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Faculty of Mechatronics, Informatics
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The growth of InGaN/GaN scintillation heterostructures

Dissertation Extended Abstract

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Preface

This doctoral thesis is a summary of my PhD study at the Faculty of Mechatronics, Informatics and Interdisciplinary Studies at the Technical University of Liberec. Most of the research work has been done in the Institute of Physics of the Czech Academy of Sciences at the Department of Semiconductors under the supervision of Prof. Hulicius and Dr. Hospodková. The doctoral thesis is written as a collection of published papers in impacted journals including a brief introduction to nitride semiconductor materials and Metal Organic Vapour Phase Epitaxy.

Abstract

Devices based on nitride semiconductors are nowadays a part of our daily life. They are for example widely spread in blue light emitting diodes. This thesis is focused on a new application of nitride semiconductors which is a scintillation detector. This detector is based on InGaN/GaN multiple quantum well heterostructures and requires very efficient and fast luminescence response without any slow defect bands in luminescence spectra. In this thesis we have used Metal Organic Vapour Phase Epitaxy for the growth of these structures. We have improved a luminescence quality of GaN buffer layers by using different growth parameters and significantly suppressed slow yellow luminescence. By increasing QW number we have increased the thickness of InGaN/GaN heterostructures up to 1 μm which is necessary for more efficient scintillation detectors. With such thick structures come a lot of problems, such as increase of the strain in the structure or too big surface defects (called V-pits). These problems are discussed in this work as well. This thesis puts emphasis on the epitaxial growth of these structures. Based on the results obtained during this work, it seems that our proposed structure is suitable for scintillation detectors and it could be used in some commercial applications in the future.

Key words: MOVPE, InGaN/GaN heterostructure, scintillator, fast decay

Abstrakt

Zařízení na bázi nitridových polovodičů jsou součástí našeho každodenního života. Rozšířená a používaná jsou například v modrých světlo emitujících diodách. Tato práce zkoumá novou možnost využití nitridových polovodičů, kterou je scintilační detektor. Detektor je tvořen heterostrukturami na bázi InGaN/GaN mnohonásobných kvantových jam a vyžaduje velice účinnou a rychlou luminiscenční odezvu bez pomalých defektních pásů v luminiscenčních spektrech. Pro růst těchto struktur jsme použili organokovovou epitaxi z plynné fáze. Pomocí různých růstových parametrů jsme zlepšili luminiscenční vlastnosti GaN podkladových vrstev, kde jsme potlačili pomalou defektní žlutou luminiscenci. Zvýšením počtu kvantových jam bylo dosaženo tloušťky InGaN/GaN heterostruktury téměř 1 μm. Takto tlustá struktura je nezbytná pro účinný scintilační detektor, avšak vzhledem k této tloušťce jsme narazili na mnoho problémů, jakými jsou například zvýšení napětí ve struktuře nebo příliš velké povrchové defekty (nazývané V-pity). Diskuze těchto problémů je také součástí práce. Disertační práce klade důraz na epitaxní růst scintilačních struktur. Na základě poznatků získaných v průběhu zkoumání nitridových scintilačních heterostruktur se zdá, že naše navrhovaná struktura je vhodná jako scintilační detektor a mohla by být v blízké budoucnosti použita v některých komerčních aplikacích.

Klíčová slova: MOVPE, InGaN/GaN heterostruktury, scintilátor, rychlý dosvit

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List of Acronyms

AFM	Atomic Force Microscopy
BB	Blue Band
CCS	Close Coupled Showerhead
CL	Cathodoluminescence
DAP	Donor-Acceptor Pair
HRTEM	High-Resolution Transmission Electron Microscopy
HRXRD	High-Resolution X-ray Diffraction
HVPE	Hydride Vapour Phase Epitaxy
LED	Light Emitting Diode
LPE	Liquid Phase Epitaxy
MBE	Molecular Beam Epitaxy
MOVPE	Metal Organic Vapour Phase Epitaxy
MQW	Multiple Quantum Well
PAS	Positron Annihilation Spectroscopy
PL	Photoluminescence
QW	Quantum Well
TCSPC	Time-Correlated Single Photon Counting
TEM	Transmission Electron Microscopy
VPE	Vapour Phase Epitaxy
YB	Yellow Band

Introduction

It is more than one hundred years when William Crookes used the first scintillation counter (called spinthariscope) in practice. In that time, scintillation process was visualised on the ZnS screen. Since that time, a lot of scintillation materials were discovered and used in scintillation detectors. However, the research in the field of scintillation materials (especially inorganic materials) is still very active nowadays and new materials need to be developed for many different applications, such as medical imaging, electron detection, high-energy physics calorimetry, homeland security or industrial control.

The requirements for new scintillation materials are very demanding and depend on the application. For example, for Time-of-flight applications sub-100 ps time resolution is necessary or energy resolution down to 2 – 3 % for large crystals is necessary for homeland security [1]. These very high demands cannot meet common scintillation materials (bismuth germanate, garnets, perovskites, ortho-silicates, etc.) and new materials have to be found. Especially performance of radiation detectors used in X-ray and nuclear medicine imaging [2], high-energy physics [3] or scanning electron microscopes needs to be improved. For example, Time-of-flight applications (positron emission tomographs) need to speed up the rise time to get sub-100ps resolution. Scanning electron microscopes need faster scintillator to increase scanning rate with the same quality of images.

In last two decades, nanomaterials gained considerable attention in the scintillation community for their suitable properties. Due to the quantum confinement effect, they can offer a very high quantum efficiency and ultrafast decay time [1]. For example, ZnO nanoparticles co-doped with Ga^{3+} or La^{3+} showed decay time around 250 ps [4] and they are promising in ultrafast X-ray imaging [5]. CdSe nanoplatelets have been also proposed as a fast emitter with sub-100 ps decay time [6]. Finally, CdSe/CdS core shell quantum dots were also investigated and showed decay time around 850 ps [6]. These two CdSe based nanocrystals are promising for fast timing applications. All of these new nanomaterials have also disadvantages, such as necessity of some matrix where these nanoparticles have to be embedded. For example, ZnO nanoparticles co-doped with Ga^{3+} were embedded in polystyrene matrix, which is not sufficiently resistant against high energy irradiation. CdSe nanocrystals are unstable in colloidal solution and appropriate matrix has to be found. Moreover, density of these materials embedded in matrix is not so high. Finally, stopping power and energy transfer efficiency can be a limitation as well.

Another nanomaterial, which was proposed for fast timing applications, is InGaN/GaN multiple quantum well (MQW) heterostructure. It was shown in our publication [7], that luminescence spectrum of this heterostructure contains fast quantum well excitonic band with the decay time of a few nanoseconds and slow defect band (called yellow band - YB), which have decay time in the range of microsecond scale. Ratio of the intensity of these two bands depends strongly on the type and density of excitation. Suppression of the YB intensity is necessary for the scintillation applications. With a proper design of the heterostructure can be reached excitonic decay time below 1 nanosecond, which is a good precondition for fast timing applications. Moreover, InGaN/GaN MQW heterostructures have high efficiency (light yield) and good radiation resistance compared to mentioned scintillating nanomaterials. They are also mechanical robust. The rise time of these structures is very fast, which is another good precondition for fast timing applications.

At the beginning of the 21st century GaN has been considered as a suitable material for scintillation detection. GaN layers were studied as a promising detector in harsh radiation environment [8] or detector for X-ray detection [9]. GaN layers grown on sapphire substrate were used and investigated for neutron detection when suitable neutron conversion layers were used [10]. Moreover, implantable dosimetric system based on GaN was proposed for real-time measurements of dose and dose rate [11,12]. Luminescence properties of epitaxially grown GaN layers were studied and compared with ZnO epitaxial layers (widely used scintillation material) by Schenk *et al.* [13]. They have shown that GaN layers doped with silicon have decay time below 1 ns and external photon yield 1.4 ± 0.2 photons per 1 keV incident electrons. Despite low planar light extraction coefficient, the external photon yield was low compared to classical single crystalline and powder scintillators (YAG:Ce, YSO:Ce, etc.).

The work contained in this doctoral thesis is concentrated on the growth of InGaN/GaN MQW heterostructures with Metal Organic Vapour Phase Epitaxy (MOVPE). These heterostructures are nowadays commercially used in blue light emitting diodes (LED) but for scintillation detectors, there are different requirements for the structure, such as very thick active region, suppression of defect bands as much as possible and others. All these growth challenges are subject of this doctoral thesis. It is written as a collection of published papers in impacted journals related to this topic. At first, a brief introduction to III-nitride properties will be given. Afterwards, aspects of MOVPE technology with in situ and ex situ measuring techniques are described and finally, collection of seven papers with a brief description of each paper and connection of these papers are shown.

1 Thesis Outline

1.1 Aims

Based on the previous works on the GaN epitaxial layers it seemed that GaN is promising material for scintillation application. Drawbacks of this material was low external photon yield due to the small thickness of epitaxial layer structure in comparison to bulk scintillators and slow luminescence defect components which are presented in GaN layers.

We have proposed an idea, that external photon yield could be enhanced by using InGaN/GaN MQW heterostructure instead of using only GaN layers doped with silicon. Thanks to the quantum confined effect the luminescence efficiency should be much higher and the external photon yield should be enhanced as well.

Undoped GaN layers are always unintentionally n-type due to the residual impurities. Creation of acceptor levels is much probable than donor levels in these n-type layers. Deep or shallow acceptor levels are the source of various defect bands, which have slow decay time, and they are detrimental for fast scintillation applications. One of this defect band is called yellow band (YB) with the maximum around 2.2 eV. The decay time of this band is in microsecond range and needs to be suppressed as much as possible. The luminescence intensity of the YB can be reduced with proper growth parameters.

Aims of my doctoral thesis can be summarized in following steps:

- Proposal of InGaN/GaN heterostructure in order to get fast excitonic decay time (around 1 ns)
- Suppression of defect luminescence
- Growth of these structures by the MOVPE technology
- Adjustment of the structure according to the results obtained by different measurement techniques

The main and the most time consuming task of my thesis was the growth of the structure by MOVPE technology. The structure is very similar to blue LED structure, which is commercially used, but there are a few important differences, which are discussed in my doctoral thesis. The advantage of our structure is the fact that we do not need p-type GaN layers (only n-type GaN layer is grown below MQW structure). On the other hand, any kind of defect bands in the luminescence spectrum is undesirable in our structure, which means having very precisely adjusted growth parameters and controlling level of impurities. Another difference is the number of quantum wells (QWs). MQW structure in LEDs contains few QWs, usually less than five. In scintillator structures, much thicker MQW region with higher QW number is necessary, to increase detected part of high energy deeply penetrating irradiation. Our structure usually contains more than 30 QWs with total MQW thickness up to 1 μm. The growth of such thick MQW region is very challenging due to increasing strain in the structure (coming from the different lattice parameters of InGaN and GaN layers) and enlarging of V-pits (surface defects with V-shape character).

1.2 Connection of thesis papers

During our project, we have focused on the growth of different parts of the structure separately. Simplified scheme of the whole structure is shown in Fig. 1.1.

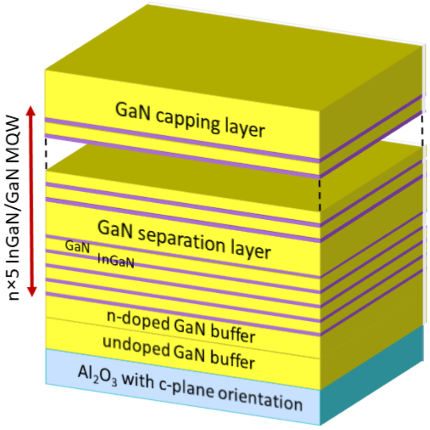


Fig. 1.1. Simplified scheme of the scintillation structure based on InGaN/GaN multiple quantum well heterostructure.

As a substrate, we have used sapphire with c-plane orientation. The growth on this substrate is well described in the literature and it is cheaper compared to GaN or SiC substrates. The initial growth of GaN on sapphire substrate is very important for the quality of the whole structure.

We have studied the first phases (nucleation and coalescence layer) of the growth in the article [i].

Very good quality of n-doped GaN buffer layer is necessary for scintillation purpose as well. That is why we have studied growth parameters of n-doped GaN layers as well (article [ii]).

Level of dopants in the layer beneath the MQW structure influences internal electric field inside the MQW structure and its luminescence properties. It has been studied in the article [iii].

Level of impurities and defects penetrating from GaN buffer layer into MQW region can be supressed by different techniques. One of them was studied in the article [iv].

MQW structure is the most important part of the whole structure. Depending on the application (different kinds of irradiation), the structure has to be optimized with respect to QW number and thickness of MQW region. Structures with different number of QWs have been studied in the articles [v] (focused on the excitation with electrons) and [vi] (focused on the X-ray excitation).

Finally, we have found the way how to supress indium desorption from InGaN QWs during the growth of the MQW structure (article [vii]).

2 III-Nitride Semiconductors

2.1 Brief history of III-nitrides

Most of the research involving III-nitride technology is dated to late 1960s, however the first synthesis of GaN occurred in 1928 by Johnson *et al.* [14]. In 1938, Juza and Hahn synthesized the first GaN by passing ammonia through hot gallium [15]. Afterwards, in 1969 Maruska and Tietjen grew epitaxially GaN layer on sapphire substrate using halide vapour phase epitaxy [16]. Two years later, Pankove *et al.* [17] fabricated the first blue GaN based LED. Violet LED was fabricated by the same group in 1972 [18]. Despite these achievements, quality of GaN epitaxial layers were not sufficient for future devices.

The growth of III-nitrides was accomplished in Czechoslovakia Academy of Sciences during 1960s as well. Pastrňák *et al.* [19,20] grew mainly AlN crystals and studied their optical properties.

In 1980s, the quality of GaN layers grown on sapphire substrate was improved by using modern growth techniques, such as Molecular Beam Epitaxy (MBE) or MOVPE. In 1983 Yoshida *et al.* [21] grew AlN layer between sapphire substrate and GaN layer for improvement of the electrical and luminescence properties of GaN (using MBE technique). Amano *et al.* [22] later improved this two-step growth technique using MOVPE technique. They grew amorphous AlN layer on the sapphire substrate and then GaN epitaxial layer at higher temperature which resulted in smooth surface with high crystallographic quality and high room temperature photoluminescence intensity. GaN layers were typically unintentionally n-type. Akasaki and Amano used zinc as an acceptor dopant for p-type GaN, but they did not succeed. They tried magnesium as a dopant with no success as well. In 1988, Amano found out that after electron beam irradiation cathodoluminescence intensity of Mg-doped GaN layer increases. One year later, Amano *et al.* [23] made first p-n junction with Mg dopant activated by electron beam irradiation. After that, Nakamura *et al.* [24] found out that acceptor activation also occurs after thermal annealing in hydrogen-free atmosphere. Also by introduction of indium into GaN matrix and formation of InGaN QWs the emission was shifted from UV to blue spectral region. Since that time, there was no obstacle to grow blue LED with sufficient quality [25]. Later on LED became commercially available from Nichia Laboratories. For these achievements the scientists (I. Akasaki, H. Amano and S. Nakamura) were awarded the Nobel Prize in Physics in 2014. In electronic devices found GaN material utilization as well due to high breakdown voltage, high saturation velocity of electrons and high density of electrons in 2D electron gas which can be obtained on heterostructure interfaces due to the polarization field. These properties are necessary for implementation in high power transistors for electrical vehicles and high frequency applications in next generation communication systems. Due to their advantageous properties nitrides became the second most important semiconductor after Si. However, Si remains unbeatable in general electronics due to the low production price, well established technology and availability of large wafers.

2.2 Crystal structure

Gallium nitride's most stable crystal structure is wurtzite, which is stable under ambient conditions. Another two structures, zincblende and rocksalt, are stable at specific conditions, such as a high pressure or growth on specific crystal planes. The wurtzite structure is in fact two interpenetrating hexagonal close packed sub-lattices, each with one type of atoms, offset along the c axis by 5/8 of the cell height. GaN hexagonal unit cell is shown in Fig. 2.1. Each gallium atom is surrounded by four nitrogen atoms and vice versa.

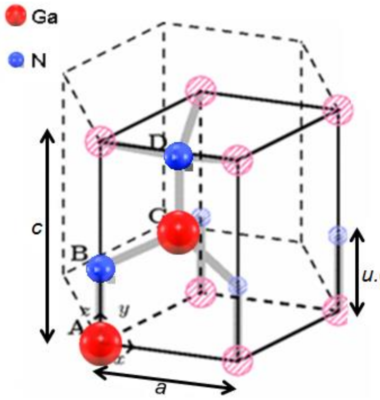


Fig. 2.1. Unit cell of the wurtzite GaN with lattice parameters a *(3.189 Å) and* c *(5.185 Å). Unit cell consists two atoms of gallium and two atoms of nitrogen. Taken from [26].*

2.3 Chemical, mechanical and thermal properties

GaN is exceedingly stable compound and exhibits significant hardness. It is chemically stable even at elevated temperatures. It was found that GaN is insoluble in water, acids or bases at room temperature, but dissolves in hot alkali solutions at a very slow rate [16]. Low quality layers can be etched at reasonably high rates in NaOH, H_2SO_4 or H_3PO_4 [27]. Especially, material around dislocations is well etched (smooth surface is much difficult to etch), so this technique can be used for estimating density of defects in GaN. This technique is destructive but gives reasonable information about the dislocation density.

Wurtzite structure is mechanically stable up to 50 GPa when changes to rocksalt phase [28]. Mean thermal expansion coefficient of GaN is in the *c* plane $\Delta a/a = 5.59\ 10^{-6}\ K^{-1}$ (300 – 900 K), $\Delta c/c = 3.17\ 10^{-6}\ K^{-1}$ (300 – 700 K) and $\Delta c/c = 7.75\ 10^{-6}\ K^{-1}$ (700 – 900 K) [16]. During epitaxial growth of GaN on sapphire substrate, slightly different thermal expansion coefficient of sapphire and GaN causes bending of the sample during cool down process. This phenomenon has to be taken into account during fabrication of devices by opposite pre-bending during the growth.

Radiation resistance of GaN layers was studied as well. Look *et al.* [29] studied formation of point defects under 1 – 2 MeV electron irradiation. They showed that GaN is quite resistant to displacement changes and the most dominant formed defect is nitrogen vacancy. Good radiation resistance predestines GaN to be used as a good scintillation material.

2.4 Optical properties of GaN

GaN is a direct semiconductor with the bandgap energy of E_g = 3.42 at 300 K [27]. It is suitable material for optoelectronic devices, such as LEDs or laser diodes. Luminescence characteristic of GaN layers is very important for optoelectronic devices and even for scintillation devices. Typical luminescence spectrum of undoped GaN layer is shown in Fig. 2.2.

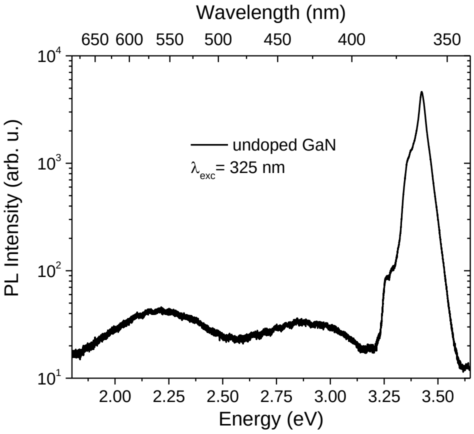


Fig. 2.2. Room temperature photoluminescence spectrum of undoped GaN layer grown on sapphire substrate by MOVPE technology at standard conditions, and pumped by 325 nm laser with 50 W/cm^2.

This spectrum consists of four recombination parts, excitonic emission, donor-acceptor pair (DAP) emission, blue luminescence and yellow luminescence bands (BB and YB respectively). The emission around 3.42 eV is attributed to bound exciton to neutral donors [30]. In some cases, free excitons associated with the A, B and C valence bands can be measured, but due to unintentionally n-type GaN layers, bound excitons are measured in most cases. Emission around 3.28 eV comes from DAP recombination, where electrons are bound to donors and holes are bound to acceptors. Broad band centred at about 2.9 eV is BB, which comes from some shallow acceptor level. The BB is observed usually in undoped, Zn-doped [31], Mg-doped [32] or C-doped [33] layers. The decay time of this band is in the range of hundreds of nanoseconds (around 400 ns) and it is unwanted for the scintillation applications. The second broad band centred at about 2.2 eV is YB. The YB is usually observed in undoped, C-doped, Si-doped or Fe-doped layers. The source of the YB is deep acceptor level but after more than 20 years of research, there is still controversy in the literature about the origin of this acceptor level. The acceptor level was attributed to V_{Ga}-related complexes [34,35] or C_N-related complexes [36,37]. Nevertheless, the decay time of the YB is very slow (in the range of microseconds) and suppression of this band is essential for fast scintillation applications.

2.5 InGaN/GaN MQW heterostructure

InGaN/GaN MQW heterostructure is in fact a stack of $In_xGa_{1-x}N$ and GaN layers with varying composition of indium. InN has larger lattice parameter a than GaN, which means that InGaN layers are compressively strained in the heterostructure. Moreover, InN has smaller bandgap, so InGaN layers, surrounded by GaN barriers with higher bandgap, act as QWs.

2.6 Polarization field

In nitride heterostructures we are dealing with a quite huge macroscopic polarization. This polarization has two components: spontaneous (P_{SP}) and piezoelectric polarization (P_{PZ}). The reason of the spontaneous polarization is an intrinsic asymmetry of the bonding in the wurtzite crystal structure. It increases from GaN (-0.034 C/m^2) over InN (-0.042 C/m^2) to AlN (-0.090 C/m^2) and it has a negative sign [38]. Bernardini and Fiorentini [39] showed nonlinear behaviour of polarization for ternary III-nitride alloys. Spontaneous polarization follows Vegards-like relationship with a bowing parameter b describing nonlinear relationship between InN and GaN. For InGaN alloy we can describe spontaneous polarization as:

$$P_{InGaN}^{SP}(x) = -0.042\,x - 0.034\,(1-x) + 0.037x(1-x)$$

where 0.037 C/m^2 is bowing parameter value for this case [40].

Knowledge of the spontaneous polarization is not sufficient for the description of the MQW heterostructure. As was already mentioned, InGaN QWs are compressively strained to match GaN lattice parameter. It leads to creation of piezoelectric polarization. In the growth along c-axis ([0001]) the strain in epitaxial layers is directed along the plane parallel to the substrate surface and crystal can relax freely in the growth direction. Assuming biaxial stress and negligible shear stresses, the piezoelectric polarization has only one non-vanishing component, which is directed along the growth direction and can be expressed as:

$$P_3^{PZ} = 2\frac{a_{InGaN} - a_{GaN}}{a_{GaN}}\left(e_{31} - e_{33}\frac{C_{13}}{C_{33}}\right)$$

where a is the lattice parameter, e_{31} and e_{33} are piezoelectric constants of InGaN and C_{13} and C_{33} are the elastic constants of InGaN [40]. P_3^{PZ} is always negative for layers under tensile strain and positive for layers under compressive strain. InGaN layers grown on GaN are compressively strained and the P^{PZ} is anti-parallel to the P^{SP}. Piezoelectric polarization is nonlinear in terms of the alloy compositions (same as P^{SP}) and can be expressed as:

$$P_{InGaN/GaN}^{PZ}(x) = 0.148\,x - 0.0424\,x\,(1-x)$$

where -0.0424 C/m^2 is the bowing parameter value for InGaN/GaN structure [40]. This equation is true when the piezoelectric polarization depends linearly on the strain. If high forces or pressures are applied to the crystal, this relation becomes nonlinear. It is the case of high indium content heterostructures, which are hard to prepare in practice.

The piezoelectric polarization has a strong contribution to the overall polarization in the structure. The piezoelectricity gives rise to an electric field pointing from the substrate side (N face) to the surface side (Ga face), which leads to a corresponding inclination of the conduction and valence band edges in QWs and barriers, see Fig. 2.3. It directly leads to a redistribution of the electrons and holes to the upper and lower surface, respectively. Decreasing of the wave function overlap can be observed, resulting in the lower recombination probability. Moreover, the effective band gap shrinks. This effect is called quantum confined Stark effect. The reduction of the overlap leads to the longer decay time and less effective recombination process, which is detrimental for the scintillators.

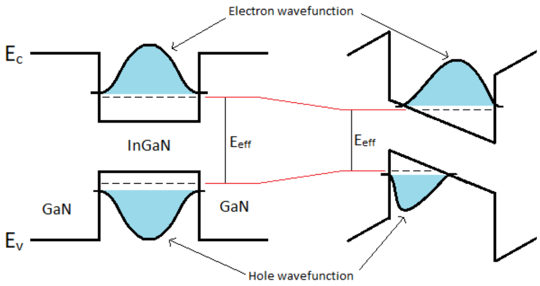


Fig. 2.3. Illustration of the band structure of InGaN/GaN heterostructure without electric field (left) and with electric field (right). Effective bandgap shrinks and the overlap of wave function decreases.

2.7 Carrier localization

MQW structures grown on sapphire substrate have dislocation density in the order of $10^8 - 10^9$ cm^{-2}. Despite of such high dislocation density, the light emission is not quenched and the room temperature photoluminescence efficiency can be very high. In InGaN/GaN heterostructures are created localization centres which confine carriers and prohibit non-radiative recombination. Localization centres are generally attributed to the fluctuation of indium concentration [41], indium clustering [42] or fluctuation in quantum well width [43]. The precise nature of the localization centres is still unknown because it is hard to directly measure them and moreover some of the measurement techniques can give rise to false localization centres (for example indium clustering in InGaN QWs caused by electron beam damage in transmission electron microscope (TEM) images [44]).

2.8 V-shape defects

Threading dislocations, which penetrate through the whole structure, are created during the initial growth of GaN on the sapphire substrate (due to 16 % lattice mismatch between sapphire and GaN). Dislocation density is typically between $10^8 - 10^9$ cm^{-2} and screw, edge and mixed type dislocations can be distinguished. During the growth of MQW structure (low temperature growth), V-shape defects (called V-pits) start to open on the dislocations with screw component. Cross sectional TEM images of such V-pits in the real structure are shown in Fig. 2.4.

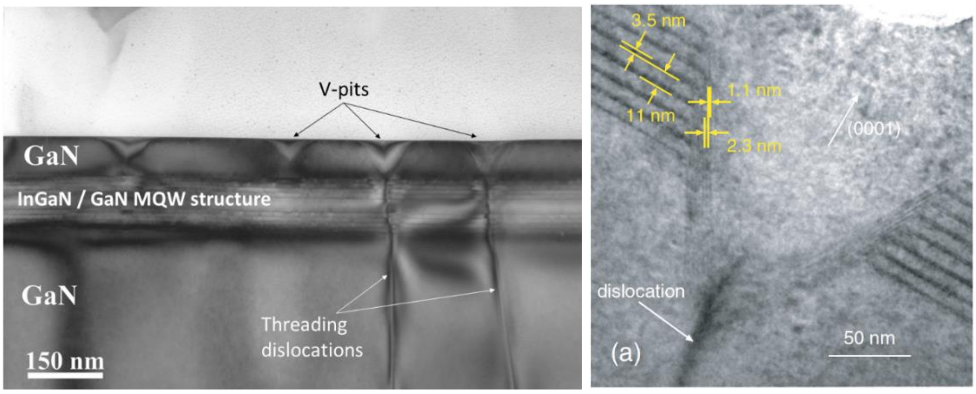


Fig. 2.4. Bright field XTEM image (g = 0002) of the InGaN/GaN MQW structure grown in our laboratory (left image) and TEM image of InGaN/GaN MQW structure (right image) with QWs thickness marked on the c-plane (3.5 nm) and sidewall of V-pit (1.1 nm). Right image was taken from [45].

Most of the surface defects are detrimental for the luminescence efficiency of the structures but it was found that role of the V-pits is different. The growth rate significantly depends on the different crystallographic planes. Sidewalls of the V-pits have {1-101} or {11-22} planes and the growth rate is much slower compared to (0001) plane. Therefore, QWs and barriers have much lower thickness, as you can see in Fig. 2.4, and with increasing layer thickness V-pits tend to be larger. Such thinner QWs act as barriers for excitons generated in c-plane QWs. Thus, excitons are screened from the non-radiative centres located around the threading dislocation by the thinner QWs in the V-pit sidewall, which act as a potential barrier [45].

2.9 MQW structure design

As explained before, quantum confined Stark effect in InGaN/GaN MQW heterostructures causes separation of electron and hole wave functions and worse recombination efficiency. To minimize this phenomenon, it is necessary to have a very thin InGaN QWs to get fast response and good recombination efficiency. Most of our structures had QW thickness between 1 and 2 nm. Higher indium composition decreases luminescence efficiency as well as higher thickness. Therefore, low indium concentration of InGaN layers was necessary for our purpose. Our scintillation structures with the fastest decay time had InGaN layers with indium concentration below 10 %.

We have also added GaN separation layers after each stack of five QWs (see Fig. 1.1). Increase of QW number (MQW thickness) causes higher strain in the structure and GaN separation layer should decrease it a little bit, so we are able to grow thicker MQW structure (higher QW number) without any cracking. GaN separation layer itself increases MQW thickness and if we choose a proper thickness (below diffusion length of excitons), we will increase detection efficiency for high energy irradiation. For example, Hocker *et al.* [46] found diffusion length of excitons in undoped GaN around (150 ± 25) nm. Our GaN separation layer had usually thickness around 30 nm.

3 Epitaxial Growth and Experimental Techniques

3.1 Introduction

Epitaxy can be described as a growth of monocrystalline layers on a monocrystalline substrate. The term “epitaxy” was established by L. Royer in 1936. The word comes from Greek words *epi* (upon) and *taxis* (ordered) meaning together “arranging upon”. Epitaxial process is carried on the temperatures below melting point of the material, which means better crystallographic perfection and purity of the layers compared to the monocrystals grown from melt by Czochralski or Bridgman growth techniques (due to role of entropy – disorder at higher temperatures) [47].

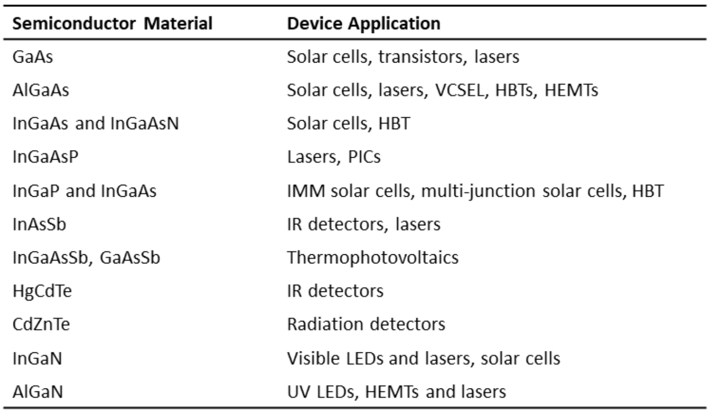
The principle of the epitaxial growth is following. Atoms or molecules of the compound, which we would like to deposit on suitable substrate, are transported to epitaxial surface, which has to be atomically clean (cleaned from oxides and sorbants) and atomically smooth (only with atomic steps due to disorientation of the monocrystalline substrate). On the surface, the atoms will be physisorbed, and after that, chemisorbed to the crystal structure. By this way epitaxial atomic layers and all structures are grown.

Family of epitaxial techniques can be divided to the three techniques: solid, liquid and vapour phase epitaxy. From the beginning, compound semiconductors were mainly grown either by liquid phase epitaxy (LPE) or vapour phase epitaxy (VPE). LPE was used for the growth of II-VI and III-V compound semiconductors since the early 1960s. This technique produced high-purity semiconductors from a very simple apparatus designed for production of thick layers (up to 100 μm). The limitation of this technique was a growth of multiple layers with different composition, which are needed in today’s complex and advanced devices. Hydride vapour phase epitaxy (HVPE) was also used since 1960s for the growth of high-quality thick epitaxial layers. Limitation of this technique is the same as for LPE, difficulty in the growth of thin layers and superlattices with different composition. Unlike LPE, it is still nowadays used thanks to very high growth rate >100 μm/h with dislocation density $<10^6$ cm^{-2}. Such grown crystals are especially used in the growth of GaN due to the lack of native GaN substrates [48].

Limits of both LPE and HVPE techniques in growing complex devices and nanostructures led to development of new techniques, such as MBE or MOVPE. Both techniques can grow nearly atomically abrupt interfaces and high quality superlattices. MBE technique was still not widely adopted for the industrial production of compound semiconductor devices due to the ultrahigh vacuum system requirements, very complex maintenance procedures and wafer size limits. On the other hand, MOVPE became the primary production technique used in the semiconductor industry. Despite the fact that the equipment and procedure is quite expensive, MOVPE was adopted worldwide for the production of most of the III-V and II-VI devices due to its versatility, simplicity, large wafer area and fast turnover of growth process [48]. Both MBE and MOVPE techniques are able to growth semiconductor heterostructures with sharp interfaces and precise composition of each layers. The MBE is a physical process while the MOVPE is a chemical one.

3.2 MOVPE technology

MOVPE technology is an epitaxial process for the deposition of very thin layers of atoms onto a (usually semiconductor) monocrystalline wafer. In principle, source materials are delivered onto the heated monocrystalline substrate which becomes atomically clean and flat by this heating. Substrate is placed in the cold-wall reactor chamber. Molecules, close to the heated substrate, are decomposed to radicals which react on the epitaxial surface and create monocrystalline layer. The epitaxial temperature must be high enough to decompose metalorganic and ammonia molecules and low enough to prevent the thermal desorption of atoms from the surface and to prevent pre-reactions of source molecules in the gas phase. The growth is done by chemical reaction (not only a physical deposition as in MBE process). The growth on the same material is called homo-epitaxy, but the growth can be done on different substrates (hetero-epitaxy). Variety of compound semiconductors for many device applications can be prepared by MOVPE technology, see summarizing table in Fig. 3.1.



Semiconductor Material	Device Application
GaAs	Solar cells, transistors, lasers
AlGaAs	Solar cells, lasers, VCSEL, HBTs, HEMTs
InGaAs and InGaAsN	Solar cells, HBT
InGaAsP	Lasers, PICs
InGaP and InGaAs	IMM solar cells, multi-junction solar cells, HBT
InAsSb	IR detectors, lasers
InGaAsSb, GaAsSb	Thermophotovoltaics
HgCdTe	IR detectors
CdZnTe	Radiation detectors
InGaN	Visible LEDs and lasers, solar cells
AlGaN	UV LEDs, HEMTs and lasers

Fig. 3.1. Summary of many kinds of semiconductor materials grown by MOVPE with different application utilization (VCSEL = vertical cavity surface emitting laser, HBT = heterojunction bipolar transistor, HEMT = high electron mobility transistor, PIC = photonic integrated circuit, IMM = inverted metamorphic multi-junction). Taken and modified from [48].

Source materials (named precursors) used for the growth of monocrystalline thin layers by MOVPE technology are hydrides and metalorganics (chemical compound containing metal atom and organic ligands). In case of III-nitrides, trimethylgallium (TMGa), triethylgallium (TEGa), trimethylindium (TMIn), trimethylaluminium (TMAl) and ammonia (NH_3) are usually used for the growth. Metalorganic precursors are placed in the stainless steel bubblers (solid form – TMIn, liquid form – TMGa, TEGa, TMAl). High purity carrier gasses (hydrogen or nitrogen at the purity level of ppb or better) go through the bubbler and take metalorganic molecules into the chamber on the heated substrate, where the layer deposition takes place. Silane (SiH_4) is usually used as n-type dopant and biscyclopentadienyl magnesium (Cp_2Mg) as p-type dopant.

The chemical reaction of precursors can occur either in the hot vapour above the surface or on the hot substrate. In case of GaN growth, summary stoichiometric reaction can be written as:

$$Ga(CH_3)_3 + NH_3 \rightarrow GaN + 3\ CH_4$$

The reaction mentioned above is a just simplified chemical reaction. During the GaN growth, complex gas-phase and surface reactions occur. Gas reactions have been extensively studied by many research groups and it was found that there are two competing paths in the gas reactions during MOVPE growth of GaN, the adduct/amide reaction formation path and the TMGa pyrolysis path [49]. Schematic diagram of these two formation paths is shown in Fig. 3.2.

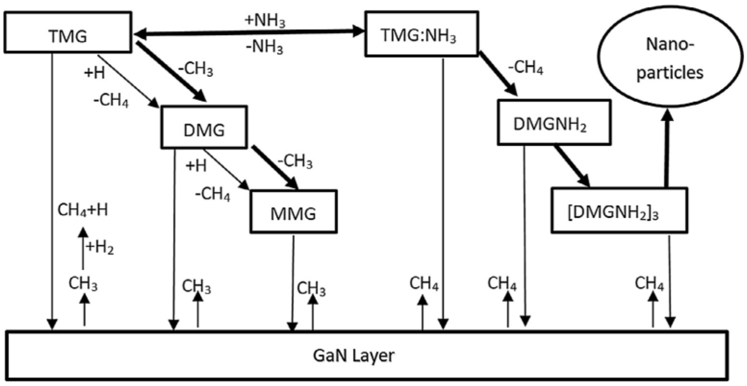


Fig. 3.2. Schematic diagram of the gas reactions paths during MOVPE growth of GaN. The pyrolysis path (the left one) and the adduct/amide path (the right one). Taken from [49]. (TMG = $(CH_3)_3Ga$, DMG = $(CH_3)_2Ga$, MMG = $(CH_3)Ga$)

TMGa and NH_3 make adduct at room temperature and at elevated temperature this adduct ($TMGa{:}NH_3$) can decompose into the amides $DMGaNH_2$. The amides are highly reactive and they can create oligomers $[DMGaNH_2]_x$, where x can be 2 or 3. This process is known as an adduct path. During the pyrolysis path are $TMGa{:}NH_3$ adducts dissociated back to TMGa and NH_3. At sufficiently high temperature TMGa decomposes to DMGa ($Ga(CH_3)_2$) and MMGa ($GaCH_3$). For this pyrolysis path is needed higher temperature and higher activation energy compared to the adduct path. Which gas reaction path dominates during the growth depends on the value of the reaction kinetics parameters[1] (activation energy and pre-exponential factor) [49]. For the modelling of GaN MOVPE growth are usually used these gas reactions (or part of them) [49]:

G1:	$(CH_3)_3Ga \rightarrow (CH_3)_2Ga + CH_3$	pyrolysis reaction of TMGa
G2:	$(CH_3)_2Ga \rightarrow (CH_3)Ga + CH_3$	pyrolysis reaction of DMGa
G3:	$(CH_3)_3Ga + NH_3 \rightarrow (CH_3)_3Ga{:}NH_3$	adduct formation
G4:	$(CH_3)_3Ga{:}NH_3 \rightarrow (CH_3)_3Ga + NH_3$	adduct decomposition
G5:	$(CH_3)_3Ga{:}NH_3 \rightarrow (CH_3)_2GaNH_2 + CH_4$	adduct decomposition
G6:	$3(CH_3)_2GaNH_2 \rightarrow [(CH_3)_2GaNH_2]_3$	formation of cyclic trimer
G7:	$CH_3 + H_2 \rightarrow CH_4 + H$	CH_3 radical reaction

---

[1] Reaction kinetic parameters, activation energy E [kcal/mol] and pre-exponential factor k_0 $[(cm^3/mol)^{\alpha-1}s^{-1}]$ are part of the equation $k = k_0 T^n \exp(-E/RT)$. This equation calculates rate constant of the chemical reaction. Values of calculated or experimentally observed kinetic parameters differ in the literature. See for example [49-51].

G8: $NH_3 + H \rightarrow NH_2 + H_2$ H radical reaction

G9: $NH_3 \rightarrow H + NH_2$ ammonia pyrolysis

G10: $(CH_3)_3Ga + H \rightarrow (CH_3)_2Ga + CH_4$ H radical reaction

G11: $(CH_3)_2Ga + H \rightarrow (CH_3)Ga + CH_4$ H radical reaction

The kinetics parameters of the reactions listed above are important for the basic idea of the GaN MOVPE growth process. For example, incorporation of hydrogen into GaN layers is very important for the layer quality. When we look at the H radical in the mentioned reactions, we can see that H formation is done by reaction G7 and G9 and depletion of H radical is done by reaction G8, G10 and G11. From the activation energies, we can conclude that G7 is the main reaction of the generation of H radical (lower activation energy compared to G9). On the other hand, G8 is the main reaction for depletion of H radical because much more NH_3 molecules are in the reactor (compared to TMGa or DMGa molecules) and the probability of the collision is higher [49].

GaN MOVPE growth contains surface reactions as well. Surface reactions usually considered in the simulations are listed below [49]:

S1: $(CH_3)_3Ga \rightarrow Ga(s) + 3CH_3$

S2: $(CH_3)_2Ga \rightarrow Ga(s) + 2CH_3$

S3: $(CH_3)Ga \rightarrow Ga(s) + CH_3$

S4: $(CH_3)_3Ga{:}NH_3 \rightarrow GaN(s) + 3CH_4$

S5: $(CH_3)_2Ga{:}NH_2 \rightarrow GaN(s) + 2CH_4$

S6: $[(CH_3)_2GaNH_2]_3 \rightarrow 3GaN(s) + 6CH_4$

S1 – S3 describe decomposition of TMGa, DMGa and MMGa. These reactions provide Ga atoms to the layer. Reactions S4 – S6 describe decomposition of adducts, amides and trimers. These reactions provide stoichiometric amounts of Ga and N atoms into the layer. Very high V/III ratio is commonly used during the GaN growth, which means that surface reactions of NH_3 are not considered in the simulations [49].

The growth temperature is usually high enough to have the growth transport-limited. The growth rate is almost independent on the growth temperature during this regime. When the temperature is low, the growth regime is kinetic-limited. Molecules and radicals have not enough energy to be sufficiently decomposed and transported to the surface. On the other hand, desorption occurs at very high temperatures and the growth rate decreases. This growth regime is called evaporation-limited [52]. Typical dependence of the growth rate on the growth temperature is shown in Fig. 3.3.

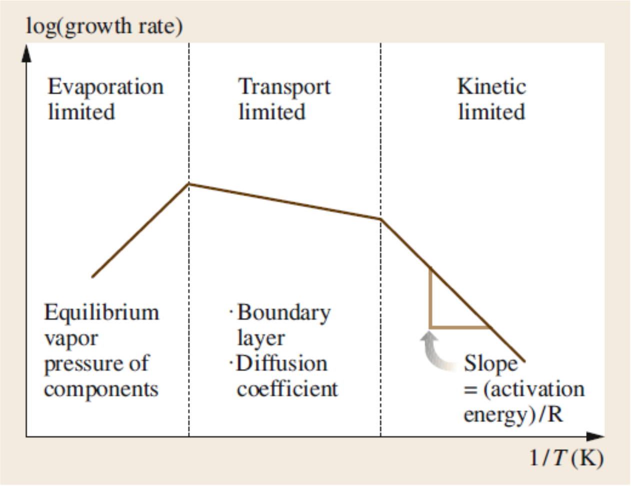


Fig. 3.3. Schematic diagram of the three different regimes during the MOVPE growth. Taken from [52].

Although the GaN MOVPE growth is much more complex, gas and surface reactions listed above can give us basic information about the growth and the processes which occur during the growth. However, details of processes during the GaN growth are still not well described and much more investigations and simulations need to be done.

The process of III-nitrides growth is significantly more complex than that of the other III-V or II-VI compounds. There are three main reasons. At first, the growth is mostly done on the lattice-mismatched substrates (sapphire, silicon, SiC, etc.) and various nucleation layers have to be implemented into the process. The second reason is a formation of adducts in the vapour phase which inhibits the mass transport of the elements to the surface. Finally, no p-type dopants with low ionization energy are available. The best choice is Mg with ionization energy around 200 meV in GaN (for AlGaN or AlN is the ionization energy much higher) resulting in only few percent of Mg atoms producing holes at room temperature [48].

3.3 Design of the reactor

There are two common types of MOVPE reactors according to the design of gas transport channel inputs, horizontal and vertical reactors. In horizontal reactors, gas flow is approximately parallel to the wafer surface. These reactors suffer from a decrease of the growth rate along the path of gas flow. Wall or wafer inclination, wafer rotation or optimized inlet flow rate were implemented to increase the homogeneity of the growth rate along the wafer. In vertical reactors, gases flow perpendicular to the wafer surface. In past two decades, different designs of the reactors were invented, for example close coupled showerhead (CCS) reactors, planetary reactors or high-speed rotating disk reactors. They are designed and used for the mass production of III-nitride devices with excellent growth homogeneity uniformity and reproducibility.

Our laboratory is equipped by Aixtron 3x2 CCS MOVPE reactor for III-nitride growth with LayTec EpiCurveTT system for in situ measurement of reflectivity, curvature and temperature. Schematic diagram of our MOVPE system is shown in Fig. 3.4. Scheme of the reactor is shown in Fig. 3.5.

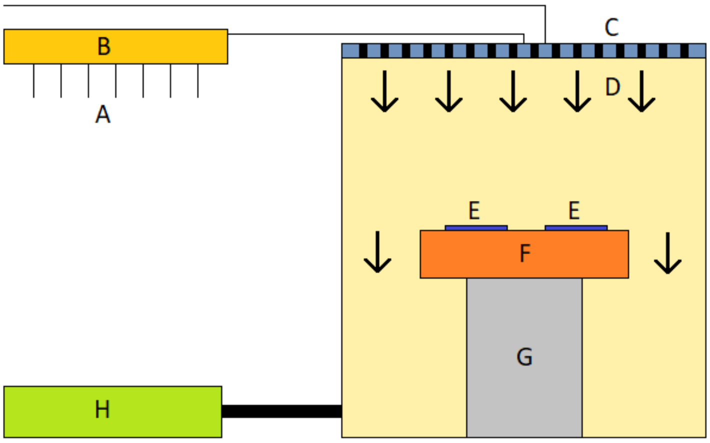


Fig. 3.4. Schematic diagram of the CCS MOVPE reactor (A – process gas supply, B – gas mixing system, C – showerhead, D – reactor chamber, E – substrates, F – susceptor, G – heater, H – pump system).

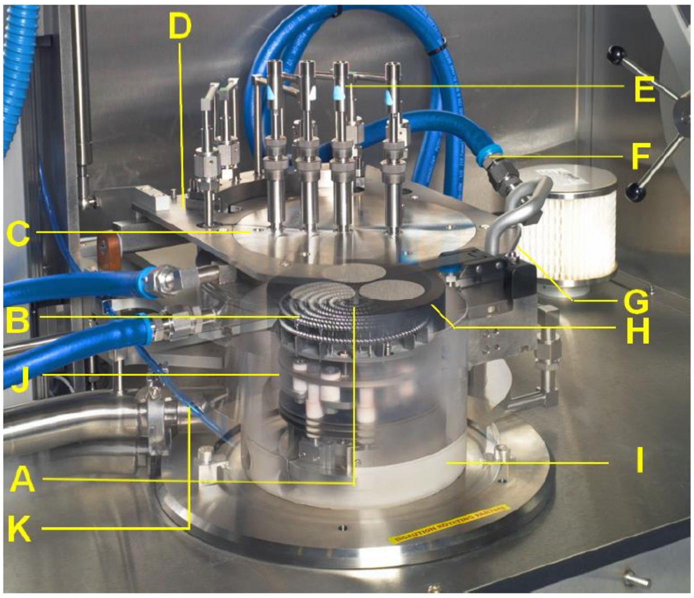


Fig. 3.5. Scheme of the 3x2 CCS MOVPE reactor (A – thermocouple, B – tungsten heater, C – showerhead, D – reactor lid, E – optical probe, F – showerhead water cooling, G – double O-ring seal, H – susceptor, I – quartz liner, J – susceptor support, K – exhaust). Taken from the Aixtron manual.

Our reactor has 3 pockets for two-inch wafers. This kind of reactor is designed for scientific research. For the mass production of epitaxial III-nitrides films in the industry are used much bigger reactors (for example 124 four-inch wafers in one run).

Wafers are located on the susceptor, which is generally a graphite disk with approximately 100 µm SiC coating. Susceptor rotates in a clockwise direction during the growth for better temperature homogeneity. Heater coils are located inside of the susceptor support and below the susceptor (see Fig. 3.5). The system is heated by a three-zone heater, see schematic diagram in Fig. 3.6(a).

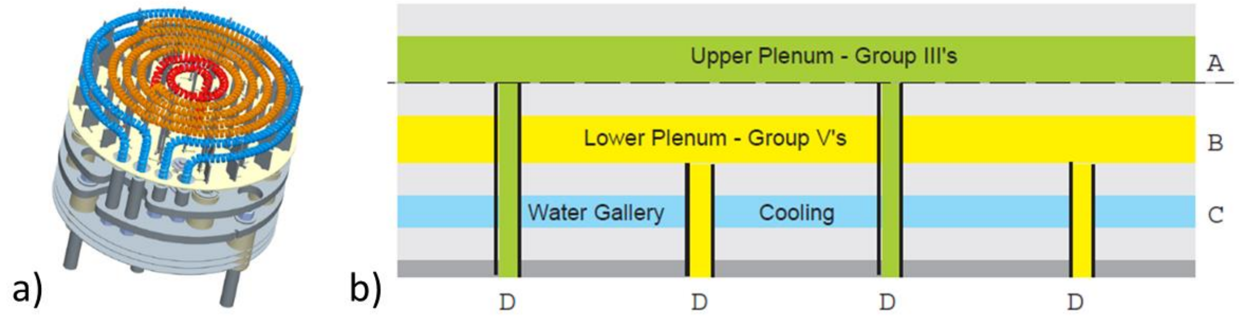


Fig. 3.6. a) Schematic diagram of the three zone heaters (red – centre, orange – middle, blue – outside) and b) cross section of the showerhead (A – upper plenum, B – lower plenum, C- water cooling, D – tubes). Taken from the Aixtron manual.

Cross section of the showerhead is shown in Fig. 3.6(b). Showerhead has normally two plenums, upper plenum for metalorganics (group III's) and lower one for ammonia (group V's). Both precursors come to the reactor from tubes with diameter 0.6 mm. Distance between showerhead and susceptor influences the growth (growth rate, amount of the pre-reactions in the gas phase, etc.) The distance can be adjusted, but it is typically around 11 mm.

3.4 Growth process of scintillation structure

The typical growth process of InGaN/GaN scintillation structure on sapphire substrate, which is the subject of this work, is performed in following technological steps:

- Substrate annealing at high temperature (1100°C) in H_2 ambient (desorption of contaminants from the surface and smoothing the surface)
- Nitridation of the sapphire substrate with ammonia flow to terminate the dangling bonds with N
- Nucleation layer deposition at low temperature (500 – 600°C)
- Annealing of the nucleation layer during the temperature ramp up to 1000°C to create monocrystalline islands
- Slow coalescence of the islands
- Growth of undoped GaN buffer layer
- Growth of n-doped GaN layer
- Growth of the InGaN/GaN heterostructure
- Cool down process in NH_3 ambient

The first steps of the growth are important when the growth is performed on the foreign mismatched substrate. In case of sapphire, the lattice mismatch is 16%, which is quite a lot and many dislocations are formed at the interface between sapphire and GaN layer. Two-step model growth (nucleation layer growth, annealing and coalescence of monocrystalline islands) helps to decrease the amount of threading dislocations and capability of the 2D growth (to get smooth surface).

At first, sapphire substrate is annealed at 1100°C in H_2 ambient for desorption of any contaminants from the surface. Afterwards, the temperature is reduced down to 550°C and surface is nitrified with ammonia flow. GaN layer with very poor crystallographic quality (called nucleation layer) is grown at the same temperature. This layer with typical thickness around 60 nm acts as a wetting layer for the next growth. During the temperature ramp up to 1000°C the nucleation layer is annealed and monocrystalline islands are created. The size and amount of these islands can be controlled by different growth parameters. It influences the quality of GaN layer. At defined point, annealing is stopped and gallium precursor is introduced into the chamber. Islands grow in all directions and the growth switches from 3D to 2D growth in the point when islands coalesce and create smooth surface. During this process, a lot of threading dislocations are bended and they annihilate with one another. The reduction of density is very significant (from almost 10^{10} cm^{-2} down to 10^{8} cm^{-2}). The growth continues with n-doped layer when SiH_4 is introduced into the chamber. MQW structure can be grown on the top of these layers.

InGaN quantum wells are grown at lower temperature (650 – 800°C) compared to the GaN barriers (higher than 800°C) because indium incorporation is very sensitive on the temperature and at lower temperature more indium is incorporated into QWs. Therefore, temperature has to be cycled during the MQW structure growth. Record of the surface temperature for the whole growth is shown in Fig. 3.7 (red curve). Reflectance record (black curve) is shown in the same figure. It gives us useful information about the growth and capability to control the growth in the real time.

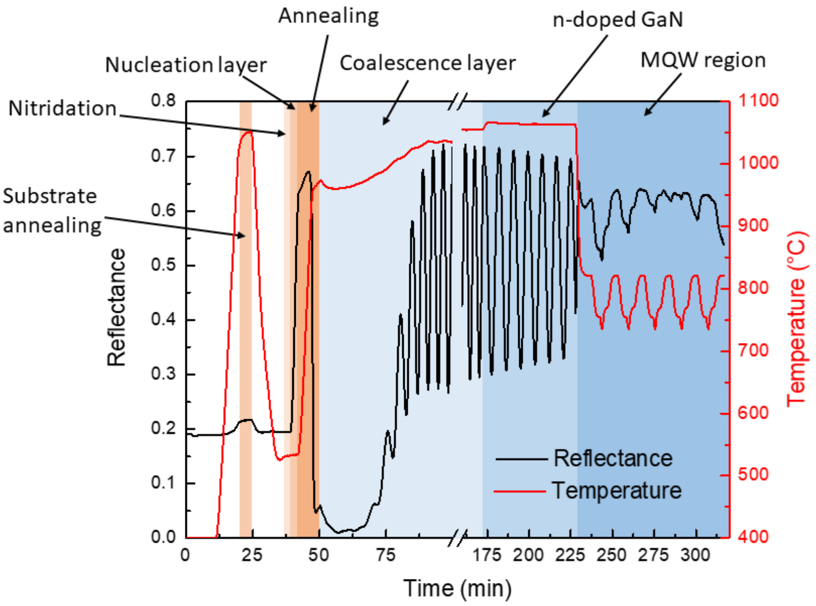


Fig. 3.7. Reflectance (black curve) and surface temperature (red curve) record during the growth of scintillation structure with each growth step marked with different background colour.

MQW structure growth is the most important part which influences significantly scintillation properties. Especially InGaN growth is very sensitive to the growth conditions and just a slight adjustment of the growth parameters can dramatically change the InGaN quality (optical, structural and electrical properties). There are a few problems with growing high-quality InGaN layers. InN has a relative high vapour pressure compared to GaN, which leads to low indium incorporation into InGaN layer. Moreover, the difference in formation enthalpies for InN and GaN leads to a strong indium surface segregation. Appropriate growth parameters (low growth temperature, high V/III ratio or slow growth rate) can minimize these problems [53]. Reduction of the growth temperature reduces desorption of indium atoms from the surface. On the other hand, cracking of the ammonia is reduced significantly at lower temperature (the percentage of decomposed ammonia varies from only a few percent at 900 °C up to 40 – 50 % at 1050 °C). It leads to lower growth rate and lower indium incorporation into InGaN layer. A compromise has to be found between these two phenomena.

Since InGaN QWs need lower growth temperature, it is necessary to use different gallium precursor. TMGa precursor is usually used during the high temperature growth of undoped and n-doped GaN layers. At lower temperatures (below 1000°C), this precursor would be inefficiently decomposed and layers would contain many carbon impurities. TEGa precursor is decomposed at lower temperatures thanks to the bigger organic ligands with weaker bond to Ga atoms and additional way of decomposition (β-hydrogen elimination process) further lower the carbon contamination in layers. That is the reason why TEGa precursor is used during the growth of InGaN QWs and GaN barriers.

Another very important difference of MQW and buffer growth is in a carrier gas. During the high temperature GaN growth, hydrogen is normally used as a carrier gas. On the other hand, during the MQW growth nitrogen has to be used, because hydrogen used during the growth of InGaN reduces significantly indium incorporation [54] and thickness [55]. Understanding of the effect of the hydrogen during InGaN growth is still not well described. Recently, increased coverage of surface with H adatoms and easy desorption of In-H species from the surface was suggested as a reason of a bad indium incorporation in InGaN layers [56].

To get good crystallographic GaN barriers, it is necessary to grow them at higher temperature than InGaN QWs. It brings problems during the growth because temperature ramp is necessary to introduce and indium can easily desorb from InGaN QWs during temperature ramp to GaN barrier growth temperature. Moreover, many defects are concentrated at this upper interface between InGaN QW and GaN barrier. A lot of growth approaches were used, such as thin low temperature GaN cap layer, GaN growth during temperature ramp or many others. Each approach brings different problems and to find a proper way how to grow the upper interface for different nitride application is quite challenging.

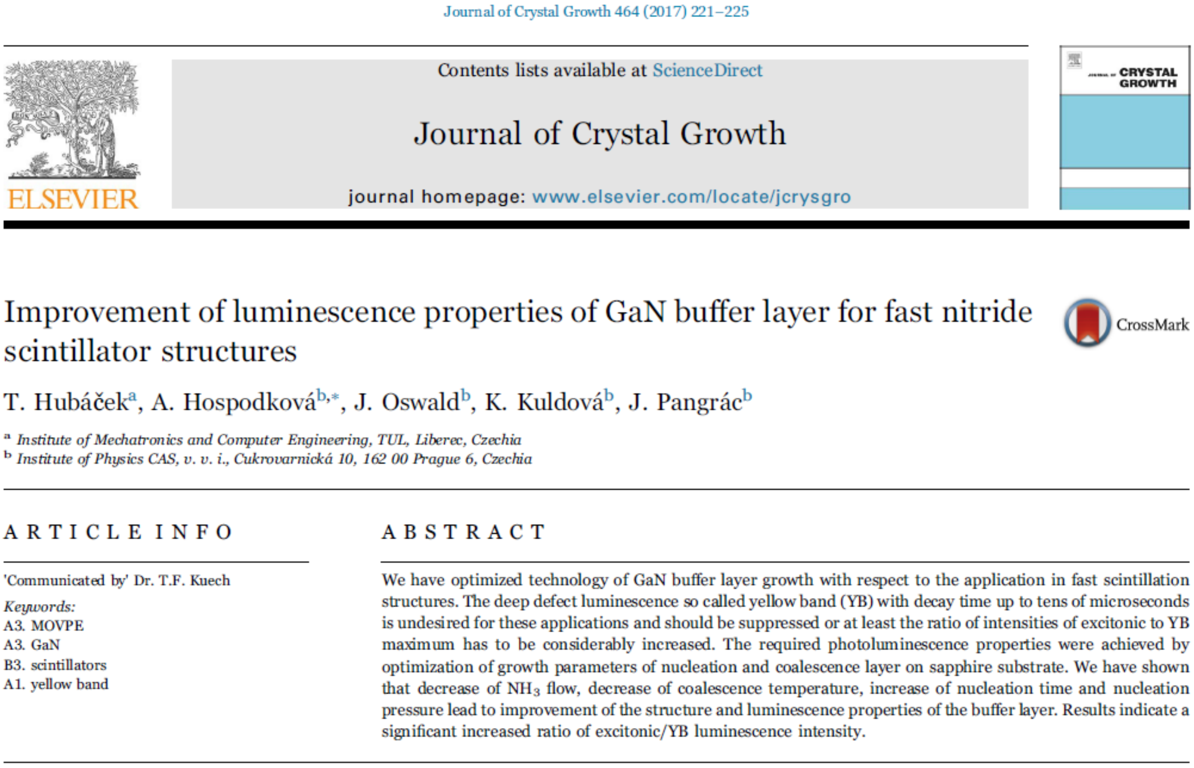
As a summary, MQW growth is much more complex than growth of high temperature GaN buffer layers and different growth conditions are necessary, such as nitrogen carrier gas, TEGa precursor, lower growth temperature, higher pressure, slower growth rate and higher V/III ratio (higher amount of NH_3 flow).

4 Collection of Papers

This chapter collects seven original papers published in the impact journals, related to the dissertation topic. Papers are ordered with respect to the scintillation structure. The first four papers are devoted to technology of GaN buffer (papers [i], [ii]) and layers surrounding the InGaN/GaN MQW active region (papers [iii], [iv]), following three papers are devoted to technology and properties of InGaN/GaN MQW active region itself (papers [v], [vi] and [vii]). The first paper is focused on the growth of GaN nucleation and coalescence layer on the sapphire substrate. In the second paper, which was accepted for publication before the finish of this doctoral thesis, we have studied the growth of n-doped GaN layer and effect of different precursors (TMGa or TEGa) used for n-doped GaN growth. The third paper deals with the influence of Si doping of buffer and GaN capping layer on the luminescence and structural properties of the MQW active region. The fourth paper suggested the improvement of the scintillation structure quality by adding the low temperature GaN layer directly below the MQW region. The fifth paper studies the effect of different QW number (10 or 30 QWs) on the luminescence properties, especially cathodoluminescence properties. In the next paper, we have increased the QW number more (up to 70 QWs) and studied the effect of the thick active region on the luminescence and structural properties of the scintillation structure. The last paper introduced the new method of the growth interface between QW and barrier in the MQW region. The new method increased the indium content in InGaN QW layer which can be useful not only for scintillation applications but also for the LED structures emitting in the green spectrum. This process was successfully patented and the author of the doctoral thesis is the co-author of the patent, see [xii].

4.1 Improvement of luminescence properties of GaN buffer layer for fast nitride scintillator structures [i]

In this paper, we have studied the initial part of the GaN growth on the sapphire substrate. The nucleation and coalescence layer growth was studied. Nucleation layer, which is the wetting layer for the subsequent high temperature GaN growth, was studied and luminescence properties were improved by higher reactor pressure and longer layer growth with subsequent longer annealing. The next part of the paper deals with growth parameters of high temperature coalescence layer. The luminescence properties were improved by lower NH_3 flow (graded flow) during coalescence layer growth. The lower temperature also improved the quality. Very good quality of GaN buffer layers is necessary for the growth of MQW region and we have successfully improved undoped GaN quality, which was indicated by significant increase of the ratio of excitonic/YB luminescence intensity from 0.65 before optimization to 16.8 after the optimization. This paper was published in Journal of Crystal Growth (IF = 1.57, Q3, 7 citations).



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Improvement of luminescence properties of GaN buffer layer for fast nitride scintillator structures

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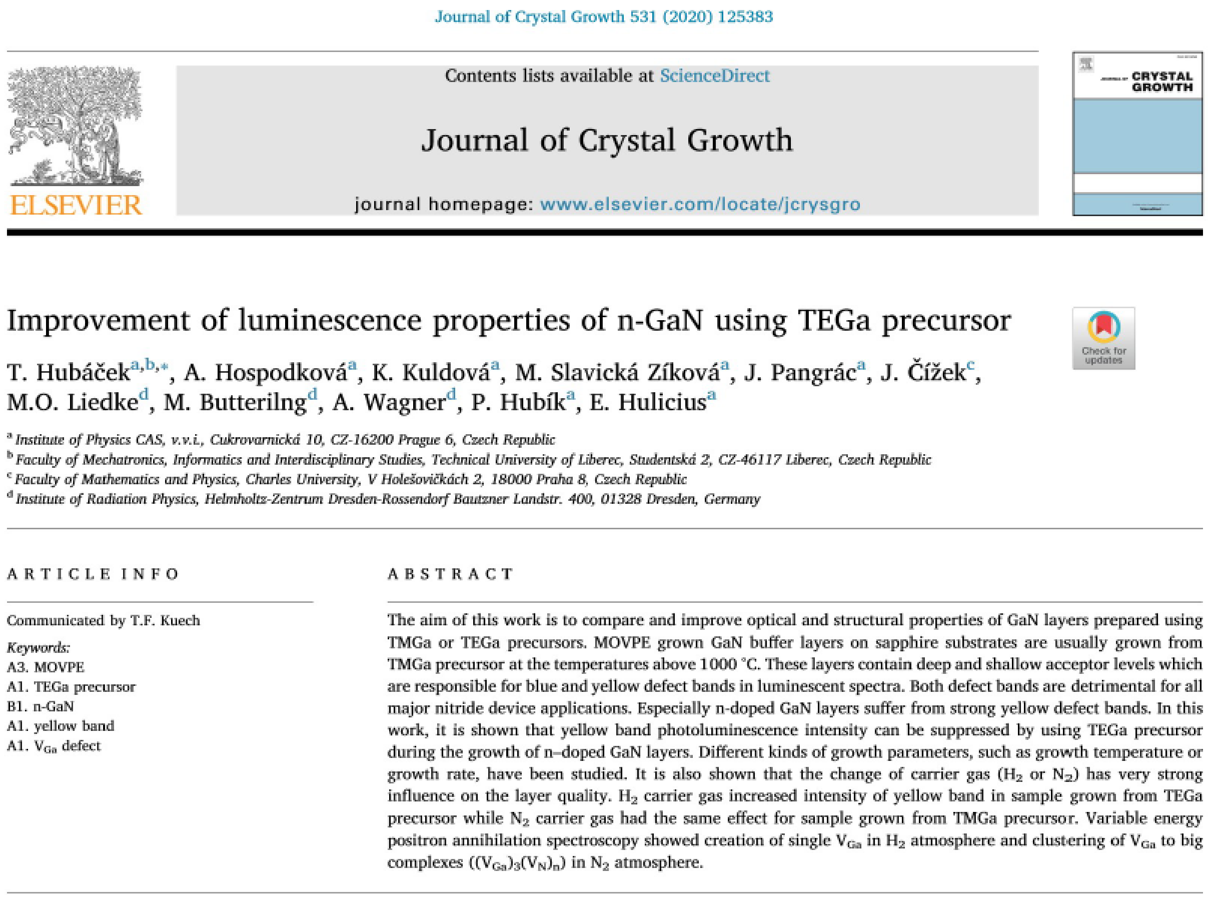
B3. scintillators
A1. yellow band

ABSTRACT

We have optimized technology of GaN buffer layer growth with respect to the application in fast scintillation structures. The deep defect luminescence so called yellow band (YB) with decay time up to tens of microseconds is undesired for these applications and should be suppressed or at least the ratio of intensities of excitonic to YB maximum has to be considerably increased. The required photoluminescence properties were achieved by optimization of growth parameters of nucleation and coalescence layer on sapphire substrate. We have shown that decrease of NH_3 flow, decrease of coalescence temperature, increase of nucleation time and nucleation pressure lead to improvement of the structure and luminescence properties of the buffer layer. Results indicate a significant increased ratio of excitonic/YB luminescence intensity.

4.2 Improvement of luminescence properties of n-GaN using TEGa precursor [ii]

This paper follows the first paper with respect to the study of GaN buffer layers. N-doped GaN layer is usually grown under the MQW region and due to the decrease of the formation energies of acceptor levels in n-doped GaN, intensity of defect bands (especially yellow band) are increased because the origin of the YB is recombination of electrons from shallow donor level and holes trapped in some kind of deep acceptor level (0.9 eV above valence band). After more than 20 years, there is still open discussion about the source of the acceptor level responsible for the YB. In our work, we have used different approach for the growth of n-doped GaN layer (different precursor). We were able to improve luminescence properties of n-doped GaN layers using TEGa precursor. Significant increase of excitonic band and consequence decrease of YB was observed. We have experimentally shown that both defects C_N as well as V_{Ga} can be responsible for YB luminescence. Using positron annihilation spectroscopy, we have identified presence of huge vacancy complexes in layers grown at N_2 atmosphere. This paper was published in Journal of Crystal Growth (IF = 1.57, Q3).



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Improvement of luminescence properties of n-GaN using TEGa precursor

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A1. TEGa precursor
B1. n-GaN
A1. yellow band
A1. V_{Ga} defect

ABSTRACT

The aim of this work is to compare and improve optical and structural properties of GaN layers prepared using TMGa or TEGa precursors. MOVPE grown GaN buffer layers on sapphire substrates are usually grown from TMGa precursor at the temperatures above 1000 °C. These layers contain deep and shallow acceptor levels which are responsible for blue and yellow defect bands in luminescent spectra. Both defect bands are detrimental for all major nitride device applications. Especially n-doped GaN layers suffer from strong yellow defect bands. In this work, it is shown that yellow band photoluminescence intensity can be suppressed by using TEGa precursor during the growth of n–doped GaN layers. Different kinds of growth parameters, such as growth temperature or growth rate, have been studied. It is also shown that the change of carrier gas (H_2 or N_2) has very strong influence on the layer quality. H_2 carrier gas increased intensity of yellow band in sample grown from TEGa precursor while N_2 carrier gas had the same effect for sample grown from TMGa precursor. Variable energy positron annihilation spectroscopy showed creation of single V_{Ga} in H_2 atmosphere and clustering of V_{Ga} to big complexes ($(V_{Ga})_3(V_N)_n$) in N_2 atmosphere.

4.3 Influence of Si doping of GaN layers surrounding InGaN quantum wells on structure photoluminescence properties [iii]

InGaN/GaN heterostructures suffer from a quite huge internal piezoelectric field which results in tilting of the band structure and consequently worse overlap of electrons and holes confined in QWs. Influence of different position of Si doped layer around MQW region on luminescence and structural properties was studied. It was found that the dominant influence of Si doping is in a modification of the tilt of the band structure. Both luminescence bands, excitonic and defect band, were influenced and we have suggested the mechanism of defect band (observed in our luminescence spectra) which could be recombination between holes confined in QWs and defect states located near the upper InGaN/GaN QW interface. The paper was published in Journal of Crystal Growth (IF = 1.57, Q3, 3 citation).

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Influence of Si doping of GaN layers surrounding InGaN quantum wells on structure photoluminescence properties

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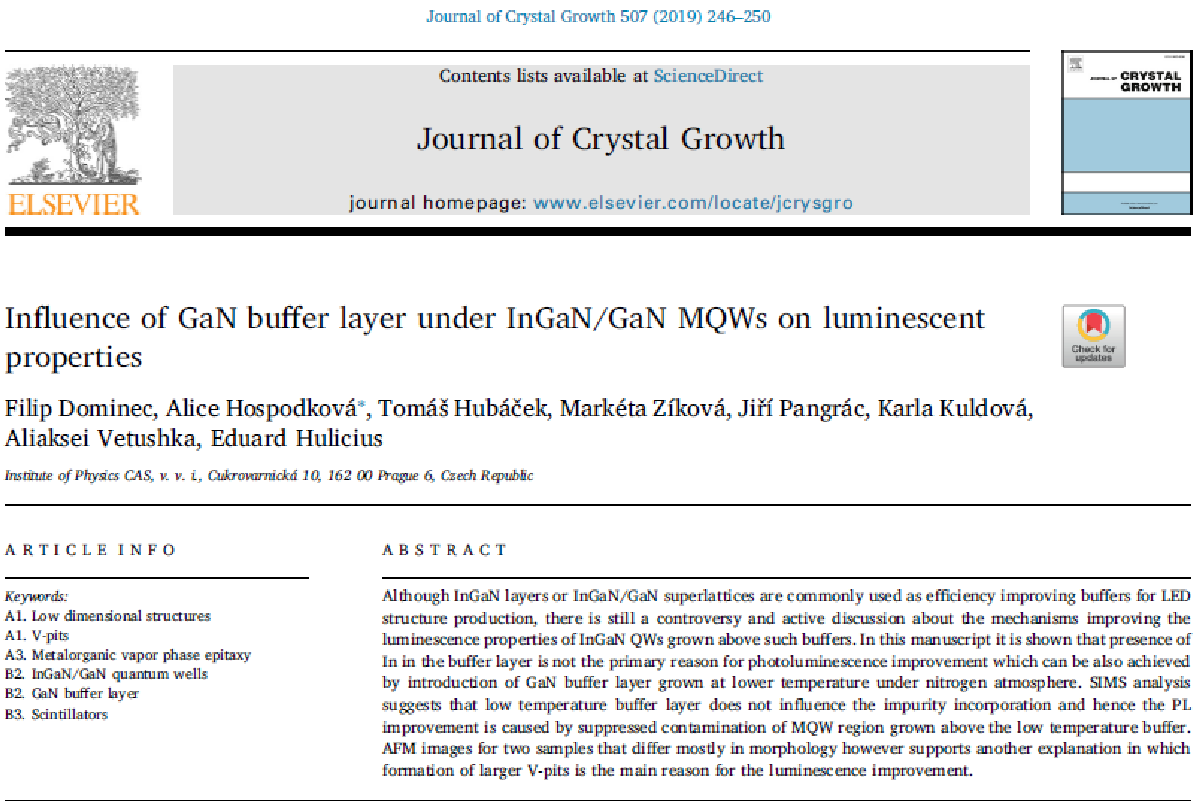
B2. Luminescent defect band

ABSTRACT

In this work, the influence of Si doping position on the photoluminescence (PL) properties of InGaN/GaN quantum wells (QWs) is studied. A set of samples with different positions of Si doping with respect to the multi quantum well (MQW) active region was prepared and studied by PL, SIMS and AFM and structure band alignments were simulated. Based on our experiments and band structure simulations, we show that the dominant influence of Si doping is in modification of the tilt of the band structure. However, the minor influence of lower dislocation density or unintentional doping of a few lowest QWs in the case of a Si doped buffer layer cannot be excluded. A probable origin of the defect band luminescence and its high sensitivity to the band structure tilting is explained. Based on gained understanding, proper Si doping position for particular applications is suggested. In the case of LED structures, the n-type buffer layer and p-type capping layer help improve the emission efficiency. In the case of an InGaN/GaN MQW structure designed for scintillators, the n-type doping immediately under the MQW region is not required, since it strongly increases the QW defect band luminescence which becomes dominant in the spectrum.

4.4 Influence of GaN buffer layer under InGaN/GaN MQWs on luminescent properties [iv]

Commercial available LED structures are grown with InGaN underlayer or InGaN/GaN superlattice under the MQW active region for increasing luminescence efficiency. The mechanism of that improvement is still not well understood and publications with new explanations are published every year. In this work we have compared structures with different buffer layers and studied photoluminescence properties. SIMS analysis showed that after decreasing of the growth temperature to the growth of InGaN layers, impurities, such as oxygen, iron or zinc, are incorporated into InGaN layers. We grew set of samples with low temperature (LT) GaN buffer layer under different growth conditions and found that LT GaN buffer layer increases excitonic emission from QWs and decreases defect band. LT GaN layer did not influence contamination incorporation and the increase of PL was explained by increased size of V-pits. This suggestion was proved by two samples grown with N_2 and H_2 carrier gas. In conclusion, we have shown that PL improvement can be done by LT GaN buffer layer without any indium and this approach can be used either in LED community or for our scintillation structure. The paper was published in Journal of Crystal Growth (IF = 1.57, Q3, 2 citation).



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Influence of GaN buffer layer under InGaN/GaN MQWs on luminescent properties

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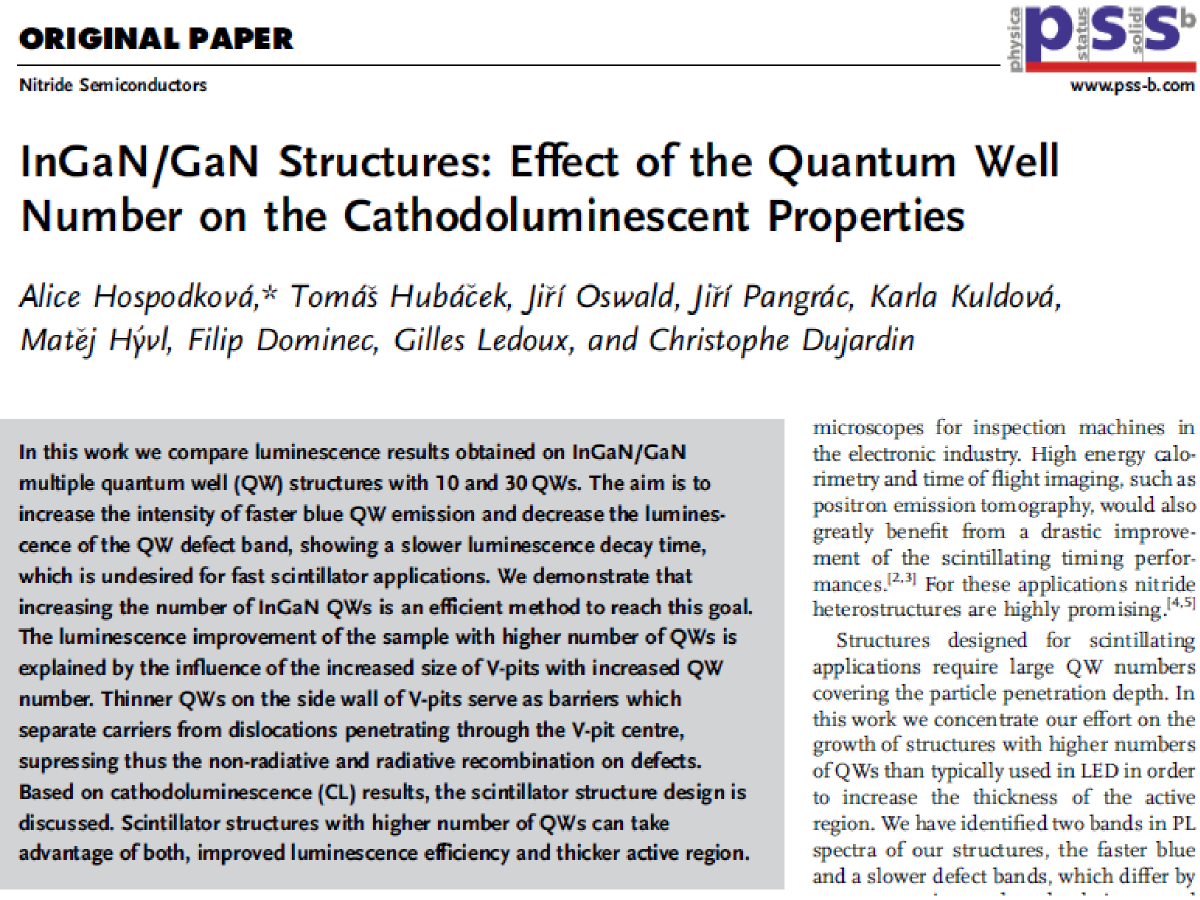
Keywords:
A1. Low dimensional structures
A1. V-pits
A3. Metalorganic vapor phase epitaxy
B2. InGaN/GaN quantum wells
B2. GaN buffer layer
B3. Scintillators

ABSTRACT

Although InGaN layers or InGaN/GaN superlattices are commonly used as efficiency improving buffers for LED structure production, there is still a controversy and active discussion about the mechanisms improving the luminescence properties of InGaN QWs grown above such buffers. In this manuscript it is shown that presence of In in the buffer layer is not the primary reason for photoluminescence improvement which can be also achieved by introduction of GaN buffer layer grown at lower temperature under nitrogen atmosphere. SIMS analysis suggests that low temperature buffer layer does not influence the impurity incorporation and hence the PL improvement is caused by suppressed contamination of MQW region grown above the low temperature buffer. AFM images for two samples that differ mostly in morphology however supports another explanation in which formation of larger V-pits is the main reason for the luminescence improvement.

4.5 InGaN/GaN Structures: Effect of the Quantum Well Number on the Cathodoluminescent Properties [v]

Very thick active region is necessary for some applications of our scintillation structure. In this paper, we have studied structures with different number of QWs (10 and 30 QWs). From the PL and CL measurements it was found out that sample with 30 QWs has stronger excitonic luminescence than sample with 10 QWs. The main cathodoluminescence signal originates only from the lowest part of the interaction volume of the incident electrons, which was found out from the CL measurement with different acceleration voltage. This observation is important for design of the scintillation structure, where active region should overlap the main CL region to get the most intensive luminescence for specific primary electron energy. Enhancement of the luminescence intensity in sample with 30 QWs was explained by bigger V-pits and screening of the non-radiative centres located around threading dislocations (in the middle of V-pits). The paper was published in Physica Status Solidi B in May 2018 (IF = 1.45, Q3, 3 citations).



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InGaN/GaN Structures: Effect of the Quantum Well Number on the Cathodoluminescent Properties

Alice Hospodková, Tomáš Hubáček, Jiří Oswald, Jiří Pangrác, Karla Kuldová, Matěj Hývl, Filip Dominec, Gilles Ledoux, and Christophe Dujardin*

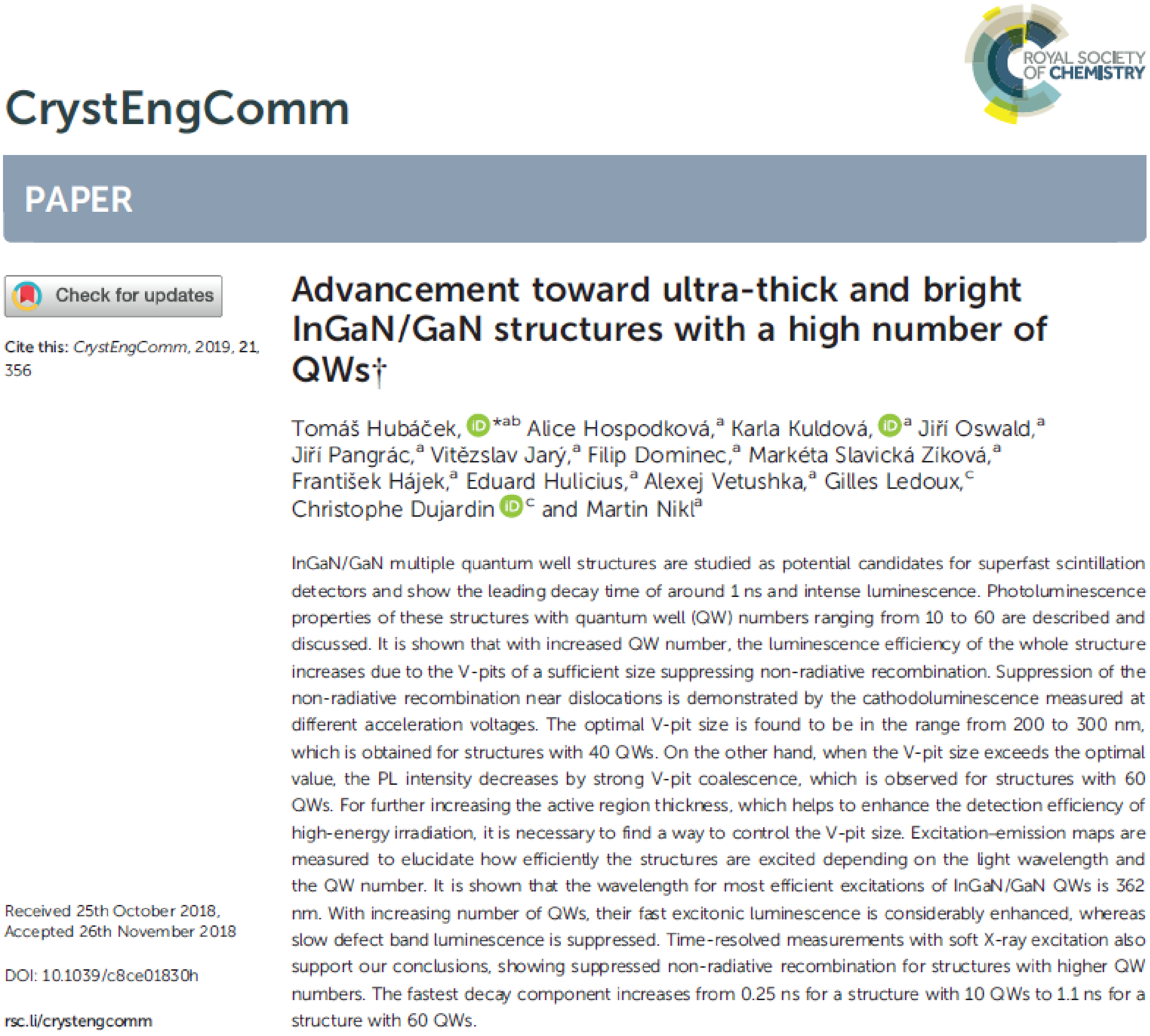
In this work we compare luminescence results obtained on InGaN/GaN multiple quantum well (QW) structures with 10 and 30 QWs. The aim is to increase the intensity of faster blue QW emission and decrease the luminescence of the QW defect band, showing a slower luminescence decay time, which is undesired for fast scintillator applications. We demonstrate that increasing the number of InGaN QWs is an efficient method to reach this goal. The luminescence improvement of the sample with higher number of QWs is explained by the influence of the increased size of V-pits with increased QW number. Thinner QWs on the side wall of V-pits serve as barriers which separate carriers from dislocations penetrating through the V-pit centre, supressing thus the non-radiative and radiative recombination on defects. Based on cathodoluminescence (CL) results, the scintillator structure design is discussed. Scintillator structures with higher number of QWs can take advantage of both, improved luminescence efficiency and thicker active region.

microscopes for inspection machines in the electronic industry. High energy calorimetry and time of flight imaging, such as positron emission tomography, would also greatly benefit from a drastic improvement of the scintillating timing performances.[2,3] For these applications nitride heterostructures are highly promising.[4,5]

Structures designed for scintillating applications require large QW numbers covering the particle penetration depth. In this work we concentrate our effort on the growth of structures with higher numbers of QWs than typically used in LED in order to increase the thickness of the active region. We have identified two bands in PL spectra of our structures, the faster blue and a slower defect bands, which differ by

4.6 Advancement toward ultra-thick and bright InGaN/GaN structures with a high number of QWs [vi]

In this article, we have studied structures with QWs number up to 70 QWs. Scintillation structures need to have thick active region (more than 1 µm) and we have studied the effect of higher QW number on the luminescence properties. The structure with 70 QWs had almost 800 nm thick active region which is up to now the highest reported QW number in the nitride community. PL intensity increased with higher QW number (as was observed in previous article) but for sample above 50 QWs the PL intensity started to decrease. This decrease was attributed to too big V-pits (strong V-pits coalescence and increase of non-radiative recombination). The best diameter of V-pits was found 200 – 300 nm (sample with 40 QWs). The decay time of the structures was measured as well and it was shown that structures had the fast excitonic band with the decay time from 0.25 ns (for sample with 10 QWs) to 1.1 ns (for sample with 60 QWs). In conclusion, we have reported InGaN/GaN structures with the highest QW number and active region thickness, but for reaching 1 µm thick active region we cannot increase only number of QWs because V-pits of the high QW number structures are too big, but we will have to find a way how to control V-pits size. The paper was published in CrystEngComm (IF = 3.38, Q1, 2 citation).



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Advancement toward ultra-thick and bright InGaN/GaN structures with a high number of QWs†

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InGaN/GaN multiple quantum well structures are studied as potential candidates for superfast scintillation detectors and show the leading decay time of around 1 ns and intense luminescence. Photoluminescence properties of these structures with quantum well (QW) numbers ranging from 10 to 60 are described and discussed. It is shown that with increased QW number, the luminescence efficiency of the whole structure increases due to the V-pits of a sufficient size suppressing non-radiative recombination. Suppression of the non-radiative recombination near dislocations is demonstrated by the cathodoluminescence measured at different acceleration voltages. The optimal V-pit size is found to be in the range from 200 to 300 nm, which is obtained for structures with 40 QWs. On the other hand, when the V-pit size exceeds the optimal value, the PL intensity decreases by strong V-pit coalescence, which is observed for structures with 60 QWs. For further increasing the active region thickness, which helps to enhance the detection efficiency of high-energy irradiation, it is necessary to find a way to control the V-pit size. Excitation–emission maps are measured to elucidate how efficiently the structures are excited depending on the light wavelength and the QW number. It is shown that the wavelength for most efficient excitations of InGaN/GaN QWs is 362 nm. With increasing number of QWs, their fast excitonic luminescence is considerably enhanced, whereas slow defect band luminescence is suppressed. Time-resolved measurements with soft X-ray excitation also support our conclusions, showing suppressed non-radiative recombination for structures with higher QW numbers. The fastest decay component increases from 0.25 ns for a structure with 10 QWs to 1.1 ns for a structure with 60 QWs.

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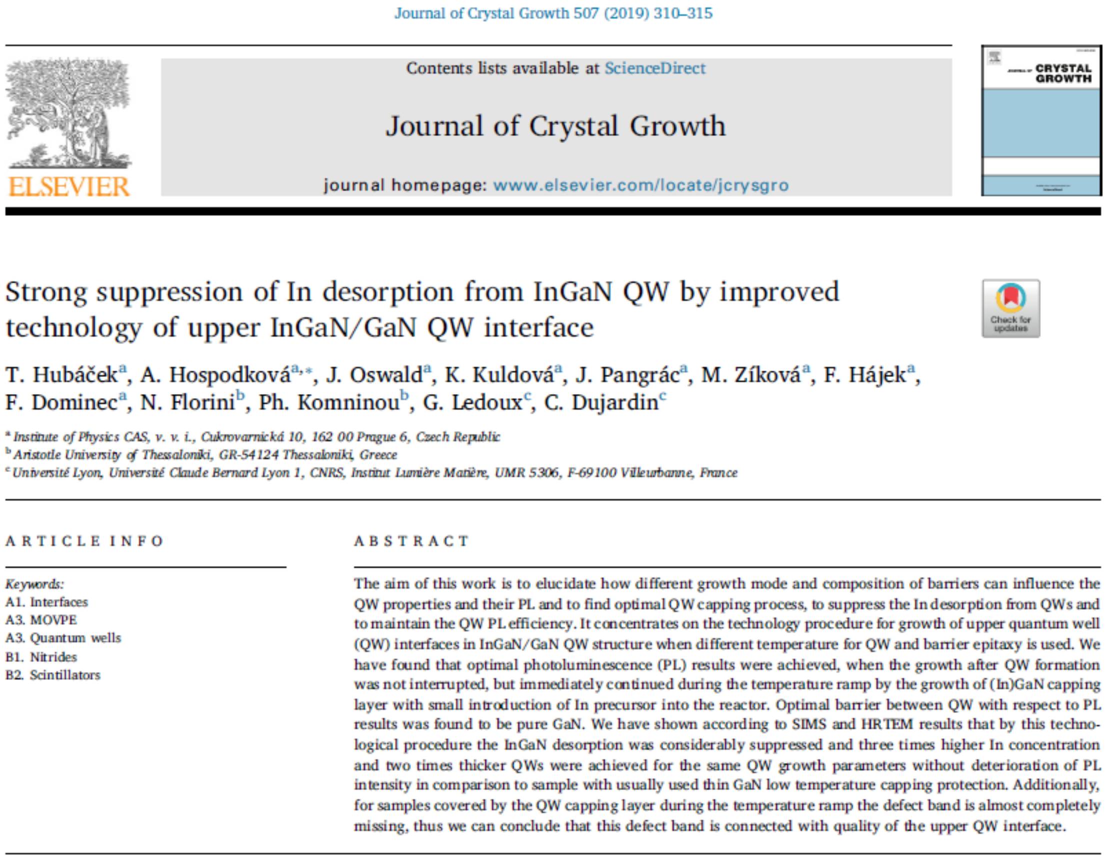
4.7 Strong suppression of In desorption from InGaN QW by improved technology of upper InGaN/GaN QW interface [vii]

The growth of upper interface between InGaN QWs and GaN barriers is always a challenge because different growth temperature is needed, which causes many problems, such as indium desorption during the temperature ramp or worse quality of GaN barrier. Many approaches of the growth were published, such as growth interruption or growth of low temperature thin GaN cap layer. We have compared different growth modes in this publication and studied their effect on the luminescence properties. From the PL point of view, we have found that the best technology was when the growth was done without any growth interruption and a small amount of indium was added during the temperature ramp and consequently barrier was pure GaN. Moreover, for the increase of indium in InGaN layers was very sufficient approach of adding indium during the temperature ramp. It increased indium concentration in InGaN in our structures three times, so we were able to grow InGaN QWs at higher temperature then other group with the same indium concentration of InGaN layers and with better quality. Moreover, structure with such increased indium content showed much smaller intensity of defect band. This result is very important for our scintillation applications, where defect band deteriorates our effort. These results confirmed the hypothesis about the source of the defect band from the previous works (recombination between holes confined in QWs and electrons trapped in defect state in the upper InGaN/GaN interface). The growth technique described in this article was successfully patented. The paper was published in Journal of Crystal Growth (IF = 1.57, Q3).



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Strong suppression of In desorption from InGaN QW by improved technology of upper InGaN/GaN QW interface

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B2. Scintillators

ABSTRACT

The aim of this work is to elucidate how different growth mode and composition of barriers can influence the QW properties and their PL and to find optimal QW capping process, to suppress the In desorption from QWs and to maintain the QW PL efficiency. It concentrates on the technology procedure for growth of upper quantum well (QW) interfaces in InGaN/GaN QW structure when different temperature for QW and barrier epitaxy is used. We have found that optimal photoluminescence (PL) results were achieved, when the growth after QW formation was not interrupted, but immediately continued during the temperature ramp by the growth of (In)GaN capping layer with small introduction of In precursor into the reactor. Optimal barrier between QW with respect to PL results was found to be pure GaN. We have shown according to SIMS and HRTEM results that by this technological procedure the InGaN desorption was considerably suppressed and three times higher In concentration and two times thicker QWs were achieved for the same QW growth parameters without deterioration of PL intensity in comparison to sample with usually used thin GaN low temperature capping protection. Additionally, for samples covered by the QW capping layer during the temperature ramp the defect band is almost completely missing, thus we can conclude that this defect band is connected with quality of the upper QW interface.

5 Conclusions

This doctoral thesis was devoted to the growth of InGaN/GaN multiple quantum well nanoheterostructures with MOVPE technology. Based on theoretical predictions, these structures should be useful as a very fast and efficient scintillation detector. It should be used especially in fast-timing applications because of its sub-nanosecond excitonic decay time. Therefore, we have modified commonly used blue LED nitride structure to get thick active MQW region as much as possible and obtain very fast excitonic decay time around 1 ns and luminescence spectra without any slow defect bands. Presented results in this thesis showed real possibility of using MOVPE grown InGaN/GaN structures as efficient and fast scintillation structures. The first tests and comparison (made in CERN) of different nanoscintillators (our MQW structures, ZnO:Ga and CdSe/CdS) showed that our structures present the best mechanical and optical properties. From all tested samples only our structures gave light yield comparable to LYSO:Ce [57]. That is a promising result for future work in the field of fast timing applications.

Perfect initial part of GaN growth on sapphire substrate predestines the whole scintillation structure quality for this application. Nucleation and coalescence layer growth on sapphire substrate was investigated at the beginning of our work. Suppression of yellow band and increase of the excitonic band was achieved by proper growth conditions, such as high growth pressure during nucleation or lower NH_3 flow during coalescence of islands. The next part of the structure, which is n-type GaN layer, was optimized as well with respect to suppression of YB intensity. Significant suppression of YB was achieved with TEGa precursor which was used instead of usual TMGa precursor. It was found that different growth conditions have to be used, such as N_2 carrier gas, higher V/III ratio or slower growth rate.

Luminescence spectra of our InGaN/GaN scintillation structures contain fast excitonic band originating from QWs and defect band which is related to QWs (assumption coming from the observation that it shifts with the position of QWs). We were not able to eliminate this kind of defect band during our work but we have suggested its origin. Influence of n-doped GaN layers surrounded MQW region on PL properties was studied. Different position of n-doped GaN layer changes internal electric field resulting in different tilting of the band structure. Theoretical simulations and PL results suggested that the defect band may originate in recombination between holes confined in QWs and electrons trapped in some defect state in the upper InGaN/GaN interface. Different growth modes of the upper interface were also investigated and results supported our hypothesis about the origin of QW defect band. Special growth of the upper interface, when after InGaN QW is without interruption grown cap layer (during the temperature ramp) and consequently grown barrier, was successfully patented. Unfortunately, the source of the defect state in the upper interface was not established up to now and defect band observed in luminescence spectra was still not fully eliminated.

Finally, we have confirmed the positive role of V-pits on the luminescence properties which was suggested in the literature. On the other hand, their positive influence can be seen when the size of V-pits is not higher than 300 nm in diameter. LED community usually does not reach such big V-pits, but for our scintillation structure, it is the limitation. We found out that bigger V-pits influence negatively the luminescence properties of our structures. Different approach or a way to control the size of V-pits will have to be found to get more than 1 μm thick active region with sufficient luminescence quality.

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