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Density of States and Interband Light Absorption in $Ga_{1-x}Al_xN$ (x 0, 0.03, 0.07) Thin Films

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The long-wave edge of the fundamental absorption band of thin $Ga_{1-x}Al_xN$ films ($x = 0$, 0.03, 0.07) obtained by radio-frequency (RF) ion-plasma sputtering in a nitrogen atmosphere is investigated. As shown, the empirical Urbach's rule well approximates the edge of interband absorption in the studied films. To analyse the experimental results, a model of a heavily doped or defective semiconductor within the quasi-classical approximation is used. The use of this model enables, depending on the films' chemical composition, the determination of the radius of the ground electronic state a, the screening radius r_s, and the root-mean-square potential Δ. The obtained results are analysed.

Досліджено довгохвильовий край смуги фундаментального вбирання тонких плівок $Ga_{1-x}Al_xN$ ($x = 0$, 0,03, 0,07), одержаних методом високочастотного (ВЧ) йонно-плазмового напорошення в атмосфері азоту. Показано, що край міжзонного вбирання у досліджуваних плівках добре апроксимується емпіричним правилом за Урбахом. Для аналізи експериментальних результатів використано модель сильнолеґованого або дефектного напівпровідника в квазикласичному наближенні. Використання даного моделю уможливило визначити, залежно від хемічного складу плівок, радіюс основного електронного стану a, радіюс екранування r_s і середньоквадратичний потенціял Δ. Проведено аналізу одержаних результатів.

Key words: gallium nitride, thin films, fundamental absorption edge.

Ключові слова: нітрид Ґалію, тонкі плівки, край фундаментального вбирання.

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1. INTRODUCTION

Compounds based on gallium nitride (GaN) are a promising material for ultraviolet detectors and semiconductor light-emitting diodes and lasers emitting in the blue and ultraviolet regions of the spectrum [1–6]. In addition, with its unique physical characteristics and high chemical and thermal stability, gallium nitride is a promising material for the creation of new-generation microelectronic and nanoelectronic devices [7–9], gas sensors, and applications in power electronics [10, 11].

In general, the physical properties of thin films are largely determined by the methods of production, application modes, subsequent technological techniques, and the targeted introduction of impurities, which create varying degrees of perfection in the samples obtained. Based on this, this work investigates thin $Ga_{1-x}Al_xN$ films, in which some of the Ga^{3+} ions are replaced by Al^{3+} ions. This replacement did not require local compensation of the electric charge. At the same time, thin AlN films are also promising components in optoelectronic devices, micro- and nanoelectronics [12–14].

Considering the above, this work investigates the long-wave edge of the fundamental absorption band of $Ga_{1-x}Al_xN$ thin films ($x = 0$, 0.03, 0.07) and analyses it using a model of a heavily doped or defective semiconductor in a quasi-classical approximation. The studied films were obtained by radio-frequency (RF) ion-plasma sputtering, the use of which leads to the deposition of the most homogeneous and perfect multicomponent semiconductor and dielectric films [15].

2. EXPERIMENTAL TECHNIQUE

Thin films of $Ga_{1-x}Al_xN$ ($x = 0$, 0.03, 0.07) on sapphire (Al_2O_3) substrates were obtained by radio-frequency ion-plasma sputtering in a nitrogen atmosphere. The film thicknesses ranged from 0.3 to 0.8 µm. The working gas pressure in the chamber ranged from $5\cdot10^{-3}$ to $5\cdot10^{-2}$ Torr. The substrate temperature during film deposition was of 600°C.

The structure and phase composition of the obtained films were

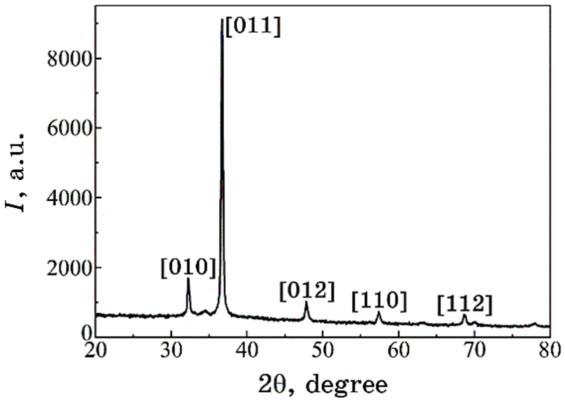

Fig. 1. X-ray diffractograms of thin GaN films obtained by RF sputtering in an N_2 atmosphere on a sapphire substrate.

studied by x-ray diffraction analysis using a Shimadzu XDR-600 device. The studies showed the presence of polycrystalline structures with a predominant orientation in the (002) plane for all types of films. The diffractograms for all films are practically identical and coincide with the diffractograms of pure GaN films. The characteristic x-ray diffractograms of thin GaN films obtained by radio-frequency ion-plasma sputtering in a nitrogen atmosphere are shown in Fig. 1. The description and analysis of the diffractogram data are given in our previous work [16].

Elemental analysis of the obtained films was performed using an OXFORD INCA Energy 350 energy dispersive spectrometer. The studies were performed at several points on the sample surface. The analysis results showed that the percentage content of the components in the obtained films corresponded to their percentage content in the $Ga_{1-x}Al_xN$ compound ($x = 0$, 0.03, 0.07).

The optical transmission spectra of the obtained films were measured on a CM 2203 spectrofluorometer with a Hamamatsu R928 measuring head at 295 K.

3. RESULTS AND DISCUSSION

The characteristic absorption spectra of thin films of $Ga_{1-x}Al_xN$ ($x = 0$, 0.03, 0.07) at a temperature of 295 K are shown in Fig. 2.

Our spectral studies show that, in the regions $h\nu < 3.50$ eV for thin GaN films, $h\nu < 3.60$ eV for thin $Ga_{0.97}Al_{0.03}N$ films, and $h\nu < 3.90$ eV for thin $Ga_{0.93}Al_{0.07}N$ films, the spectral dependence of the absorption coefficient $\alpha(h\nu)$ is described by the empirical Urbach's rule [17]. Analytically, the dependence of the Urbach's rule

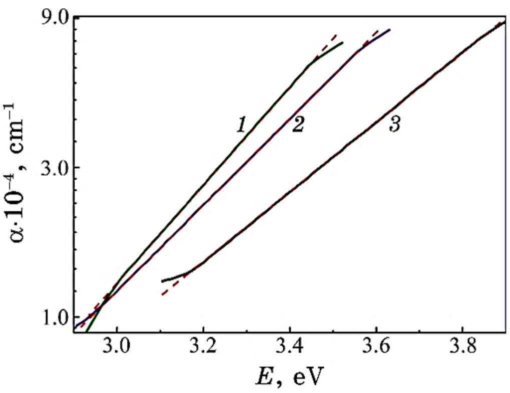

Fig. 2. Edge absorption spectrum of thin films of GaN (*1*), $Ga_{0.97}Al_{0.03}N$ (*2*), and $Ga_{0.93}Al_{0.07}N$ (*3*) obtained by RF sputtering in a nitrogen atmosphere at 295 K.

is given by the expression [18]

$$\alpha = \alpha_0 \exp\left[-\frac{\sigma}{kT}(h\nu_0 - h\nu)\right], \tag{1}$$

where the value σ, which characterizes the slope of the spectral dependence $\ln\alpha = f(h\nu)$, is given as

$$\sigma = \sigma_0 \frac{2kT}{h\nu_{ph}} \operatorname{th} \frac{h\nu_{ph}}{2kT}. \tag{2}$$

Here, α_0, $h\nu_0$ and σ_0 are approximation parameters, and $h\nu_{ph}$ generally corresponds to the average energy of phonons that interact with excitons in the sample and make the main contribution to the fundamental absorption edge.

The exponential form of the fundamental absorption edge is also observed in strongly doped or defective semiconductors. Therefore, in general, the screened Coulomb interaction caused by defects in the crystal structure, including phonons, is considered [19]. Since the studied films have a polycrystalline structure [16], it is necessary to take into account the presence of structural defects, among which grain boundaries and surfaces play an important role.

Based on the above, the fundamental absorption edge region is approximated by a slightly modified relation (1):

$$\alpha = \alpha_0 \exp\left[-\frac{1}{\gamma}(h\nu_0 - h\nu)\right], \tag{3}$$

where the parameter γ characterizes the disorder of the crystal lattice [16]:

$$\frac{1}{\gamma} = \begin{cases} \sigma/(kT), & \alpha \geq \alpha'; \\ 1/\gamma, & \alpha < \alpha'. \end{cases} \tag{4}$$

In expression (4), the upper term describes 'phonon' disorder, while the lower term describes 'defect' disorder due to structural defects (vacancies, dislocations, impurities, intergranular boundaries, surfaces). Considering that the edge absorption measurements for all three types of films were performed at the same temperature of 295 K (Fig. 2), the differences in the absorption coefficients for the $Ga_{1-x}Al_xN$ ($x = 0$, 0.03, 0.07) are mainly determined by the lower term in expression (4), which is caused by the peculiarities of structural defects. Having determined the crystal lattice disorder parameter γ from Fig. 2, we can conclude that the least disorder is observed in thin GaN films. The parameter γ determined by the slope of the dependence $\ln\alpha = f(h\nu)$ at 295 K is 0.31 eV in thin GaN films, 0.35 eV in thin $Ga_{0.97}Al_{0.03}N$ films, and 0.43 eV in $Ga_{0.93}Al_{0.07}N$ films. The characteristic values of the γ parameters in $Ga_{1-x}Al_xN$ thin films ($x = 0$, 0.03, 0.07) are given in Table.

To describe the obtained spectral dependence of edge absorption in thin films of $Ga_{1-x}Al_xN$ ($x = 0$, 0.03, 0.07), we used a model of a heavily doped or defective semiconductor. The choice of this model is fully consistent with our previous studies [20], which showed that the concentration of free charge carriers in thin films of $Ga_{0.97}Al_{0.03}N$ is $N \approx 9.38 \cdot 10^{17}$ cm^{-3}, and in thin films of $Ga_{0.93}Al_{0.07}N$, the value is $N \approx 6.75 \cdot 10^{18}$ cm^{-3}. At the same time, according to Ref. [21], in heavily doped degenerate semiconductors, the concentration of charge carriers exceeds 10^{16} cm^{-3} and can reach up to 10^{20} cm^{-3}.

Based on the theoretical model of a heavily doped or defective semiconductor in a quasi-classical approximation [22], the density of energy states caused by fluctuations in the concentration of charged anionic vacancies decreases into the forbidden zone according to an exponential law:

$$\rho(E) = \frac{m^{*3/2}\Delta^{1/2}}{4\pi^2\hbar^3}(\Delta/E)^{3/2}\exp(-E^2/\Delta^2)\,. \tag{5}$$

TABLE. Parameters of the quasi-classical approximation for describing edge absorption in thin $Ga_{1-x}Al_xN$ films ($x = 0$, 0.03, 0.07).

Thin film	γ, eV	m^*/m [20]	N, cm^{-3} [20]	a, nm	r_s, nm	Δ, eV
GaN	0.31	0.058		5.25		
$Ga_{0.97}Al_{0.03}N$	0.35	0.133	$9.38 \cdot 10^{17}$	2.29	3.84	$5.31 \cdot 10^{-2}$
$Ga_{0.93}Al_{0.07}N$	0.43	0.198	$6.75 \cdot 10^{18}$	1.54	2.27	$10.94 \cdot 10^{-2}$

In expression (5), Δ is the root-mean-square potential, which determines the blurring of zones due to the disordered arrangement of vacancies:

$$\Delta = \left(\frac{4\pi N r_s e^4}{\varepsilon^2} \right)^{1/2}, \qquad (6)$$

where N is the vacancy concentration, r_s is the screening radius, which is equal to

$$r_s = \frac{a}{2} \left(\frac{\pi}{3} \right)^{1/6} \frac{1}{(Na^3)^{1/6}}, \qquad (7)$$

and a is radius of the ground state:

$$a = \frac{\hbar^2 \varepsilon}{m^* e^2}, \qquad (8)$$

m^* is effective mass of charge carriers, ε is dielectric permeability of the sample.

The physical meaning of the root-mean-square potential Δ is that the root-mean-square fluctuation of the number of impurities or defects in the volume r_s^3 is of the order of $(Nr_s^3)^{1/2}$, and the potential energy of an electron in the field of such a fluctuation is $\Delta = e^2(\varepsilon r_s)^{-1}(Nr_s^3)^{1/2}$. Based on the results of Ref. [22], the main contribution to the root-mean-square potential is made by fluctuations of scale r_s. The energy of the ground state in the well is higher than the bottom of the well by an order of magnitude $E_s = \hbar^2/(mr_s^2)$.

To find the values included in expressions (5)–(8), we will use the results of a previous study [20]. The values of the refractive index n required to determine the dielectric permeability $\varepsilon = n^2$ were determined by extrapolating the dependence $n(h\nu)$ defined for the region of transparency and weak absorption [20] to the studied energy region. The values of the effective mass of free charge carriers m^* in thin films of $Ga_{1-x}Al_xN$ ($x = 0$, 0.03, 0.07) are also taken from Ref. [20].

The obtained values of the parameters of the quasi-classical approximation model for describing edge absorption in thin $Ga_{1-x}Al_xN$ films ($x = 0$, 0.03, 0.07) are given in Table.

When analysing the results obtained, it should be noted that they are consistent with the results of studies of a number of other semiconductor compounds. For example, the Bohr radius a in n-InSb is quite large: $a \approx 60$ nm [22]. At the same time, in oxide compounds, it is significantly smaller; in particular, in the $0.9ZrO_2$–$0.1Y_2O_3$ fannite, the radius $a = 0.4$ nm [23]. In thin films of β-Ga_2O_3, depending on the heat-treatment atmosphere, a varies from 0.6 to 0.8 nm [24], and in thin films of Y_2O_3, depending on the heat-treatment atmosphere, the value of a varies from 0.91 to 0.99 nm [25]. As can be seen from Table, the values of a obtained by us are slightly higher than in oxide compounds, although significantly lower than in *n*-InSb.

It is characteristic that with an increase in the Al content in thin films of $Ga_{1-x}Al_xN$, there is a decrease in the values of both the ground-state radius a and the screening radius r_s. At the same time, it has been established that in the studied range of Al concentrations, the value of the screening radius r_s a.

The results we obtained for the root-mean-square potential Δ also agree quite well with the results of studies of a number of wide-bandgap oxide semiconductors. In particular, according to Ref. [23], for fannite, $\Delta = 7.22 \cdot 10^{-2}$ eV. In thin films of β-Ga_2O_3, depending on the conditions of preparation, the value of Δ varies from $4.78 \cdot 10^{-2}$ eV to $23.30 \cdot 10^{-2}$ eV [24]. In thin films of Y_2O_3, when the heat treatment atmosphere is changed, the value of Δ varies from $1.51 \cdot 10^{-2}$ eV to $4.98 \cdot 10^{-2}$ eV. As can be seen from Table, the values of Δ obtained by us for thin films of $Ga_{1-x}Al_xN$ ($x = 0$, 0.03, 0.07) are quite close to the above values.

4. CONCLUSIONS

The studies show that the edge of the long-wave band between the zone absorption in thin films of $Ga_{1-x}Al_xN$ ($x = 0$, 0.03, 0.07), obtained by radio-frequency sputtering in a nitrogen atmosphere, is well described by the empirical Urbach's rule. To analyse the experimental results, previous studies were analysed and a theoretical model was used, which is applied to describe a heavily doped or defective semiconductor in a quasi-classical approximation. The use of this model made it possible, depending on the composition of the film, to determine the ground-state radius a, the screening radius r_s, and the root-mean-square potential Δ. It was found that an increase in the Al content in $Ga_{1-x}Al_xN$ films reduces the values of a and r_s and leads to an increase in the root-mean-square potential Δ.

REFERENCES

1. Lakshman Srinivasan, Cyril Jadaud, François Silva, Jean-Charles Vanel, Jean-Luc Maurice, Erik Johnson, Pere Roca i Cabarrocas, and Karim Ouaras, *J. Vac. Sci. Technol. A*, **41**, Iss. 5: 053407 (2023); https://doi.org/10.1116/6.0002718
2. F. Roccaforte and M. Leszczynski, *Nitride Semiconductor Technology. Power Electronics and Optoelectronic Devices* (Wiley-VCH Verlag GmbH & Co.

KGaA: 2020).
3. C. M. Furqan, Jacob Y. L. Ho, and H. S. Kwok, *Surfaces and Interfaces*, **26**: 101364 (2021); https://doi.org/10.1016/j.surfin.2021.101364
4. Sujan Rajbhandari, Jonathan J. D. McKendry, Johannes Herrnsdorf, Hyunchae Chun, Grahame Faulkner, Harald Haas, Ian M. Watson, Dominic O'Brien and Martin D. Dawson, *Semicond. Sci. Technol.*, **32**: 023001 (2017); https://doi.org/10.1088/1361-6641/32/2/023001
5. Bing Xiong, Lai Wang, Zhibiao Hao, Jian Wang, Yanjun Han, Hongtao Li, Jiadong Yu, and Yi Luo, *Laser Photonics Rev.*, **16**, Iss. 1: 2100071 (2022); https://doi.org/10.1002/lpor.202100071
6. Michael A. Reshchikov, *Solids*, **6**, Iss. 3: 52 (2025); https://doi.org/10.3390/solids6030052
7. M. Monisha, Shyam Mohana, D. S. Sutarb, and S. S. Majora, *Semicond. Sci. Technol.*, **35**, Iss. 4: 045011 (2020); doi:10.1088/1361-6641/ab73ec
8. Aoxue Zhong, Lei Wang, Yun Tang, Yongtao Yang, Jinjin Wang, Huiping Zhu, Zhenping Wu, Weihua, Tang, and Bo Li, *Chin. Phys. B*, **32**: 076102 (2023); doi:10.1088/1674-1056/accb8a
9. V. Bondar, I. Kucharsky, B. Simkiv, L. Akselrud, V. Davydov, Yu. Dubov, and S. Popovich, *phys. stat. sol.* (*a*), **176**, No. 1: 329 (1999); https://doi.org/10.1002/(SICI)1521-396X(199911)176:1<329::AID-PSSA329>3.0.CO;2-E
10. Sarmad Fawzi Hamza Alhasan, Mothana A. Hassan, Zaid T. Salim, Reem M. Khalaf, Makram A. Fakhri, Motahher A. Qaeed, Ahmed A. Al-Amiery, and Subash C. B. Gopinath, *Int. J. of Nanoelectronics and Materials*, **18**: 227 (2025); https://doi.org/10.58915/ijneam.v18iJune.2358
11. Salvatore Musumeci and Vincenzo Barba, *Energies*, **16**: 3894 (2023); https://doi.org/10.3390/en16093894
12. Nanxi Li, Chong Pei Ho, Shiyang Zhu, Yuan Hsing Fu, Yao Zhu, and Lennon Yao Ting Lee, *Nanophotonics*, **10**, No. 9: 2347 (2021); https://doi.org/10.1515/nanoph-2021-0130
13. W. Alan Doolittle, Christopher M. Matthews, Habib Ahmad, Keisuke Motoki, Sangho Lee, Aheli Ghosh, Emily N. Marshall, Amanda L. Tang, Pratyush Manocha, and P. Douglas Yoder, *Appl. Phys. Lett.*, **123**: 070501 (2023); https://doi.org/10.1063/5.0156691
14. Milena Beshkova and Rositsa Yakimova, *Vacuum*, **176**: 109231 (2020); https://doi.org/10.1016/j.vacuum.2020.109231
15. Kiyotaka Wasa, Makoto Kitabatake, and Hideaki Adachi, *Thin Film Materials Technology: Sputtering of Compound Materials* (William Andrew Inc. publishing–Springer-Verlag GmbH&Co. KG: 2004).
16. O. M. Bordun, I. Yo. Kukharskyy, M. V. Protsak, I. I. Medvid, I. M. Kofliuk, Zh. Ya. Tsapovska, and D. S. Leonov, *Nanosistemi, Nanomateriali, Nanotehnologii*, **22**, Iss. 2: 287 (2024); https://doi.org/10.15407/nnn.22.02.287
17. Franz Urbach, *Phys. Rev.*, **92**, Iss. 5: 1324 (1953); https://doi.org/10.1103/PhysRev.92.1324
18. M. V. Kurik, *phys. stat. sol. (a)*, **8**, Iss. 1: 9 (1971); https://doi.org/10.1002/pssa.2210080102
19. J. I. Pankove, *Optical Processes in Semiconductors* (New York: Dover Publications, Inc.: 1971).
20. O. M. Bordun, I. Yo. Kukharskyy, I. M. Kofliuk, I. I. Medvid, and

M. V. Protsak, *Physics and Chemistry of Solid State*, **26**, No. 2: 203 (2025); https://doi.org/10.15330/pcss.26.2.203-208
21. E. F. Schubert, *Physical Foundations of Solid-State Devices* (New York: Rensselaer Polytechnic Institute Troy: 2006); http://nadirpoint.de/Physik_Lit_PDF/65.pdf
22. A. L. Éfros, *Soviet Phys. Uspekhi*, **16**, No. 6: 789 (1974); https://doi.org/10.1070/PU1974v016n06ABEH004090
23. N. D. Dovga, *Phys. Electron.*, **33**: 86 (1986) (in Russian).
24. O. M. Bordun, B. O. Bordun, I. Yo. Kukharskyy, and I. I. Medvid, *J. Appl. Spectrosc.*, **88**, Iss. 2: 257 (2021); https://doi.org/10.1007/s10812-021-01166-8
25. O. M. Bordun, I. O. Bordun, I. M. Kofliuk, I. Yo. Kukharskyy, and I. I. Medvid, *J. Appl. Spectrosc.*, **88**, Iss. 6: 1152 (2022); https://doi.org/10.1007/s10812-022-01292-x