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GaInN/GaN-Heterostructures and Quantum Wells Grown by Metalorganic Vapor-Phase Epitaxy

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Abstract

The dependence of the In-incorporation efficiency and the optical properties of MOVPE-grown GaInN/GaN-heterostructures on various growth parameters has been investigated. A significant improvement of the In-incorporation rate could be obtained by increasing the growth rate and reducing the H_2-partial pressure in the MOVPE reactor. However, GaInN layers with a high In-content typically show an additional low energy photoluminescence peak, whose distance to the band-edge increases with increasing In-content. For GaInN/GaN quantum wells with an In-content of approximately 12%, an increase of the well thickness is accompanied by a significant line broadening and a large increase of the Stokes shift between the emission peak and the band edge determined by photothermal deflection spectroscopy. With a further increase of the thickness of the GaInN layer, a second GaInN-correlated emission peak emerges. To elucidate the nature of these optical transitions, power-dependent as well as time-resolved photoluminescence measurements have been performed and compared to the results of scanning transmission electron microscopy.

1. Introduction

The past several years have witnessed a rapid development in the growth of group III nitrides by metalorganic vapor phase epitaxy (MOVPE), that eventually resulted in the realization of high-brightness blue, green, and yellow light emitting diodes (LEDs) based on GaInN quantum well structures [1]. Furthermore, room temperature cw-operation of purple GaInN injection laser diodes (LDs) has recently been demonstrated [2]. However, despite these promising achievements, the fabrication of blue and green laser diodes remains a major challenge, that seems to be closely related to certain fundamental problems inherent in the epitaxial growth of GaInN.

While high growth temperatures are essential for an efficient decomposition of the ammonia usually employed as group-V precursor at the epilayer surface (a growth temperature of typically 1000°C yields best results for GaN), the thermal instability of InN necessitates a considerable reduction of the growth temperature in order to incorporate a significant amount of InN in the GaInN alloy. This is, however, only achieved at the expense of a diminished crystalline quality of the epilayer [3]. Even at growth temperatures of 700-800°C, an extremely high V/III-ratio is required to prevent the formation of In-droplets on the epilayer surface [4]. The enhanced tendency of In-segregation that goes along with a reduction of the V/III-ratio [4] also limits the possibility of increasing the In-content in the GaInN layer by simply raising the In partial pressure in the reactor. We, therefore, focused our investigations on other methods of improving the In incorporation efficiency (growth rate, carrier gas composition) and their influence on the optical transitions observed in GaInN layers.

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Recent studies [5] [6] [7] indicate that the emission spectra of GaInN LED- and LD-structures can be explained by exciton localization at subgap states possibly originating from In-rich regions in the GaInN alloy. The formation of large compositional fluctuations may be promoted by the miscibility gap in this ternary system [8]. It has been speculated [6] [9] that a localization of excitons at In-rich regions with the size of a quantum dot might hinder non-radiative recombination via defect states, thereby increasing the quantum efficiency of a GaInN-based laser diode. However, this would only be effective for a high density of small In-rich dots. A phase separation of the GaInN alloy that results in an large spread of composition and size of In-rich regions could, on the other hand, represent a severe problem in the quest for blue and green laser diodes.

In order to gain further insight into the connection between the mechanisms involved in the optical transitions and the structural properties of GaInN epilayers, we investigated GaInN/GaN quantum wells and heterostructures of various thickness by optical methods like cw- and time-resolved photoluminescence and photothermal deflection spectroscopy (PDS), high resolution X-ray diffraction (HRXRD), and scanning transmission electron microscopy (STEM).

2. Experimental

2.1. Epitaxial Growth

The GaInN/GaN-layers described in this paper were grown in a home-made low-pressure MOVPE system using a horizontal quartz-glass reactor with rectangular cross section . The SiC coated graphite susceptor was heated by halogen lamps, and the temperature was measured by a thermo-couple directly within the susceptor. Triethyl-gallium (TEGa), trimethyl-indium (TMIn), trimethyl-aluminum (TMAl), and ammonia (NH_3) were used as group III and group V sources, respectively. All epilayers were grown on c-plane sapphire substrates at a reactor pressure of 100 hPa.

After an in situ nitridation of the substrate, a thin (ca. 15 nm) AlN nucleation layer was grown at 750-800°C, followed by approximately 0.5 μm of GaN deposited at 1000°C with a V/III-ratio of 5500 at a growth rate of about 13 nm/min. Under these conditions, single GaN-crystals were of excellent quality, with XRD-linewidths of about 50 arcsecs and 100 arcsecs for the [0 0 2] and [1 0 4] reflections, respectively, and low temperature PL-linewidths of less than 3 meV for the donor bound exciton.

GaInN layers were grown on top of these high-quality GaN layers. In our first experiments on GaInN-growth, we could only obtain a significant In-incorporation for growth temperatures around 700°C and V/III-ratios in the range of 20000 [10]. Now, we have carefully optimized our growth conditions, as described below, which enabled the use of higher growth temperatures and lower V/III-ratios ranging from 700-800°C and 20000-4000 respectively. The In/Ga ratio was varied between 1.3 and 10.4, and GaInN growth rates between 1.1 and 5.4 nm/min were employed. Hydrogen was used as carrier gas in the metalorganic bubblers while the ammonia was diluted with nitrogen and either hydrogen or nitrogen could be flown to the main dilution gas line.

To optimize the growth conditions for GaInN, uncapped GaInN/GaN heterostructures with a 100 nm thick GaInN layer were studied, whereas the GaInN film in quantum well structures was covered by a GaN cap of about 65 nm.

2.2. Characterization Methods

All layers were characterized by high-resolution x-ray diffraction (HRXRD, Philips MRD) and photoluminescence (PL) measurements at liquid helium temperature using the 300 nm line of an Ar-ion laser as excitation source.

The In-content of the GaInN layers was determined from a measurement of the [00 2] reflections in HRXRD using Vegard's law for the lattice constant c. A complete relaxation of the mismatch strain was assumed and the difference in the thermal expansion coefficients of GaN and (Ga)InN was neglected.

The room temperature bandgap of thin GaInN quantum films was determined by photothermal deflection spectroscopy (PDS). This method enables the measurement of absorbance values as low as $\alpha\ d = 10^{-5}$, where α is the absorption coefficient and d the well thickness. A detailed description of the experimental set-up can be found in [11].

Additionally, the optical transitions in GaInN quantum wells were characterized by excitation power dependent PL as well as PL-measurements with an excitation energy below the band gap of GaN and below the main

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PL-peak of GaInN, respectively, employing a frequency-doubled Ti/Sa laser. High excitation power PL measurements were performed using the 308 nm line of a pulsed excimer laser with a pulse width of 10 ns and a repetition rate of 10 Hz. Furthermore, measurements of PL-decay dynamics were performed using the measurement set-up described in [12].

The chemical composition of GaInN/GaN quantum wells was investigated by atomic number (Z)-contrast imaging in an analytical scanning transmission electron microscope (STEM) [13]. A cold field-emission STEM equipped with a high-resolution pole piece was used where the minimum diameter of the electron probe is approximately 0.3 nm at an energy of 100 keV.

3. Optimization of Thick GaInN Layers

3.1. Influence of Carrier Gas

Hydrogen of very high purity can easily be obtained by diffusion through a heated Pd-wall. Therefore, hydrogen has traditionally been used as carrier and dilution gas in MOVPE. With the availability of efficient nitrogen purifiers, the use of nitrogen as carrier gas in MOVPE has become an interesting alternative.

3.2. In-Incorporation Behavior

We have previously reported an increase of the In-incorporation in MOVPE obtained by reducing the H_2-flow of the main dilution gas line [10] [14]. Here, we present a more detailed study of the influence of the hydrogen partial pressure in the reactor. In our MOVPE system, H_2 is used as carrier gas for the metalorganic precursors, while either H_2 or N_2 can be employed as dilution gas. The H_2 partial pressure in the reactor can thus be changed by varying the N_2/H_2-ratio in the carrier/dilution gas. Figure 1 demonstrates a roughly exponential increase of the In-content with decreasing H_2 partial pressure in GaInN layers grown at 700°C with an In/Ga-ratio of 5 and a growth rate of about 1 nm/min. The large effect of even small amounts of H_2, that has also been observed by Piner *et al.* [15] , cannot be explained by the different thermal properties of H_2 and N_2. It seems that hydrogen directly influences the reaction mechanisms at the surface of the growing epilayer. A possible explanation might be the formation of indium hydrides at the surface resulting in a decreased amount of adsorbed In-atoms that can be incorporated into the crystal.

3.3. Effects on Optical Transitions

Figure 2 shows the PL-spectra of the GaInN layers described above, measured at 4.2 K and 300 K respectively. While at first, an increase of the In-content only results in a broadening of the PL-peak, In-rich layers show an additional low-energy band whose distance to the band gap increases with increasing In-content. This deep transition dominates the PL-spectra at room temperature. There is a possibility that the deep transitions are actually caused by a phase-separation. The latter would be more pronounced for a high In-content. Moreover, the formation of mismatch dislocations due to the increased lattice mismatch between the GaInN layer and the underlying GaN layer is likely to play an important role.

3.4. Influence of Growth Rate

It is obvious that the In desorption will be hindered by raising the growth rate of the GaInN epilayer, thereby covering the growing GaInN instantaneously with the next layer and reducing the time available for a re-evaporation of adsorbed In-Atoms. To put it another way, a higher growth rate drives the system further away from a thermal equilibrium condition, that hinders the In incorporation due to the high In volatility and the miscibility gap in the GaInN system.

The increased In-incorporation in the MOVPE of GaInN at high growth rates has previously been mentioned by Keller et al. [4]. To study the extent of this improvement of the In-incorporation efficiency and the influence on the layer quality, we raised the TEGa-flux under otherwise unchanged growth conditions. X-ray diffraction measurements revealed an increase of the In-content from 18% to 24% and 26% with a respective increase of TEGa-flux by a factor of 2 and 4, although the latter also results in a decrease of the In/Ga-ratio by a factor of 2 and 4, respectively.

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While no deterioration of the surface quality could be observed, low-temperature PL-spectra of In-rich GaInN layers deposited with high growth rates at 700°C were dominated by a deep, broad emission band. The deterioration of the optical quality of these GaInN-layers could be partly explained by a reduction of the effective lateral mobility of In-adatoms with increased growth rate that favors the formation of compositional fluctuations in the alloy. Again, a partial phase-separation due to the miscibility gap for GaInN layers with high In-content may also play an important role. STEM investigations (Z-contrast image), that will give some information on the microstructure of these layers, are currently underway.

3.5. Result of Optimized Growth Conditions

In the previous sections, we have shown that the In-incorporation efficiency can be drastically improved by lowering the H_2 partial pressure in the reactor and increasing the growth rate. This enables a significant In-incorporation even at higher growth temperatures resulting in an improvement of the crystalline quality. Figure 3 compares the PL-spectra of a GaInN-layer grown at 700°C and another one grown at 800°C employing a lower H_2-partial pressure and a higher growth rate (optimized conditions). Although both spectra show the same peak energy, the In-content (as determined by XRD) of the sample grown under optimized conditions is higher. Furthermore, the FWHM could be halved by using optimized growth conditions. These observations can be understood by assuming a significant reduction of compositional fluctuations in the alloy. Under optimized growth conditions, a PL-FWHM of about 50 meV at low temperature and 100 meV at room temperature and an XRD-linewidth of about 200 arcsecs was obtained for 100 nm thick GaInN samples with an In-content of about 7.5%.

Figure 4 shows the influence of the TMIn-flow under two different growth conditions summarized in Table 1. For the samples grown at 700°C, the increased In-content obtained by raising the TMIn-flow is accompanied by a large increase of the FWHM of the low temperature PL-peak. Eventually, the In-content in the sample drops again due to the formation of In-droplets on the surface of the GaInN layer. The samples grown at 800°C exhibit a slower increase of the In-content with increasing TMIn-flow. However, under these optimized conditions, a slight decrease of the PL-FWHM with increasing TMIn-flow is observed.

4. Optical Transitions in GaInN/GaN Quantum Wells

A detailed understanding of the optical transitions involved in GaInN quantum wells of different thickness and composition is essential for an effective design of GaInN-based LEDs and LDs emitting in the visible spectral region.

4.1. Results of Optical Spectroscopy

In Figure 5, low temperature PL-spectra of $Ga_{0.88}In_{0.12}N$/GaN double heterostructures with different thickness of the GaInN film are depicted. The arrows in Figure 5 indicate the position of the effective band edge (at room temperature) as determined by PDS. As the well thickness increases, so does the Stokes shift between the PL-peak and the position of the effective band edge. Furthermore, the linewidth of the PL-peak also increases with increasing well width (Figure 6). Eventually, for thicker GaInN films, a PL-peak (labelled I_1 in Figure 5) emerges whose position is again (as for the thinnest well) close to the band edge. These thicker GaInN films do, however, show a second PL-peak (labelled I_2 in Figure 5) about 200 meV below the I_1-peak that behaves like a donor-acceptor pair transition in temperature and power dependent PL-measurements and also exhibits a strongly non-exponential decay on a very long time scale of a few microseconds [14] that is typical for a DA-pair transition.

PL measurements with different excitation wavelengths (Figure 7) clearly indicate that these PL-peaks really originate from the GaInN-films because they can still be detected at an excitation energy below the band edge of GaN. Moreover, as expected from the position of the effective band edge, the PL-peak of the 4 nm well vanishes if an excitation energy slightly above the position of the PL-peak is employed. Finally, the low energy peak I_2 of thicker GaInN-wells can only be observed for excitation energies above the effective bandgap.

We have previously shown [12] that the decay dynamics and temperature dependence of the radiative lifetime of our thinnest quantum wells (well width l_z<2 nm) can be explained by a localization of excitons at low temperature due to well width or compositional fluctuations. Similarly, the high-energy PL-peak I_1 of thicker GaInN-films originates from localized excitons as determined by measurements of PL decay dynamics [14] and optical gain [9]. The observed increase of the Stokes shift and the PL line width with increasing well width

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might be explained by a localization effect if the depth of the localization centers increases with increasing well width. This rules out interface fluctuations as the main reason for the large localization effects in quantum wells with a thickness of several nanometers. Similar localization effects that have been observed by Chichibu *et al.* [7] and Narukawa *et al.* [5] in GaInN single and multiple quantum well structures were attributed to the formation of dot-like In-rich regions within the GaInN layers [6] [7]. Whether such compositional fluctuations are also responsible for the observed optical properties of our quantum wells will be discussed in conjunction with the presentation of STEM studies in section 4.2.

Another indication of large localization effects is obtained from PL-measurements of the 4 nm quantum well with varying excitation power. While the I_2-peak of thick GaInN-films exhibits a blue shift with increasing excitation power of the Ar-ion laser used for measuring cw-PL-spectra, no such shift was observed for any of the quantum wells with l_z<5 nm under these low excitation conditions. Hence it is unlikely that the observed Stokes shift in these quantum wells originates from DA-pair transitions. On the other hand, high excitation PL-measurements of a 4 nm quantum well using a pulsed excimer laser (Figure 8) do show a shift of the PL-peak that can be explained by a filling of the localized states. With increasing excitation power, the PL-peak moves towards the band edge, and finally the advent of amplified spontaneous emission (ASE) can be observed. The position of the ASE peak about 100 meV below the band edge at the high energy tail of the cw-photoluminescence indicates that the ASE may originate from localized states.

Further insight into the behavior of the optical transitions can be obtained from measurements of the PL decay traces shown in Figure 9. While thinnest quantum wells exhibit a monoexponential decay, as expected for an excitonic transition, an increase of the well width is accompanied by an increasingly non-exponential decay with long decay times [14]. Such a transition is not observed for GaInN/GaN-quantum wells with an In-content of only 6%. For these quantum wells, the decay behavior is independent of the well width as shown in Figure 10. This indicates that the observed dependence of the nature of the optical transitions on the width of the GaInN well only occurs for wells with a high In-content.

4.2. STEM studies

Obviously, the behavior of the optical transitions is closely related to the microstructure of the GaInN quantum wells. Reasons for an increase of the Stokes shift with increasing well width might be found in compositional fluctuations in the GaInN alloy and/or a partial relaxation of the misfit strain leading to inhomogeneous strain fields within the GaInN layer.

We have investigated the local chemical composition of the $Ga_{0.88}In_{0.12}N$ quantum wells by Z-contrast imaging in an STEM. The image of a 17 nm well depicted in Figure 11 reveals fluctuations of the In-content in the GaInN layer. Assuming an average In-content of 12%, the brightness modulations of the Z-contrast image correspond to variations in the In-content of about 3%. However, an STEM measurement always represents an average across a specimen thickness of a few hundred Ångstroms. Therefore, the actual fluctuations in the composition of the GaInN film may be somewhat larger.

In a 2.7 nm thick GaInN well, however, no significant variations of the composition could be detected although optical measurements do show indications of a strong localization effect. Localization centers in these samples might be caused by inhomogeneous strain fields due to a partial relaxation of the misfit strain explaining the increase of the Stokes shift with increasing thickness of the GaInN film. It is likely that a phase-separation is also effected by the strain in the GaInN layer, (ie: the existence of regions with different strain could ease the formation of compositional fluctuations in the alloy). This might explain why the latter are only observed in thicker GaInN films. The low energy peak I_2 observed in thicker GaInN films could be due to defect states caused by misfit dislocations. Considering the strong piezoelectric effect in group III-nitrides, there is, however, also a possibility of a spatially indirect transition in a material exhibiting large local strain fields connected with the observed compositional fluctuations on a nanometer scale.

For In-rich layers necessary to obtain an emission wavelength in the blue or even green spectral region, a phase separation might already occur in thinnest films. Therefore, this represents a severe problem for the realization of blue or even green laser diodes.

5. Summary

The In-incorporation efficiency in GaInN/GaN heterostructures could be drastically improved by reducing the H_2 partial pressure in the reactor and increasing the growth rate. However, In-rich GaInN layers exhibit a low

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energy PL-peak that might be caused by a phase separation. The increased In-incorporation efficiency enabled a growth at higher temperatures resulting in a significant improvement of the layer quality.

Optical measurements on GaInN quantum wells with an In-content of about 12% indicate strong localization effects that are more pronounced for thicker layers. While the PL-transitions in thin quantum wells exhibit an exponential decay, an increase in the well width is accompanied by an increasingly non-exponential decay on a large time scale. No such transition is observed in GaInN wells with an In-content of only 6%. These observations might be explained by a combination of inhomogeneous strain fields and large compositional fluctuations in In-rich layers. Indications for such compositional fluctuations have been found by an STEM analysis using Z-contrast imaging.

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Table 1

Comparison of growth conditions of the two series of GaInN samples depicted in Figure 4. The NH_3-flow was set to 4.25 slm in both cases.

Symbol used in Figure 4	Growth temperature	Carrier gas flow: N_2 [sccm] / H_2[sccm]	TEGa flow [µmol/min]
blue star	700°C	1000 / 300	1.6
red triangle	800°C	2000 / 200-350	6.4

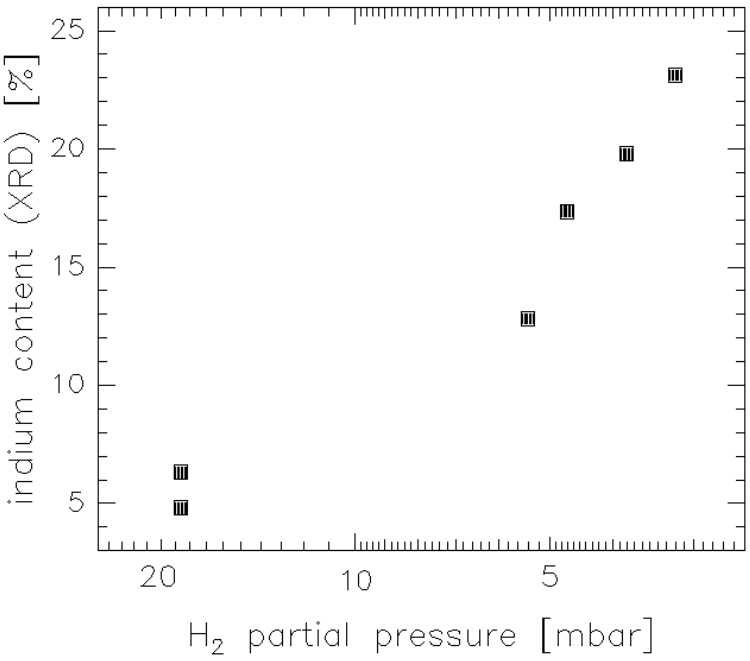

Figure 1. Dependence of In-content in GaInN/GaN heterostructures on the H_2-partial pressure in the reactor.

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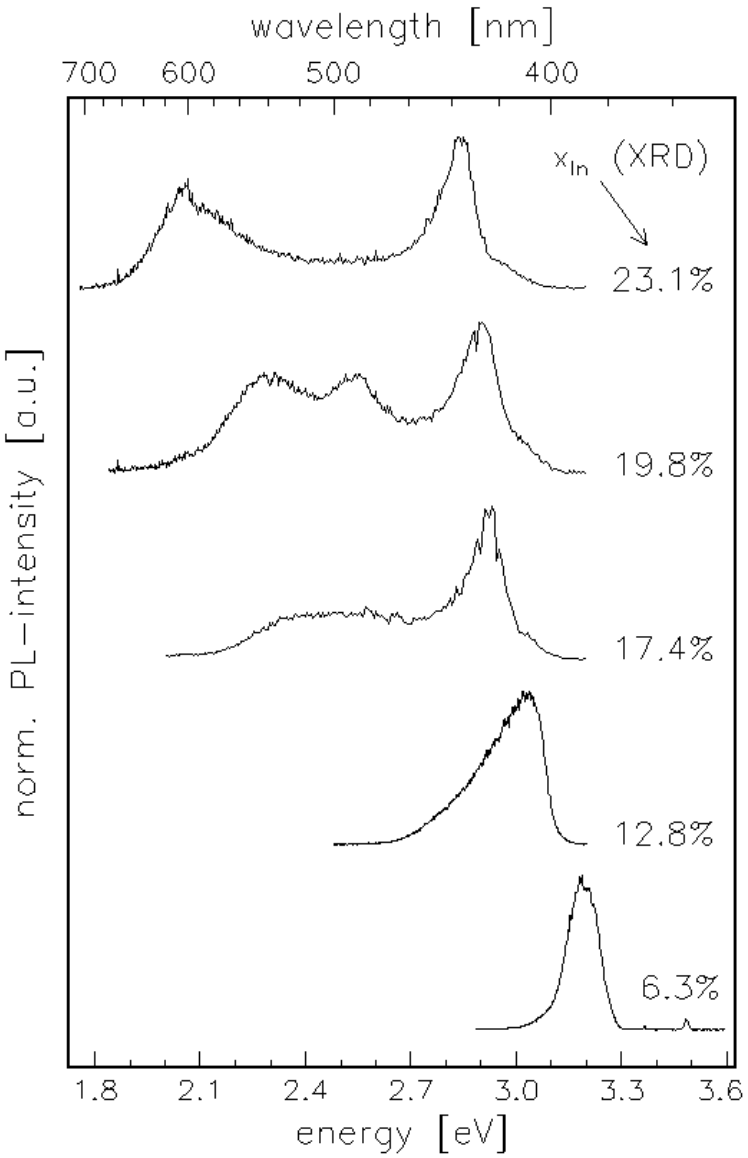

Figure 2a. PL-spectra of GaInN/GaN heterostructures taken at 4.2 K . The In-content specified in the figure was determined by HRXRD. The variation of the In-content was obtained by changing the carrier gas composition.

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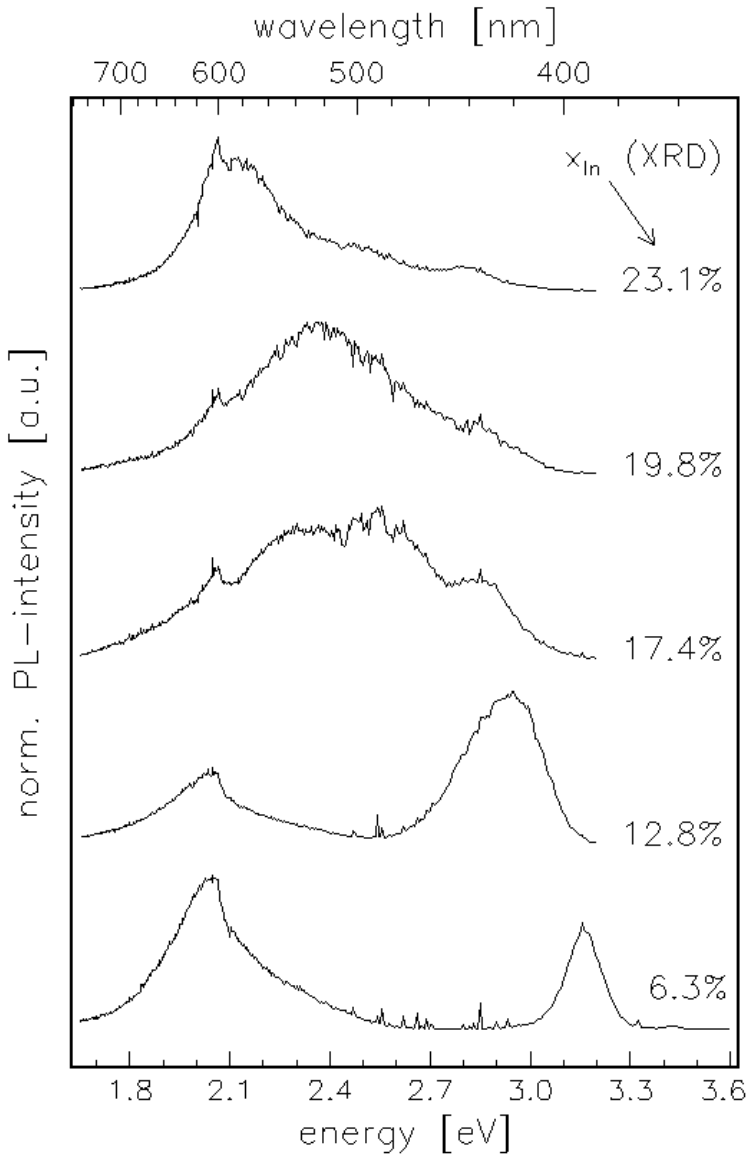

Figure 2b. PL spectra of GaInN/GaN heterostructures taken at 300K. The samples are the same as those in Figure 2a.

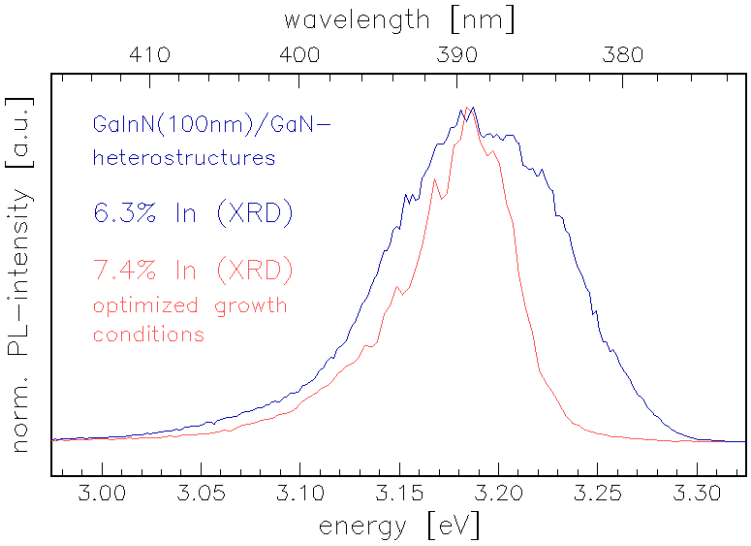

Figure 3. Influence of optimized growth conditions on low temperature PL-spectrum of GaInN/GaN heterostructures. The distance of the PL-peak to the band edge and the FWHM are reduced.

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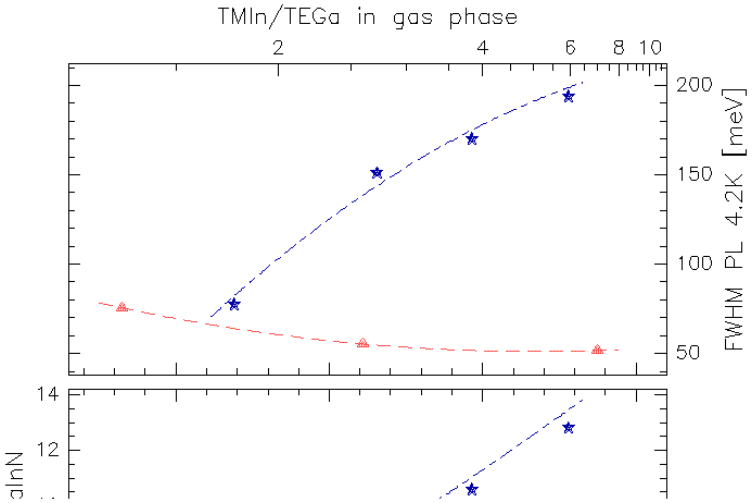

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