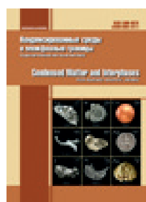

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Residual strain evaluation in GaN/AlN multiperiod superlattices grown on SiC/Si

P. V. Seredin[1]✉, Sh. Sh. Sharofidinov[2], D. L. Goloshchapov[1], N. S. Buylov[1], K. A. Eremeev[2], S. A. Yusupova[2], S. A. Kukushkin[3]

*[1]1Voronezh State University,
Universitetskaya pl. 1, Voronezh 394018, Russian Federation*

*[1]Ioffe Institute,
26 Polytechnicheskaya st., St. Petersburg 194021, Russian Federation*

*[3]Institute for Problems in Mechanical Engineering of the Russian Academy of Science,
61 Boljshoy prospekt V.O., St. Petersburg 199178, Russian Federation*

Abstract

In our study, we formed a multilayer heterostructure consisting of periodic GaN and AlN layers by means of chloride-hydride epitaxial growth on a hybrid SiC/Si substrate synthesized using the method of the coordinated substitution of atoms.

A comprehensive study of the heterostructure by means of nanoscale mapping of elastic strain demonstrated that in the upper GaN layer the dual-axis strain σ_{xx} is minimal (~ –0.12 GPa). There is practically no strain in the superlattices located in the upper part of the heterostructure.

Keywords: GaN, AlN, Superlattice, Raman spectroscopy

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✉ Pavel V. Seredin, e-mail: paul@phys.vsu.ru

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1. Introduction

Group III nitrides (GaN, AlN, AlGaN) have unique physical and chemical properties as compared to other semiconductors [1–3]. They have high hardness, good thermal conductivity, and high resistance to radiation and chemicals. These properties make Group III nitrides good candidates for the role of semiconductors in modern high-frequency equipment [3–6].

Group III nitrides are usually grown on substrates including sapphire and silicon carbide (SiC). However, silicon substrates, including porous ones [7–9], are becoming increasingly popular, because they have large diameters and, what is more important, have the required thermal characteristics and electrical properties. However, due to the considerable mismatch of crystal lattice parameters between group III nitride films and foreign substrates, as well as the difference in the coefficient of thermal expansion (CTE) of these materials, large elastic strain occurs during the growth process [10]. Therefore, it is important to lower the elastic strain in the epitaxial layers of the superlattice. At the same time, the misfit deformation in epitaxial systems with mismatched lattices can be reduced by the high density of structural defects and the growth of transition buffer layers based on multiperiod superlattices. Therefore, strain engineering in group III nitrides and its analysis present an important problem [11]. X-ray powder diffraction is often used to control strain, because it is a powerful and reliable method of nondestructive analysis of heterostructures [12, 13]. However, lately, Raman spectroscopy has been the most preferable method [14, 9]. Its main advantage over X-ray powder diffraction is that it allows for spatially resolved evaluation of inhomogeneous deformations. Raman spectra and motorized sample stages used to adjust the position of the sample within the scanning plane at submicron steps make it possible to register residual strain and its fluctuations in the layers of heterostructures with a high spatial resolution. Considering the fact that strain engineering is one of the most powerful tools for adjusting the optical and electronic properties of AIIIN semiconductor compounds, it is important to investigate residual strain in epitaxial layers of gallium nitride grown by means of transition buffer layers based on multiperiod GaN/AlN superlattices.

Earlier experiments demonstrated [15,16] that group III nitrides of good structural quality (AlN, GaN, and AlGaN) can be grown on a hybrid substrate SiC/Si and then separated from it. Thus, in [16] we grew single-crystal crack-free layers of AlN (with a thickness up to 300 μm), AlGaN (with a thickness up to 400 μm, and GaN (with a thickness up to 200 μm), as well as GaN films of the semipolar $(11\bar{2}4)$ orientation and a thickness up to 35 μm.

Therefore, the purpose of this study was to analyze residual elastic strain in the epitaxial periodic heterostructure and the corresponding GaN/AlN multiperiod superlattices after the separation from the hybrid substrate.

2. Materials and methods

To grow a bulk GaN layer with a good crystal structure which could then be separated from the substrate, we used hybrid vapor phase epitaxy (HVPE), which is well-known to be a relatively inexpensive method of obtaining bulk III-nitride layers on silicon or sapphire substrates. In our experiment, we used a hybrid SiC/Si(111) substrate synthesized using the method of coordinated substitution of atoms [17–19]. Taking into account the mismatch of crystal lattice parameters and the difference in the coefficients of thermal expansion, to avoid cracking we used the method of deposition of superlattices between the main layers of AlN and GaN. First, we deposited a thin layer of AlN, after which the second element was added (Ga). Then we grew an AlN/GaN superlattice layer in a 50:50 ratio for 20 min. During the next stage, another AlN layer was grown followed by the growth of yet another AlN/GaN superlattice layer. The final layer was a GaN layer with a thickness of about 3.5 μm. The structure was grown in a reactor at high temperatures (T ~ 1000 °C). Ammonia (NH_3) and argon (Ar) were used as a gas mixture, the flow rate was 1000 and 4000 ml/min respectively. The flow rate of Al and Ga was 100 ml/min. After the growth of the structure, the substrate was removed.

The diagnostics of the samples was carried out using microstructural and spectroscopic methods. Microscopic studies were performed

using a JSM-7001F scanning electron microscope (Jeol, Japan). Raman spectra were measured using a RamMics 532 confocal Raman microscope (EnSpectr, Moscow, Russia) with a radiation wavelength of 532 nm. The scanning was performed using a 60× lens. The power at the focus was 30 mW. The spectra were registered in the range of 100–2000 cm^{-1} with a spectral resolution of 1 cm^{-1}. Analysis of the spatial domains of the samples was carried out using a dual-axis motorized stage with a step of 0.25 μm along the whole structure of the samples. As a result, we obtained the spectra in the $z(xy)\bar{z}$ and $x(xy)\bar{x}$ geometry.

3. Results and discussion

Fig. 1 demonstrates a scheme of the GaN/AlN multilayer heterostructure and microscopic images of the cross-section of the sample on different scales obtained using scanning electron microscopy.

We have already mentioned that information about the structural properties of free thin layers based on GaN/AlN multiperiod superlattices was obtained by means of Raman light scattering. Raman spectroscopy is a very effective tool for non-destructive testing of semiconductor nanostructures.

Fig. 2 presents the Raman spectrum of the sample in the $z(xy)\bar{z}$ geometry.

Due to the optical transparency of GaN and AlN and a large depth of the Raman spectroscopy profiling in the $z(xy)\bar{z}$ geometry the spectrum demonstrates Raman light scattering modes from various layers of the heterostructure.

In accordance with the geometry of Raman light scattering and the selection rules for the wurtzite crystal structure (spatial group *P3m1*) observed in phases GaN and AlN, for each phase the Raman spectra might demonstrate a characteristic set of six longitudinal (LO) and transverse (TO) phonon modes [20,21]. An analysis of the experimental data (Fig. 2) demonstrated that there are four vibrations in the spectrum. The first and the most intense maximum at about 567 cm^{-1} is the phonon mode E_2^{high} of the wurtzite-like GaN [22,23]. A less intense peak at about 735 cm^{-1} is the A_1(LO) mode of GaN. The peak at about

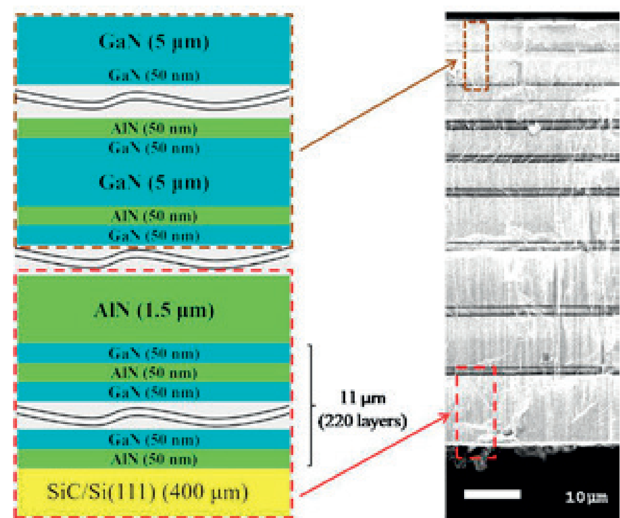

Fig. 1. SEM image of the heterostructure and schematic images of two types of superlattices

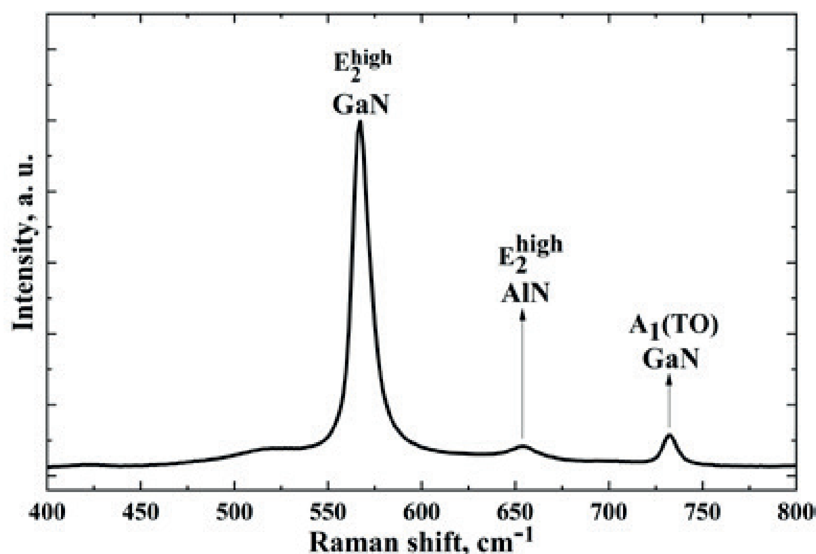

Fig. 2. Raman spectrum of the film in the geometry $z(xy)\bar{z}$

653 cm⁻¹ is the E_2^{high} mode of AlN, the strongest of the modes allowed in the films of wurtzite AlN in the $z(xy)z'$ backscattering geometry used in our experiment [24].

To perform a layer-by-layer analysis of the structure with a high spatial resolution we performed the scanning in the $x(xy)\bar{x}$ geometry with a step of 250 nm. As a result, we obtained a set of phonon modes from the region of multiperiod superlattices GaN/AlN (Fig. 3) as well as from AlN buffer layers (Fig. 4)

Based on the obtained results, we can say that in the selected $x(xy)\bar{x}$ geometry, the spectra of the GaN/AlN superlattice (Fig. 3) demonstrate an intense nonpolar phonon mode E_2^{high} of GaN (Fig. 2) together with active polar vibrations A1(TO) of GaN and E1(TO) of GaN at about 535 and 555 cm⁻¹ respectively. These vibrations are characteristic for GaN crystals with a wurtzite structure [25]. We can see that depending on the distance between the substrate and the studied region, a shift in the frequencies of phonon modes A1(TO), E1(TO), and E_2^{high} of GaN is observed as well as a change in their relative intensities.

As for the Raman spectra of the AlN buffer layers (Fig. 4), there are three active modes: E_2^{high}, A1(TO), and E1(TO), whose intensity practically does not depend on the location of the AlN layer in the film. We should also note that the spectra of the AlN buffer layer demonstrate vibrations at about 530–580 cm⁻¹ (Fig. 4) attributed to A1(TO) and E_2^{high} modes of GaN. This can be explained by the fact that during the scanning, the region of generation of the desired signal occupied the neighboring layers of the superlattice, which in turn means that the cleavage plane was not perpendicular to the surface of the sample.

The observed shifts of the phonon modes of various symmetry must be connected with the deformations of the layers caused by the difference in the crystal lattice parameters and the thermal expansion coefficients of the materials of the layers that occurred during the growth of the heterostructure. We can see that the shifts in phonon vibrations belonging to phonons of AlN and GaN in various layers of superlattices and buffer layers have different directions, which indicates different types of deformations in these layers.

By performing micro Raman spectroscopy of the cleavage of the heterostructure using coordinated spectral scanning, we can obtain a scheme of the structure in the cross-section of the layers based on the variations on the intensity

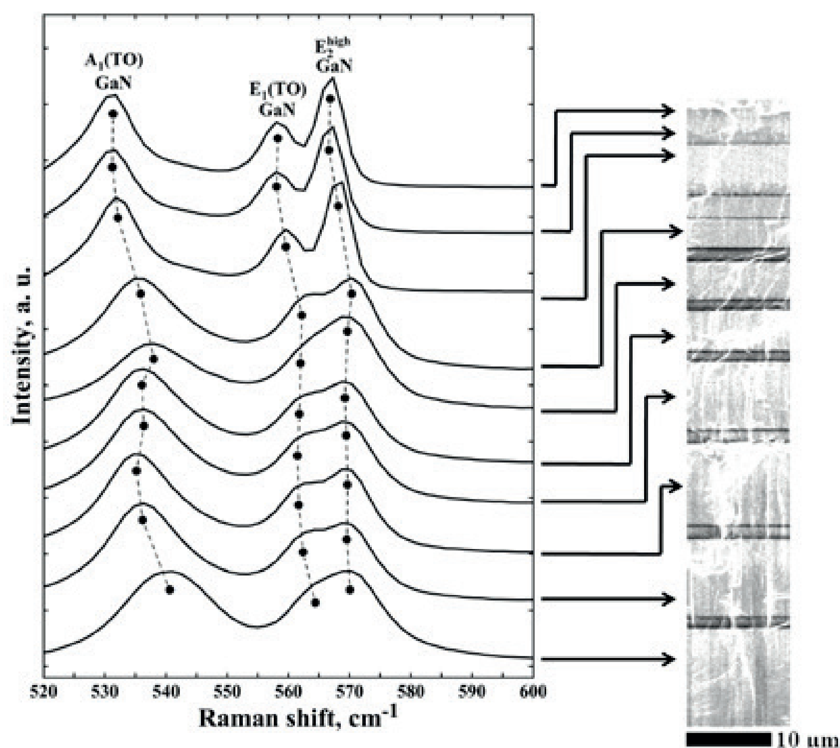

Fig. 3. Raman spectra from regions of GaN/AlN superlattices, taken in geometry $z(xy)\bar{z}$

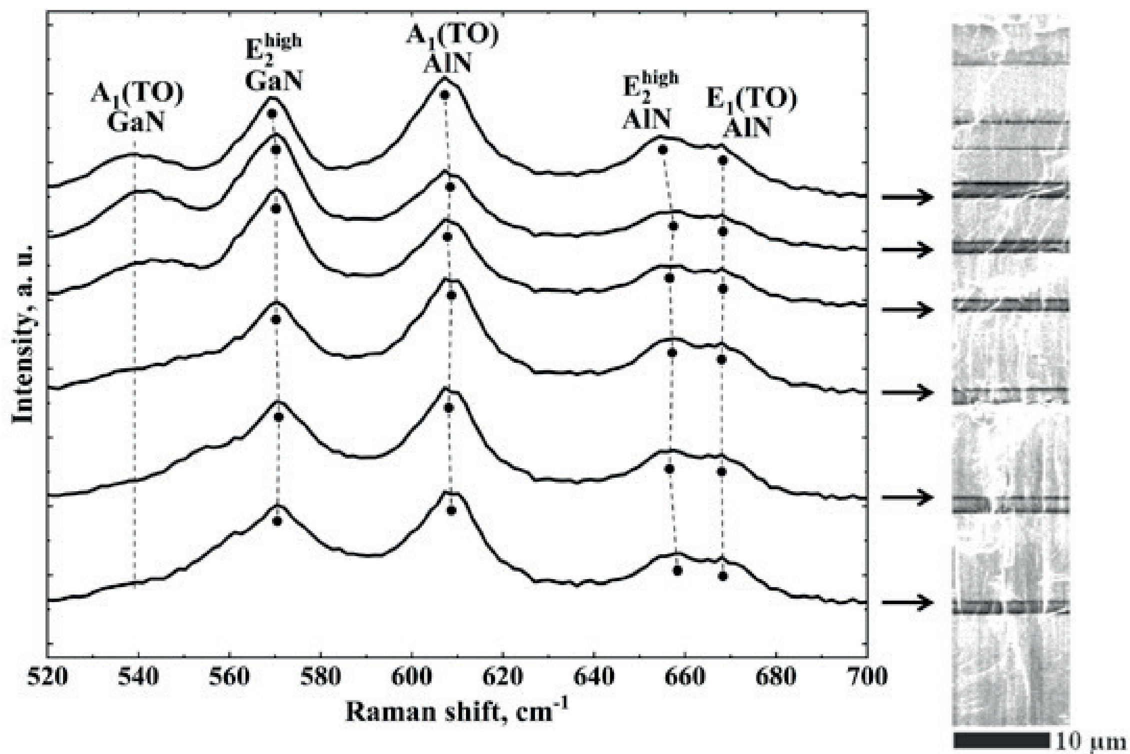

Fig. 4. Raman spectra from AlN buffer layers taken in geometry $z(xy)\bar{z}$

of spectral lines reflecting the distribution of nonpolar E_2^{high} vibrational modes of GaN and AlN near the interface. In order to do this, we determined integral areas under the selected spectral lines in each spectrum corresponding to a particular point in the scanning region.

Fig. 5a, b demonstrate the results of the hyperspectral mapping based on the distribution of intensities of the selected vibrations and a SEM image of the scanned region. The results of the chemical mapping are color coded. The warmer the color, the greater the intensity of the corresponding phonon and therefore the composition of the phase in the region.

An analysis of the results of the hyperspectral mapping (Fig. 5a, b) visualizes the structure of the layers in the sample: the maps demonstrate bands of the greatest/smallest intensity of GaN/AlN, and the distance between the bands correlates well with the SEM image.

At the same time, we should note that in the layers forming the GaN/AlN superlattices, the quantitative composition and the intensity of the localized modes depend on the localization region as well as on the period of the superlattice. We can see that the nonpolar E_2^{high} mode of GaN has a maximum intensity in upper layers of the superlattices changing gradually from layer to layer.

As we have already mentioned, the residual strain in thin epitaxial films is an important issue for the production of various devices. During the growth of multilayer heterostructures based on group III nitrides on foreign substrates, the residual strain observed in the films is the result of a balance between two competing deformation components: misfit deformation caused by the difference in the thermal expansion coefficients and the deformation caused by the defects in the structure [26]. Results of numerous studies have demonstrated that the frequencies of the E_2^{high} modes of GaN and AlN depend on the deformations in the crystal lattice. Therefore, the evaluation of residual strain in various layers of the heterostructure can be carried out based on the frequency shifts in the Raman spectrum of the main vibrational modes: E_2^{high} modes of GaN and AlN.

The calculation of residual strain at the cleavage of the epitaxial layer was performed based on the frequency of the E_2^{high} mode of GaN using the equation:

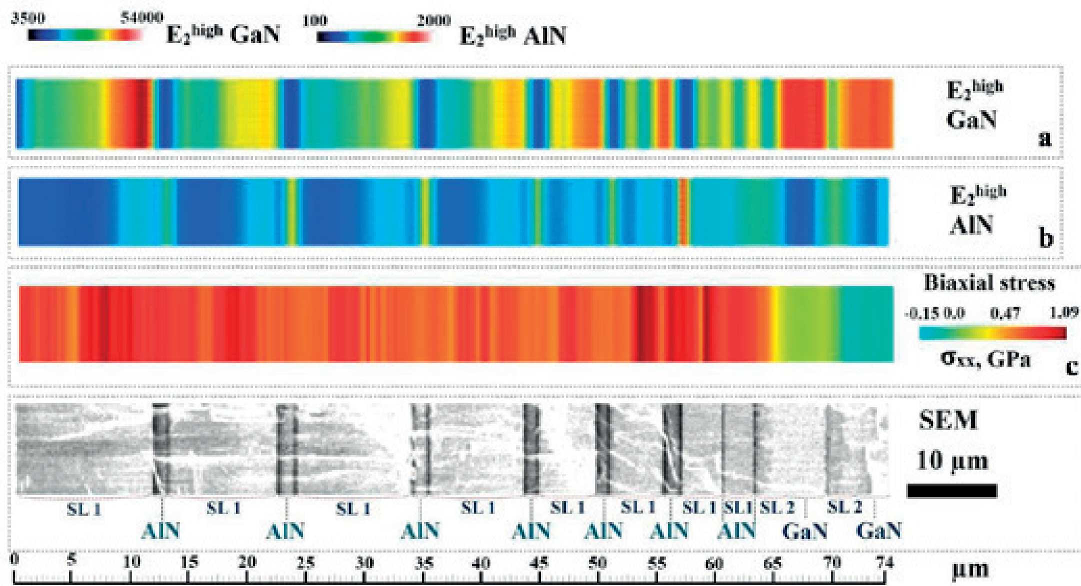

Fig. 5. Hyperspectral Raman mapping of the film cleavage region based on the intensity distribution of the E_2^{high} GaN (a) и E_2^{high} AlN (b), phonon modes, as well as the distribution of elastic stresses in a multilayer heterostructure (c)

$$\sigma_{xx} = \frac{\Delta\omega}{K}. \quad (1)$$

Where $\Delta\omega$ is the Raman shift with regard to the strain-free layer, K is a constant value for GaN GaN KGaN = 4.3 cm^{-1}·GPa

Fig. 5c demonstrates a map of dual-axis strain near the cleavage of the film. We can see that in the upper GaN layer the dual-axis strain σ_{xx} is minimal (~ –0.12 GPa). At the same time, the strain is minimal in the upper SL2 superlattices (with a constant period).

4. Conclusions

In our study, we formed a multilayer heterostructure consisting of periodic GaN and AlN layers by means of chloride-hydride epitaxial growth on a hybrid SiC/Si substrate synthesized using the method of coordinated substitution of atoms.

The thickness of the obtained structure was ~ 78 µm. Using nanoscale mapping in the upper GaN layers we determined the dual-axis strain σ_{xx} to be minimum (~ 0.12 GPa). There is practically no strain in the superlattices located in the upper part of the structure.

Contribution of the authors

The authors contributed equally to this article.

Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

References

1. Zou C., Zhao Z., Xu M., … Li S. GaN/Gr (2D)/Si (3D) Combined high-performance hot electron transistors. *ACS Nano*. 2023;17(9): 8262–8270. https://doi.org/10.1021/acsnano.2c12435

2. Das P., Wu T.-L., Tallur S. Design and analysis of high electron mobility transistor inspired: III-V electro-optic modulator topologies. *Semiconductor Science and Technology*. 2020;35(9): 095028. https://doi.org/10.1088/1361-6641/ab9ea9

3. Kohen D., Nguyen X. S., Yadav S., … Fitzgerald E. A. Heteroepitaxial growth of In0.30Ga0.70As high-electron mobility transistor on 200 mm silicon substrate using metamorphic graded buffer. *AIP Advances*. 2016;6(8): 085106. https://doi.org/10.1063/1.4961025

4. Jang W.-H., Kim H.-S., Kang M.-J., Cho C.-H., Cha H.-Y. Recessed AlGaN/GaN UV phototransistor. *Journal of Semiconductor Technology and Science*. 2019;19(2): 184–189. https://doi.org/10.5573/JSTS.2019.19.2.184

5. Encomendero J., Faria F. A., Islam S. M., … Xing H.G. New tunneling features in polar III-nitride resonant tunneling diodes. *Physical Review X*. 2017;7(4): 041017. https://doi.org/10.1103/PhysRevX.7.041017

6. Singh M. M., Siddiqui M. J., Saxena A. Comparative simulation of GaAs and GaN based double barriers-resonant tunneling diode. *Procedia Computer Science*. 2016; 85581–85587. https://doi.org/10.1016/j.procs.2016.05.224

7. Seredin P. V., Lenshin A. S., Mizerov A. M., Leiste H., Rinke M. Structural, optical and morphological properties of hybrid heterostructures on the basis of GaN grown on compliant substrate por-Si(111). *Applied Surface Science*. 2019; 4761049–4761060. https://doi.org/10.1016/j.apsusc.2019.01.239

8. Seredin P. V., Goloshchapov D. L., Lenshin A. S., Mizerov A. M., Zolotukhin D. S. Influence of por-Si sublayer on the features of heteroepitaxial growth and physical properties of In x Ga 1-x N/Si(111) heterostructures with nanocolumn morphology of thin film. *Physica E: Low-dimensional Systems and Nanostructures*. 2018; 104101–104110. https://doi.org/10.1016/j.physe.2018.07.024

9. Seredin P. V., Goloshchapov D. L., Arsentyev I. N., Sharofidinov S., Kasatkin I. A., Prutskij T. HVPE fabrication of GaN sub-micro pillars on preliminarily treated Si(001) substrate. *Optical Materials*. 2021; 117111130. https://doi.org/10.1016/j.optmat.2021.111130

10. Ansah-Antwi K. K., Soh C. B., Liu H., Chua S. J. Growth optimization and characterization of GaN epilayers on multifaceted (111) surfaces etched on Si(100) substrates. J*ournal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*. 2015;33(6): 061517. https://doi.org/10.1116/1.4933201

11. Gao N., Chen J., Feng X.,...Kang J. Strain engineering of digitally alloyed AlN/GaN nanorods for far-UVC emission as short as 220 nm. *Optical Materials Express*. 2021;11(4): 1282. https://doi.org/10.1364/OME.422215

12. Kuchuk A. V., Kryvyi S., Lytvyn P. M., ... Salamo G. J. The peculiarities of strain relaxation in GaN/AlN superlattices grown on vicinal GaN (0001) substrate: Comparative XRD and AFM study. *Nanoscale Research Letters*. 2016;11(1): 252. https://doi.org/10.1186/s11671-016-1478-6

13. Seredin P. V., Glotov A. V., Ternovaya V. E., ... Tarasov I.S . Effect of silicon on relaxation of the crystal lattice in MOCVD–hydride $AlxGa_{1-x}As$:Si/GaAs(100) heterostructures. *Semiconductors*. 2011;45(4): 481–492. https://doi.org/10.1134/S106378261104021X

14. Davydov V., Roginskii E., Kitaev Y., ... Smirnov M. Phonons in short-period GaN/AlN superlattices: Group-theoretical analysis, ab initio calculations, and Raman spectra. *Nanomaterials*. 2021;11(2): 286. https://doi.org/10.3390/nano11020286

15. Sharofidinov Sh. Sh., Kukushkin S. A., Red'kov A. V., Grashchenko A. S., Osipov A. V. Growing III–V semiconductor heterostructures on SiC/Si substrates. *Technical Physics Letters*. 2019;45(7): 711–713. https://doi.org/10.1134/S1063785019070277

16. Kukushkin S. A., Sharofidinov Sh. Sh. A new method of growing AlN, GaN, and AlGaN bulk crystals using hybrid SiC/Si substrates. *Physics of the Solid State*. 2019;61(12): 2342–2347. https://doi.org/10.1134/S1063783419120254

17. Kukushkin S. A., Osipov A. V. Theory and practice of SiC growth on Si and its applications to wide-gap semiconductor films. *Journal of Physics D: Applied Physics*. 2014;47(31): 313001. https://doi.org/10.1088/0022-3727/47/31/313001

18. Kukushkin S. A., Osipov A. V. Nanoscale single-crystal silicon carbide on silicon and unique properties of this material. *Inorganic Materials*. 2021;57(13): 1319–1339. https://doi.org/10.1134/S0020168521130021

19. Kukushkin S. A., Osipov A. V. Epitaxial silicon carbide on silicon. Method of coordinated substitution of atoms (a review). *Russian Journal of General Chemistry*. 2022;92(4): 584–610. https://doi.org/10.1134/S1070363222040028

20. Olivier A., Wang H., Koke A., Baillargeat D. Gallium nitride nanowires grown by low pressure chemical vapour deposition on silicon substrate. *International Journal of Nanotechnology*. 2014;11(1/2/3/4): 243. https://doi.org/10.1504/IJNT.2014.059826

21. Borowicz P., Gutt T., Malachowski T. Structural investigation of silicon carbide with micro-Raman spectroscopy. In: *2009 MIXDES-16th International Conference Mixed Design of Integrated Circuits Systems*. 2009; 177–180.

22. Davydov V. Yu., Kitaev Yu. E., Goncharuk I. N., ... Evarestov R. A. Phonon dispersion and Raman scattering in hexagonal GaN and AlN. P*hysical Review B*. 1998;58(19): 12899–12907. https://doi.org/10.1103/PhysRevB.58.12899

23. Feng Y., Saravade V., Chung T.-F., ... Lu N. Strain-stress study of $AlxGa_{1-x}N$/AlN heterostructures on c-plane sapphire and related optical properties. *Scientific Reports*. 2019;9(1): 10172. https://doi.org/10.1038/s41598-019-46628-4

24. Lughi V., Clarke D. R. Defect and stress characterization of AlN films by Raman spectroscopy. *Applied Physics Letters*. 2006;89(24): 241911. https://doi.org/10.1063/1.2404938

25. Zeng Y., Ning J., Zhang J., ... Wang D. Raman analysis of E2 (High) and A1 (LO) phonon to the stress-free GaN grown on sputtered AlN/graphene buffer layer. *Applied Sciences*. 2020;10(24): 8814. https://doi.org/10.3390/app10248814

26. Hushur A., Manghnani M. H., Narayan J. Raman studies of GaN/sapphire thin film heterostructures. *Journal of Applied Physics*. 2009;106(5): 054317. https://doi.org/10.1063/1.3213370

Information about the authors

Pavel V. Seredin, Dr. Sci. (Phys.–Math.), Full Professor, Head of the Department, Department of Solid State Physics and Nanostructures, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0002-6724-0063
paul@phys.vsu.ru

Shukrilo Sh. Sharofidinov, Cand. Sci. (Phys.–Math.), Research Fellow, Ioffe Institute (St. Petersburg, Russian Federation).

https://orcid.org/0000-0003-0354-5981
shukrillo71@mail.ru

Dmitry L. Goloshchapov, Cand. Sci. (Phys.–Math.), Assistant Professor, Department of Solid State Physics and Nanostructures, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0002-1400-2870
goloshchapov@phys.vsu.ru

Nikita S. Buylov, Cand. Sci. (Phys.–Math.), Educator, Department of Solid State Physics and Nanostructures, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0000-0003-1793-4400
buylov@phys.vsu.ru

Konstantin A. Eremeev, student, Department of Solid State Physics and Nanostructures, Voronezh State University (Voronezh, Russian Federation).

https://orcid.org/0009-0004-9798-6642
kjcnz2001@gmail.com

Shaira A. Yusupova, Cand. Sci. (Phys.–Math.), Researcher, Laboratory of Power Semiconductor Devices, Department of Solid State Electronics, Ioffe Institute (St. Petersburg, Russian Federation).

sh.yusupova@mail.ioffe.ru

Sergey A. Kukushkin, Dr. Sci. (Phys.–Math.), Professor, Head of Laboratory, Institute for Problems in Mechanical Engineering of the Russian Academy of Sciences (St. Petersburg, Russian Federation).

https://orcid.org/0000-0002-2973-8645
sergey.a.kukushkin@gmail.com

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