# PA MBE growth of intermediate-composition InGaN layers for red and near-IR laser sources

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This paper presents the results of studying the growth of InGaN layers with a high (50−80%) indium content by molecular beam epitaxy with nitrogen plasma activation on sapphire substrates with GaN/AlN buffer layers. It is shown that the processes of dissociation and phase separation of the growing InGaN layer, which occur in structures with an indium fraction of about 50%, cannot be suppressed due to the transition to a lower temperature growth (470°C → 390°C) without significant degradation of the crystalline quality of the formed structures and a sharp decrease in their emissivity. As an alternative approach to suppressing diffusion processes on the growth surface and, as a result, obtaining homogeneous InGaN layers with an [In] content ∼ 50%, high-temperature (470°C) growth under highly nitrogen-enriched conditions (flux ratio III/V ∼ 0.6) was tested. The InGaN layers grown in this way show intense photoluminescence, while at the same time showing no signs of phase separation according to X-ray diffraction data. This is critically important for the possibility of implementing optical amplification and laser generation in such structures in the red region of the spectrum and in the immediately adjacent part of the near infrared region.

**Keywords:** indium and gallium nitride, molecular beam epitaxy, spinodal decomposition, photoluminescence.

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## 1. Introduction

Semiconductor structures formed on the basis of III-nitrides (AlN, GaN, InN and their triple compounds) are of interest as a basis for light emitting devices overlapping the entire spectral range from deep ultraviolet to near infrared region. At present, the potential of such structures is realized to a sufficient extent only in the ultraviolet and blue-green spectral regions for GaN, as well as for AlGaN and for InGaN with small fraction of indium [1,2]. Advancement to the longer-wavelength, „red" region of the spectrum, is limited by a rather low level of crystalline quality of currently obtaining InGaN epitaxial films with large fraction of indium [3]. Here, the key factors are the low temperature of decomposition of InGaN with a high fraction of indium, as well as the processes of spinodal decomposition of the triple solution and segregation of indium [4–6]. Together with the absence of consistent substrates for the growth of III-nitrides (and, accordingly, the initially high level of defectiveness of the obtained etipaxial layers), these circumstances contributed to the shift of research interest towards the construction of InGaN-based sources of coherent radiation for the red region of the spectrum and near IR range towards low-dimensional heterostructures with quantum dots (for example, [7]), most often implemented in recent works on the type „quantum dot in a wire" [8]. However, such structures also have certain disadvantages in comparison with planar structures, the main of which are the complexity of processing during the formation of laser structures, as well as a relatively low output radiation power. This work is also aimed at studying the possibilities of advancement InGaN emitters to the red region of the spectrum from the side of long waves, from binary InN and InGaN layers with a small (up to 20−25%) fraction of Ga. The authors of this work recently demonstrated stimulated emission (SE) in such structures with a bulk active layer [9,10] and showed that the threshold for stimulated emission decreased as the fraction of indium in the InGaN active layer decreased to 80%, which was explained by a decrease in the Auger recombination coefficient. However, with a further decrease in the content of In, to 75%, the sharp increase in the SE threshold was observed, associated with an increase in optical losses on free charge carriers (the concentration of which increased as a result of a deterioration in the crystalline quality of InGaN). Therefore, the possibility of further advancement of InGaN-based coherent radiation sources to shorter wavelengths is currently not obvious.

In this work, the effect of growth conditions on the formation, structural quality, and photoluminescence (PL) of InGaN layers with an indium content of 50 to 80% is studied. It should be noted here that the early works devoted to the growth of similar structures

The main parameters of the structures under study are: the nominal fraction of indium in the InGaN layer ($x^{\text{nom}}_{[\text{In}]}$) and the corresponding value refined from XRD data ($x^{\text{XRD}}_{[\text{In}]}$); growth temperature of the InGaN layer ($T_g$) and flux ratio III/V ($R_{\text{III/V}}$); the width of the X-ray peak corresponding to the InGaN layer ($\Delta\Theta_{\text{InGaN}}$) for reflection (0004); concentration ($n_e$) and mobility ($\mu_e$) of free electrons according to Hall measurements

| Sample number | #1 | #2 | #3 | #4 | #5 | #6 | #7 | #8 | #9 |
|---|---|---|---|---|---|---|---|---|---|
| $x^{\text{nom}}_{[\text{In}]}$% | 80 | 70 | 60 | 50 | 50 | 50 | 50 | 50 | 50 |
| $x^{\text{XRD}}_{[\text{In}]}$, % | 83 | 69 | 60 | 52 | 54 | 54 | 48 | 51 | 53 |
| $T_g$, °C | 470 | | | | 440 | 420 | 400 | 380 | 470 |
| $R_{\text{III/V}}$ | 0.9 | | | | | | | | 0.6 |
| $\Delta\Theta_{\text{InGaN}}$ [0004], $^0$ | 0.28 | 0.31 | 0.36 | 0.52 | 0.55 | 0.81 | 1.05 | 1 | 0.55 |
| $n_e$, $10^{19}$ cm$^{-3}$ | 1.8 | 1.2 | 1.4 | 1.2 | 2 | 3.2 | 4.3 | 7.3 | 2 |
| $\mu_e$, cm$^2$/(B · c) | 680 | 536 | 134 | 84 | 73 | 72 | 41 | 21 | 55 |

(for example, [11]) dealt exclusively with the structural properties of the obtained layers, while the emphasis on the study of radiative characteristics has been made only recently [12,13]. It should be noted also the revival of interest in issues of fundamental nature, for example, the effects of charge carrier localization in such layers of InGaN [14]. On the whole, there are not many works in the literature devoted to detailed study of the luminescent properties of InGaN „layers of intermediate“ compositions.

The purpose of the experimental studies described in this paper is better quantitative understanding of the features of growth regimes that determine the boundaries of the decomposition and phase decay processes of InGaN layers with an average indium content (from 50 to 80%). As a result, the possibility of suppressing these processes by optimizing the growth modes of InGaN layers is demonstrated, which leads to increase in their emission activity.

## 2. Experimental procedure

The samples were grown on a STE 3N3 facility (ZAO „NTO“) by molecular beam epitaxy with nitrogen plasma activation (MBE PA) on sapphire ($c$-$Al_2O_3$) substrates with diameter of 2″ with Ti layer 400 nm thick deposited on the reverse side. Buffer layers AlN (200 nm) and GaN (700 nm) were successively grown at growth temperatures ($T_g$) 820 and 710°C, respectively, and then InGaN layer 700 nm with indium content within 50–80%. In the work, two series of samples were studied, the data on which are given in the Table. Within the framework of the first series of structures (samples #1–4), the composition of the InGaN triple solution was varied, while the values $T_g \sim 470$°C and the ratio of the fluxes of atoms of the third group and active nitrogen $R_{\text{III/V}} \sim 0.9$, which corresponded to the nitrogen-enriched growth mode. These parameters were chosen as providing the lowest stimulated emission threshold in InGaN layers with $x_{[\text{In}]} \sim 80\%$ [15] content. Undoubtedly, the transition to noticeably wider gap InGaN layers (with fraction of $x_{[\text{In}]} \sim 50\%$) should be accompanied by optimization of the growth conditions. For this reason, in the second series of structures (samples #4–8 containing nominally 50% In), different growth temperatures were tested within $T_g \sim 380$–470°C, as well as high-temperature growth of InGaN under highly nitrogen-enriched conditions ($R_{\text{III/V}} \sim 0.6$, sample #9). For all structures under study, the growth rate of the InGaN layer, determined by the total flow of metals (Ga + In), was $\sim 0.35\,\mu$m/h. The consumption of molecular nitrogen during the growth of all InGaN layers remained unchanged and amounted to 2 sccm (standard cubic centimeters per minute), while the discharge power of the nitrogen plasma source (RF Atom Source HD25) was selected to provide the required flux ratio $R_{\text{III/V}}$. The grown samples were characterized by X-ray diffraction (XRD) analysis, photoluminescence (PL) spectroscopy, and Hall effect measurements.

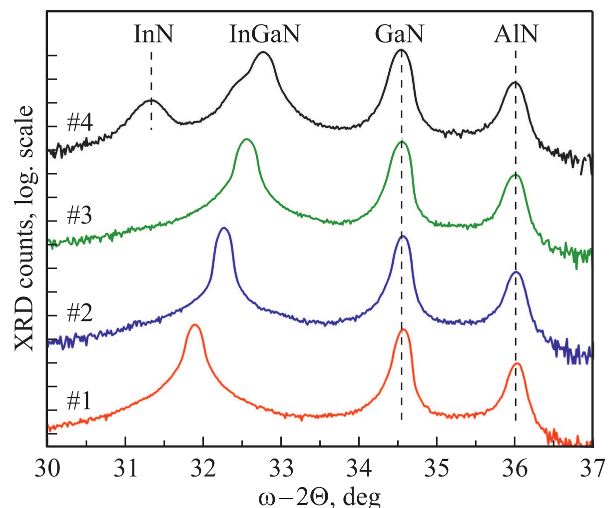


**Figure 1.** (0004) $\omega$–$2\theta$ X-ray diffraction spectra of samples with InGaN layers of various compositions grown at $T_g = 470$°C and RIII/V $\sim 0.9$ (samples #1–4 in table).

## 3. Results and discussion

Let's first consider InGaN layers grown under fixed growth conditions ($T_g \sim 470^\circ$C and $R_{\text{III/V}} \sim 0.9$); layers differ in fraction of indium in the triple solution (see samples #1–4 in the table). For these layers, when the content of $x_{[\text{In}]}$ decreases to $\sim 60\%$ inclusive, a single symmetric reflection peak is observed in the X-ray diffraction spectra (see Fig. 1), which indicates the formation of a structurally homogeneous layer of InGaN without traces of phase decomposition and segregation. Nevertheless, the width of the [0004] reflection peaks noticeably increases as the fraction of In decreases, which may indicate increase in fluctuations in the composition of the deposited layers and general deterioration in their crystalline quality. With further decrease in the content of $x_{[\text{In}]}$ to 50%, reflections appear in the XRD spectrum of the InGaN layer (sample #4) corresponding to the phases of metallic indium and InN, which clearly indicates the inclusion of decomposition processes material during the growth of such layers. On the whole, the results obtained agree with the data of the work [16], in which the non-monotonic behavior of the critical growth temperature of InGaN layers of various compositions was pointed out at fixed flux ratio III/V. Thus, in the work [16] the decomposition temperature of the deposited layer increased from 475°C to InGaN with fractions of > 500°C upon transition from growth of InN layers to layers of indium 80 –90%. Similar „stabilization“ of the InGaN ternary solution with the addition of a small amount of Ga was explained by stronger Ga–N bond compared to In–N. However, a further increase in the fraction of Ga (and corresponding decrease in the fraction of In to 60–70%) in the work [16] led to decrease in the decomposition temperature of InGaN to 485°C, which was associated with the processes phase decay. In the present work, we observed signs of decay of the growing InGaN layer only at a noticeably higher fraction of Ga ($x_{[\text{Ga}]} \sim x_{[\text{In}]} \sim 50\%$), which can be associated both with somewhat lower (than [16]) growth temperatures and with differences in the flow of active nitrogen in comparison with the flow of metals. At the same time, the general decrease in the crystalline quality of InGaN as the content of indium decreases in the 1–4 series of structures is confirmed by both XRD data and luminescence measurements. The corresponding PL spectra are shown in Fig. 2. With decrease in the In content in the InGaN layer from 80 to 50%, in addition to the expected shift of the PL maximum to the region of high energies due to increase in the band gap of the material [17], a monotonic decrease in the integrated PL intensity is observed . Since the balance of recombination processes in wider-gap structures is shifted, as a rule, towards radiative processes (both due to the higher probability of radiative recombination and the smaller role of nonradiative Auger processes), the observed decrease in PL upon transition to more wide-bandgap InGaN layers, it is logical to associate it with a higher defectiveness of the resulting layers and, accordingly, with a higher rate of defect-impurity recombination according to the Shockley–Read mechanism.

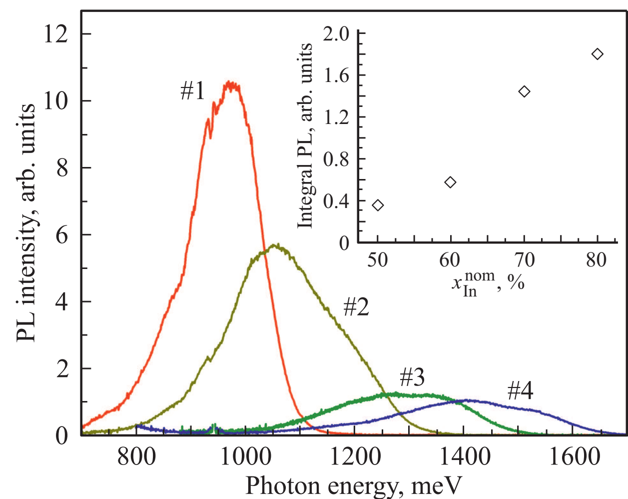


**Figure 2.** Spontaneous PL spectra of InGaN layers of various compositions (samples #1–4 in the table). The insert shows the integral PL intensity for the same samples. All measurement data are given for temperature $T = 77$ K when the structures are pumped by a diode laser with a radiation wavelength of 650 nm in the weak excitation mode (pumping power density $\sim 3$ W/cm$^2$).

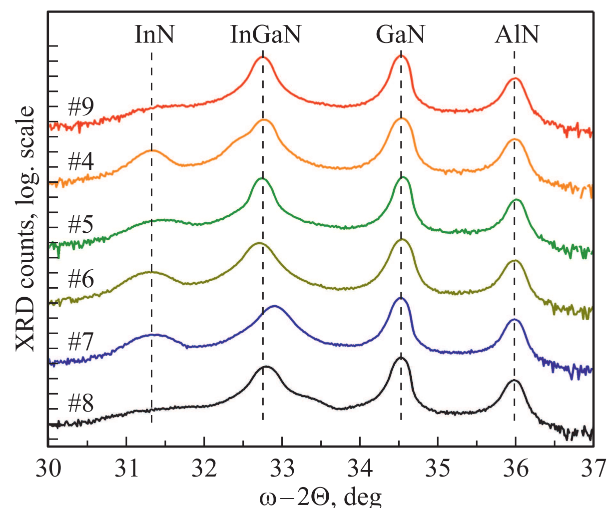


**Figure 3.** (0004) $\omega{-}2\theta$ X-ray diffraction spectra of samples with InGaN layers with $x_{[\text{In}]} \sim 50\%$ grown under various conditions: at $R_{\text{III/V}} \sim 0.9$ and various temperatures (#4–8, see table), as well as grown at $R_{\text{III/V}} \sim 0.6$ and $T_g = 470^\circ$C (#9 in table).

To study the possibility of suppressing InGaN decomposition processes and obtaining homogeneous layers „middle“ ($\sim 50\%$ In) of compositions, a series of InGaN layers was grown at different growth temperatures, which varied in the range $T_g \sim 380{-}470^\circ$C. It was found (see Fig. 3) that the signal in the XRD spectra of these InGaN layers, corresponding to the InN phase, is observed in layers grown at high temperatures $T_g = 470{-}400^\circ$ C inclusive.

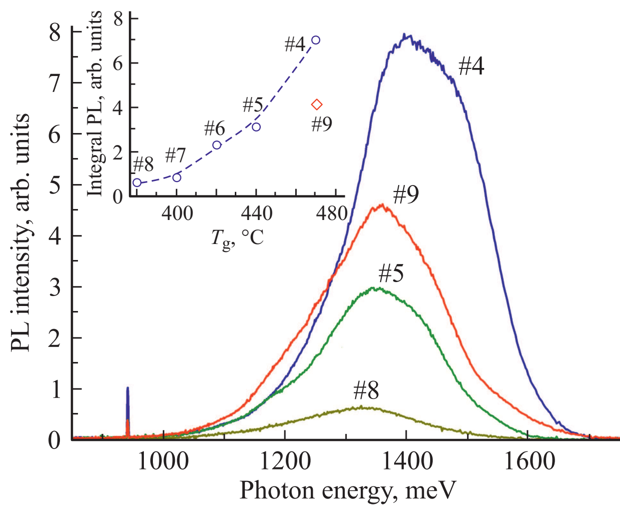


**Figure 4.** Spontaneous PL spectra of InGaN layers with a fraction of indium in the $x_{[\mathrm{In}]} \sim 50\%$ ternary solution: samples #4, 5, 8 grown at $R_{\mathrm{III/V}} \sim 0.9$ and different temperatures (see table) and sample #9 ($R_{\mathrm{III/V}} \sim 0.6$). The insert shows the integrated PL intensity of the studied InGaN layers. All the measurements were performed at temperature $T = 77\,\mathrm{K}$.

Only for the sample #8, grown at $T_g \sim 380°\mathrm{C}$, the XRD spectrum does not contain reflections corresponding to InN and InGaN with a composition different from the nominal one, as well as from the indium metal phase. However, the homogeneity of this InGaN layer is achieved due to the degradation of its crystalline quality, as evidenced by a twofold increase in the width of the XRD rocking curve. Additionally, the data of Hall measurements show the increase in the background electron density by a factor of 5 and decrease in their mobility by a factor of 4 as the growth temperature of InGaN layers decreases from 470 to 380°C (see table). This also affects the emitting properties of the formed InGaN layers. As shown in Fig. 4, the integrated PL intensity drops by more than an order of magnitude as the growth temperature decreases from 470 to 380°C.

Thus, high-temperature growth of InGaN is preferable from the point of view of better crystalline and optical quality of the deposited layers, under the condition of suppressing the decomposition of the material. In the work [18] for III-nitrides, the possibility of increasing the decomposition temperature of the material (and, correspondingly, the admissible temperature of epitaxy) due to an increase in the flow of active nitrogen was predicted. Higher nitrogen flux makes it possible to compensate for nitrogen desorption from the growth surface and to carry out epitaxial growth at higher temperatures [18]. In addition, the transition to highly nitrogen-enriched ($R_{\mathrm{III/V}} < 1$) MBE PA growth conditions limits the surface diffusion of adatoms, which hinders the development of decomposition and phase separation processes in InGaN triple solid solutions.

To test the possibility of obtaining homogeneous InGaN layer with content of $x_{[\mathrm{In}]} \sim 50\%$ at high-temperature ($T_g = 470°\mathrm{C}$) epitaxy, the sample was grown #9 (see table), which differs from the „reference“ sample #4 by noticeably higher nitrogen flux ($R_{\mathrm{III/V}} \sim 0.6$ and 0.9, respectively). For sample #9, a symmetrical reflection peak from the InGaN layer was observed in the XRD spectrum, while there were no additional signals from InN, metallic In, or InGaN phase of different composition (Fig. 3). This confirms the possibility of suppressing the decomposition of the InGaN layer with $x_{[\mathrm{In}]} \sim 50\%$ even at sufficiently high ($T_g = 470°\mathrm{C}$) growth temperature due to increased nitrogen flow. It is important that sample #9 exhibited very strong luminescence in the IR range (comparable to „reference“ sample #4, Fig. 4), having at the same time significantly better structural homogeneity. Consequently, from the point of view of laser applications of InGaN „layers of intermediate“ compositions, their high-temperature growth under highly nitrogen-enriched conditions may be preferable to the low-temperature epitaxy proposed earlier in the papers [12,13] at a flux ratio III/V close to stoichiometric.

## 4. Conclusion

Thus, the problem of obtaining homogeneous and optically active InGaN layers with an average indium content in the range of 80−50% by MBE PA method is considered in this work. It is shown that this problem for InGaN layers with indium content of $\sim 50\%$ during growth under slightly nitrogen-enriched conditions ($R_{\mathrm{III/V}} \sim 0.9$) cannot be solved by reducing the growth temperature without significant degradation of their crystalline quality and radiative properties. At the same time, the possibility of solving this problem by switching to highly nitrogen-enriched growth conditions ($R_{\mathrm{III/V}} \sim 0.6$) at relatively high (470°C) growth temperatures was demonstrated, which makes it possible to preserve the intense PL characteristic of high-temperature InGaN layers and at the same time achieve the required layer homogeneity. We believe that these results are due to the limitation of surface diffusion and suppression of material degradation. The results obtained may turn out to be critically important for the implementation of InGaN-based laser radiation sources. At the same time, apparently, to obtain planar structures with layers of InGaN „medium“ ($x_{[\mathrm{In}]} \sim 50\%$) compositions of high crystalline quality, their growth must be carried out at the highest possible ($> 470°\mathrm{C}$) temperatures, and practical limitations here will be related to providing the necessary flow of active nitrogen to realize ever smaller values of $R_{\mathrm{III/V}}$.


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### Conflict of interest

The authors declare that they have no conflict of interest.

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