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Effect of buffer layer on the characteristics of GaPN layers grown by molecular beam epitaxy on silicon substrates

© E.V. Nikitina[1,2], E.V. Pirogov[1], A.K. Kaveev[2], V.V. Fedorov[1]

[1] 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
[2] Ioffe Institute, St. Petersburg, Russia
E-mail: mail.nikitina@mail.ru

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This paper presents a comparative study of the effect of buffer layers on characteristics of GaPN layers synthesized by molecular beam epitaxy on silicon substrates. Structures with a GaP- buffer grown using the "migration-enhanced epitaxy" (MEE-GaP- buffer) and a low-temperature GaP- buffer with a smoothly increasing growth temperature were studied. It was shown that the photoluminescence intensity for the structures with MEE-GaP and optimized GaP- buffer is almost equal, but the stress relaxation mechanisms are different.

Keywords: dilute nitrides, heterostructures, molecular beam epitaxy, silicon substrate.

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Since the efficiency of silicon-based solar cells has almost reached its theoretical limit [1], further development of photovoltaics necessitates a constant search for new approaches and the use of novel materials. The use of multi-junction (cascade) heterostructures is one of the most promising ways to increase the efficiency of solar cells (SCs). Three-, four-, and even five-junction SCs with an efficiency as high as 46 % [2] have already been fabricated based on $A^{III}B^{V}$ compounds. Silicon used as a substrate or a lower cascade is of interest not only as a cheap and easy-to-process material, but also as a fine heat sink ensuring stable SC operation.

One of the possible ways to obtain monolithic multijunction SCs on silicon is the use of GaPNAs solid solutions, which may be lattice-matched with a silicon substrate within a wide range of band gap values (from 1.5 to 2.0 eV) [3,4] due to the fact that nitrogen and arsenic reduce and raise the lattice constant, respectively. It was demonstrated theoretically [5] that the limit efficiency of lattice-matched three-junction SCs (GaPNAs(2 eV)/GaPNAs(1.5 eV)/Si) is 44.5 % at AM1.5D 50 W/cm^2. However, these theoretically predicted efficiency values may be achieved only with a lifetime of minority carriers in GaPNAs layers greater than 1 ns [5], which has not been demonstrated yet. Therefore, the study of techniques for fabrication of GaPN(As) materials on silicon substrates is relevant.

Migration-enhanced epitaxy (MEE), which involves layer-by-layer (atomic) growth of a GaP buffer layer at low temperatures, is one of the approaches to fabrication of dislocation-free GaPN layers on silicon substrates [6]. Another possible method is to perform low-temperature growth of a buffer layer [7] and to use aluminum-containing buffer layers [8]. The present study is focused on the influence of buffer layers on the characteristics of the GaPN solid solution.

The examined structures were synthesized using a Veeco Gen III molecular beam epitaxy system with a high-frequency inductively coupled nitrogen plasma source on Si (100) substrates with a 4° misalignment in the [110] direction.

Their structural properties were studied by X-ray diffraction (XRD). Diffraction rocking curves were obtained using a DRON-8 X-ray diffractometer with a BSV 29 LLF X-ray tube. The anode material was copper with $K_{\alpha1}$ ($\lambda = 1.5405$ Å) radiation type. An Accent Optical Technologies setup was used to record photoluminescence spectra. A solid-state UV laser provided optical pumping ($\lambda = 266$ nm).

The samples featured a 200-nm-thick GaPN layer grown on buffer layers of various configurations. To prevent the emergence of antiphase regions at the silicon−gallium phosphide heterointerface, silicon substrates misaligned in the [110] direction were used, and a monolayer of phosphorus was formed on the silicon surface after annealing in the growth chamber. Sample No. 1 had a GaP buffer layer synthesized by the MEE method based on 45 periods of layer-by-layer growth of gallium and phosphorus [9] at a temperature of 450 °C with a further GaP layer (50 nm). The overall thickness of the MEE-GaP- buffer was 100 nm. The buffer layer of sample No. 2 had a thin (1 nm) AlP sublayer grown at a temperature of 450 °C. On top of it were a 36-nm-thick GaP layer with the growth temperature increasing gradually to 600 °C, a 10-nm-thick GaP layer grown at 600 °C, and a GaP layer 8 nm in thickness with the temperature decreasing smoothly to 540 °C. The buffer layer of sample No. 3 had a configuration similar to the one detailed above; the only difference was that the top

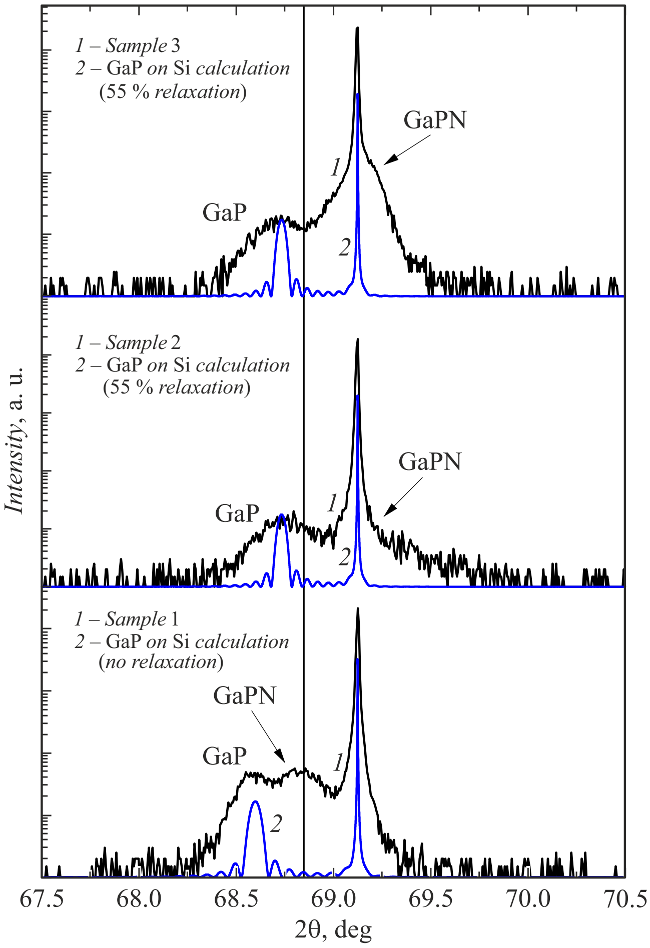

Figure 1. XRD rocking curves around the symmetrical reflection of Si for samples with an epitaxial GaPN layer on the Si surface with different buffer layers. A color version of the figure is provided in the online version of the paper.

GaP layer was grown at a temperature of 600 °C. The AlP layer in the second and third samples serves to suppress the mutual diffusion of silicon and gallium atoms from the buffer layer.

Figure 1 presents the XRD rocking curves around the symmetrical reflection of Si for epitaxial GaPN layers on the Si (100) surface with different buffer layers. The black vertical line indicates the theoretical position of the diffraction maximum of a mechanically unstressed (relaxed) GaP layer. The calculated diffraction curves from GaP layers with different degrees of relaxation on a silicon substrate are also shown in blue. These simulated diffraction curves were plotted using the PANalytical X'Pert Epitaxy software. The relaxation percentage is used in the sample files to model the change in lattice cell distortion that occurs at imperfect interfaces forming in the presence of mismatch dislocations. This parameter helps calculate the correct peak positions in the simulated rocking curves. Relaxation is the difference between the actual dimensions of a lattice cell parallel to the interface divided by the difference in undistorted values. If a layer is distorted elastically in such a way that lattice cells have the same width parallel to the interface plane, the relaxation is 0 % and the interface does not contain mismatch dislocations. This layer is called a fully deformed (elastically stressed, pseudomorphic) one. When a layer is not deformed, the relaxation is 100 %. Such a layer is called a fully relaxed one.

The lower panel of Fig. 1 shows the calculated curve for a fully stressed GaP layer on a silicon substrate. It can be seen that the position of the diffraction peak maximum of sample No. 1 is consistent with the model. Therefore, it may be concluded that sample No. 1 has fully stressed (pseudomorphic) GaP and GaPN layers and, as will be shown below, the molar fraction of nitrogen in GaPN approaches its value for the layer in sample No. 3 (despite the significant difference in positions of the diffraction maximum). The intensities and positions of the diffraction maxima of the GaP layers in samples Nos. 2 and 3 are similar, but the maxima are shifted toward larger angles to the silicon substrate. The calculated curves indicate an approximate degree of relaxation of 55 % in the GaP layers, which follows from the comparison of experimental and simulated data. The emergence of dislocations at the initial stages of epitaxy probably leads to partial relaxation of elastic stresses of the epitaxial layer in these samples, and the lattice constant of the GaP epitaxial layer approaches the lattice constant of a mechanically unstressed GaP layer. The GaPN layers in samples Nos. 2 and 3 also demonstrate stress relaxation; however, since the conditions of growth of the buffer layer differed, the GaPN layer in sample No. 2 does not, unlike the layer in sample No. 3, feature a clearly defined maximum that is virtually coincident with the maximum from the silicon substrate. This may be indicative of a significant nonuniformity of nitrogen distribution in the GaPN layer in sample No. 2 and of the presence of a large number of mismatch dislocations.

Microphotographic images of the cross section and surface of the studied samples with a GaP buffer layer on the silicon substrate are shown in Fig. 2. These images were obtained using a Supra 25 Zeiss scanning electron microscope (SEM). The sample with a MEE-GaP- buffer (sample No. 1) has a well-developed surface morphology, but there are few pronounced dislocations in the layer. This is consistent with the XRD data on the pseudomorphic nature of growth of both the buffer layer and the studied GaPN layer. Samples Nos. 2 and 3 with a low-temperature GaN buffer layer have a smooth surface of the upper GaPN layer and a large number of threading dislocations formed as a result of partial relaxation of elastic stresses of the epitaxial layer.

Figure 3 shows the room-temperature photoluminescence spectra of the samples. Despite the large number of dislocations, sample No. 3 has a high photoluminescence intensity. The photoluminescence intensity of sample No. 1 with a MEE buffer is also high (comparable to that of sample No. 3). Close positioning of the maximum wavelengths of photoluminescence indicates that the molar fractions of nitrogen in samples Nos. 1 and 3 are also virtually identical.

The FWHM values of the photoluminescence line for samples Nos. 1 and 3 were equal and quite large (close to 65 nm), indicating that the ternary GaPN solution has a nonuniform composition. The growth of an additional high-temperature GaP- layer in the buffer layer of sample No. 2 leads to a shift of photoluminescence toward longer wavelengths, broadening of the photoluminescence line, and a reduction in intensity. This suggests that the GaPN layer is highly nonuniform and is characterized by intense nonradiative recombination of carriers due to a large number of threading dislocations, which is also confirmed by X-ray data.

The samples with an optimized low-temperature GaP buffer layer and with a MEE-GaP buffer layer demonstrate high (almost equal) photoluminescence intensities. The GaPN layer stress relaxation depends on the buffer used. The sample with a MEE-GaP- buffer has a pseudomorphic non-relaxed buffer and a GaPN layer, a small number of threading dislocations, and a relief surface. Partial relaxation of elastic stresses in the GaPN layer is observed in the form of threading dislocations in the samples with a low-temperature gradient GaP- buffer.

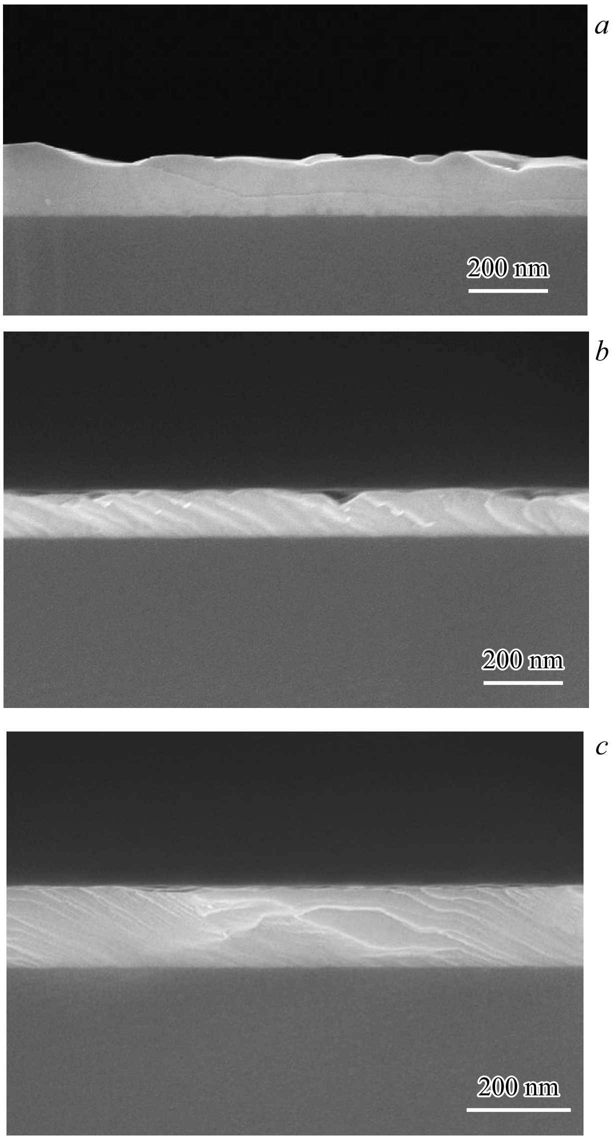

Figure 2. Microphotographic images of the cross section and surface of samples Nos. 1 (*a*), 2 (*b*), and 3 (*c*).

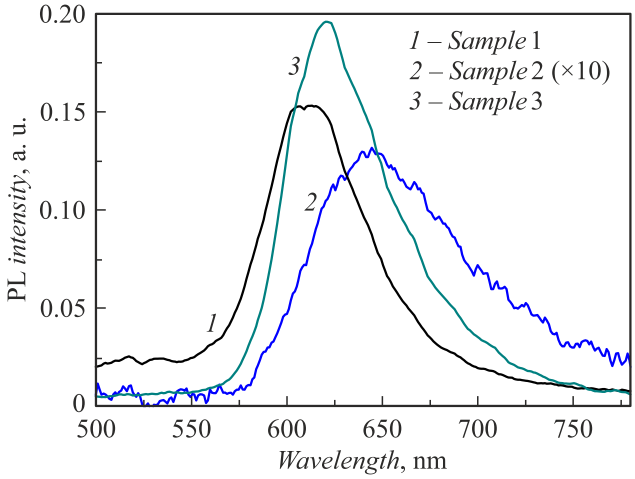

Figure 3. Photoluminescence spectra of the studied samples with an epitaxial GaPN layer on the Si surface with different buffer layers.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] K. Yoshikawa, W. Yoshida, T. Irie, H. Kawasaki, K. Konishi, H. Ishibashi, T. Asatani, D. Adachi, M. Kanematsu, H. Uzu, K. Yamamoto, Solar Energy Mater. Solar Cells, **173**, 37 (2017). DOI: /10.1016/j.solmat.2017.06.024

[2] M.A. Green, E.D. Dunlop, M. Yoshita, N. Kopidakis, K. Bothe, G. Siefer, X. Hao, Prog. Photovolt.: Res. Appl., **32**, 3 (2024). DOI: 10.1002/pip.3750

[3] J.F. Geisz, D.J. Friedman, Semicond. Sci. Technol., **17**, 769 (2002). DOI: S0268-1242(02)37904-5

[4] R. Kudrawiec, J. Appl. Phys., **101** (11), 116101 (2007) DOI: 10.1063/1.2736618

[5] D.A. Kudryashov, A.S. Gudovskikh, E.V. Nikitina, A.Yu. Egorov, Semiconductors, **48**, 381 (2014). DOI: 10.1134/S1063782614030154.

[6] Y. Takagi, H Yonezu, K. Samonji, N. Ohshima, J. Cryst. Growth, **187** (1), 42 (1998) DOI: 10.1016/S0022-0248(97)00862-2

[7] V.V. Fedorov, S.V. Fedina, A.K. Kaveev, D.A. Kirilenko, N.N. Faleev, I.S. Mukhin, Nauchno-Tekh. Vedomosti S.-Peterb. Gos. Politekh. Univ. Fiz.-Mat. Nauki, **17** (2), 120 (2024) (in Russian). DOI: 10.18721/ JPM.17209

[8] G.A. Sapunov, O.Yu. Koval, V.V. Fedorov, A.D. Bolshakov, J. Phys.: Conf. Ser., **1697**, 012127 (2020). DOI: 10.1088/1742-6596/1697/1/012127

[9] M.S. Sobolev, A.A. Lazarenko, E.V. Nikitina, E.V. Pirogov, A.S. Gudovskikh, A.Yu. Egorov, Semiconductors, **49**, 559 (2015). DOI: 10.1134/S1063782615040235.

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