STABILIZATION OF INDIUM-RICH IN_{1-X} Ga_{X}N HETEROSTRUCTURES - THE EXPLORATION OF A C

Nikolaus Dietz
GEORGIA STATE UNIVERSITY RESEARCH FOUNDATION INC.

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Final Report

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Stabilization of indium-rich In1-xGaxN heterostructures: the exploration of a common processing window

During the grant period, the growth and optimization of indium-rich InGaN layers grown by high-pressure metalorganic chemical vapor deposition (MOCVD) was explored at reactor pressures from 5 to 20 bar and at growth temperatures of 700-900°C. The goal was to evaluate the reactor pressure and growth temperature relation at which indium-rich In1-xGaxN layers can be stabilized. The results showed that for a pressure at 15 bar, the growth temperatures for InGaN varies from 850°C (InN) to 950°C (In0.7Ga0.3N), reducing the temperature gap in the ternary InGaN system compared to low-pressure MOCVD. An unexpected effect was the significant reduction in growth rate with increasing reactor pressures, which is due to smaller surface diffusion layers with incr. pressures. The results on forming single phase InGaN alloys using simultaneous and sequential group-III precursor injection sequences worked only partially: We obtained single phase alloys for In1-xGaxN [0<x<0.15] and [0.25<x<0.3] but mixed phases between. The experiments indicate the presence of Ga- and In-adlayers that may play a major role for the observed mixed InGaN phases. Additional studies will be needed to relate the precursor deployment with surface decomposition and surface chemistry processes.

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<td>Dr. Kenneth C. Goretta AFOSR/RTD</td>
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Final Report on AFOSR Grant FA9550-10-1-0097

Stabilization of indium-rich InGaN heterostructures: the exploration of a common processing window

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Abstract
During the grant period, the growth and optimization of indium-rich In_{1-x}Ga_xN layers grown by high-pressure metalorganic chemical vapor deposition (MOCVD) was explored at reactor pressures from 5 to 20 bar and at growth temperatures of 700-900°C. The goal was to evaluate the reactor pressure and growth temperature relation at which indium-rich In_{1-x}Ga_xN layers can be stabilized. The results showed that for pressures around 15 bar, the growth temperatures for InGaN varies from 850°C (InN) to 950°C (In_{0.7}Ga_{0.3}N), significantly reducing the temperature gap in the ternary InGaN system compared to low-pressure MOCVD. An unexpected side effect found was the significant reduction in growth rate with increasing reactor pressures, which is due to smaller surface diffusion layers at higher pressures. The results on forming single phase indium-rich ternary InGaN alloys using simultaneous and sequential group-III precursor injection sequences was only partial successful: We obtained single phase alloys for In_{1-x}Ga_xN [0 < x < 0.15] and [0.25 < x < 0.3] but observed mixed phases for compositions between for the digital alloying concept explored. The experiments indicate the presence of Ga- and/or In-adlayers - and oscillations between them – that may play a major role for the observed mixed InGaN phases. Additional studies will be needed to obtain a better understanding on how the deployment of precursors to the surface relates to the surface decomposition and chemistry processes that influence the Ga- and In-fragment incorporation and the subsequent InGaN phase formation.
Outline of the report

Accomplishments - Summary

I. HPCVD growth of indium-rich InGaN epilayers – Background/Motivation

II. Accomplishments: Growth of InN and InGaN under HPCVD conditions

III. Patent, Theses, Publications and Presentation of research results

III.1 Patent filed

III.2 Completed theses

III.3 Referred Publications

III.4 Presentations at conferences/seminars

Accomplishments - Summary

During the reporting period, we explored the growth parameter space for indium-rich In$_{1-x}$Ga$_x$N layers growth under sequential metalorganic precursor injection and compared the results with simultaneous metalorganic precursor injection, performed in the previous years. The reactor pressure was kept between 8 and 15 bar, with growth temperatures ranging from 700°C - 900°C, depending on the targeted gallium content, which was varied from $x=0.0$ to $x=0.4$. The epitaxial growth was carried out on Sapphire substrates, GaN/Sapphire- and InN/GaN/Sapphire templates.

The growth and analysis of the In$_{1-x}$Ga$_x$N epilayers showed that the growth temperature for InN can be increased by 120°C as the reactor pressure increases from 1 to 18 bar. For In$_{0.85}$Ga$_{0.15}$N the growth temperature increases by 110°C in the same pressure range. At the same time however, the growth rate linearly decreases with a slope of 5.6 nm/h for each bar of reactor pressure increase. Significant progress has been made in the growth of InN epilayers grown with various nucleation conditions in order to improve the InN/GaN/Sapphire templates used for InGaN growth. The structural quality of the InN templates varied from 200 to 150 arcsec for the full-width-half-maximum (FWHM) values of the InN(0002) Bragg reflex. The photoluminescence (PL) from these epilayers showed emission peak maxima varying from 0.7eV to 0.95 eV depending on the free carrier concentration analyzed to Fourier transform infrared (FTIR) spectroscopy. The limiting factor in reducing the free carrier concentration in these layers is related to residual oxygen-contamination during the sample loading in at the present reactor, even after an improvised nitrogen glove box attached to the reactor during the loading process was used.

Ternary In$_{1-x}$Ga$_x$N layer growth studies to achieve single-phase alloys showed that the pulse separation between the ammonia and the group III-precursor pulse has to be increased with increasing TMG concentration. These studies suggest that the surface reaction chemistry for the group III-precursors - TMI and TMG - differs significantly and contribute to the observed phase instabilities. We explored therefore the growth of ternary In$_{1-x}$Ga$_x$N alloys with simultaneous and sequential Indium and Gallium MO injections. A significant effort was dedicated to formulate and rewrite the reactor control software, allowing the sequential indium and gallium precursor injection - denoted as digital alloy injection approach.

The analysis of the In$_{1-x}$Ga$_x$N layers grown with this approach showed improved structural quality with no phase segregation observed below 15% gallium incorporation. However, InGaN layers with gallium incorporation higher than 15% showed small second phases, indicating that the parameter space explored so far was not sufficient to eliminate the gallium and/or indium adlayer formation at the growth interface, responsible for the InGaN phase segregation in the grown bulk layers. This can be addressed by expanding the parameter space, evaluating a larger process parameter window that includes pulse separation times, precursor fluxes and flux ratio,
or reactor nitrogen pressures in order to stabilize the difference partial pressures above indium-rich and gallium-rich growth surfaces.

As shown in this final report, substantial progress has been made in the structural quality of indium-rich In$_{1-x}$Ga$_x$N epilayers. The HPCVD system employed narrows the presently encounters growth temperature gap by suppressing the decomposition of indium-rich alloys at growth temperatures required for wider band-gap group III-nitrides. Employed real-time optical diagnostics such as Principal-angle-reflectance (PAR) spectroscopy have been utilized to analyze the surface chemistry during nucleation and steady state growth at a sub-monolayer level. Laser light scattering (LLS) was applied to characterize the surface morphology during nucleation and growth. These techniques provided critical insights into gas phase and surface chemistry processes during the HPCVD growth process and helped to adjust the growth process parameters. Further studies are needed to improve the structural, optical and electrical properties of ternary In$_{1-x}$Ga$_x$N layers. At this point, we demonstrated that the HPCVD approach allows the stabilization of highly volatile constituents/alloys such as encountered in the growth of indium-rich In$_{1-x}$Ga$_x$N epilayers under process conditions not possible by MBE or low-pressure MOCVD.

**Highlights:**

- During the research program, three graduate students completed and received their PhD degree and four graduate students completed their MS degree (see section III.2). Three students are still working on various aspects related to this research.
- The research results have been published in 19 referred publications and have been presented in 10 invited publications, 35 oral conference contributions, and 18 conference poster presentations (see section III.3).
- A full national and international patent application, entitled "High pressure chemical vapor deposition apparatuses, methods, and compositions produced therewith," has been filed Aug. 12, 2010 (after provisional filing in Aug. 2010). This patent application describes critical design aspects of a next generation of HPCVD reactor, which integrates discoveries related to research supported during this research program.
- We showed that HPCVD enables the successful growth of high crystalline quality layers of InN on sapphire and GaN/sapphire templates. At a reactor pressure of 15 bar, the growth temperature for InN can be raised to about 850°C. Detailed studies were carried out on the precursor pulse separations and correlated to the crystalline quality of the epilayer. We also carried out extended studies on the optimum group V/III precursor ratio and its influence and the surface chemistry, crystalline quality and the reduction of the free carrier concentration in the layers. A large difference in free carrier concentrations in layers grown on GaN/sapphire templates compared to InN layers grown directly on sapphire was observed.
- The growth results on indium-rich In$_{1-x}$Ga$_x$N alloys showed that macroscopic single phase InGaN epilayers can be stabilized. However, significant broadening of the FWHM values in the XRD Bragg reflexes indicate high point defect densities. At present the process conditions have to be adjusted of each composition region in order to stay single phase, requiring more detailed microscopic structural and optical defect studies on potential compositional fluctuations.
- In the compositional region 0.3<x<0.4 of In$_{1-x}$Ga$_x$N, a significant reduction of the measured free carrier concentration is observed. The reason is not clear and further experimental studies are needed.
I. High-pressure chemical vapor deposition (HPCVD) growth of indium-rich InGaN epilayers

However, all presently employed low-pressure deposition techniques encounter significant temperature gaps in the growth of binary group III-nitrides. For instance, the optimum growth temperatures of InN and GaN differ by more than 300°C under low-pressure organometallic chemical vapor deposition growth conditions. Such a temperature gap severely limits the ternary InGaN alloy formations and their integration in wider band-gap alloys that have to be grown at higher growth temperatures. One consequence of this problem is discussed in the context of spinodal decomposition/compositional fluctuations in the ternary InGaN\(^{1-8}\) system – an added problem to compositional induced lattice strain, interfacial piezoelectric polarization effects, and extended defect related effects that have to be addressed.

A potential pathway to address and overcome the difficulties associated with the phase stability, stoichiometry fluctuations and the growth temperature gap between the group III-N binaries, is to assess the pressure dependency of surface chemical reactions and growth surface stabilization, one potential pathway explored at GSU.

High-pressure chemical vapor deposition (HPCVD): Motivation and History

Research on extending OMCVD to super-atmospheric pressure is motivated by the sensitive relation between the properties of compounds and their native defect chemistry. In turn, the defects depend on the control of compound stoichiometry, that is, on the partial pressure of volatile constituents in thermal equilibrium. For many materials utilized in today’s industry, the decomposition pressures are sufficiently low to permit processing at reduced pressure, which avoids fluid dynamics perturbations of process uniformity. However, there are important merging materials systems, where stoichiometry control is limited under conditions of low total pressure. For example, limitations are encountered at present in the control of the stoichiometry and defect formation for InN and indium-rich group III-nitride solid solutions in processing at reduced pressure, due to the high decomposition pressure and their vastly different partial pressures. MacChesney et al.\(^9\) assessed within the thermodynamic limitations the growth of high-quality InN, suggesting that high pressures are needed to stabilize the compound. The calculation indicated that substantial nitrogen pressure is required to prevent thermal decomposition of bulk InN, a relationship captured by

\[
p(N_2) \rightarrow p_0 \exp \left[ \frac{-H_r}{R} \left( \frac{1}{T} - \frac{1}{T_0} \right) \right],
\]

which results in the p-T\(^{-1}\) relation shown in Fig. 1\(^9\). This relation suggests that, for pressures \(p_{N_2} \leq 10^2\) bar and substrate temperatures \(\leq 900\) K, the surface decomposition of InN can be effectively suppressed. Also, recent studies in the indium-gallium-nitrogen system\(^{10}\) show much uncertainty in the p-T-x relations (where x stands for Ga/In ratios) due to missing experimental validation.

Even though the transition from bulk crystal growth techniques towards thin film growth techniques (e.g., MBE, MOCVD, MOVPE, CVD, etc.) opens unique off-equilibrium approaches to stabilize growth surfaces at temperatures and pressures not possible otherwise, the integration of such highly dissimilar alloys remain a main challenge due to mismatched processing windows or stoichiometric instabilities and low dissociation temperatures that may lead to inconsistent and process dependent material properties.
Keeping this in mind, Dr. Bachmann and Dr. Banks at North Carolina State University (NCSU) addressed this problem in 1995, in a MURI research program entitled "Modeling and Control of Chemical Vapor Deposition Processes: The Control of Defects in Mixed III-V Compound Heterostructures," and started the modeling and design of reactor systems, suitable to operate at elevated pressures,\textsuperscript{11-15}, an effort which was funded by AFOSR under DOD-MURI F49620-95-1-0447.

![Graph: Thermal decomposition pressure vs. reciprocal temperature for AlN, GaN and InN.]

The research program simulated and analyzed various reactor geometries and provided a theoretical assessment of a well-suited high-pressure CVD flow geometry. Based on the predictions, a flow channel reactor design was singled out. The experimental constructed differential HPCVD reactor system is depicted in Fig. 2. In order to confine pressures up to 100 bar, a large outer pressure confinement vessel was required, which made its operation very cumbersome and difficult to control. However, over the three years of operation, significant experience was gained in assessing the flow kinetics of the flow channel and the pressure balancing requirements during inserting of precursor plugs in the gas carrier stream. The knowledge accumulated during this time led to the design of a 2nd-generation reactor, the construction of which Drs. Bachmann and Dietz started in 1998. The PI completed the reactor at GSU 2001. The involvement of the PI in the MURI project focused initially on the development of real-time process monitoring\textsuperscript{16-18} and control methodology\textsuperscript{18,19} using Ga\textsubscript{1-x}In\textsubscript{x}P as an example\textsuperscript{20-23}. The involvement expanded as the PI closely interacted with Dr. Bachmann in the design and construction of a compact HPCVD reactor, which is schematically shown in Fig. 3. Besides of the drastic reactor size reduction, the most significant advances implemented in the 2nd-generation of HPCVD system were

\begin{itemize}
  \item[a)] a reduction of the flow channel height from 10 mm to 1 mm,
  \item[b)] a symmetric flow channel and substrate arrangement, and
  \item[c)] the integration of optical diagnostics for gas phase and growth surface analysis.
\end{itemize}

A more detailed description of the reactor design and the optical characterization capabilities can be found at \texttt{http://www.phy-astr.gsu.edu/dietzrg/HPCVD.html}.

The construction of the compact HPCVD reactor was completed at GSU with support of NASA Grant# NAG8-1686 (from 2000 to 2006; Dr. Bachmann was Co-PI on the project and he retired}
with a main emphasis on demonstrating the flow kinetics and abilities of the real-time growth diagnostics.\textsuperscript{24-27}

Fig. 2: \textbf{a)} 1\textsuperscript{st} generation HPCVD reactor assembly constructed at NCSU in 1996. B = Base Plate; C = 2nd Confinement Shell; R = Fused Silica Reactor; 1&2 = Window Connections for PRS Laser Beams; RF = Radio Frequency Coil; 3&5 = Process Gas Inlet & Outlet; 4 = Tube on R For substrate wafer exchange. \textbf{b)} top view of inner flow channel assembly.

Fig. 3 \textbf{a)} 2\textsuperscript{nd} generation HPCVD reactor assembly. The flow channel is designed with a constant cross sectional area for the maintenance of laminar flow and the substrates are embedded in ceramic plates; \textbf{b)} Schematic cross section of the reactor containing the optical access ports and the center of the substrates. Optical ports provide access to the flow channel and to the growth surface.
Accessing the growth regime at super-atmospheric pressures brings significant challenges in suppressing gas phase reactions, while controlling the nutrient support through a reduced diffusion layer to the growth surface and optimizing the growth surface chemistry. An essential component in the exploration of high-pressure CVD growth is the integration of real-time optical characterization techniques that allow to monitor and analyze the gas flow kinetics, the precursor decomposition dynamics, as well as growth surface reactions. The PI has a long track record of developing optical diagnostic tools\textsuperscript{28,55,23} and of applying them for real-time process monitoring\textsuperscript{23} and process control\textsuperscript{18,19}. For high-pressure CVD, the PI integrated principal angle reflectance spectroscopy (PARS)\textsuperscript{30} - a derivation of p-polarized reflectance spectroscopy (PRS)\textsuperscript{16}, which is able to follow the film growth process with sub-monolayer resolution. The link between the surface sensitive PARS response to the gas phase analysis via ultra-violet absorption spectroscopy (UVAS) allows for the link between gas phase decomposition kinetics and surface chemistry processes, which will provide critical insights in the film growth process at high pressures. With support by AFOSR (award# FA9550-07-1-0345), the PI focused in recent years on the optimization of InN and indium-rich InGaN growth in the pressure regime of 5 to 15 bars, the results of which are presented in more details below.

\textbf{InN and InGaN specific material challenges:}

InN is predicted to have an electron affinity of 5.8 eV, the largest of any known semiconductor\textsuperscript{31}. The consequences of the large electron affinity of InN and indium-rich InGaN can be considered within the amphoteric defect model (ADM). Within the ADM, the formation energy of native defects depends on the location of the Fermi energy ($E_F$) with respect to a common energy reference, the Fermi stabilization energy ($E_{FS}$). Therefore, native donor formation is predicted to be dominant in InN and indium-rich InGaN. The low formation energy of native donor defects in InN and indium-rich InGaN creates challenges for producing p-type materials\textsuperscript{32}. Degenerate doping may be a solution to achieve p-type InN and indium-rich InGaN, due to the high n-type background of undoped InN.

The pulsed precursor injection scheme employed in HPCVD to minimize gas phase reactions bears also significant advantages for the prevention of phase segregation and for the exploration of the surface chemistry during growth. An important research aspect is the study and
understanding of the growth kinetics on a micro-/nanometer scale, in order to develop an optimum pulse timing. Once this understanding is established, it can be applied to the digital alloying of InGaN, which will not only allow the prevention of phase segregation but also the fabrication of III-nitride superlattices\textsuperscript{33,34}.

For the fabrication of indium-rich In\textsubscript{1−x}Ga\textsubscript{x}N alloys and embedded heterostructures, the thermal stability of InN and indium-rich alloys at growth temperatures that are compatible with GaN growth conditions, needs to be advanced. Our initial InGaN growth results in the pressure regime up to 15 bars indicate that pressures above 20 bars may be required - a regime that provides some technical challenges and has not been investigated to date. In this pressure regime, the role of turbulent gas flow becomes decisive.

Another critical issue is the type of growth mode: 2-dimensional (2-dim) versus 3-dimensional (3-dim) film growth. In 2-dim growth mode, material is deposited layer-by-layer. On the other hand, 3-dim growth consists of formation of islands and their subsequent coalescence. The latter results in grain boundaries that detrimentally influence the topographical and electrical properties of the deposited epilayer, e.g., carrier mobility and free carrier concentration\textsuperscript{35}. Good topographic properties of Ga\textsubscript{1−x}In\textsubscript{x}N layers (i.e., a smooth surface) are essential for the fabrication of heterostructures. Benchmarks of 3-dim growth are the size, shape, height and density of the islands.

The growth mode during the initial stage of epitaxy (nucleation) is of particular interest, as the quality of the epilayer is governed by the quality of the nucleation layer. Therefore, a good understanding and control of the nucleation and nuclei coalescence is decisive. Moreover, the growth of In\textsubscript{1−x}Ga\textsubscript{x}N alloys brings along the issue of phase segregation and spinodal decomposition. The here explored high-pressure CVD approach is promising for enabling new Ga/In ratios (i.e., new x values) that have not been achieved before. Thus phase homogeneity becomes a very important goal of our work. Finally, new alloys may exhibit new defects related to ordering processes in a microscopic scale or cubic/wurtzite lattice instabilities. A careful analysis and identifications of such defects is required. A major effort in our research will pursue a deep understanding of occurring defects, how they differ as a function of growth pressure, and how they affect the materials properties. A beneficial effect of HPCVD is the potential decrease in the native point defect concentrations with increased growth temperature at higher reactor pressures.

The epitaxial growth of ternary III-V systems is characterized by the segregation of one of the constituent column III element at the growth front and at the interfaces with the binary material. This segregation results in poor composition profiles and poor interfacial width control. Chemical stability can be influenced by several factors, a number of which have been explored in the literature, such as heat of formation, ion size, and interfacial strain. The driving force for this segregation in InGaN can be considered to be a replacement reaction of Ga for the In in the substrate. The heat of formation for GaN is –156.8 kcal/mole whereas that for InN is –28.6 kcal/mole. The ejection of In from an underlying InGaN layer with Ga deposition thus results in a lower free energy for the surface. The transport of In to the surface is mediated by the surface exchange of Ga for In. The lower free energy of the GaN layer accounts for the asymmetry in the In diffusion profile with growth order in compositional modulated structures. This preferential segregation may be limited by migration enhanced epitaxy techniques in MBE and by variation of the III/V ratio in MOCVD and CBE. Segregation is also seen with annealing processes and current injection techniques.

Other aspects of scientific interest arise from the strong polarity of Group III-nitride crystals. A higher concentration of indium in InGaN/GaN quantum wells (QW) results in more strain and
more polarization. The quantum confined Stark effect (QCSE) is caused by spontaneous polarization and by a strain induced piezoelectric field. Increasing the indium composition increases the piezoelectric field. The resulting QCSE will cause a blue shift at high current densities moving further away from the desired wavelength, and at lower current densities, efficiency will be low due to charge separation.

The challenges given by the stabilization of indium-rich group III-nitride alloys and embedded heterostructures in wide bandgap group III-nitrides (e.g., In$_{1-x}$Ga$_x$N) can be addressed by the PI’s successful development of an advanced 2nd-generation version of the high-pressure growth reactor capable of operating at pressures of up to 100 bar. The pulsed injection of precursor gases is a prerequisite for high-pressure operation and, at the same time, it facilitates control of the growth process on sub-monolayers, as well the thorough investigation of surface processes during growth.

II. Accomplishments

*Growth of InN and InGaN under high-pressure CVD conditions*

**InN layer characterization**

A promising approach to tackle the challenges outlined in the previous section has been developed by the PI at Georgia State University. A unique high-pressure chemical vapor deposition (HPCVD) reactor allows the extension of the thin film growth parameter space by utilizing the pressure dependency of chemical reactions. Growing indium-rich In$_{1-x}$Ga$_x$N alloys at high pressures and high temperatures (T > 850 °C) is promising since this approach may overcome problems of off-equilibrium techniques arising from different partial pressures and low growth temperatures. Over the last years our research group demonstrated the capability of HPCVD to produce high-quality, single-phase InN layers. The InN layers exhibit XRD (0002) Bragg reflexes with a full width at half maximum (FWHM) at 150 arcsec and rocking curve values around 1600 arcsec. Further rocking curve analysis for the symmetric and skew-symmetric reflections indicate that within the experimental resolution - InN grew single phase and epitaxially on the GaN template. A reciprocal XRD map scan shows a nearly relaxed InN epilayer on top of GaN.

**InGaN layer characterization**

High quality InGaN layers were achieved for growth temperatures in the range of 830°C to 850°C, which is about 250°C higher than under low-pressure OMCVD conditions. As depicted in Fig. 5, the growth temperatures of InN and InGaN can be increased by more than 120°C in the pressure regime between 1 and 20 bar, which is a significant advantage over conventional low-pressure metalorganic chemical vapor deposition (MOCVD or OMCVD), where the growth temperatures are around 650 °C. For InGaN, the increase of growth temperature as function of reactor pressure decreases due to the reduced temperature gap between InGaN and GaN. Therefore the MOCVD reactor pressure (high-pressure versus low-pressure) is critical balance between the partial pressures of the alloy compositions that have to be integrated / stabilized at a specific growth temperature.
Figure 5: Growth temperature versus reactor pressure for the growth of InGaN epilayers in HPCVD growth conditions (see text). The increased growth temperature narrows the processing gap between the binaries InN and GaN.

The XRD analysis for selected indium-rich In$_{1-x}$Ga$_x$N layers from 0 < x < 0.65 are summarized in Fig. 6. Under these pressure and temperature conditions, macroscopic InN-InGaN phase segregations have been observed in the compositional regime 0.1 < x < 0.30, while macroscopic a single-phase material can be obtained in the compositional regime 0.3 < x < 0.65. The $\omega$-scan InGaN(0002) rocking curve analysis reveals FWHM's around 5000 – 7000 arcsec (x=0.31), indicating a high density of point defects and dislocations.

Figure 6: In$_{1-x}$Ga$_x$N(0002) Bragg reflexes of XRD 2Q-w scans for In$_{1-x}$Ga$_x$N layer grown by high-pressure CVD at 850°C and 15 bar reactor pressure.

The In$_{1-x}$Ga$_x$N phase segregations observed differ for In$_{1-x}$Ga$_x$N growth on GaN versus sapphire, indicating that not only the pressure/temperature processing parameter contributes to the
segregation process. Potentially, induced lattice strain, interfacial piezoelectric polarization effects, and extended defects may contribute to the compositional fluctuations.

To improve the thermal stability of indium-rich alloys at the desired growth temperatures that are compatible with GaN growth conditions, the growth may have to be expanded to reactor pressures well above 20 bar. Even though this pressure regime inevitably leads to turbulent growth flow conditions, the potential benefits will be the merged temperature processing window that allows the fabrication of indium rich In$_{1-x}$Ga$_x$N alloys with wider bandgap group III-nitride layers, an essential step for many of the envisioned device structures.

**Indium add-layer problem**

The indium adlayer formation$^{42-44}$ during InN and InGaN growth is a well-known phenomenon. Its ability to act as surfactant has been described for the AlGN/GaN heterostructure growth.$^{45}$ Figure 7 shows the 2Θ-ω XRD scans for a InN layer grown on a GaN template before and after etching in a HCl:H$_2$O (1:10) solution. The In(101) Bragg reflex disappears after typically 2 min etch time, indicated the complete removal of the surface indium.

For the growth of InGaN and InGaN/GaN heterostructures, however, it has to be avoided, requiring precise adjustments of the surface chemistry (precursor pulse separation, growth temperature, reactor pressure). Initial studies during InN growth showed that the indium adlayer formation can be suppressed by adjusting the precursor injection sequence. Detailed studies are required to optimize the surface chemistry for each InGaN target composition.

![Figure 7: XRD Bragg reflex of InN(101) is related to an indium adlayer formed during InN growth on a GaN template. The indium add-layer is completely removed by a 2 min HCl:H$_2$O (1:10) etch.](image)

**2.3.2 Real-time growth control and optical growth monitoring**

The progress in understanding and controlling thin film growth processes has been very slow, considering how little is known about chemical reaction pathways and reaction kinetics parameters during the decomposition process of the metal-organic (MO) precursors. These demands led to the development of advanced surface-sensitive optical diagnostics that can be integrated in CVD reactors$^{46,47,23,26}$. These diagnostic techniques move the monitoring and control point close to where the growth occurs which, in a chemical beam epitaxy process, is the surface reaction layer, built up of physisorbed and chemisorbed precursor fragments between the ambient and film interface. In recent years, we developed and explored p-polarized reflectance...
spectroscopy (PRS)\textsuperscript{23,16,48} as a highly surface sensitive sensing technique, and demonstrated the closed-loop control of deposition processes at low pressure pulsed chemical beam epitaxy\textsuperscript{22}. With advancing progress in the growth of indium-rich In\textsubscript{1-x}Ga\textsubscript{x}N, the employed optical real-time monitoring techniques will allow for the investigation of fundamental questions regarding surface chemistry. In this context, the competing incorporation of In and Ga atoms is of particular interest for an understanding of compositional questions and segregation processes. During the growth of In\textsubscript{1-x}Ga\textsubscript{x}N/GaN heterostructures, we will be able to investigate the physical and chemical processes during the transition from indium-rich to gallium-rich In\textsubscript{1-x}Ga\textsubscript{x}N layers which govern the quality of such heterostructures and which will bring upon clarity about the interfacial phenomena discussed above.

The HPCVD reactor utilizes real-time optical diagnostic techniques - as well as a pulsed precursor injection scheme - to gain insights and to control the gas phase and surface chemistry processes that govern the growth of indium-rich group III-nitride alloys. This is of crucial importance for understanding and controlling their materials properties. We deployed “principal angle reflectance spectroscopy” (PARS),\textsuperscript{30} and ultra-violet absorption (UVA) spectroscopy to analyze the kinetics of gas phase constituents above the growth surface.\textsuperscript{26} The link between the surface sensitive PARS response to the real-time gas phase analysis (UVAS) provided insights in the gas phase decomposition kinetics, surface chemistry processes, and the film growth process at high pressures. Advanced growth models as established for the growth of GaInP\textsuperscript{23} is essential for the exploration of high-pressure growth process parameters. Adjusting the pulse separations between the precursors - as well as the length of each precursor pulse - are additional process control parameters that can be utilized in optimizing surface chemistry and materials properties.\textsuperscript{49}

**InGaN gas phase and surface chemistry at elevated reactor pressures**

The formation of In\textsubscript{1-x}Ga\textsubscript{x}N ternary alloys in the whole composition range is of great interest, since it would allow to tune the direct bandgap from the near infrared (InN around 0.7 eV) to the near UV wavelength regions (GaN at 3.5 eV). However, experimental and theoretical predictions indicate that the In\textsubscript{1-x}Ga\textsubscript{x}N ternary alloys might be unstable with a tendency toward clustering and phase separations.\textsuperscript{50} For instance, it is well known that indium phase separation (or fluctuation) induced localized states in the InGaN layers play major roles in achieving highly efficient blue and green InGaN multiple quantum wells (MQW). The large differences in the tetrahedral radii between InN and GaN may induce strain that can either lead to the formation of particular sublattices (phase separations) or to an atomic ordering within the sublattice, resulting in a deviation from homogeneity (nano-clustering).\textsuperscript{51,50}

Nevertheless, the growth of single phase In\textsubscript{1-x}Ga\textsubscript{x}N alloys by rf-PMBE at growth temperatures between 400-435°C has been demonstrated by Iliopoulos et al.\textsuperscript{52} in the entire composition range, which suggests that under proper processing conditions, clustering and phase separations in the ternary InGaN alloy system can be suppressed. Under low-pressure MOCVD growth conditions with typical growth temperatures between 700 and 800 °C, metastable In\textsubscript{1-x}Ga\textsubscript{x}N alloys are predicted for regions of low and high gallium concentrations (0.94>x<0.64 and 0.1>x<0.3) and compositional unstable In\textsubscript{1-x}Ga\textsubscript{x}N alloy regions, where phase separations occur due to spinoidal decomposition.\textsuperscript{50} Contrary to these predictions, recent In\textsubscript{1-x}Ga\textsubscript{x}N layers grown by MOCVD indicate that single phase In\textsubscript{1-x}Ga\textsubscript{x}N alloys in the compositional range 0.33 > x < 0.75 can be achieved by adjusting the growth temperature as function of composition.\textsuperscript{53,54}

The question left open is to which extend a processing window exists where In\textsubscript{1-x}Ga\textsubscript{x}N layers with different compositions can be stabilized at the same growth temperature. The high-pressure
CVD reactor system - together with the digital injection system – explored in this research indicated a potential pathway to establish such common processing window, by

- adjusting the reactor pressure to stabilize a compositional alloy at the temperatures at which the alloy would either decompose or exhibit phase separation, and by
- adjusting the group V/III precursor ratio and surface chemistry as function of composition x with sub-monolayer precision.

The present 2nd generation of HPCVD reactor will have to be modified in to integrate a research results over the last 15 years and to address the main limitations in the present HPCVD system, which are

- lack of a load lock system,
- 1 sq-inch substrate size restriction,
- precursor intermixing in the flow channel due to run-time issues, and
- fixed flow channel height.

Even though the cylindrical pressure vessel design employed in the 2nd HPCVD reactor system is ideally suited for reactor pressures well above 100 bars, it became apparent in our research studies that the loading and unloading of the substrates is too complex and exposes the inner reactor to atmosphere after each growth run – even if a glove box enclosure was used. Even if the reactor was purged several times after the substrate loading, the remaining impurity contaminations limit at present the quality of the grown InGaN epilayers.

The next 3rd generation HPCVD design will have to integrate reactor design elements formulated in our patent to address the above mentioned shortcomings. It should be able to handle ø2-inch substrates, which are loaded via a load-lock station. The outer pressure vessel of formed by a Stainless Steel (SS) block with a rectangular inner cutout, in which the inner MOCVD reactor will be embedded. All components of the pressures confining outer reactor consists of machined and bolted together components, avoiding any welded parts. The outer reactor has to be designed to maintain reactor pressures of up to 25 bars. Both – the lower part of the pressure vessel as well as the top flange – are water cooled to maintain well-defined process conditions. The loading and unloading of the samples is done via a load-lock station, such that the outer pressure vessel reactor and the embedded inner MOCVD reactor of the HPCVD system isn’t exposed to atmosphere during the sample transfer process. This will drastically reduce the impurity level in the HPCVD system and will lead to improved InGaN epilayer structures.

The most critical modification in the 3rd generation HPCVD reactor addresses the MO precursor injection and gas flow kinetics to engineer the gas- and surface chemistry during ternary III-N alloy formation. As schematically depicted in Fig. 8, the adjustable center flow channel is formed through a lower base plate and an upper u-shaped element clung around the lower base (the upper cutout for the showerhead injection elements is not shown in Figure). This allows for an adjustable height of the flow channel as function of reactor pressure. The showerhead element(s) are embedded on the upper u-shaped flow channel as schematically illustrated in Fig. 9(a) and (b). The additional vertical injection element contains engineered injection ports/areas above and/or in front of the reaction zone. These showerhead elements are shaped to obtain/tailor a desired precursor concentration profile in the reaction zone. Since the upper flow channel position is adjustable, a flexible SS-bellow decouples the push flow from the MO-precursor injection element.
Figure 8. Schematics of the center section of the inner 3rd-gen. HPCVD reactor, which consist of an adjustable flow channel height arrangement (from 10 mm down to 1 mm).

Figure 9. Schematic illustration of showerhead arrangements for the injection of the MO-precursors perpendicular to the flow channel above and/or in front of the growth surface.

a) spatial engineered area injection element above reaction zone,

b) line injection in front of the reaction zone, perpendicular to flow channel.
Citations:


III. Patent, Theses, Publications and Presentation of research results

III.1 Patent filed


III.2.1 Graduate Students supported during award period and still working on…

Ms. Indika Senevirathna, graduate PhD-student: June 2014 - open; “optical characterization of III-N alloys by IR reflectance”

Mr. Daniel Seidlitz (MS from Technical University Berlin);
Research PhD-student scholar: Jan 2014 - open; "Optical diagnostics and real-time characterization of MOCVD growth of group III-nitrides”

Mr. Mark Veron, MS-student: May 2014 – open; “Growth and analysis of InGaN alloys”

III.2.2 Graduate Students supported during award period with completed theses:

MS Title: “Optical Properties of In1-xGaxN epilayers grown by HPCVD”
http://digitalarchive.gsu.edu/phy_astr_theses/9

Mr. Ramazan Atalay Aug. 2006 - Nov. 2012
PhD Title: "Optical and Structural Properties of InN epilayers grown by High-Pressure Chemical Vapor Deposition”

Mr. Max Buegler March 2008 - Sept. 2012
PhD Title: "Optical and structural properties of Indium-Nitride epilayers and their growth by High Pressure Chemical Vapor Deposition”

Mr. Ananta Acharya Aug. 2009 – July 2013
PhD Title: "Indium nitride surface structure, desorption kinetics and thermal stability”
PhD-Thesis completed Aug. 2013

Ms. Indika Senevirathna Aug. 2011 – June 2014
MS Title: "Properties of Group III-Nitride Materials studied using FTIR Reflection Spectroscopy,” MS-Thesis completed June 2014; continued PhD program

Mr. Sampath Gamage Aug. 2010 – Feb. 2015
MS Title: "Growth and characterization of InN and In-rich InGaN alloys by HPCVD”
MS-Thesis completed Nov. 2014

Mr. Rasanga Samaraweera Aug. 2011 – Feb. 2015
MS Presentation: "Growth and analysis of InGaN alloys and epilayers”
MS-Thesis completed Jan. 2015

III.3 Referred Publications (published) during award period:


III.4 Presentations at conferences/seminars during award period:

Invited Presentation:


**Conference - oral contributions**


Conference - poster contributions


1. Report Type

F na Report

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Organization / Institution name
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STABILIZATION OF INDIUM-RICH IN1-XGAXN HETEROSTRUCTURES - THE EXPLORATION OF A COMMON PROCESSING WINDOW

Grant/Contract Number
AFOSR assigned control number. It must begin with "FA9550" or "F49620" or "FA2386".

FA9550-10-1-0097

Principal Investigator Name
The full name of the principal investigator on the grant or contract.

N ko aus D etz

Program Manager
The AFOSR Program Manager currently assigned to the award

Dr. Kenneth C. Goretta

Reporting Period Start Date
04/01/2010

Reporting Period End Date
03/31/2015

Abstract
During the grant period, the growth and optimization of indium-rich In1-xGaxN layers grown by high-pressure metal-organic chemical vapor deposition (MOCVD) was explored at reactor pressures from 5 to 20 bar and at growth temperatures of 700-900°C. The goal was to evaluate the reactor pressure and growth temperature relationship at which indium-rich In1-xGaxN layers can be stabilized. The results showed that for pressures around 15 bar, the growth temperatures for InGaN vary from 850°C (InN) to 950°C (In0.7Ga0.3N), significantly reducing the temperature gap in the ternary InGaN system compared to low-pressure MOCVD. An unexpected decrease in growth rate with increasing reactor pressures, which is due to smaller surface diffusion at higher pressures, was observed. The results presented on forming single-phase indium-rich ternary InGaN alloys using simultaneous and sequential group-III precursor injection sequences were only partially successful: we obtained single-phase alloys for In1-xGaxN \[0 < x < 0.15\] and \([0.25 < x < 0.3]\) but observed mixed phases for compositions between the data points. The experiments indicate the presence of Ga- and/or In-
adayers - and oscations between them – that may play a major role for the observed mixed InGaN phases. Addtional studies will be needed to obtain a better understanding on how the deployment of precursors to the surface relates to the surface decomposition and chemistry processes that influence the Ga- and In-fragment incorporation and the subsequent InGaN phase formation.

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Archival Publications (published) during reporting period:


Changes in research objectives (if any):
None

Change in AFOSR Program Manager, if any:

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Extensions granted or milestones slipped, if any:
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AFOSR LRIR Number

LRIR Title

Reporting Period

Laboratory Task Manager

Program Officer
Research Objectives

Technical Summary

Funding Summary by Cost Category (by FY, $K)

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Appendix Documents

2. Thank You

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