. Ley, P.C. Kemeny, The electronic band structure of indium selenide: photoemission and theory, *J. Phys. C: Solid State Phys.*, Vol. 10, No. 8, 1977, pp. 1211–1222, https://doi.org/10.1088/0022-3719/10/8/023
9. O.Z. Alekperov, M.O. Gogjaev, M.Z. Zarbaliev, R.A. Suleimanov, Interband photoconductivity in layer semiconductors GaSe, InSe and GaS, *Solid State Commun.*, Vol. 77, No. 1, 1991, pp. 65–67, https://doi.org/10.1016/0038-1098(91)90428-X
10. M. Ohyama, H. Ito, M. Takeuchi, Growth, optical and structural characterisation of layered GaS films prepared by reactive RF sputtering method, *Jpn. J. Appl. Phys.*, Vol. 44, 2005, pp. 4780–4783, https://doi.org/10.1143/JJAP.44.4780
11. V.Ye. Lashkarev, A.V. Lyubchenko, M.K. Sheynkman, *Nonequilibrium Processes in Semiconductors*, Kiev: Naukova Dumka, 1981.
12. G. Micocci, R. Rella, P. Siciliano, A. Tepore, Investigation of electronic properties of gallium sulfide single crystals grown by iodine chemical transport, *J. Appl. Phys.*, Vol. 68, 1990, pp. 138–142, https://doi.org/10.1063/1.347105
13. V.S. Vavilov, H.A. Ukhin, *Radiation Effects in Semiconductors and Semiconductor Devices*, Moscow: Atomizdat, 1969, 270 p.
14. V.V. Emchev, T.G. Mashovech, *Alloys and Defects in Semiconductors*, Moscow: Radio i Svyaz, 1981, 247 p.
15. L.S. Smirnov, *Physics Processes in Irradiated Semiconductors*, 1977, 253 p.

16. R.S. Madatov, T.B. Tagiev, A.Sh. Khaligzadeh, Photoluminescence of undoped and Yb-doped GaS single crystals irradiated with γ-quanta, *Probl. At. Sci. Technol.*, Vol. 135, No. 5, 2021, pp. 42–43, https://doi.org/10.46813/2021-135-042
17. R.S. Madatov, T.B. Tagiev, A.Sh. Khaligzadeh, The effect of γ-irradiation on the volt-ampere characteristics (VAC) of GaS monocrystal doped with Yb, *J. Radiat. Res.*, Vol. 8, No. 2, 2021, pp. 60–64, Avvailable at: Issue page, PDF

ХАРАКТЕРИСТИКИ ТОКОНЕСЕНИЯ В СЛОИСТЫХ МОНОКРИСТАЛЛАХ GaS(Yb), ОБЛУЧЁННЫХ ГАММА-КВАНТАМИ

Р.С. Мадатов, Т.Б. Тагиев, М.А. Мамедов, Р.М. Мамишова, А.Ш. Халигзаде

Резюме: Исследованы электрические и фотоэлектрические свойства монокристаллов GaS<Yb> 0,1 ат.% после облучения γ-квантами с дозой ≤ 50 крад. Установлено, что облучение приводит к образованию как донорных, так и акцепторных дефектов, среди которых преобладают вакансии галлия. Повышение электропроводности в облучённом кристалле при низких температурах связано с образованием комплекса с участием атома иттербия (~ 0.039 эВ), а подавление электропроводности в интервале температур 200 ÷ 250 К с формированием глубокого донорного уровня с энергией активации ~ 1.48 эВ. Установлено, что с увеличением дозы облучения глубина подавления уменьшается, а температура подавления смещается в сторону высоких температур.

Ключевые слова: концентрация, легирование, акцептор, донор, доза, фотоэлектрические.

QAMMA KVANTLARI İLƏ ŞÜALANMIŞ GaS(Yb) LAYLI MONOKRİSTALINDA CƏRƏYANIN DAŞINMA XARAKTERİSTİKALARI

R.S. Mədətov, T.B. Tağıyev, M.Ə. Məmmədov, R.M. Məmişova, A.Ş. Xalıqzadə

Xülasə: D ≤ 50 krad dozada γ-kvantları ilə şüalanmış GaS<Yb>0.1 at.% tərkibli monokristalların elektrik və fotoelektrik xassələri tədqiq edilmişdir. Məlum olmuşdur ki, şüalanma həm donor, həm də akseptor tipli defektlərin yaranmasına səbəb olur və bu zaman əsasən qalium vakansiyası üstünlük təşkil edir. Aydınlaşdırılmışdır ki, aşağı temperaturlarda şüalanmış kristalda elektrik keçiriciliyinin artması itterbium atomunun iştirakı ilə yaranan kompleks (~0.039 eV) səbəbilə baş verir, 200 ÷ 250K temperatur intervalında keçiriciliyin sönməsi isə aktivləşmə enerjisi təqribən ~1.48 eV olan dərin donor səviyyəsinin formalaşması ilə əlaqəlidir. Həmçinin müəyyən edilmişdir ki, şüalanma dozası artdıqca keçiriciliyin sönmə dərinliyi azalır və sönmə temperaturu yüksək temperaturlara doğru sürüşür.

Açar sözlər: konsentrasiya, qatqı, akseptor, donor, doza, fotoelektrik.