11

The Effect Of Surface Passivation Of GaAs-based Cylindrical Mesa Structures On Their Optical Properties

© I.A. Melnichenko [1,2,¶], N.V. Kryzhanovskaya [1], K.A. Ivanov [1], A.M. Nadtochiy [1,4], I.S. Makhov [1], M.G. Kozodaev [3], R.R. Khakimov [3], A.M. Markeev [3], A.A. Vorobyev [2], A.M. Mozharov [2], Yu.A. Guseva [4], A.I. Likhachev [4], E.S. Kolodezny [5], A.E. Zhukov [1]

[1] National Research University Higher School of Economics, St. Petersburg, Russia
[2] Alferov Federal State Budgetary Institution of Higher Education and Science Saint Petersburg National Research Academic University of the Russian Academy of Sciences, St. Petersburg, Russia
[3] Moscow Institute of Physics and Technology (National Research University), Dolgoprudniy, Moscow Region, Russia
[4] Ioffe Institute, St. Petersburg, Russia
[5] ITMO University, St. Petersburg, Russia

¶e-mail: imelnichenko@hse.ru

Received May 17, 2023
Revised May 17, 2023
Accepted June 02, 2023.

The optical properties of GaAs-based cylindrical mesa-structures were studied before and after passivation using hydrogen plasma treatment followed by atomic layer deposition of an Al_2O_3 layer. The $In_{0.2}Ga_{0.8}As$/GaAs quantum well and the GaAs/AlAs superlattice were used as the light-emitting region of the mesa structures. The diameter of the mesas varied from 3 to 20 μm. The result of passivation was an 8-fold increase in the photoluminescence intensity of 9 μm-diameter mesa at room temperature, and time-resolved photoluminescence studies of such mesa structures demonstrated an increase in charge carrier lifetime from 0.13 to 0.9 ns.

Keywords: InGaAs, quantum well, surface passivation, atomic layer deposition.

DOI: 10.61011/EOS.2023.08.57289.4894-23

Introduction

The study of surface passivation of GaAs-based structures is paid much attention [1]. The miniaturization of sizes of light-emitting devices down to submicron scale [2,3] and the creation of mesa structures with etching through the light-emitting active region [4] leads to degradation of optical properties of the structures due to non-radiative surface recombination [1]. The high density of surface states (10^{13} cm^{-2}) in GaAs and, as a result, the high surface recombination rate (10^5-10^6 cm/s) necessitates the development of passivation methods [5,6]. It should be noted that for the etching-formed mesa structures the method of producing clean semiconductor surface by chipping in vacuum is not suitable. The problem of optical properties deterioration with the active region approaching the side surface of a light-emitting device in the course of its miniaturization is especially acute when using two-dimensional layered structures (quantum wells and superlattices), where the lateral transport of charge carriers in the plane of the active layer is not limited and the role of non-radiative recombination of carriers on the surface increases significantly [7].

There is a belief that the high density of surface states in GaAs is largely due to the presence of natural Ga and As oxides on the surface [8], as well as the presence of arsenic itself [9]. The surface of the structure can be passivated using a chemical reaction of sulfides or thiols [10,11] to remove oxides and elemental arsenic from the GaAs surface. Sulfur partially fills the dangling bonds on the surface of the semiconductor and prevents re-oxidation. However, the formed bonds quickly degrade under the effect of the environment due to the stronger bond of Ga−O and As−O compared to, for example, Ga−S or As−S and require an additional layer to protect the passivation [12,13]. Another option is passivation by forming oxides or wide-gap materials on the surface, such as GaP, GaN, Al_2O_3 [10,14,15]. For example, passivation by epitaxy of InP and GaN monolayers has demonstrated, in particular, an enhancement of the PL signal of an InGaAs/GaAs quantum well by two orders of magnitude [14].

As_2O_3 oxide and arsenic can be effectively removed from the GaAs surface by treating the surface in hydrogen plasma [16,17]. The resulting surface requires subsequent encapsulation with a continuous covering layer. Thus, when covering a surface treated in hydrogen plasma with layers of Si_3N_4 or AlO_x, the effect of surface passivation was also observed. The atomic layer deposition (ALD) method makes it possible to produce conformal surface coatings, which is necessary for structures with a large aspect ratio, such as disk microlasers and micropillars. For example, in [18] for InP whisker nanocrystals, coating with 15 nm thick aluminum oxide using ALD resulted in an increase in intensity by a factor of 20. For GaN whisker nanocrystals, also passivated with ALD of SiN_x and Al_2O_3, an increase in the internal quantum efficiency was observed by 88% and 45%, respectively [19].

This study investigated the effect of treating the surface of structures in hydrogen plasma followed by deposition of a protective layer of Al_2O_3 using the ALD method on the photoluminescence of mesas with $In_{0.2}Ga_{0.8}As$/GaAs quantum well and GaAs/AlAs superlattice at room temperature. Also, the attenuation of photoluminescence intensity in mesas of different diameters was investigated with time resolution at room temperature, which made it possible to evaluate the effect of passivation on the lifetime of charge carriers.

Experiment

The epitaxial structure was created on a GaAs(100) substrate using the molecular beam epitaxy method. First, a GaAs buffer layer was deposited, then a $Al_{0.25}Ga_{0.75}As$ layer with a thickness of 50 nm was formed to limit the leakage of charge carriers into the substrate area. Then a GaAs layer with a thickness of 200 nm was grown, in the middle of which a layer of $In_{0.2}Ga_{0.8}As$ quantum well (QW) with a thickness of 10 nm was placed, after which 10 periods of a superlattice (SL) consisting of GaAs/AlAs layers with thicknesses of 10 nm/10 nm were grown. The structure was completed with a 10 nm thick GaAs layer. Fig. 1, *a* schematically represents the sequence of layers of the grown structure.

Using photolithography and plasma-chemical etching, microdisk mesas of various diameters were created: 20 μm, 9 μm, 4 μm and 3 μm. Moreover, the mesa with a diameter of 20 μm was formed as a single mesa, and mesas of smaller diameters were formed in the form of arrays of mesas enclosed in a circle with a diameter of 20 μm, so that when illuminated from top by a laser spot with a diameter of $\sim 20\,\mu$m, all mesas were within the area of this spot and the surface area of the mesas did not change much. As a result, the region of laser illumination during further research included 1 mesa with a diameter of 20 μm, 2 mesas with a diameter of 9 μm, 7 mesas with a diameter of 4 μm, and 12 mesas with a diameter of 3 μm.

The structure was etched through the QW and SL layers down to the GaAs substrate. Fig. 1, *b* shows an image obtained by scanning electron microscopy using a JSM 7001F electron microscope (JEOL, Japan) for mesas with a diameter of 3 μm.

To passivate the mesa surface, the samples were first treated with hydrogen radicals in the chamber of a Picosun R200adv setup at a pressure of about 0.8 mbar (40 sccm Ar+100 sccm H_2) for 10 minutes (the discharge power was recorded equal to 2500 W). Under these conditions, the ion flux near the substrate with mesas can be considered negligible. After that, in the same setup (without violating the conditions of vacuum), a layer of Al_2O_3 with a thickness of 10 nm was deposited using the ALD method. TMA (trimethylaluminum) and water were used as precursors. Both processes were carried out at a temperature of 250°C.

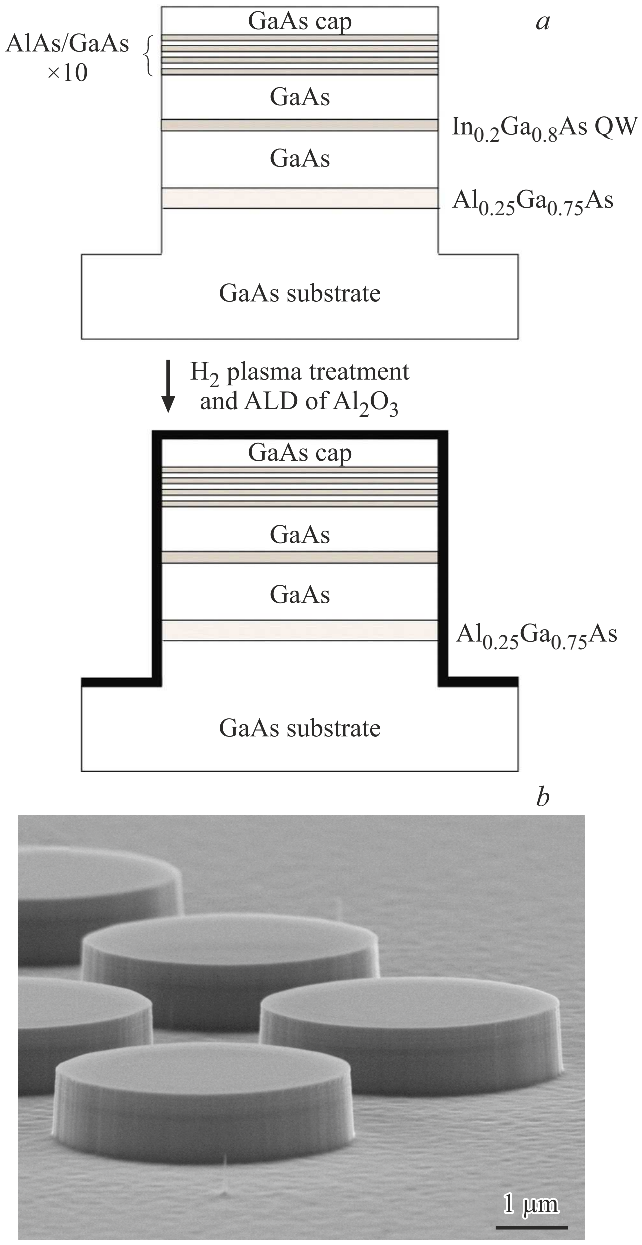

Figure 1. (*a*) Schematic representation of the sequence of layers of the grown structure and the process of its passivation. (*b*) SEM image of a group of mesa structures with a diameter of 3 μm.

Studies of the photoluminescence intensity of mesas at room temperature before and after passivation of the structure were performed using an Ntegra Spectra C optical confocal microscope (NT-MDT). To excite nonequilibrium charge carriers, a YAG:LF pump laser operating in a continuous mode (with a radiation wavelength of 527 nm) was used. The exciting laser radiation was focused using a 5x microlens (Mitutoyo, M Plan APO NIR) into a spot with a diameter of up to $\sim 20\,\mu$m. The same lens was used to collect the mesa photoluminescence signal. The radiation was directed using mirrors to the entrance slits of a monochromator (Sol Instruments MS5204i).

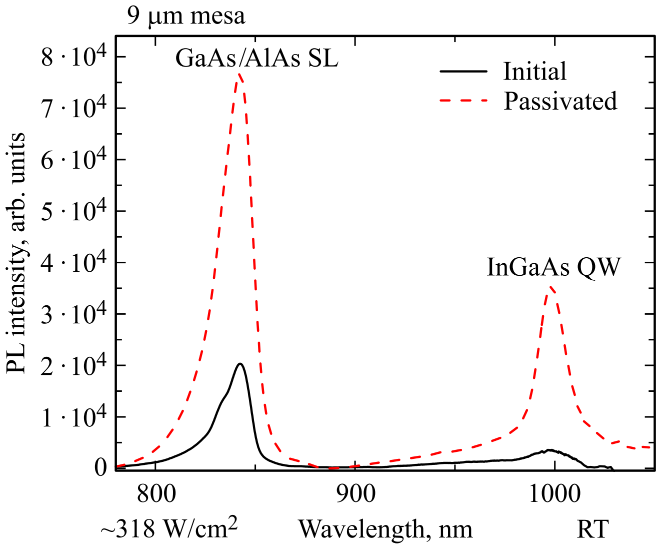

Figure 2. PL spectra obtained at room temperature for the initial structure and after passivation for mesas with a diameter of 9 μm.

Detection was performed using a cooled silicon chamber (Andor iVac). Time-resolved photoluminescence studies were performed using the up-conversion method, which allows a time resolution of up to hundreds of femtoseconds. A Coherent Mira 900 titanium-sapphire laser with a pulse duration of 130 fs, a repetition rate of 76 MHz, and a wavelength of 780 nm was used as a source of femtosecond radiation. The optical up-conversion signal was detected in the synchronous detection mode using a monochromator and a photomultiplier.

Results and discussion

The photoluminescence (PL) spectra of all structures with mesas contain two emission bands, one of which with the spectral position of the maximum PL intensity at ~ 841.5 nm corresponds to transitions in the GaAs/AlAs superlattice, and the second mesa near 980 nm corresponds to ground state transitions in the $In_{0.2}Ga_{0.8}As$/GaAs QW. Fig. 2, *a* shows the PL spectra obtained for mesas with a diameter of 9 μm before and after passivation of the structure, measured at a pump power density of 630 W/cm^2. As a result of passivation of the mesa surface, the PL intensity of both the superlattice line and the QW line increases by approximately 8 times.

We have carried out a study of the dependence of the integrated PL intensity of samples with mesas of various diameters as a function of the optical pump power density (Fig. 3, *a*). The presented intensity dependences are normalized to the total area of mesas. As the mesa diameter decreases, a decrease in PL intensity is observed, which can be explained by an increase in the contribution of non-radiative recombination on the lateral surface of the structures. With an increase in the optical pump power, an increase in the PL intensity is first observed, and then, when the optical pump power exceeds ~ 400 W/cm^2, the growth saturation occurs, and the dependence reaches a plateau, which may be associated with local heating of the mesas under the effect of the incident power, as well as with the filling of states in the QW.

Fig. 3, *b* shows the dependence of the PL line intensity of the GaAs/AlAs superlattice on the optical pump power before and after passivation for mesas with a diameter of 9 μm. An increase in the PL intensity is observed after passivation over the entire range of optical pump power studied.

The PL intensity of a structure with a QW is usually described by the following relationship:

$$I_{PL} = \eta I_0^{\alpha},$$

where I_{PL} is integrated PL intensity, I_0 is power density of the exciting laser. The exponent α depends on the dominant recombination mechanism; it is close to unity if radiative recombination dominates, and close to 2 if non-radiative recombination at defects predominates. The coefficient η is related (within the accuracy of a certain constant factor reflecting the efficiency of radiation extraction from the material, the efficiency of radiation collection, and other experimental parameters) to the ratio of radiative and non-radiative recombination coefficients in the QW. The coefficients η and the exponent α were obtained by simply fitting the experimental data. The value of the exponent α is the same for both cases and is ~ 1.7, which is indicative of the fact that recombination at defects still predominates. The coefficient η for the initial structure has a value of 2.6 and increases to 16 as a result of passivation, which is indicative of the effective suppression of non-radiative processes in the structure.

The factor of increase in PL intensity as a result of passivation (I_{PL}/I_0) differs for mesas of different diameters, and the dependence is non-monotonic (Fig. 4). The maximum increase in PL intensity by 8 times was observed for mesa structures with a diameter of 9 μm. For mesa structures with a diameter of 20 μm, non-radiative recombination on the surface makes a smaller contribution, and the increase in PL intensity was about 3 times. For mesa structures with diameters of 4 μm and 3 μm, no significant improvement in optical properties was also observed under the selected passivation modes. The low efficiency in the case of small diameters can be explained by the strong contribution of non-radiative processes on the surface due to the comparable size of the mesa and the diffusion length of charge carriers.

Time-resolved photoluminescence studies were carried out to investigate the differences in charge carrier dynamics of the initial and passivated structures. Fig. 5, *a* shows the time dependence of the PL intensity decay of $In_{0.2}Ga_{0.8}As$/GaAs QW, obtained at room temperature for mesas with a diameter of 20 ,μm for a wavelength of 980 nm. The lifetime of charge carriers τ_{decay} in the

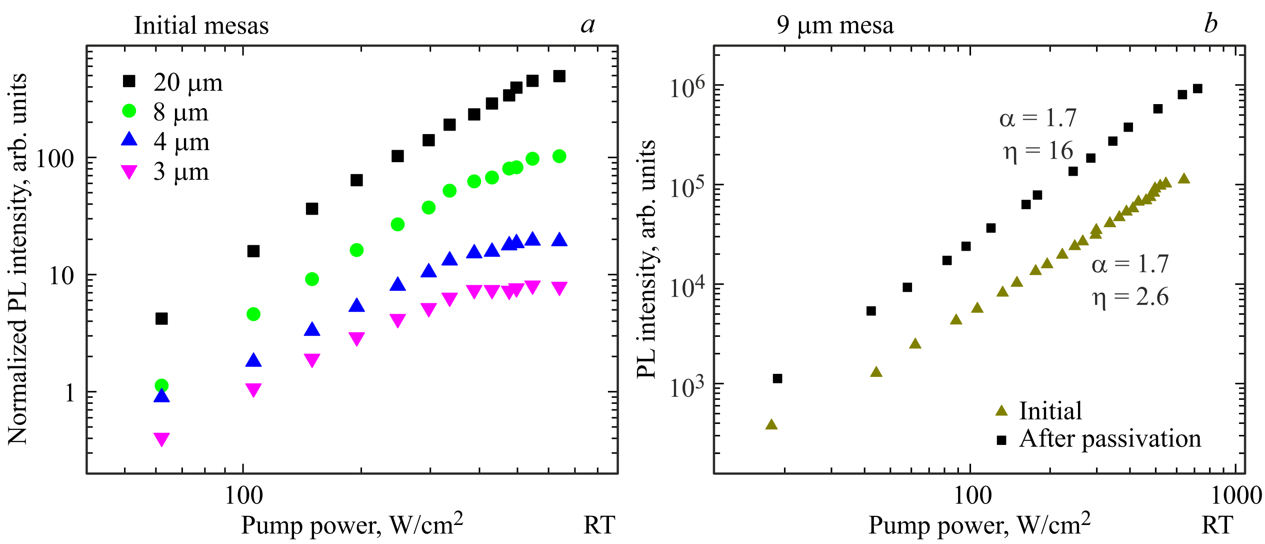

Figure 3. (*a*) Dependence of the integrated PL intensity of samples with mesas of different diameters normalized to the mesa area as a function of the optical pump power density before passivation. (*b*) Dependence of the integral PL intensity of the GaAs/AlAs superlattice line as a function of the optical pump power density for mesas with a diameter of 9 μm before and after passivation.

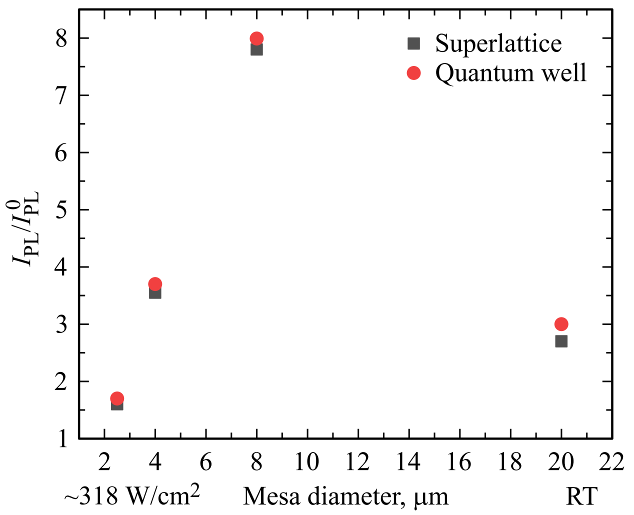

Figure 4. Factor of increase in PL intensity as a result of passivation (IPL/I0) depending on the mesa diameter of the $In_{0.2}Ga_{0.8}As$/GaAs QW and GaAs/AlAs SL.

QW was obtained using the monoexponential function $I_{PL}(t) = Ae^{-t/\tau_{decay}}$, which well describes the experimental data. In the initial samples, the PL intensity decays quickly, and the decay time changes insignificantly as the mesa diameter changes (Fig. 5, *b*). As a result of passivation, a significant increase in the lifetime of charge carriers is observed for a mesa structure with a diameter of 20 μm compared to the initial structure: from ~ 0.14 ns to ~ 2.3 ns. For mesas of other diameters, an increase in the decay time of the PL intensity as a result of passivation is also observed, but only up to 1 ns for mesas with a diameter of 9 μm and up to 0.3 ns for mesas with a diameter of 3 μm.

Conclusions

This study has investigated the effect of treatment in hydrogen plasma followed by deposition of an Al_2O_3 layer on the surface of mesa structures with a diameter from 3 μm to 20 μm with an emitting region based on an InGaAs/GaAs quantum well and a GaAs/AlAs superlattice on their optical properties. An 8 times increase in PL intensity was obtained for mesas with a diameter of 9 μm. The effect is long-term; the PL intensity of mesas remained at the same level during repeated tests for 6 months. The results of time-resolved PL studies demonstrated an increase in the lifetime of charge carriers in the 20 μm mesa structure from 0.14 ns to 2.3 ns and to 1 ns for the 9-m μm mesas. The results obtained can be used for the development of GaAs-based microlasers with a 2D active region with a characteristic lateral size of a few micron to tens of microns (microdisk lasers, vertically emitting lasers), etc.

Funding

This study was supported by grant No. 22-72-10002 from the Russian Science Foundation (https://rscf.ru/project/22-72-10002/). The investigations using time-resolved microscopy were carried out within the framework of the Fundamental Research Program of the HSE National Research University. Optical studies were carried out using the equipment of the „Integrated Optoelectronic Stand“ unique research setup. The treatment of samples with hydrogen radicals and the subsequent growth of an aluminum oxide film were carried out with the support of the Ministry of Education and Science of the Russian Federation (Agreement № 075-03-2023-106 dated 13.01.2023). SEM studies were carried out on the equipment of the „Materials Science and Characterization in Advanced Technologies “ Federal

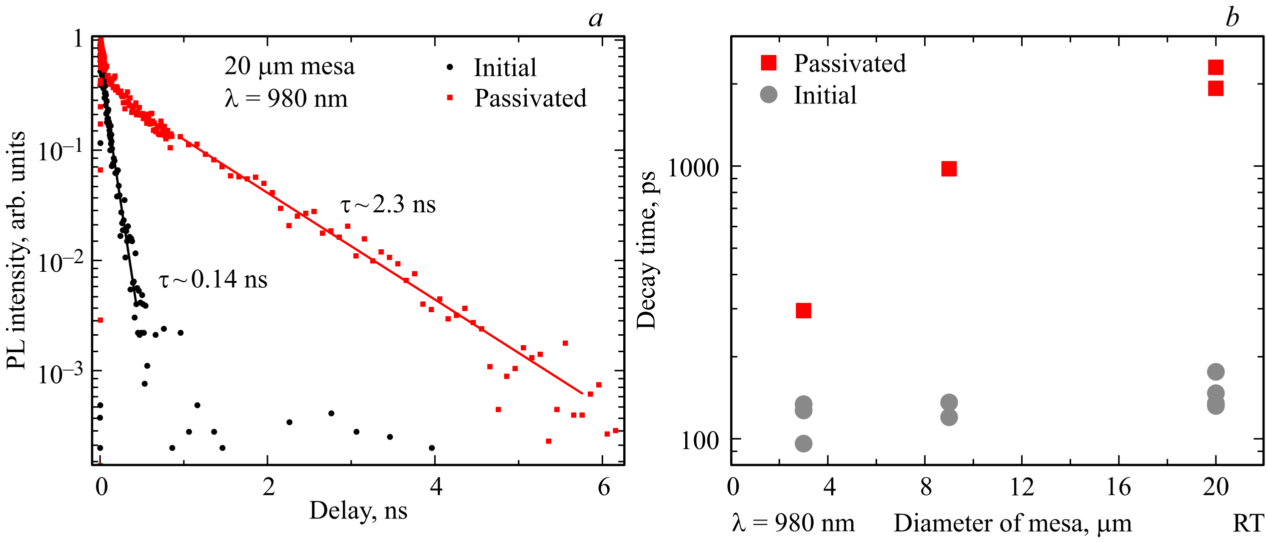

Figure 5. (*a*) Time dependences of the PL intensity decay obtained at room temperature for mesas with a diameter of 20 μm, a wavelength of 980 nm. (*b*) Lifetime of charge carriers in the initial and passivated samples with mesas with diameters of 3 μm, 9 μm, and 20 μm.

Joint Research Center. The work of the authors from ITMO University was carried out with the support of the federal project „Advanced Engineering Schools" in terms of preparing samples for the studies.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] P. Laukkanen, M.P.J. Punkkinen, M. Kuzmin, K. Kokko, J. Lång, R.M. Wallace. Appl. Phys. Rev., **8** (1), 011309 (2021). DOI: 10.1063/1.5126629
[2] H. Deng, G.L. Lippi, J. Mørk, J. Wiersig, S. Reitzenstein. Adv. Optical Mater., **9** (19), 2100415 (2021). DOI: 10.1002/adom.202100415
[3] S.H. Pan, S.S. Deka, A.El Amili, Q. Gu, Y. Fainman. Progress in Quantum Electronics, **59**, 1–18 (2018). DOI: 10.1016/j.pquantelec.2018.05.001
[4] R.T. Ley, J.M. Smith, M.S. Wong, T. Margalith, S. Nakamura, S.P. DenBaars, M.J. Gordon. Appl. Phys. Lett., **116** (25), 251104 (2020). DOI: 10.1063/5.0011651
[5] A. Baca, C. Ashby. *Fabrication of GaAs Devices* (The Institution of Engineering and Technology, London, 2005). DOI: 10.1049/PBEP006E
[6] M. Boroditsky, I. Gontijo, M. Jackson, R. Vrijen, E. Yablonovitch, T. Krauss, Chuan-Cheng Cheng, A. Scherer, R. Bhat, M. Krames. J. of Appl. Phys., **87** (7), 3497–3504 (2000). DOI: 10.1063/1.372372
[7] T.S. Shamirzaev, K.S. Zhuravlev, A.Yu. Kobitski, H.P. Wagner, D.R.T. Zahn. Phys. B: Condensed Matt., **308**, 761–764 (2001). DOI: 10.1016/S0921-4526(01)00831-6
[8] L. Zhou, B. Bo, X. Yan, C. Wang, Y. Chi, X. Yang. Crystals, **8** (5), 226 (2018). DOI: 10.3390/cryst8050226
[9] J. Robertson, Y. Guo, L. Lin. J. Appl. Phys., **117** (11), 112806 (2015). DOI: 10.1063/1.4913832
[10] S. Arab, C. Chi, T. Shi, Y. Wang, D.P. Dapkus, H.E. Jackson, L.M. Smith, S.B. Cronin. ACS Nano, **9** (2), 1336–1340 (2015). DOI: 10.1021/nn505227q
[11] S.R. Lunt, G.N. Ryba, P.G. Santangelo, N.S. Lewis. J. Appl. Physics, **70** (12), 7449–7467 (1991). DOI: 10.1063/1.349741
[12] C.I.H. Ashby, K.R. Zavadil, A.J. Howard, B.E. Hammons. Appl. Phys. Lett., **64** (18), 2388–2390 (1994). DOI: 10.1063/1.111623
[13] M. Oshima, T. Scimeca, Y. Watanabe, H. Oigawa, Y. Nannichi. Japanese J. Appl. Physics, **32** (1S), 517 (1993). DOI: 10.1143/JJAP.32.518
[14] A. Aierken, J. Riikonen, J. Sormunen, M. Sopanen, H. Lipsanen. Appl. Phys. Lett., **88** (22), 221112 (2006). DOI: 10.1063/1.2208557
[15] J. Schmid, A. Merkle, B. Hoex, M.C.M. Van De Sanden, W.M.M. Kessels, R. Brendel. In: 2008 33rd IEEE Photovoltaic Specialists Conference (IEEE, 2008), p. 1–5. DOI: 10.1109/PVSC.2008.4922636
[16] A. Paccagnella, A. Callegari, E. Latta, M. Gasser. Appl. Phys. Lett., **55** (3), 259–261 (1989). DOI: 10.1063/1.101922
[17] E. Yoon, R.A. Gottscho, V.M. Donnelly, H.S. Luftman. Appl. Phys. Lett., **60** (21), 2681–2683 (1992). DOI: 10.1063/1.106894
[18] L.E. Black, A. Cavalli, M.A. Verheijen, J.E.M. Haverkort, E.P.A.M. Bakkers, W.M.M. Kessels. Nano Letters, **17** (10), 6287–6294 (2017). DOI: 10.1021/acs.nanolett.7b02972
[19] Z.L. Wang, Z.B. Hao, J.D. Yu, C. Wu, L. Wang, J. Wang, C.Z. Sun, B. Xiong, Y.J. Han, H.T. Li, Y. Luo. J. Phys. Chem. C, **121** (11), 6380–6385 (2017). DOI: 10.1021/acs.jpcc.7b00578

Translated by Y.Alekseev