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Photoluminescence of GaPNAs/GaP(N) superlattices and bulk GaPN layers on GaP substrates

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Abstract

The addition of a few percent of nitrogen to GaP or GaPAs allows obtaining GaPNAs solid solutions that are lattice-matched to the silicon substrate over a wide range of band gaps, which makes it possible to obtain optoelectronic silicon integrated circuits. However, materials with a small fraction of nitrogen are understudied due to the difficulty in epitaxial growth of quaternary solid solutions with three materials of group V. The purpose of the study was the investigation of the influence of the substrate temperature during the epitaxial growth of dilute nitride materials (GaPN solid solution and GaPNAs/GaP(N) superlattices) on their optical properties, as well as the influence of the growth temperature and superlattice design on the bandgap of the resulting material.

It was shown that there is an optimal growth temperature for samples: at temperatures below the optimal, non-radiative recombination at defects predominates, and at a temperature higher than the optimal one, the solid solution of the GaPN layer material decomposes into components with a larger and smaller fraction of nitrogen. Studies were also carried out on the decay of photoluminescence intensity over time in the studied structures at room temperature, which allowed us to evaluate the influence of growth parameters and structure design on the lifetime of nonequilibrium charge carriers. The best lifetime for structures with superlattices was obtained for the GaPNAs/GaPN superlattice and amounted to ~0.2 ns.

As a result, the optimal growth temperatures were determined for bulk GaPN layers and for GaPNAs/GaP(N) superlattices, which leads to an increase in the PL intensity and lifetime of the carrier.

Keywords: GaPN(As), Superlattices, Photoluminescence

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1. Introduction

Now, silicon is the main material of electronics, integrated circuit technology, and solar energy. On the other hand, multi-junction solar converters based on AIIIBV materials are the most efficiently used in solar energy, their efficiency for concentrated solar radiation exceeds 47% [1]. The use of a silicon substrate for a multi-junction solar converter based on AIIIBV materials as upper stages impairs significant mismatch between silicon lattice and the main AIIIBV materials. Among all binary AIIIBV materials, GaP has the lowest lattice mismatch with Si[1] (~0.37% at room temperature [2]). Under normal conditions, GaP is an indirect-bandgap material, which to a certain extent limits its use in optoelectronics, photonics, and photovoltaics [3]. In recent decades, much attention has been paid to the study of chemical compounds of gallium phosphide with nitrogen and arsenic [4, 5], which is associated with the unusual properties of these materials, as well as their great potential for various applications in optoelectronics and photonics. It was found [6] that when a small amount of nitrogen (~0.5%) is added to GaP, the band structure of the material becomes a direct bandgap, and the band gap energy decreases. The advantages of GaPN over GaP also include an improved ability to integrate with Si, since the lattice constant of this material with the addition of nitrogen decreases and can be closer to the lattice constant of silicon [7], which allows the growth of high-quality layers. It was shown in [8] that the additional introduction of arsenic allows one to obtain GaPNAs solid solutions, which are consistent in lattice parameter with Si in a wide range of band gap values (from 1.5 to 2.0 eV). Theoretically, it was shown [9] that the potentially achievable efficiency values of triple-junction solar cells based on lattice-matched GaPNAs (2 eV)/GaPNAs (1.5 eV)/Si heterostructures are 44.5% at AM 1.5D.

However, despite the advantages of dilute nitrides, the addition of nitrogen to the layers leads to the emergence of deep centers of non-radiative recombination, which leads to the need for further improvement of technology and the search for new approaches to the creation of materials based on GaPNAs solid solutions, lattice-matched with silicon, suitable for device applications. One possible solution is to use a superlattice instead of a bulk material. It was shown in [10] that the use of a short-period GaAsSb/GaAsN superlattice led to an improvement in the crystalline and optical qualities of the material compared to the GaAsSbN solid solution.

In this study we investigated the effect of the substrate temperature during the epitaxial growth of structures with a bulk GaPN layer on the intensity of photoluminescence (PL) spectra, and also studied structures with GaPNAs/GaP and GaPNAs/GaPN superlattices grown by molecular beam epitaxy with a nitrogen plasma source at GaP substrates. We also carried out studies of the decay of photoluminescence intensity over time in the studied structures at room temperature, which allowed us to evaluate the influence of growth parameters and structure design on the lifetime of nonequilibrium charge carriers.

2. Experimental

The epitaxial structures studied were produced by molecular beam epitaxy with a nitrogen plasma source on GaP(100) substrates.

To study the effect of substrate temperature during epitaxial growth on the optical properties of the GaPN material, samples N1, N2, and N3 were prepared. In these samples, a GaP buffer layer with a thickness of 100 nm was grown on a GaP(100) substrate, then a GaPN layer with a thickness of 200 nm was grown with a nitrogen mole fraction of about 0.01 at substrate temperatures of 490, 470, and 505 °C, respectively, after which the structure was completed with a GaP layer with the thickness of 20 nm.

We also produced samples containing 12 periods of a superlattice consisting of GaPNAs/GaP layers in a GaP matrix (samples N4 and N5) and GaPNAs/GaPN in a GaPN matrix (samples N6 and N7) with thicknesses of 7 nm with a nitrogen mole fraction of about 0.01. The mole fraction of arsenic in the superlattice of samples N4 and N5 was 0.1 and 0.17, respectively, and the growth temperature was 510°C. The mole fraction of arsenic in the superlattice of samples N6 and N7 was 0.2, and the growth temperature of the superlattice was 520 and 490 °C, respectively (the parameters of the studied samples are shown in Table 1).

These structures were studied by photoluminescence (PL) in the spectral range

Table 1. Growth parameters and obtained characteristics of samples

Material of light emitting area	Layer GaPN			Superlattice GaPNAs/GaP		Superlattice GaPNAs/GaPN	
Sample	N 1	N 2	N 3	N 4	N 5	N 6	N 7
As mole fraction	–	–	–	0.1	0.17	0.2	0.2
Epitaxial growth temperature, °C	490	470	505	510	510	520	490
α	1.8–1	1.8–1	1	1.15	1.1	1.2	1.6
$\tau_{1/e}$, ps	81	65	99	69	65	200	82

from 500 to 800 nm at room temperature. The structures were pumped by a He-Cd laser (wavelength 325 nm, continuous mode). When studying the evolution of the PL spectra of samples from the pump optical power, the latter was varied in the range of 0.05 – 3 mW using a neutral gradient filter installed in the path of the laser beam. The laser beam was focused using a lens at a normal angle of incidence, and the PL signal was collected using the same lens. To detect the PL signal passed through the AndorSolis monochromator (the grating contained 1200 lines/mm, the blaze angle was 500 nm), a silicon CCD matrix (Andor) was used.

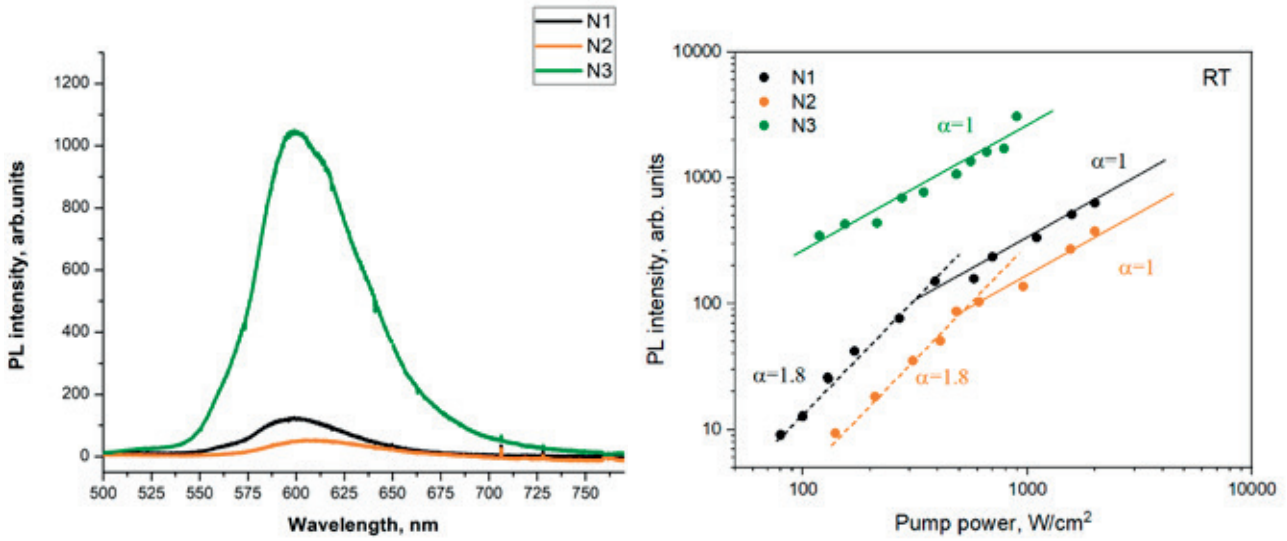
The PL study with the time resolution was carried by the up-conversion method using a FOG-100-DX-IR device for differential fluorescence kinetics measurements in the visible range. Laser pulses with a duration of 120 fs, a frequency of 80 MHz, and a wavelength of 780 nm, generated by a tunable titanium-sapphire laser CoherentMira 900D with a maximum average power of 1.5 W were used for gating and pumping samples. The gating of the optical PL signal occurred due to its up-conversion with the laser pulse (i.e., the addition of photon energies) on a nonlinear BBO crystal (β-BaB_2O_4 or β-barium borate), which allowed us to obtain a time resolution of ~0.2 ps. To excite the PL of the samples, the pulse energy of a titanium-sapphire laser was doubled using a nonlinear BBO crystal. The optical up-conversion signal was detected in a continuous mode by a synchronous detection method using a monochromator and a photomultiplier.

3. Results and discussion

The PL spectra of heterostructures with a GaPN layer (N1, N2, and N3) at room temperature are shown in Fig. 1a. The composition of the ternary and quaternary solid solutions was determined by X-ray diffraction analysis. The rocking curves for the symmetric reflection (004) of gallium phosphide for samples N1, N2, and N3 showed that the composition of the GaPN layer for the samples was the same and corresponded to a nitrogen mole fraction of about 0.01. The PL intensity increases sharply with increasing temperature of epitaxial growth of the GaPN layer and differed by more than 10 times from the sample with a growth temperature of 470 °C to sample N3 with a growth temperature of 505 °C. A further increase in the substrate temperature during epitaxial growth of the bulk GaPN layer led to the decomposition of the solid solution of the GaPN layer material into components with a larger and smaller fraction of nitrogen and a sharp decrease in the PL intensity.

The dependence of the PL intensity of structures with a bulk GaPN layer on the pump optical power density for three samples is shown in Fig. 1b. For sample N3 this dependence is well described by the dependence $IPL = \eta I\alpha$, where IPL – integrated PL intensity, I – the power density of the exciting laser, η – the coefficient. In sample N3, the α index was almost equal to unity over the entire range of studied powers, which indicated that the main recombination mechanism was radiative recombination. The dependence for samples N1 and N2 had two pronounced sections. In the region of low powers, the dependence had an exponent close to 2, which was associated with a significant contribution of nonradiative transitions. An increase in the power led to the linear behavior of the dependence, which was associated with saturation of nonradiative recombination in GaPN layers.

A mole fraction of nitrogen of 0.01 in the GaPN solid solution was not sufficient to obtain a lattice-matched material with silicon. An increase in the mole fraction of nitrogen in a GaPN



a b

Fig. 1. PL spectra of structures with a bulk GaPN layer on a GaP substrate, obtained at room temperature at a pump optical power density of 800 W/cm^2(a); dependence of the integrated PL intensity on the pump optical power density (b)

layer led to a sharp decrease in the PL intensity [11], which indicated an increasing density of nonradiative recombination centers and the impossibility of using this material as an active part of photoelectric converters.

One possible solution to this problem is the use of nanoscale superlattices. The photoluminescence spectra of samples with GaPNAs/GaP (samples N4 and N5) and GaPNAs/GaPN (samples N6 and N7) superlattices at room temperature are shown in Fig. 2. The PL spectra of samples with superlattices showed a shift of the PL wave to longer wavelengths compared to samples with a bulk GaPN layer and an increase in the peak PL intensity. As we mentioned above, samples N4 and N5 with GaPNAs/GaP superlattices were grown under the same growth conditions with arsenic mole fractions of 0.1 and 0.17,

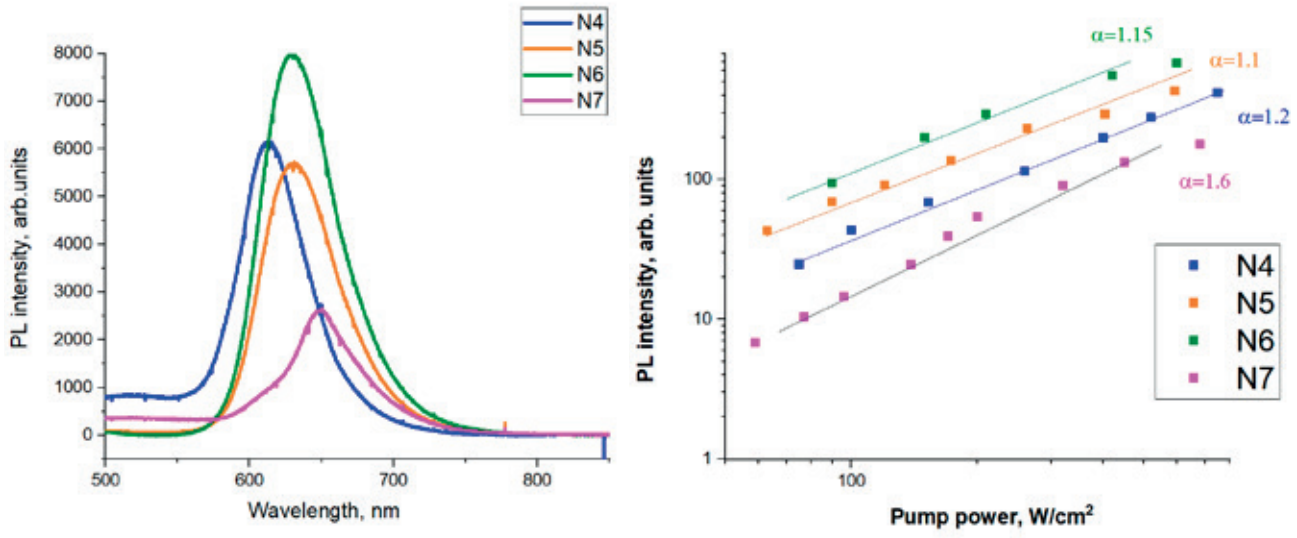


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Fig. 2. PL spectra of structures with GaPNAs/GaP (samples N4 and N5) and GaPNAs/GaPN (samples N6 and N7) superlattices on a GaP substrate at room temperature with a pump optical power density of 600 W/cm^2(A); dependence of the integrated PL intensity on the pump optical power density at room temperature (b)

respectively. With an increase in the mole fraction of arsenic in the superlattice, the PL intensity remained almost unchanged, and the wavelength of the maximum intensity of the PL band shifted from 615 to 630 nm. A further shift of the PL wave to longer wavelengths is possible when using GaPNAs/GaPN superlattices. Samples N6 and N7 with GaPNAs/GaPN superlattices were grown at the same arsenic and nitrogen flows (arsenic mole fraction 0.2, nitrogen mole fraction 0.01), but had different growth temperatures of the active region – 520 and 490 °C, respectively. The wavelength corresponding to the peak of the PL band of sample N6 coincided with the wavelength for sample N5 and is 630 nm, which indicated the re-evaporation of arsenic from the surface at elevated temperatures during epitaxial growth. A decrease in the growth temperature led to a significant increase in the wavelength of the PL peak intensity up to 650 nm, which indicated a greater incorporation of arsenic and nitrogen into the epitaxial layers, while the PL intensity decreased by approximately 3 times compared to a similar superlattice grown at 520 °C.

The dependence of the PL intensity of structures with GaPNAs/GaP and GaPNAs/GaPN superlattices at room temperature on the pump optical power density are shown in Fig. 2b. The comparison of the slopes of the dependences allowed us to estimate the contribution of nonradiative recombination and the defectiveness of the structures. It can be seen that for samples N4, N5, and N6 the dependence was well described by the relation $IPL = \eta I\alpha$ with the α index was almost equal to unity (1.1–1.2), which indicated that the main recombination mechanism is radiative recombination. In sample N7 with a GaPNAs/GaPN superlattice, recombination at defects predominated ($\alpha = 1.6$).

It was shown in [9] that the operating efficiency of multi-junction GaPNAs/Si solar cells is also strongly influenced by such an important material parameter as the lifetime of minority charge carriers. Therefore, we carried out studies of the photoluminescence kinetics of structures with a bulk GaPN layer and GaPNAs/GaP superlattices and GaPNAs/GaPN at room temperature. The dependence of the PL intensity decay on time for the light wavelength corresponding to the PL intensity peak is shown in Fig. 3.

Thus, the structures demonstrated a time evolution of the PL intensity that slightly deviated from a monoexponential decay. We estimated the characteristic times of decline in PL intensity based on 1/*e* level. The structures showed a similar PL decay time of about 100 ps, except sample N6. Sample N3 showed the longest lifetime among all the studied samples with a GaPN layer ~0.1 ns. The best lifetime for structures with superlattices was obtained for the GaPNAs/GaPN superlattice for sample N6 and amounted to ~0.2 ns.

The main parameters of the studied samples and the main obtained characteristics are shown in Table 1.

4. Conclusions

In this study the effect of epitaxial growth temperature on the optical properties of the GaPN material was investigated. It was shown that increasing the temperature up to 505 °C for bulk GaPN layers and 520 °C for GaPNAs/GaP(N) superlattices leads to a significant decrease in nonradiative recombination at defects, which leads to an increase in PL intensity and carrier lifetime. The use of GaPNAs/GaP and GaPNAs/GaPN superlattices allows changing the emission wavelength up to 650 nm.

Contribution of the authors

The authors contributed equally to this article.

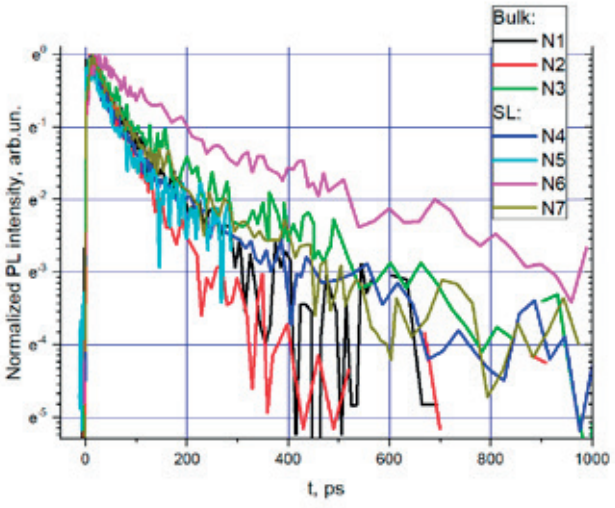

Fig. 3. Dependence of the decay of normalized PL intensity on time, obtained at room temperature

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. Green M. A., Dunlop E. D., Siefer G., … Hao X. Solar cell efficiency tables (Version 61) *Progress in Photovoltaics: Research and Applications*. 2023;31: 3–16. https://doi.org/10.1002/pip.3646

2. Ang Zhou. *Analyse structurales de pseudo-substrats Gap/Si et d'hétérostructures CIGS/GaP/Si pour des applications photovoltaïques*. Matériaux. INSA de Rennes, 2019. Français. Available at: https://theses.hal.science/tel-02924619/document

3. Greil J., Assali S., Isono Y., … Haverkort J. E. M. Optical properties of strained wurtzite gallium phosphide nanowires. *Nano Letters*. 2016;16(6): 3703–3709. https://doi.org/10.1021/acs.nanolett.6b01038

4. Kunert B., Volz K., Koch J., Stolz W. Direct-band-gap Ga(NAsP)-material system pseudomorphically grown on GaP substrate. *Applied Physics Letters*. 2006;88: 182108. https://doi.org/10.1063/1.2200758

5. Ilahi S., Almosni S., Chouchane F., … Cornet C. Optical absorption and thermal conductivity of GaAsPN absorbers grown on GaP in view of their use in multijunction solar cells. *Solar Energy Materials and Solar Cells*. 2015;141: 291. https://doi.org/10.1016/j.solmat.2015.06.003

6. Shan W., Walukiewicz W., Yu K. M., … Tu C. W. Nature of the fundamental band gap in GaN_xP_{1-x} alloys. *Applied Physics Letters*. 2000;76: 3251. https://doi.org/10.1063/1.126597

7. Furukawa Y., Yonezu H., Morisaki Y., Moon S.-Y., Ishiji S., Wakahara A. Monolithic implementation of elemental devices for optoelectronic integrated circuit in lattice-matched Si/III–V–N alloy layers. *Japanese Journal of Applied Physics*. 2006;45(9L): L920. https://doi.org/10.1143/jjap.45.l920

8. Geisz J. F., Friedman D. J. III–N–V semiconductors for solar photovoltaic applications. *Semiconductor Science and Technology*. 2002;17(8): 769–777. https://doi.org/10.1088/0268-1242/17/8/305

9. Kudryashov D. A., Gudovskikh A. S., Nikitina E. V., Egorov A. Yu. Design of multijunction GaPNAs/Si heterostructure solar cells by computer simulation. *Semiconductors*. 2014;48(3): 381–386. https://doi.org/10.1134/s1063782614030154

10. Gonzalo A., Utrilla A. D., Reyes D. F., … Ulloa J. M. Strain-balanced type-II superlattices for efficient multi-junction solar cells. *Scientific Reports*. 2017;7: 4012. https://doi.org/10.1038/s41598-017-04321-4

11. Henini M. *Dilute nitride semiconductors*. Elsevier; 2005. https://doi.org/10.1016/B978-0-08-044502-1.X5000-8

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