PHYSICS AND CHEMISTRY OF SOLID STATE
V. 25, No. 2 (2024) pp. 297-302
Section: Physics

DOI: 10.15330/pcss.25.2.297-302

Vasyl Stefanyk Precarpathian National University

ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 25, № 2 (2024) С. 297-302
Фізико-математичні науки

PACS: 85.60.Jb

ISSN 1729-4428 (Print)
ISSN 2309-8589 (Online)

M.M. Slyotov[1], O.M. Slyotov[1], H.V. Potsiluiko-Hryhoriak[2], M.P. Mazur[3], T.M. Mazur[3]

GaN based light emitters

[1]*Yuri Fedkovich Chernivtsi National University, Chernivtsi, Ukraine, m.slyotov@chnu.edu.ua*
[2]*Chernivtsi Industrial Professional College, Chernivtsi, Ukraine*
[3]*Ivano-Frankivsk National Technical University of Oil and Gas Ivano-Frankivsk, Ukraine, tetiana.mazur@nung.edu.ua*

The article discusses the preparation of epitaxial layers and *GaN* crystals, as well as the results of studies of their optical and luminescent properties. The parameters of the band structure of the resulting hexagonal modification materials $\Delta_{CR} \approx 10$ meV and $\Delta_{SO} \approx 48$ meV were determined. The mechanisms of the main recombination processes that determine the formation of radiation from undoped and *Zn*-doped materials have been established. The role of interband recombination and annihilation of excitons in the formation of radiation in the high-energy region and transitions of carriers through energy states that are formed and created by intrinsic point defects of the crystal lattice and dopant has been established. The role of response recombination processes in the formation of short-wave radiation spectra is analyzed.

Keywords: gallium nitride, layers and crystals, optical properties, mechanisms of radiative recombination.

Received 06 December 2023; Accepted 8 May 2024.

Introduction

Currently, an important task in solid-state electronics is to expand the functionality of the devices used [1-3]. In the case of light emitters, the issue of improving the materials used becomes relevant. They require obtaining high radiation intensity and expanding the spectral range into the little developed short-wave region [4,5]. Practical use predetermines the need to ensure the stability of the obtained parameters, characteristics and properties of radiation sources. In addition, the ability to use them under extreme conditions, in particular elevated temperatures, is important [6,7]. These problems for heterolayers of II-VI compounds are successfully solved through the development of doping technology with isovalent impurities [8,9]. However, other materials are widely used, especially III-V compounds. Among them, group III nitrides are attracted. Gallium nitride deserves special attention [10]. Its direct gap and large band gap are an important condition for obtaining high radiation efficiency, which, in accordance with existing developments, can cover the short-wave range. This is evidenced by the successes in obtaining various types of emitters based on group III nitrides [8,10]. At the same time, an important issue for *GaN* remains the further improvement of properties and the establishment of factors influencing them. Setting this for basic *GaN* is important for developing processes for obtaining the material and creating on its basis appropriate designs of highly efficient light emitters for the short-wave range.

I. Objects and methods of research

The properties of epitaxial layers and *GaN* single crystals were studied. They were obtained by deposition from the gas phase using the chloride-hydride method [11]. The production of epitaxial layers and single crystals behind it was carried out in a quartz reactor according to the main reaction

$$GaCl + NH_3 \rightarrow GaN + HCl + H_2 \quad (1)$$

The source of metallic gallium and the leucosapphire substrate (or graphite in the case of crystals) were placed in the region of the temperature plateau in accordance with

its distribution curve. The temperature conditions for which the studied samples were obtained were determined. It has been established that when producing epitaxial layers and crystals, deposition temperatures differ by 150-200 ^{0}C. At T = 1150-1200 ^{0}C, transparent colorless crystals of hexagonal shape are obtained, up to 5 mm long and 1 mm thick, Fig. 1.

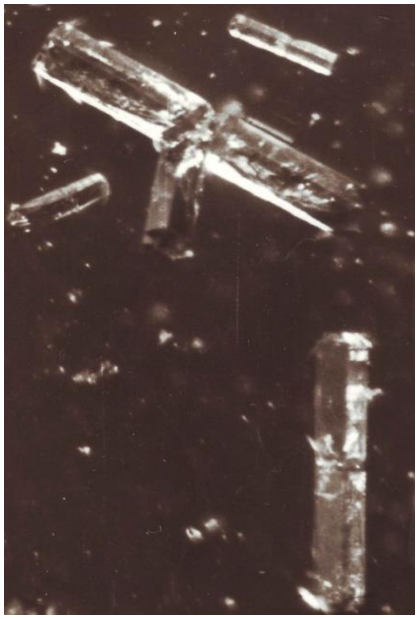

Fig. 1. Photograph of gallium nitride crystals taken at ×20 magnification.

Epitaxial layers were produced on leucosapphire substrates oriented in the [10$\bar{1}$2] plane and prepared using appropriate technology to obtain a structurally perfect material. The optimal arrangement of sources and substrates in the reactor has been established to obtain optically transparent colorless epitaxial layers up to 20 microns thick [12].

The structural perfection of the experimentally obtained samples was studied using a standard X-ray diffraction setup using a well-known technique [613,14]. Based on their results, the process of obtaining structurally perfect material was improved. To establish the optimality of technological modes, studies were carried out on optical transmission T_ω, reflection R_ω and photoluminescence N_ω. The studies were carried out on a complex experimental setup based on an MDR-23 monochromator and systems for synchrodetection and registration of optical signals with photomultipliers for the corresponding range. The measurement results were recorded on recorders. To determine the fine structure in the measured spectra, the λ-modulation method was used [14,15]. The measurement accuracy was 3%. The experimental results were processed using known methods [15-17].

II. Research results

The regimes were established and the studied epitaxial layers and *GaN* crystals were obtained using the specified widely known chloride-hydride method. They are characterized by intense photoluminescence in the short-wave region $\Delta\lambda$ = 0.42÷0.35 μm. The high radiation efficiency indicates the optimal growth modes for the formation of a perfect crystal structure [18]. This is confirmed by studies of the parameters of their band structure using the methods of long-wave optical absorption T_ω and reflection R_ω. The use of the modulation method significantly increased the sensitivity of the studies, Fig. 2. According to the obtained measurement results, their band gap is E_g = 3.42 eV at 300 K and E_g = 3.47 eV at 78 K.

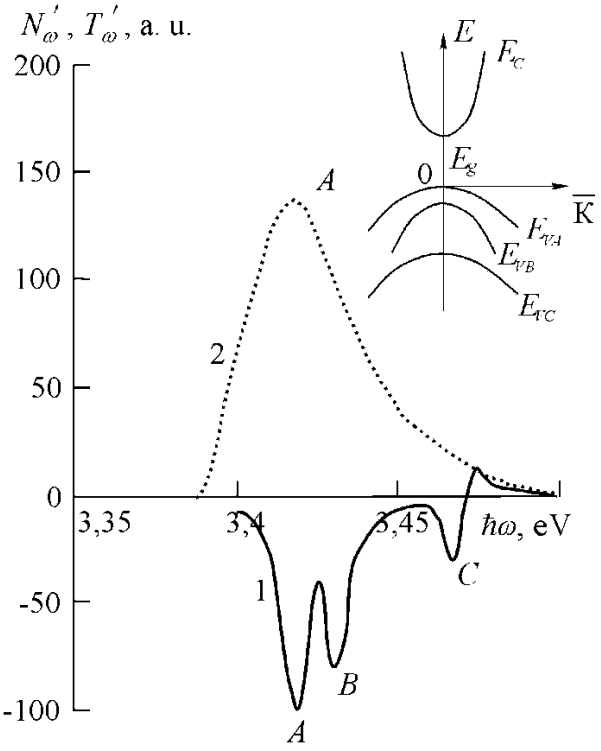

Fig. 2. Spectra of λ-modulated reflection (1) and transmission (2) of undoped *GaN*. T = 300 K. The inset shows the band structure of *GaN*.

The basic parameters of the band structure of *GaN* crystals have been determined, namely the energy of splitting the valence band into subbands due to the spin-orbit interaction Δ_{SO} and the action of the crystal field Δ_{CR}. Based on the obtained differential curves, their values $\Delta_{SO} \approx 48$ meV and $\Delta_{CR} \approx 10$ meV were established. The established parameters of the band structure indicate a hexagonal crystal lattice of the resulting *GaN*.

The established growth conditions made it possible to obtain intense photoluminescence in the short-wave region on undoped *GaN* films and crystals. In particular, the radiation of undoped crystals is characterized by a spectrum at $\Delta\lambda$ = 0.355÷0.360 μm, which at 77 K is described by two components (Fig. 3).

The maximum of band *A* occurs at the photon energy $\hbar\omega$ = 3.473 eV at 77 K. The position of the maximum does not depend on the photoexcitation level *L* when its value changes by 3 orders of magnitude, and the temperature dependence of its position is similar to the temperature dependence of the band gap. The nature of the spectral distribution is well approximated by the theoretical expression of interband radiative transitions [19]

$$N_\omega = (\hbar\omega)^2(\hbar\omega - E_g)^{1/2} exp\left[-\frac{\hbar\omega - E_g}{kT}\right], \qquad (3)$$

where k is Boltzmann constant, T is temperature. Thus, according to the information obtained for theoretical representation, the established properties indicate interband radiative recombination, which determines the formation of radiation from *GaN* crystals in the photon energy region $\hbar\omega \geq E_g$.

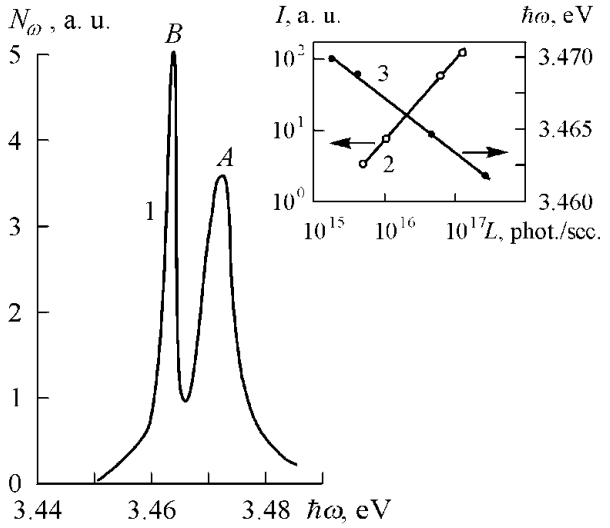

Fig. 3. Emission spectrum of *GaN* crystals during interband *A* and exciton *B* transitions. Inset: dependence of the intensity position (2) of band *B* and its maximum (3) on the excitation level *L*. *T* = 77 K.

The second band of their radiation with a maximum at $\hbar\omega \leq E_g$ (3.642 eV) is characterized by the following properties: 1) the intensity of radiation *I* changes with increasing excitation level *L* according to the law $I \sim L^{1.5}$; 2) the maximum $\hbar\omega_m$ shifts with increasing *L* to the region of lower quantum energies. Such properties are inherent in excitonic photoluminescence [20,21]. This nature of radiation is characteristic of structurally perfect materials. Accordingly, its observation, as well as the presence of interband recombination, indicate successfully determined conditions for obtaining structurally perfect crystals. In general, the resulting material can be used in the manufacture of effective emitters for the violet and ultraviolet ranges.

Note that the quantum efficiency of *GaN* crystal radiation is $\eta \approx$ 6-8%. The corresponding analysis and measurement were carried out according to a well-known method [22,23]. For typical *ZnS* crystals $\eta \approx$ 1-3%, and for *ZnSe* – $\eta \approx$ 0.5-0.8%.

It has been established that the luminescence of undoped *GaN* layers falls in the photon energy range $\hbar\omega$ = 3.1÷3.5 eV, Fig. 4. The radiation covers both the edge region $\hbar\omega \geq E_g$ and the violet range at $\hbar\omega < E_g$. In the first of them, the properties of the radiation and the correlation of the experimental spectrum with the curve calculated by expression (3) at E_g = 3.42 eV indicate interband radiative recombination, band *A* in Fig. 4.

In the $\hbar\omega \leq E_g$ region, the intensity of the radiation and its spectrum indicate transitions of charge carriers involving energy states. Due to the lack of doping of *GaN* layers, their formation is caused by intrinsic point defects (IPDs) of the crystal lattice. This is confirmed by the subsequent analysis of their nature and corresponding properties.

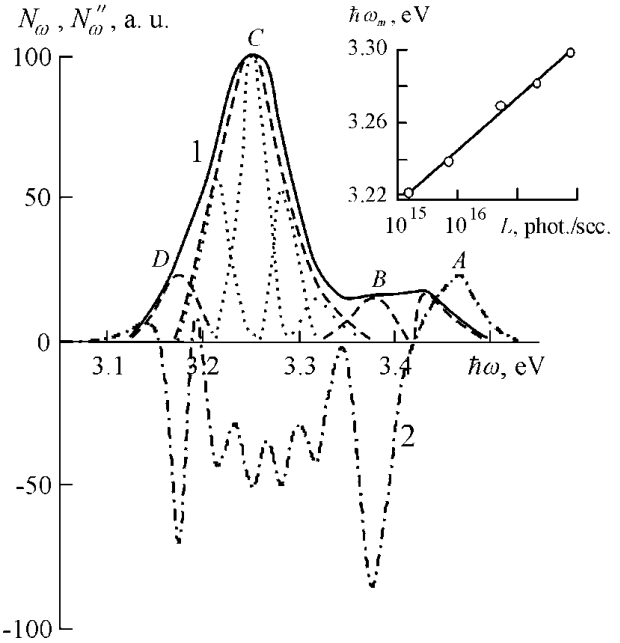

Fig. 4. Spectras of conventional N_ω (curve 1) and λ-modulated N'_ω (curve 2) PL of undoped epitaxial films and *GaN* components, calculated by the Alentsev-Fock method due to interband recombination (*A*) with the participation of donor $V_N^{\cdot}$ (*B*) and acceptor V'_{Ga} (*D*) and their associates ($V_N^{\cdot}V'_{Ga}$) (*C*). The inset shows the dependence of the position of the *C*-band maximum on the excitation level.

It has been established that the emission of the studied undoped *GaN* at $\hbar\omega < E_g$ is formed with the participation of components *B*, *C* and *D*, Fig. 4. Bands *B* and *D* in the spectrum are characterized by the following qualities: firstly, their contour is symmetrical, half-width ~1.5 *kT*; secondly, the position of the maxima of the $\hbar\omega_m$ bands does not depend on *L* within three orders of magnitude of its change; thirdly, the energy difference $E_g - \hbar\omega_m + kT/2$ is 0.045 eV and 0.24 eV for zones *B* with $\hbar\omega_m$ = 3.375 eV and *D* with $\hbar\omega_m$ = 3.18 eV, respectively. The temperature dependences of the radiation intensity *I(T)* in the region of the maxima of the spectra are plotted in lnI coordinates from *1/T* and, according to the well-known classical expression, are approximated by straight lines in the range 80-300 K. The values of Em determined from their slope are 0.042 eV and 0.23 eV for $\hbar\omega_m$ = 3.375 eV and $\hbar\omega_m$ = 3.18 eV and correlate well with those obtained from $E_g - \hbar\omega_m + kT/2$. Certain properties and analysis of their nature indicate donor and acceptor centers formed by a charged positive nitrogen vacancy $V_N^{\cdot}$ (band *B*) and a negative single-charge gallium vacancy V'_{Ga} (band *D*). Accordingly, the nature of the radiation is determined by transitions according to the Lambe-Click and Schön-Clazens models [23]. In addition, for them, a change in the excitation level *L* does not affect the position of the maxima, which are one of the most important signs of recombination processes involving individual centers. The

indicated components *B* and *D* in the optical spectra are clearly manifested in studies of λ-modulation spectroscopy.

At the same time, the dominant component in the spectrum at $\hbar\omega < E_g$ is the broad C band with $\hbar\omega_m$ = 3.26 eV. Research has revealed a change in the position of the maximum of the *C* component with a change in *L*, inset in Fig. 4. This emission property is the main feature of recombination on donor-acceptor pairs (DAP). Most likely, they are formed by oppositely charged centers located $V_N^{\cdot}$ and V_{Ga}' at appropriate distances *r* in the crystal lattice. Its possible values were established by studies using the λ-modulation method, which revealed the presence of at least four bands in the differential spectrum N_ω' based on its oscillating nature, Fig. 4. Their maxima are located at 3.33, 3.28, 3.24 and 3.21 eV, which corresponds to distances between DAP partners $V_N^{\cdot}$ and V_{Ga}' of 6.6, 8.1, 10.7 and 16.2 Å according to calculations using the Apple model -Williams-Prener [24]. The presence of these bands is confirmed by analytical calculations using the Alentsev-Fock method [25].

Effective radiation in the blue-violet region of the spectrum is obtained by doping *GaN* with a *Zn* impurity. There is a significant (4 orders of magnitude) increase in its intensity and a spectrum maximum at a photon energy of $\hbar\omega$ = 2.95 eV, Fig. 5. Quantum efficiency takes on a value of $\eta \approx$ 9-12%. One explanation for this increase may be changes in the spectral distribution of their radiation [22].

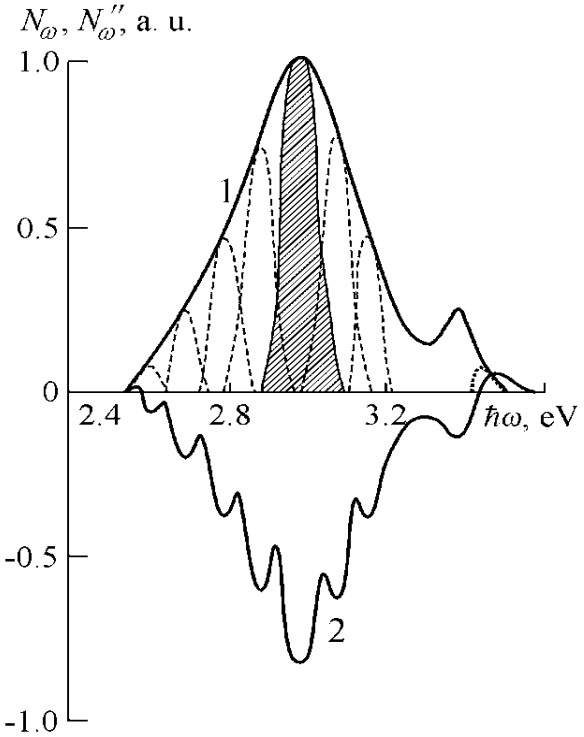

Fig. 5. Spectra of ordinary (1) and λ-modulated (2) luminescence of *GaN:Zn* layers doped to a zinc concentration of 10^{18} cm^{-3}. *T*=300 K.

The properties of radiation correspond to recombination processes involving one local center [19,21]. In particular, $\hbar\omega_m$ depends linearly on *L* when it changes within the range of 10^{14}-10^{18} phot/s. The energy difference $E_g - \hbar\omega_m + kT/2$ is 0.483 eV, which is consistent with the thermal activation energy of the center – E_t = 0.46 eV. A study of the threshold for infrared optical quenching of PL due to charge carrier transitions of the valence band – acceptor type gives a value of 0.48 eV. It has been shown [26] that such a center is an acceptor and is formed when gallium is replaced by zinc Zn_{Ga}. Accordingly, radiation is formed due to the recombination of free electrons with holes localized on acceptors. The half-width of the emission spectrum $\hbar\omega_{½} \sim$ 0.7 eV is much greater than *2kT* at 300 K. It increases significantly with increasing concentration of *Zn* and *L* dopant impurities. We also note that the depth of the Zn_{Ga} centers corresponds to the criterion $E_a > 3\hbar\omega_0$. This indicates the electron-phonon interaction of deep levels. As is known [19,21,22], in this case, in addition to the main band, the components of its phonon repetitions are formed. In this case, they are clearly observed during studies using the λ-modulation method. In the spectrum of the second derivative N_ω'' they correspond to equidistant bands from $\hbar\omega_0 \approx$ 89 meV, curve 2 in Fig. 5. The distance between them corresponds to the *LO* phonon energy (~90 meV) in *GaN*. Thus, the luminescence spectrum of *GaN*<*Zn*> layers is formed by the emission of four and absorption of two *LO* phonons [26]. This explains the wide emission band.

Increasing the temperature (up to 380-410 ^{0}C) slightly reduces the intensity and does not affect the spectral composition. The temperature and time measurements carried out revealed the stability and repeatability of the properties, parameters and characteristics of *GaN* layers and crystals to thermal irradiation up to 420 ^{0}C.

Conclusion

Thus, epitaxial films and *GaN* crystals with stable parameters and characteristics can be obtained by the chloride-hydride method. Behind it, a perfect hexagonal lattice is formed, the band structure of which is described by the parameters E_g = 3.42 eV, $\Delta_{CR} \approx$ 10 meV and $\Delta_{SO} \approx$ 48 meV. The luminescence of base undoped materials is determined by effective interband recombination, and for crystals also by emission of excitons at *T* = 78 K. For undoped layers at $\hbar\omega < E_g$, a broad band $\hbar\omega_m$ = 3.26 eV is formed, the components of which are determined by recombination processes through local donor and acceptor centers and on donor-acceptor pairs. They are formed by positively charged nitrogen vacancies $V_N^{\cdot}$ and negatively charged singly charged gallium vacancies V_{Ga}'. The emission of undoped *GaN* films is characterized by a high quantum efficiency η = 6-8%. When gallium is replaced by zinc Zn_{Ga}, $\eta \approx$ 9-12% is obtained due to the formation of deep acceptors. Accordingly, the radiation is caused by the recombination of free electrons with holes localized on acceptors. In this case, the recombination of carriers is accompanied by electron-phonon interaction of the formed deep levels. Radiating processes are characterized by resistance and repeatability of properties, parameters and characteristics to thermal radiation up to 420°C.

Slyotov *M.M.* – Professor, Doctor of Physics and Mathematics, Professor of the Department of Optics and Publishing and Printing;
Slyotov O.M. – Doctor of Engineering, Assistant of the Department of Electronics and Energy;
Potsiluiko-Hryhoriak H.V. – teacher at Chernivtsi Industrial Vocational College;
***Mazur* M.P. –** PhD (Physics and Mathematics), Associate Professor, Director of the Institute of architecture, Construction and Power Engineering;
Mazur T.M. – Doctor of Philosophy, Associate Professor of the Department of Physical and Mathematical Sciences.

[1] A. Sadao, Properties of Semiconductor Alloys: Group-IV, III-V and II-VI Semiconductors. (New Jersey: Wiley, 2009).
[2] T. Mazur, M. Mazur, M. Halushchak, *Surface-Barrier CdTe Diodes for Photovoltaics*, Journal of Nano- and Electronic Physics, 15(2), 02004-1 (2023); https://doi.org/10.21272/jnep.15(2).02006.
[3] V.B. Kopei, O.R. Onysko, V.G. Panchuk, *Component-oriented acausal modeling of the dynamical systems in Python language on the example of the model of the sucker rod string*, PeerJ Computer Science, 5, e227 (2019); https://doi.org/10.7717/peerj-cs.227.
[4] M. Slyotov, A. Slyotov, *The sources of radiation in the short-wave range on the basis of II-VI heterolayers*, Journal IAPGOS, 4(4), (2018).
[5] B. Dzundza, O. Kostyuk & T. Mazur, *Software and Hardware Complex for Study of Photoelectric Properties of Semiconductor Structures*, 39th International Conference on Electronics and Nanotechnology (ELNANO), Kyiv, 635 (2019); https://doi.org/10.1109/ELNANO.2019.8783544.
[6] B. Naidych, T. Parashchuk, I. Yaremiy, M. Moyseyenko, O. Kostyuk, O. Voznyak, ... & L. Nykyruy, *Structural and thermodynamic properties of Pb-Cd-Te thin films: Experimental study and DFT analysis*, Journal of Electronic Materials, 50, 580 (2021); https://doi.org/10.1007/s11664-020-08561-5.
[7] H. Nykyforchyn, V. Kyryliv, O. Maksymiv, V. Kochubei, R. Boyko, V. Dovhunyk, *Wear resistance of the surface nanocrystalline structure under an action of diethyleneglycol medium*, Applied Nanoscience, 9(5), 1085 (2019); https://doi.org/10.1007/s13204-018-0690-3.
[8] Харків, МОНУ.- -396 С. Е. І. Chernyakov, Yu. P. Machekhin, M. P. Kukhtin, Optoelectronics. (Kharkov, MONU, 396, 2015).
[9] Mazur T.M., Prokopiv V.V., Slyotov M.M., Mazur M.P., Kinzerska O.V., Slyotov O.M. Optical properties of CdTe doped Ca. Physics and chemistry of solid state. 21(1), 52 (2020); https://doi.org/10.15330/pcss.21.1.52-56.
[10] O. Ermakov Applied optoelectronics. (M.: Tekhnosfera, 416, 2004).
[11] A.I. Kurnosov, V.V. Yudin, Technology of production of semiconductor devices and integrated circuits. (M.: Higher school, 368, 1986).
[12] M.M. Slyotov, O.M. Slyotov, *Preparation and luminescent properties of zinc sulfoselenide thin films*, Physics and Chemistry of Solid State. 20(4), 354 (2019).
[13] Yu.V. Vorobiev, V.I. Dobrovolsky, V.I. Stryha, Semiconductor research methods. (Vyshcha schola: Kyiv, 232, 1988).
[14] T. Mazur, M. Slyotov, M. Mazur, V. Prokopiv, O. Kinzerska, O. Slyotov, *Features of the cadmium chalcogenide substrates with surface nanostructure*, Materials Today: Proceedings. 35(4), 661 (2019); https://doi.org/10.1016/j.matpr.2019.12.112.
[15] V. Kyryliv, O. Maksymiv, V. Gurey, I. Hurey, Y. Kyryliv, O. Zvirko, *The mode deformation effect on surface nanocrystalline structure formation and wear resistance of steel 41Cr4*, Coatings. 12(2), 249 (2023); https://doi.org/10.3390/coatings13020249.
[16] V. Kopei, O. Onysko, C. Barz, P. Dašić, V. Panchuk, *Designing a multi-agent plm system for threaded connections using the principle of isomorphism of regularities of complex systems*, Machines, 11(2), 263 (2023); https://doi.org/10.3390/machines11020263.
[17] I. V. Horichok, L. I. Nykyruy, T. O. Parashchuk, S. D. Bardashevska, & M. P. Pylyponuk, *Thermodynamics of defect subsystem in zinc telluride crystals*, Modern Physics Letters B, 30(16), 1650172, (2016); https://doi.org/10.1142/S0217984916501724.
[18] M. Cardona, Modulation spectroscopy. (M.: Mir, 416, 1972).
[19] V.P. Gribkovsky, The theory of absorption and emission of light in semiconductors (Science and technology, Minsk, 464, 1975).
[20] Koh Era, D.W. Langer, *Luminescence of ZnSe near the band edge under strong laser light excitation*, J. Luminescence, 1-2, 514 (1970).
[21] M. Fox, Optical Properties of Solids. (Oxford, New York, 396, 2010).
[22] M. Slyotov, T. Mazur, V. Prokopiv, O. Slyotov, M. Mazur, *Sources of optical radiation based on ZnTe/ZnSe/ZnS heterostructures*, Materials Today: Proceedings, 62, 5763 (2022); https://doi.org/10.1016/j.matpr.2022.03.476.
[23] A.N. Georgobiani and M.K. Sheinkman, Physics of A2B6 compounds (M. Mir, 320, 1986).
[24] P. Yu, M. Cardona, Fundamentals of semiconductor physics (M. Fizmatlit, 560, 2002).
[25] Gavrilenko V.I, Grekhov A.M., Korbutyak D.V., Litovchenko V.G. Optical properties of semiconductors. Directory (Naukova Dumka, Kyiv, 608, 1987).
[26] W.A. Melton, J.I. Pankove, *GaN growth on sapphire*, J. Cryst. Growth, 178, 168 (1997).

М.М. Сльотов[1], О.М Сльотов[1], Г.В. Поцілуйко-Григоряк[2], М.П. Мазур[3], Т.М. Мазур[3]

Світловипромінювачі на основі *GaN*

[1]*Чернівецький національний університет імені Юрія Федьковича, Чернівці, Україна, m.slyotov@chnu.edu.ua*
[2]*Чернівецький індустріальний фаховий коледж, Чернівці, Україна*
[3]*Івано-Франківський національний технічний університет нафти і газу, Івано-Франківськ, Україна, tetiana.mazur@nung.edu.ua*

У роботі розглядається отримання епітаксійних шарів *GaN* і кристалів та результати досліджень їх оптичних та люмінесцентних властивостей. Визначені параметри $\Delta_{CR} \approx 10$ меВ і $\Delta_{SO} \approx 48$ меВ зонної структури отриманих матеріалів гексагональної модифікації. Встановлено механізми основних рекомбінаційних процесів, що визначають формування випромінювання нелегованих і легованих *Zn* матеріалів. Встановлено роль міжзонної рекомбінації і анігіляції екситонів при формуванні випромінювання у високоенергетичному діапазоні та переходи носіїв через енергетичні стани, що формуються і утворюються власними точковими дефектами кристалічної гратки та легуючою домішкою. Аналізується роль відповідних рекомбінаційних процесів у формуванні спектрів короткохвильового випромінювання.

Ключові слова: нітрид галію, шари і кристали, оптичні властивості, механізми випромінювальної рекомбінації.