INDOT

Contract number 016956

INDOT

MOCVD technology for production of indium nitride based nanophotonic devices

STREP, Specific Targeted Research Project
NMP (Nanotechnologies and nano-sciences, knowledge-based multifunctional materials and new production processes and devices)

Final Activity Report

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RE	*Restricted to a group specified by the consortium (including the Commission Services)*	
CO	*Confidential, only for members of the consortium (including the Commission Services)*	

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1. Introduction

1.1. State-of-the-art before InDot

The Indium Nitride (InN) has been the least material studied in the family of nitride semiconductors, due to its extremely challenging growth. During the last years work, before InDot was started, good quality material was already achieved, and it was demonstrated that the bandgap of InN is close to 0.7 eV. By alloying the material with GaN, it is possible to cover a range of wavelength from 1.77 µm (infrared) to 0.36 µm (UV) which makes this material system interesting for emitters and detectors for telecommunication applications at 1.55 µm and for high efficiency solar cells. It was also demonstrated experimentally and theoretically that InN has excellent transport properties, both at low and high electric field. The discovery that InN has a bandgap lying close to the infrared telecommunication wavelengths and its excellent transport properties led to a huge interest worldwide. But the main part of the material has been grown on small pieces using MBE (Molecular Beam Epitaxy) whereas only very few reports on MOCVD growth were available. CNRS had demonstrated that high quality InN epitaxial films could be grown onto 2 inch sapphire substrates using MOCVD but the InN growth rate was extremely low, typical values were in the range of 0.05 to 0.2 µm per hour, which is too low for efficient production processes. The low growth rates are linked to special challenges for the InN growth. The InN deposition requires much lower growth temperatures (500 – 650 °C) than conventional group-III nitride compound semiconductors like GaN or AlGaN (850 – 1250 °C) but the common standard precursors for group-III-N growth like ammonia are too stable to decompose efficiently at these low temperatures. Also residual contaminations in process gases and precursors like oxygen and moisture are more serious in the low temperature growth range than at higher temperatures.

Therefore the goal of InDot was to overcome the given limitations for the MOCVD growth of high quality InN and InN quantum dot based heterostructures by the development of an optimized MOCVD technology.

1.2. The InDot Project objectives

The main goal of INDOT was to develop an MOCVD technology (Equipment, Precursors, Gas purification and Growth processes) for the industrial production of Indium Nitride (InN) quantum dot based devices. The know-how produced in the frame of the project should also be applicable to the production of InN and In-rich InGaN alloy based devices. On a purely scientific basis, this project addressed the epitaxy of a new, challenging and extremely promising semiconductor material, InN, and its nanostructures. This material has a huge potential for applications in infrared emission and detection, for telecommunication applications, high efficiency solar cells and electro-optic modulators.

Another aspect of the project was linked to environmental issues. Nitride semiconductor growth is a much more environmental friendly technology compared to the state of the art since it involves non-toxic precursors.

INDOT had to extend the existing knowledge in the following directions:

- Control of InN quantum dots size and density
- Growth of In rich $In_{1-x}Ga_xN$ alloys ($x < 15\%$)
- Encapsulation of the InN quantum dots
- Realization of a InN quantum dot based LED as a demonstrator

On the technical side, the following challenges were addressed:

- Development of new precursors for the low temperature growth of In rich $In_{1-x}Ga_xN$ alloys ($x < 15\%$).
- MOCVD equipment optimization for the growth of InN quantum dots and In rich InGaN
- Development of purification processes/equipment for the process gases

1.3. List of participants

Part. Role	**Part. no.**	**Participant Name**	**Participant short name**	**Country**
CO	1	AIXTRON	AIXTRON	Germany
CR	2	CNRS	CNRS	France
CR	3	SAFC HITECH LIMITED	HITECH	UK
CR	4	SAES Getters SpA	SAES	Italy

The consortium consisted of three industrial partners (AIXTRON, SAFC HITECH, SAES Getters) and one international level academic laboratory (CNRS). They joined their complementary expertise to develop the advanced MOCVD technology for InN based nanophotonic devices.

1.4. Coordinator contact details

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2. Execution of InDot

2.1. Work performed and main results achieved

To achieve the InDot goal, the development of a MOCVD technology (equipment, precursors, gas purification and growth processes) for the industrial production of Indium Nitride (InN) quantum dot based devices, the following technical workpackages have been addressed:

Work-package No	Workpackage title	Lead contractor No		End month
WP2	New precursors	3	0	36
WP3	InN QD on GaN and InGaN	2	0	30
WP4	In-rich InGaN growth	2	0	30
WP5	Encapsulation of InN QD	2	6	30
WP6	Demonstrator	2	30	36
WP7	Wide range Temperature Control System	1	0	12
WP8	Adaptation/optimization of gas lines and reactor design	1	0	36
WP9	Mapping of characterizations	1	0	36
WP10	Purifier design	4	0	36

WP1 was devoted to management issues. In the following the main project achievements will be summarized per WP:

2.1.1. WP2 New Precursors

Leader: SAFC

Objectives

- Develop new precursors suitable for high quality InN QD and In-rich InGaN layers
- Ensure a reliable fabrication process

- Scale up synthesis and purifications procedures to production level
- Establish a leading position on the upcoming InN related market

Description of WP activities and progress towards objections, deliverables and milestones (devided by tasks)

The initial phase of the project focussed on supply of baseline precursors for study by the deposition team to highlight deficiencies in their performance. Quickly the feedback received enabled a number of alternative strategies to be devised and the precursor chemistry developed to provide different chemicals for investigation. The first series of compounds were alternative N sources to access lower growth temperatures followed by compounds containing both In and N to enhance stoichiometry control and finally improved In compounds to fully optimise the deposition parameters accessible. Having determined the best source combinations for the matrix deposition a range of dopant materials was developed to enable device structures to be targeted. The progress in identification, synthesis, characterisation, purification and supply of samples followed the planned sub task schedule as outlined below with all milestones and deliverables met in a timely fashion.

Task 2.1: Synthesis and supply of first In precursor (precursor #1)

The deposition of In based materials (InP, InGaAs, GaInN) by MOVPE has historically been accomplished from the In precursor TrimethylIndium (TMI, Me_3In). This compound has been extensively investigated at SAFC to allow optimum purity product to be isolated and supplied into the Compound Semiconductor market place. A number of batches of the highest grade available were therefore prepared, characterised and supplied to Montpellier for growth trials to meet D3 and M1.

Task 2.2: Synthesis and supply of first N precursor (precursor #2)

For high temperature growth of nitride semiconductors NH_3 is employed however at lower temperatures the efficiency is much reduced hence alternative N sources are of interest. A reduced stability compound that generates similar species to the theorised decomposition products from NH_3 but at lower temperatures was identified from prior work in the InGaAsN deposition area. Dimethylhydrazine (DMHz, Me_2NNH_2) was therefore purified, characterisaed and supplied for growth studies at Montpellier to meet D8.

Task 2.3: Fabrication, characterisation and supply of first alternative In-N sources (precursor #3)

To improve performance a second N source was identified to again provide similar decomposition products to those proposed for NH_3 but at lower temperatures. Tertiarybutylhydrazine (TBHz, $tBuNHNH_2$) was synthesised, purified, characterised and supplied for evaluation at Montpellier to meet D14. This source was found to perform better than DMHz and so was deemed the optimum alternative N precursor for M10.

Task 2.4: Fabrication, characterisation and supply of second alternative In-N sources (precursor #4)

The results of trials using the sources from previous tasks highlighted the desire for further precursor development to fully achieve high quality structures.

The first approach attempted to solve the issue of potential unwanted reactions on mixing prior to the deposition zone leading to depletion effects and film quality degradation when using individual In and N sources. One of the proposed intermediates formed on gas phase mixing of the In and N sources was identified, prepared and characterised. The material isolated, DimethylIndiumDimethylhydrazine complex ($Me_2InHNNMe_2$), was much less reactive offering potential uniformity benefits in growth, however, its low volatility yielded prohibitively low growth rates in tests at Montpellier. A second compound with direct In-N bonding was prepared and a sample supplied for testing at Montpellier. This precursor, Tris(trimethylsilylamino)indium ($In(N(SiMe_3)_2)_3$) also possesses a relatively low vapour pressure but has the advantage of thermal stability such that elevated source temperatures can be employed to enhance transport rates. However, both of the In-N containing species proved too involatile to be used in the MOCVD equipment even after an upgrade by Aixtron to allow source heating.

The second approach addressed the inability to use H_2 as a carrier gas with InN growth coupled with the surprising deposition problems using N_2 that led to a desire to generate active H at the surface from the precursor. Triethylindium (TEI, Et_3In) was identified as a potential candidate due to a facile beta-hydride elimination process. Samples were prepared and supplied for evaluation and indeed found to significantly improve deposition control and quality.

Task 2.5: Identification and target specification for optimum source

On completion of the previous subtasks the optimum precursor combinations for InN and InGaN deposition were established. Similarly by the end of the project the p-type dopant had also been confirmed. The quality of these chemicals was assessed using physical characterisation techniques (ICP-OES and ICP-MS for metallic impurity levels, 1H NMR for organic contamination, TGA for involatile species) and based on the feedback from CNRS where excellent results were achieved a specification for impurity levels in the sources was set and issued in D21. All samples supplied on the project have met this specification.

Task 2.6: Larger scale synthesis of target precursor

Upscaling of Et_3In synthesis to afford larger batches in a reliable fashion proved to be the greatest challenge due to its low thermal stability and the requirement to apply heat to separate the pure product from the reaction mixture. After significant effort a methodology was refined to afford high purity product in acceptable yield and employing protocols that are fully compatible with those used in full scale production environment to ensure upscaling can be achieved to meet demand as required. The other sources were also studied to ensure robust preparation techniques were in place and this is now the case. All the optimum precursors established during the project are ready for HVM hence M21 has been completed in a timely fashion.

Task 2.7: Continuing supply of chemicals to growth teams

Ongoing supply of precursors was maintained throughout the project. Batches of precursors for the matrix (InN, GaN, InGaN), QD's (InN) and dopants (Mg, Zn, C) were delivered to CNRS and in-house analysis coupled with detailed deposition results highlighted the high purity achieved. Metals in all cases were below detection limits and by NMR organic impurities are also not seen.

2.1.2. InN QD on GaN and InGaN

In this task, CNRS studied the growth of InN quantum dots using TMIn and NH_3 as precursors. The parameters which were investigated in order to control the dots size and density were:

- The growth temperature
- The V/III ratio
- The molar flow rate of TMIn and NH_3
- The reactor pressure
- The deposition time

These parameters had to stay within given boundaries in order to ensure that the InN quality in the dots is high; for example the growth temperature had to be within 500 and 600 °C.

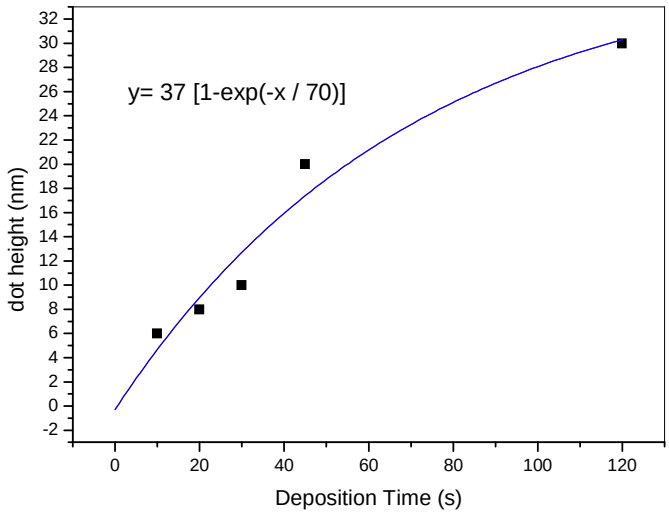


Fig. 1: Dot height versus deposition time at 550°C.

In fig. 1 above, the effect of the deposition time on the dot height is illustrated. Our goal for milestone M4 was to achieve 3 nm high dots, with density of 10^{10} cm^{-2}, which requires a deposition time of 5 seconds, as extrapolated from fig.1. It appeared that the growth temperature influenced simultaneously the dot size and density, but deposition time and ammonia flow allowed us to separately tune the sizes and densities of the dots. Preliminary experiments had led us to think that the carrier gas could play a major role in the nucleation of

InN, and we had included in the workplan the use of alternative carrier gases. We decided to make these tests earlier than planned, in order to increase the limited dot density, and AIXTRON and SAES made the effort of delivering a gas blending system for alternate carrier gases (deliverable D11) and a Ar/He purifier (deliverable D12) earlier than scheduled. We compared the effect of Argon, Helium and Nitrogen carrier gases on the growth of InN quantum dots, using the otherwise same growth conditions. This is summarized in the AFM pictures of fig. 2.

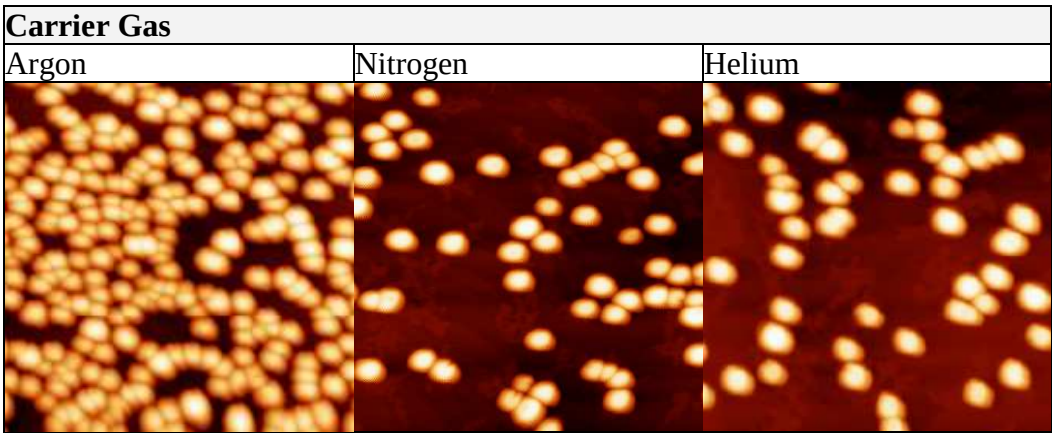


Fig. 2: Effect of the carrier gas on the dot density (image size: 2µmx2µm).

The effect of the carrier gas on the initial nucleation is huge: Argon tends to strongly increase the nucleation density, while Helium has the opposite effect. Growth conditions were re-tuned, using Ar carrier gas, in order to achieve both high nucleation density and small dot height:

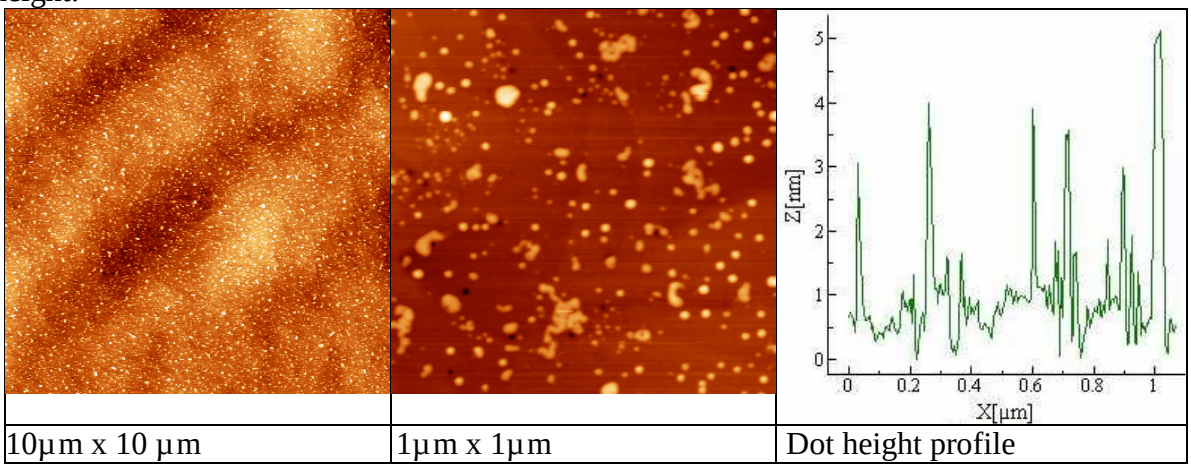


Fig. 3: AFM images at different scales and height profile for InN quantum dots grown under Ar carrier gas. From the 1x1µm picture, the dot density can be determined as $7x10^{10}cm^{-2}$.

The results in fig. 3 clearly demonstrate that project milestone M4 (mean 3nm dot height and density > $10^{10}cm^{-2}$) is achieved, indicating that reproducible control of size and density of InN quantum dots is achieved.

The process improvement linked to the use of Argon led us to apply for a French patent, further extended to international coverage. Once the patent was officially deposited, we were allowed to communicate on these results, so we published them in Applied Physics Letters Vol 90, page 153102 (2007).

However, at the time of writing the INDOT contract, we thought that even higher dot densities would be required for an efficient emitter to be realized, so we included Milestone M11, which states that a dot density equal or above 10^{11} cm^{-2} had to be achieved. In order to realize that, we studied the growth of InN dots at lower growth temperatures, which was made possible, thanks to the new TCS system designed and installed by AIXTRON.

Milestone M11: Choice of process conditions allowing the growth of QD with density>=$10^{11}$$cm^{-2}$.

We found that a quantum dot density above 10^{11} cm^{-2} could be obtained by growth at 450°C, under a V/III molar ratio of 5000, under Argon carrier gas. In fig. 4a below, an AFM picture demonstrates that a density of $1.1x10^{11}$ cm^{-2} is obtained. Using the extremely sensitive x-ray diffraction setup that we bought within the contract, we could check that the dots are indeed monocrystalline, although they are a few nanometers high. This is depicted in Figure 4b, where the ω-2θ scan shows that only the 002 dot orientation is recorded. The width of the peak is not correlated to the dot quality, but is broadened due to finitness effect, linked to their nanometric size.

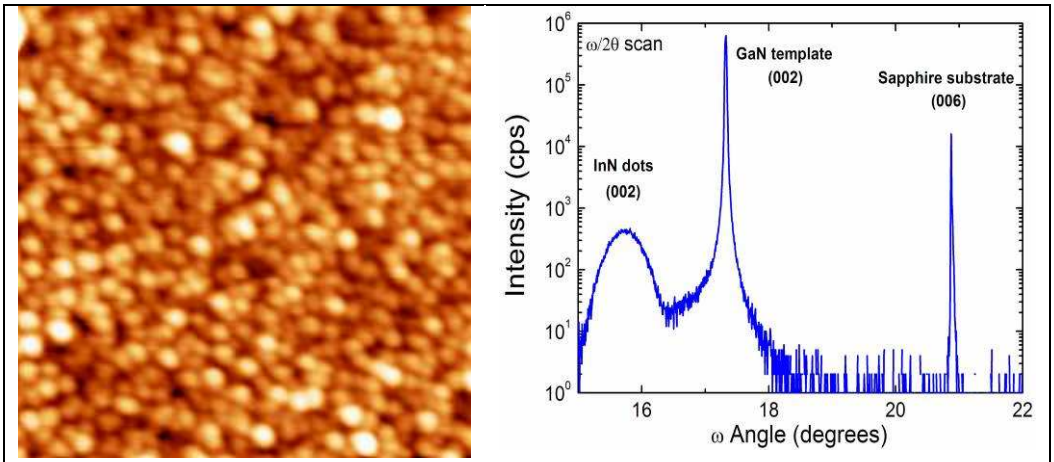


Fig. 4: (a) left side : AFM picture 600x600nm. The mean dot height is about 7 nm, with a density of $1.1x10^{11}$$cm^{-2}$. (b) right side : X-Ray diffraction pattern (ω-2θ scan) showing the monocrystalline character of the InN dots.

While analyzing recent literature regarding quantum dots devices made of « classical » III-V compounds (InAs, InP, GaAs), dot densities in the range of 10^{10} cm^{-2} were used in optoelectronic devices. Since nitride semiconductors (GaN, AlN, InN and their alloys) usually exhibit very high emission efficiency, we will probably not need to use such extreme dot densities, although we have the know-how for it.

For other purposes, we have studied the recrystallization by annealing of InN (performed in-situ in the MOCVD reactor). We had the idea that this know-how could be used as an alternative way of realizing InN dots, possibly with an improved crystalline quality

A very thin layer of amorphous InN is deposited onto GaN at low temperature. Then, this thin layer is recrystallized at a temperature close to the dissociation temperature of InN (650 to 720°C). Rippening occurs, along with recrystallization, and InN dots are formed. In fig. 5, we show an AFM image of these dots and the corresponding height profile. Dots of 6-8 nm high, with a density of $5x10^{9}$ cm^{-2} are obtained. Their crystalline quality was assessed using Grazing Incidence Diffraction (GID). This experiment, which can be performed in-house on

the setup bought for the contract, is very sensitive to the sample surface, and allows to make accurate measures on our quantum dots. The full width at half maximum (fwhm) was recorded for the (100) diffraction peak of InN for different sets of dots.
In dots grown directly by MOCVD, a fwhm mean value of 5000 arc-seconds is obtained, while for recrystallized dots, an average fwhm of 3100 arc-seconds is measured. This is a very significant improvement of the crystalline quality.

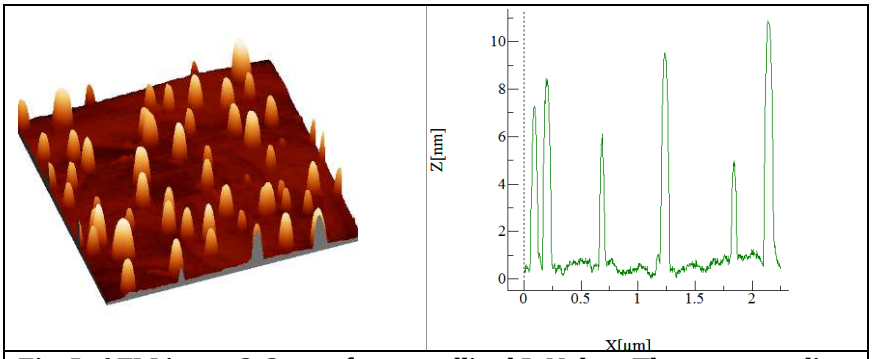


Fig. 5: AFM image 2x2 µm of recrystallized InN dots. The corresponding height profile is shown; the dots are 6 to 8 nm high, and their density is $5.1x10^{9}$ cm^{-2}.

As mentioned above, such dot density could be enough for the design of a light emitter. As explained above, we have established a large know-how on the fabrication of InN quantum dots, which allow us to grow dots of high quality with well-controlled geometrical parameters (size and density).

2.1.3. In-rich InGaN growth

In order to be able to realize different structures for optical and electronic confinement, in view of realizing devices, it was necessary to demonstrate the growth of InGaN alloys, on the In rich side. Our initial objectives were to introduce up to 15% of gallium in InN, but we soon realized that the whole concentration range could be covered by the MOCVD growth method. Results obtained after optimizing the MOCVD growth conditions are depicted in fig. 6. In this figure, we display diffraction peaks for InGaN alloys covering the whole concentration range. It can be seen that no significant broadening of the diffraction peaks occurs with increasing Ga composition, reflecting the fact that the crystalline quality is comparable in the different samples.

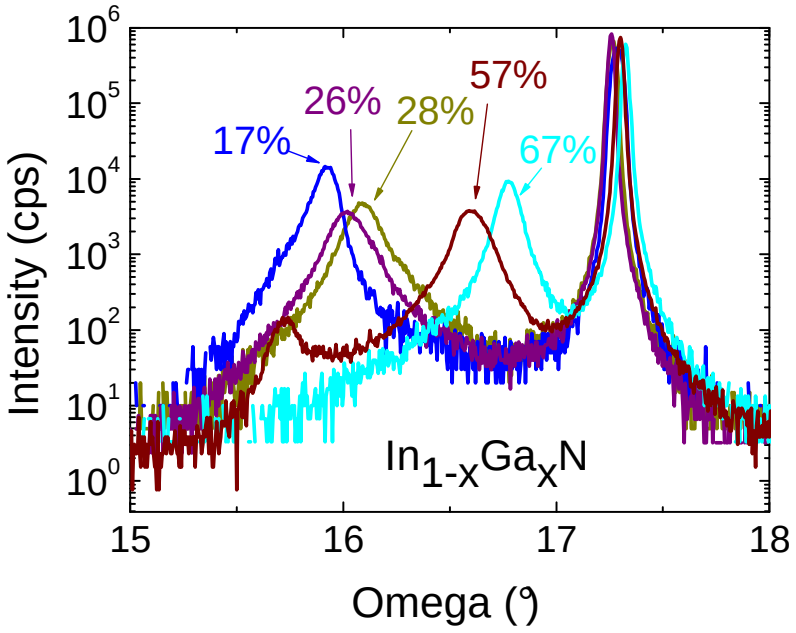


Fig. 6: ω-2θ scans for In1-xGaxN layers with different compositions, grown onto GaN templates.

Different Ga precursors were used to achieve a good control of the alloy composition: for the lower composition, i.e. below 17% of Ga, TEGa was preferably used, due to its lower vapour pressure. Above an alloy composition of 17%, TMGa was used. This is plotted in fig. 7 below.

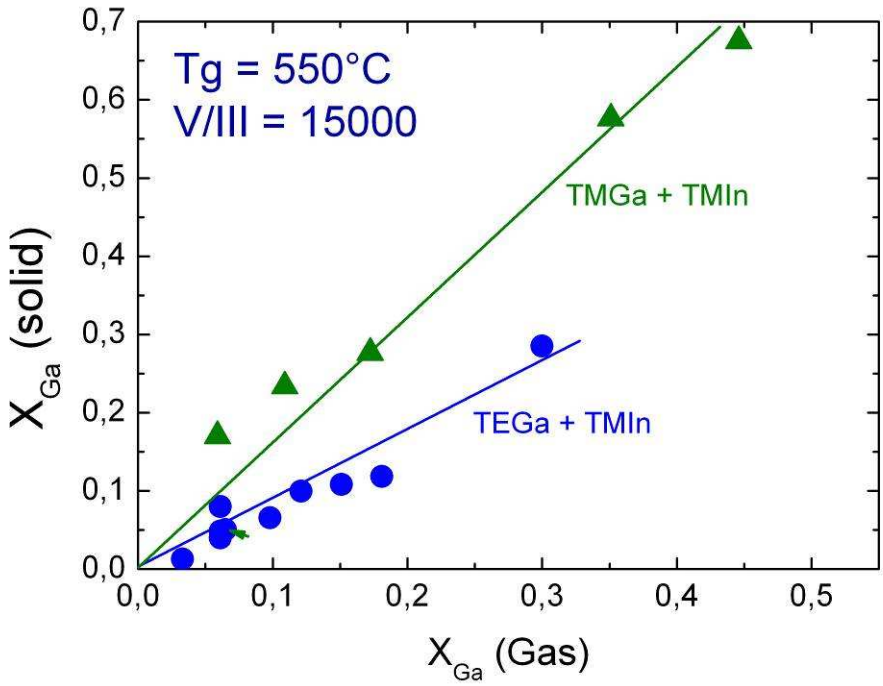


Fig. 7: relation between gas phase and deposited alloy composition, for different Ga precursors (TEGa and TMGa).

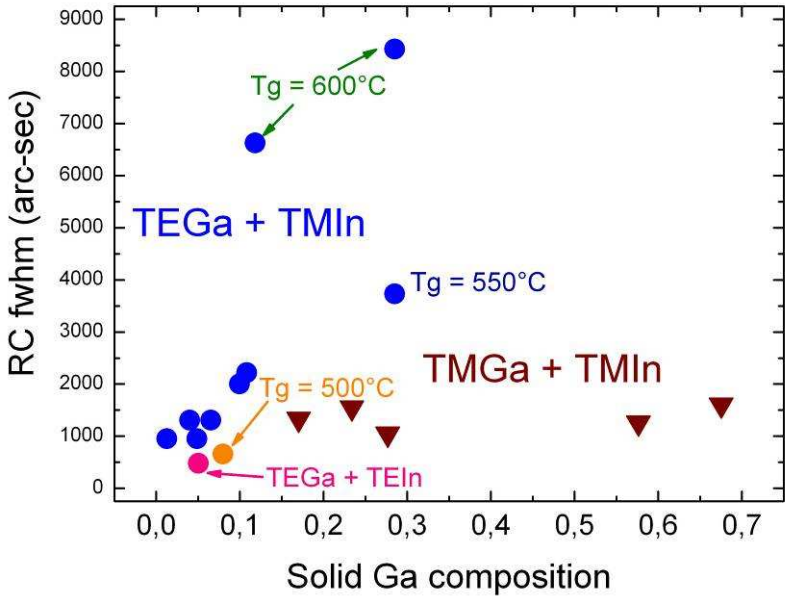


Fig. 8: full width at half maximum (fwhm) of the InGaN alloys rocking curves measurements, indicating the crystal quality, for different Ga precursors and solid compositions.

The crystal quality results reported in fig. 8 clearly indicate that TMGa must be preferred to TEGa at higher compositions to improve material quality. The effect of growth temperature Tg is also shown; A degradation of crystal quality occurs above 550°C.

Doping of InGaN Alloys

Doping of the alloy is an essential task in view of realizing devices. We spent much efforts in this direction, as discussed below.

a) n-type doping

n-type doping was easily achieved. InN has a residual background doping of n-type, and we could easily increase this residual doping by performing silicon doping. SiH_4 precursor gas was used, and doping levels up to $10^{21}cm^{-3}$ were realized.

b) p-type doping

p-type doping was studied, using magnesium (Mg) as dopant species. Cp_2Mg was used as a MOCVD precursor for Mg. Theoretically, no particular problem is to be expected, since the InN material bandgap is small, the ionization energies of dopant should be accordingly small, and the difficulties encountered in the doping of wide bandgap materials, such as GaN, should not been encountered.

However, direct doping with Mg was not successful. This is not very surprising, since in the case of GaN doping in MOCVD, it has been demonstrated that Magnesium – Hydrogen complex are formed, which are not electrically active. It is then necessary to remove the hydrogen by annealing the samples. A lot of experiments were conducted to first incorporate

Mg in InN, then to characterize it optically and electrically, and then to establish proper annealing treatments to activate Mg in InN, by removing the passivating hydrogen.

Using Cp_2Mg as a precursor, Mg was incorporated in InN in sufficient quantities, as demonstrated by SIMS measurements. Mg concentrations up to $10^{20}cm^{-3}$ were achieved. We noted that the incorporation yield is between 2 and 6%, depending upon experimental conditions. This is much less than in the case of Mg doping of GaN, but it can be understood by considering the low growth temperature of InN (500-600°C), which probably results in a moderate decomposition rate of Cp_2Mg.

The as-grown InN:Mg already demonstrates an optical activity of Mg : in the figure below, the photoluminescence of a highly magnesium doped sample of InN has been plotted versus sample temperature, in the range 9 – 300K. A striking feature is that a blue-shift of the luminescence is observed (peak displacement toward higher energies), which does not reflect the variation of the material bandgap with temperature which would cause *a red-shift*. Another mechanism has to be present in the sample and is related to magnesium. Further studies are ongoing to obtain more details on the exact nature of the mechanism, but it clearly demonstrates that optical properties of InN are affected by the presence of Mg.

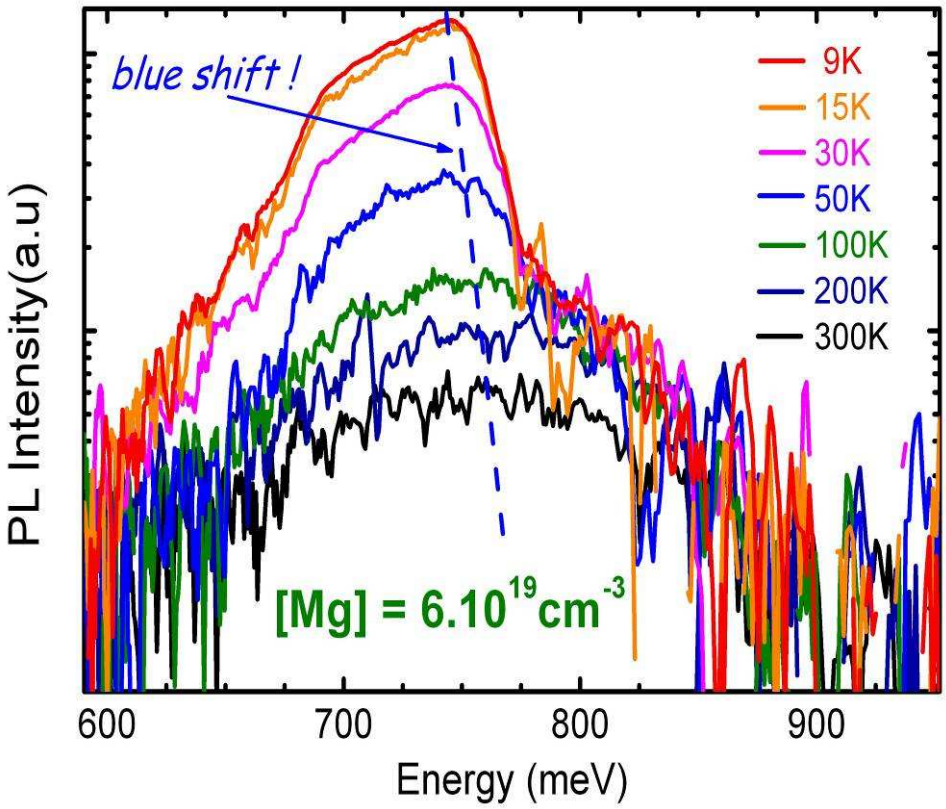


Fig. 9: Photoluminescence versus temperature of a highly magnesium doped sample of InN. A blue-shift of the PL with temperature is observed.

Then, detailed systematic experiments were conducted to find proper annealing conditions that can activate the magnesium dopant, as in the case of GaN:Mg. The difficulty here is that successful annealing leading to a dissociation of the Mg-H complex occurs in GaN at a temperature of 700°C. Here, such an elevated temperature would degrade the material. After

many experiments, we observed that a long annealing step performed at 550°C gives the best results as illustrated on figure 10 below.

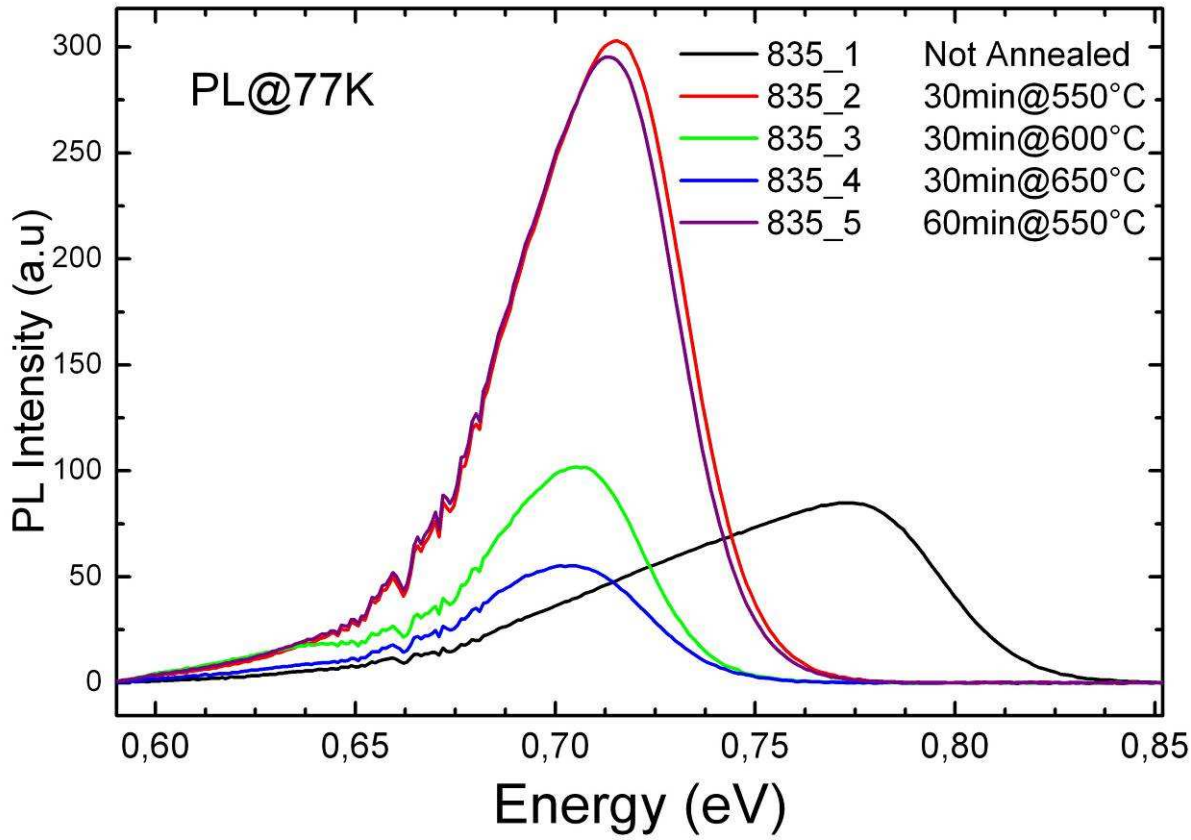


Fig. 10: 77K photoluminescence of highly magnesium doped InN samples annealed in various conditions. A strong increase of the PL signal is observed after an optimal annealing of 30 minutes at 550°C, accompanied by a shift of the peak energy at lower values.

A shift of the luminescence peak towards lower energies is observed, along with a strong increase of the intensity, for optimized annealing conditions (30 min. at 550°C). This can be interpreted as described in fig. 11: The annealing treatment removes the hydrogen which is passivating Mg, and allows for the emergence of an acceptor level above the valence band. The observed luminescence is the changing in nature, from a band to band transition to e-Ao transition in the doped activated sample. The magnitude of the shift is 60 meV, which corresponds clearly to the activation energy of Mg in InN, as reported by Japanese groups (Yoshikawa et al. Appl.Phys.Lett. 90 (2007) 201913).

Although p-type doping was successful, as demonstrated by PL results, it was not possible to make accurate Hall effect measurements of the hole concentration: a parasitic conduction channel exists in the samples, corresponding to a n-type conduction, that masks the p-type conduction.

Indeed, mobilities in the n-type material are higher typically by a factor of 10 to 40. Electron densities can easily be achieved with concentration of an order of magnitude higher than typical hole concentrations. The conductivity being the product of these last two factors, any parasitic n-type conduction can easily mask the p-type conduction in transport experiments.

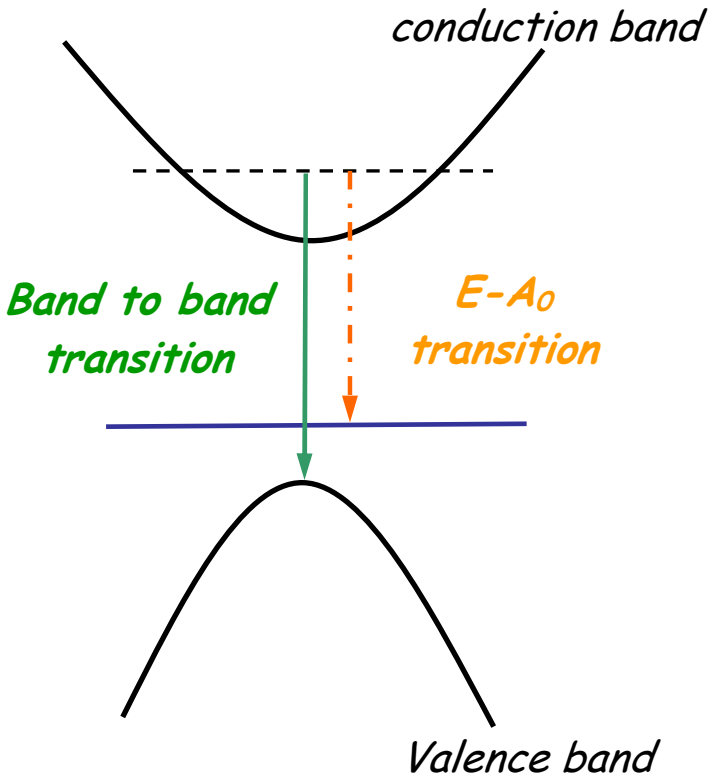


Fig. 11: band structure of Mg doped InN explaining the different optical transitions observed.

Different hypothesis may be invoked to explain this parasitic n-type conductivity.

- **surface electron accumulation** : this hypothesis is very popular in the literature, and such phenomenon has already been observed in small bandgap materials like InAs. Although it has been advanced that it could be an intrinsic feature of the InN band structure, it has been recently observed that some samples were clearly free of such phenomenon. (Wu et al. Phys.Rev.Lett. 101 (2008) 106803). Simpler hypothesis may be invoked that explain the results as well.

- **Conduction in the underlying GaN**: all the high quality InN samples are grown on top of GaN in order to reduce the lattice mismatch with the sapphire substrate. GaN is residually n-type, this can explain easily the parasitic conduction observed, as the metallic contact easily diffuse down to this bottom layer. Growing InN without an underlying GaN layer results in poor quality material, which is prone to impurities incorporation, also resulting in n-type material.

- **Conduction at grain boundaries**: the best InN samples at the state of the art have all a mosaic structure. This is common in material grown on mismatched substrates, and can be checked by AFM, looking at the surface morphology, and also by x-ray diffraction experiments, where the average grain size can be determined. From data in the literature, it was

found that the best samples produced in the USA (Cornell University) have a grain diameter of 290 nm, while the INDOT samples grown at CNRS Montpellier have a grain size of 320 nm. The larger the grain size the less grain boundaries there are. These sizes are typically 20 to 40 times less than in GaN. The existence of grain boundaries corresponds to numerous crystal defects, where impurities easily collect. This may be an important source of parasitic conduction and must be reduced.

We have made a lot of efforts to try to reduce the grain size. It appears that lateral growth of InN is severely limited in the usual growth processes, be it in MBE or MOCVD. This is the main reason for numerous grain formation, since surface diffusion remains very limited, and no coalescence occurs, even at very advanced stages of the growth. The resulting material is highly 3D, and presents numerous grains. Improving the surface diffusion by increasing the growth temperature is a very limited solution, since InN decomposes readily.

Within INDOT, the collaboration between the partners has resulted in a very innovative solution, which consists in injecting $CBrCl_3$ during growth, to modify the growth mechanisms, and improve lateral growth. The idea is to form volatile halides of Indium, which improve the mobility of existing species on the growth surface. This major breakthrough in the growth of high quality InN is illustrated in the two figures below: in fig. 12, x-ray diffraction pattern exhibit interference fringes, which are more pronounced as the amount of $CBrCl_3$ injected during growth increases. These fringes, known as "Pendellosung" fringes, witnesses of a high in-plane coherence of the sample, and demonstrates that the morphology is now extremely flat, due to the addition of $CBrCl_3$.

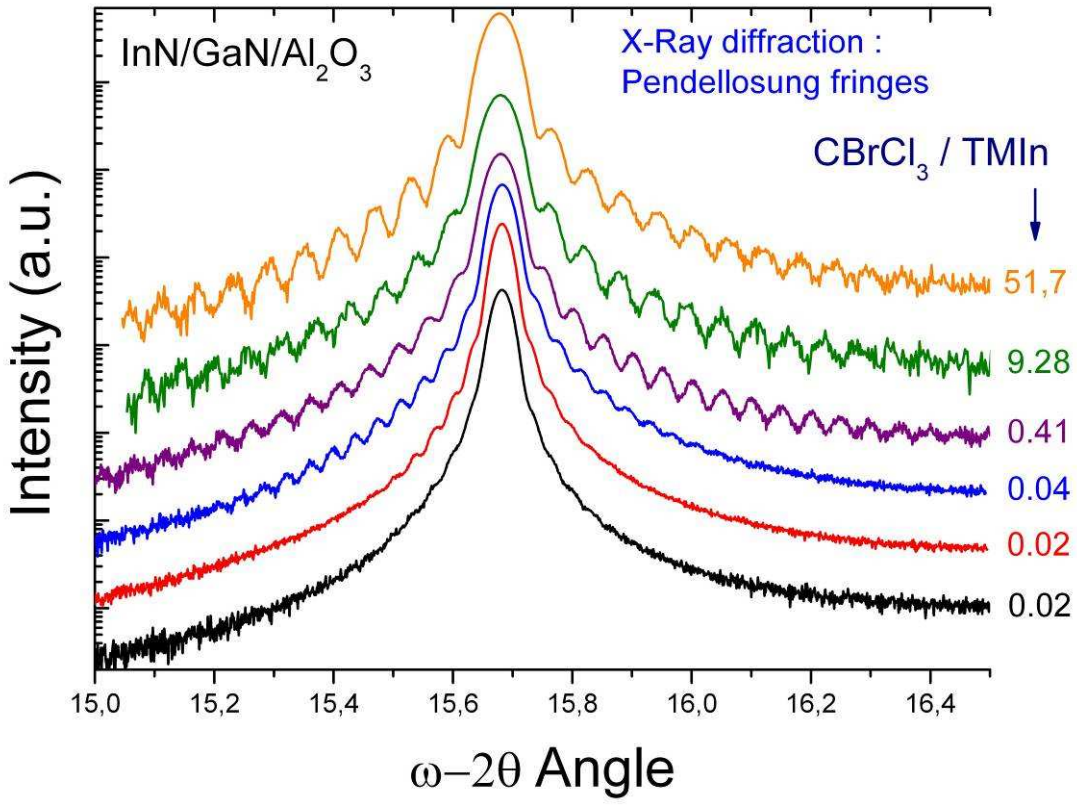


Fig. 12: x-ray diffraction Patterns of InN grown in presence of increasing $CBrCl_3$ amounts.

A direct evidence is provided in fig. 13, where AFM images of the InN surface are given for increasing CBrCl3 amounts added in the growth ambient.

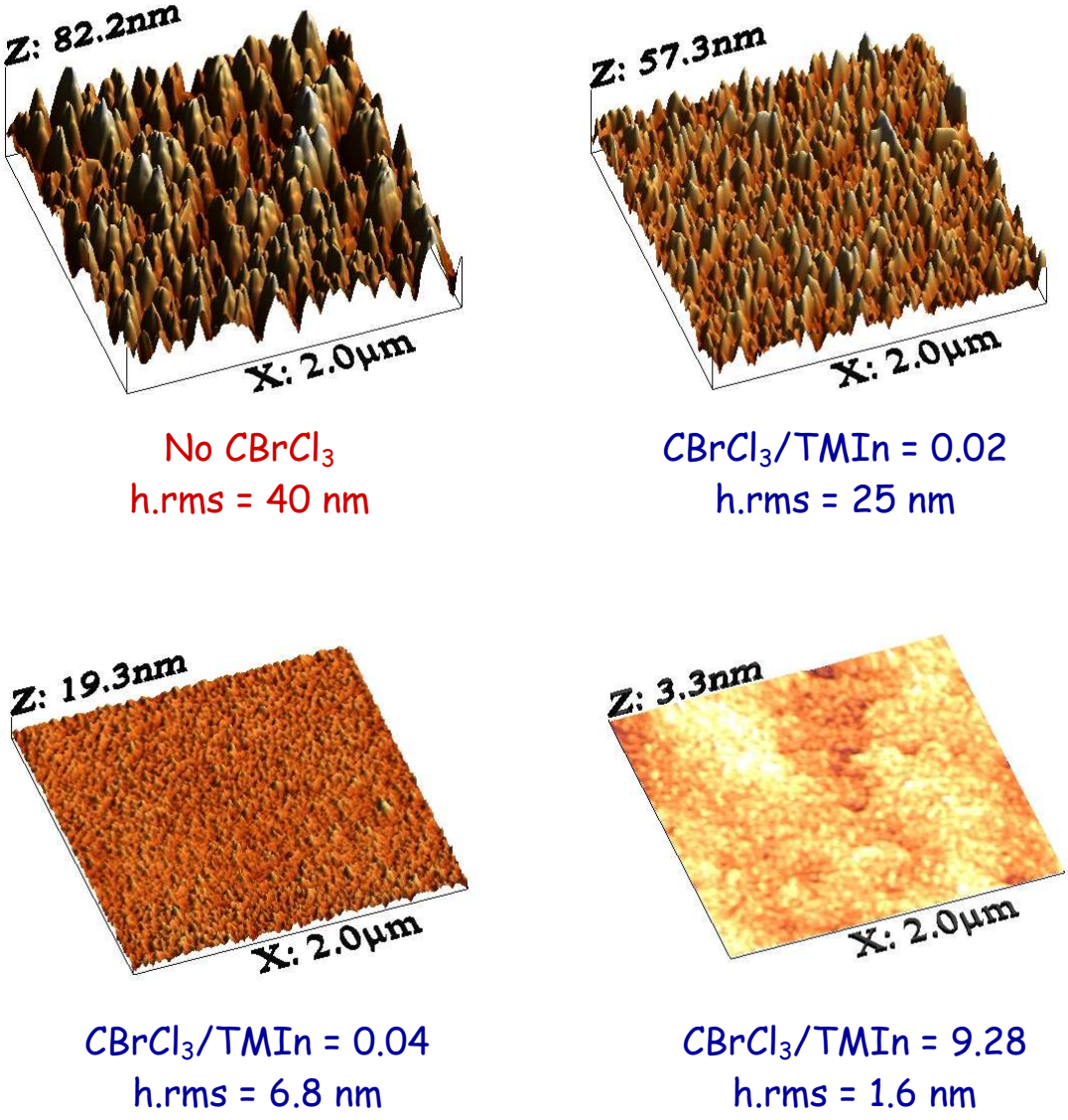


Fig. 13: AFM images and roughness values for InN grown under increasing amounts of $CBrCl_3$ in the gas phase.

This major breakthrough will enable us to get rid of parasitic conduction occurring at grain boundaries, and constitutes a major step towards usable p-doped InN for a device structure. Further work is ongoing to take advantage of this, combining it with the use of high resistivity GaN buffers.

2.1.4. Encapsulation of InN QD

The major problem that occurs in the encapsulation of InN quantum dots is that a wider bandgap material has to be grown on top of the InN dots. The available materials of the same family (GaN, AlN) are usually grown at much higher temperatures, and thus cannot be deposited directly on top of the dots, without destroying it.
We investigated the possibility of lowering the growth temperature of the capping layer. First, we have grown GaN at 600 °C, using NH_3, to encapsulate the InN dots. The capping layer In fig.14, a TEM (Transmission Electron Microscopy) image is shown, on which the InN dot and capping layer is clearly visible. A continuous capping layer is formed on top of the dot (the dot height being 12 nm). Although the capping is successful, the GaN cap layer quality is moderate, due to the low growth temperature (optimal growth temperature for GaN, in our equipment: 1090 °C). The capping process in itself, however, is not harmful to the InN dots, as demonstrated by fig.15, where a X-ray diffraction pattern is shown. The contribution of the InN dots is clearly detectable after capping with GaN, and shows no additional broadening, compared to uncapped dots. In addition, a local chemical analysis was performed during TEM imaging by EDX, which showed no quantitative interdiffusion between the InN dot and the capping layer. Thickness was targeted to be in the range of 25 nm.

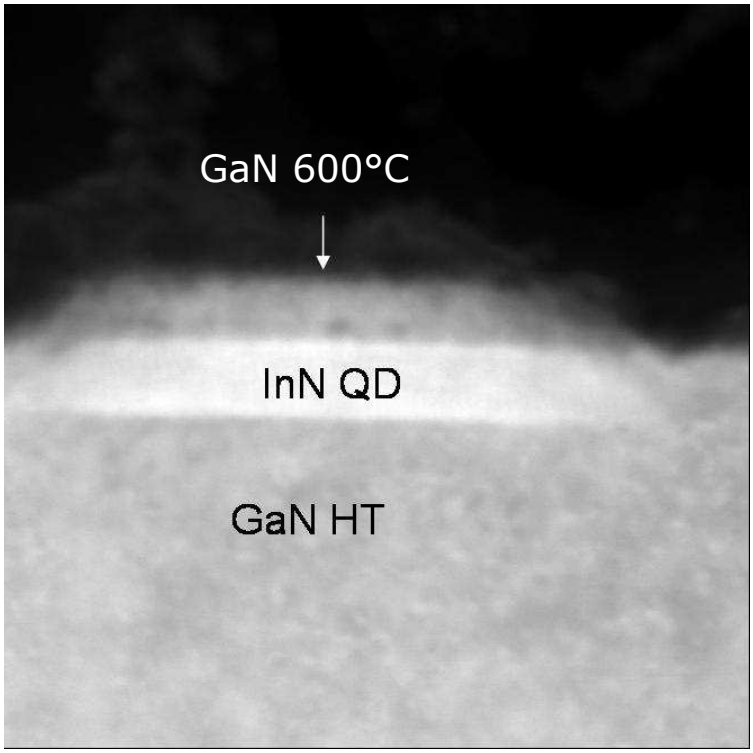


Fig. 14: Low resolution TEM cross section image showing an InN quantum dot (12 nm high) grown on GaN (high quality – grown at 1090 °C), and capped with low temperature GaN grown at 600 °C, using NH_3.

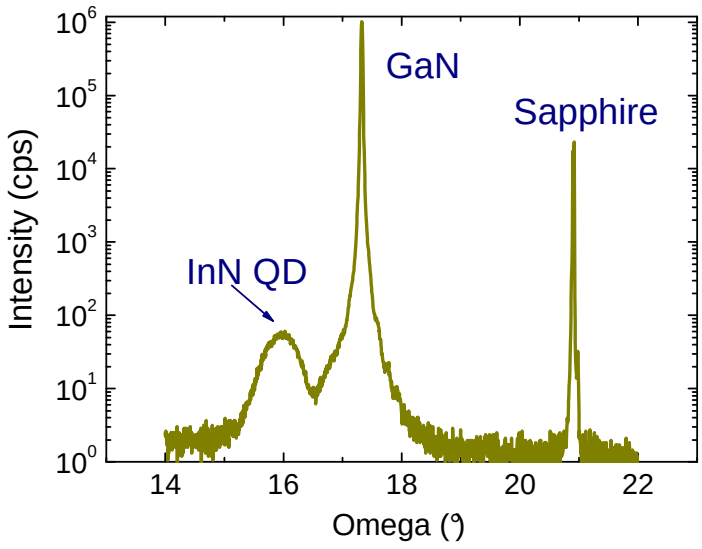


Fig. 15: X-ray diffraction pattern of GaN capped InN dots. The capping layer was grown using NH_3 at 600 °C.

The dot crystal quality is unaffected by the capping process However, no photoluminescence emission attributable to the dots was measured in these samples. This can be attributed to the low crystalline quality of the GaN encapsulation layer, which is grown at a temperature (600 °C) far too dissimilar from its optimal growth temperature (1090°C). This probably induces defects at the interface, which trap electron/holes and induce non-radiative recombination. These results demonstrate that low temperature growth of GaN will not be the easiest solution.

In order to overcome this difficulty, we decided to turn to InGaN encapsulation, since the results demonstrated that InGaN could be obtained at low temperature (550 °C) with similar crystalline quality as compared to InN. In fig.16, we compare the x-ray diffraction patterns obtained on three different samples:

- a thin film (typically 25 nm) of $In_{0.83}Ga_{0.17}N$ grown onto GaN, as a reference for the capping material.
- InN dots grown onto GaN and capped with a 25 nm $In_{0.83}Ga_{0.17}N$ film.
- The previous samples of InN capped at 600 °C with GaN.

From this figure, one notice that the diffracted intensity for the $In_{0.83}Ga_{0.17}N$ capped dots is the result of two contributions: the $In_{0.83}Ga_{0.17}N$ capping layer itself, and the InN dots. We have fitted this data using two Gaussian contributions centred on the alloy and InN positions, and deduced that the intensity contribution from the dots capped with $In_{0.83}Ga_{0.17}N$ is 10 times higher than the intensity diffracted by the GaN capped dots. This result demonstrate that $In_{0.83}Ga_{0.17}N$ capped dots have a much higher crystalline quality.

Then we performed 77K photoluminescence measurements on the $In_{0.83}Ga_{0.17}N$ capped dots. The result is displayed in fig. 17, along with the 77K PL of the $In_{0.83}Ga_{0.17}N$ alloy thin film used as a reference.

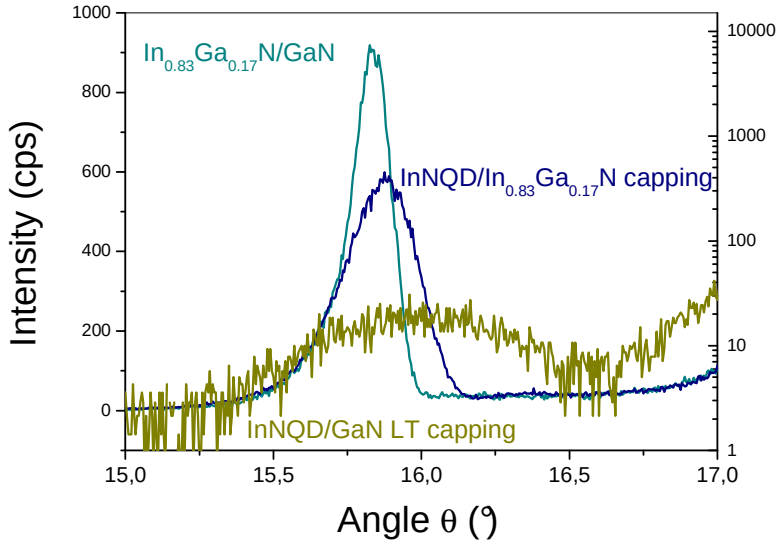


Fig. 16: ω-2θ scans for InN dots capped with GaN and $In_{0.83}Ga_{0.17}N$, and for the capping In0.83Ga0.17N film alone. The diffracted intensity for the GaN capped sample is much lower, corresponding to the logarithmic scale on the right side.

The PL emitted by the capped dots is shifted at higher energy, and the alloy luminescence is no longer detected. This is to be expected since a majority of the electron-hole pairs will now diffuse into the InN dots and recombine there. The collected luminescence is still weak, indicating that some defects/traps are still present, giving rise to non-radiative recombination.

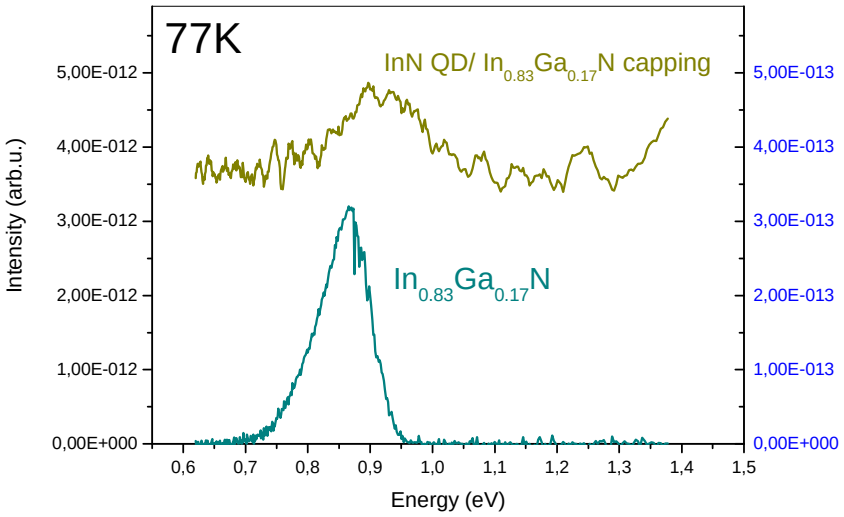


Fig. 17: 77K photoluminescence of $In_{0.83}Ga_{0.17}N$ and InN quantum dots encapsulated with $In_{0.83}Ga_{0.17}N$.

To summarize, successful encapsulation of the InN dots has been realized both using GaN and InGaN grown at low temperature, a continuous capping layer is deposited and photoluminescence is emitted by the dots.

2.1.5. Demonstrator

The realization of a simple demonstrator structure was planned for the last six months of the contract. However, many unexpected scientific difficulties were encountered, regarding growth of InN, dots encapsulation. We also spent a lot of efforts on the use of alternative precursors (DMHy, TBuHy, signle source precursor containing N and In simultaneously) to reduce the growth temperatures and improve growth rates. However, we found that these precursors were extremely inefficient when nitrogen carrier gas is used, which is mandatory in the growth of InN. Still, they can be of great interest for the low temperature growth of GaN, where hydrogen can be used as carrier gas. We demonstrated that good quality GaN can then be obtained at low temperatures.

Also, although p-type doping was successfully achieved, as demonstrated by photoluminescence, huge problems of parasitic n-type conduction were encountered. When spent a lot of efforts in analyzing these effects and finding a solution to improve growth in order to increase grain size and improve surface structure.

All these difficulties have resulted in delays, and although we are now very close to achieve our goal, we have not been able to produce a simple device in time. However, due to all the successful achievements made during INDOT, we will continue the work after this contract terminates.

2.1.6. WP7 Wide range Temperature Control System

Leader: AIXTRON

Objectives

- Improvement of the MOCVD equipment control system in order to be able to make growth both at low temperatures and high temperatures (250°C to 1200°C)

Description of WP activities and progress towards objections, deliverables and milestones (devided by tasks)

Task 7.1: Design of the Temperature Control System (TCS)

In its original design the temperature control system (TCS) of the MOCVD reactor in Montpellier was optimized for the high temperature growth of Group-III-N. The temperature in the reactor chamber is measured with a light pipe (pyrometer) from the bottom of the susceptor. The output of the light pipe is connected to a detector in the Accufiber readout. The commonly used Si detector operates at temperatures between 400°C and 1900°C. The output of this Si detector is fed into the Eurotherm controller and is used to control the susceptor temperature. To allow also the control of temperatures below 400 °C the Accufiber was upgraded with an additional low band gap detector made from InGaAs. The InGaAs detector operates in the lower temperature range between 100°C and 1000°C. In the new design, the output of the light pipe is split and connected to the two detectors in the Accufiber readout to cover the temperature range between 100 °C and 1900 °C. The control software had to be modified in a way that for the low temperature range the signal coming from the InGaAs detector is used by the Eurotherm controller. For the high temperature range still the Si detector output is used.

Task 7.2: Optimization of the Temperature Control System

The new designed TCS has been implemented in the AIX200/4RF-S reactor in Montpellier. The new system was calibrated using a second pyrometrical temperature measurement from the top side of the susceptor. The PID parameters were adjusted and optimized for the precise control of temperatures between 250 °C and 1200 °C. Finally the new system was extensively tested. The results of the heat tests can be seen in fig. 18. After a short stabilization phase the temperatures are very constant with time for the whole range between 250 °C and 1200 °C. The maximum minimum deviation was less than ± 0.5 °C.

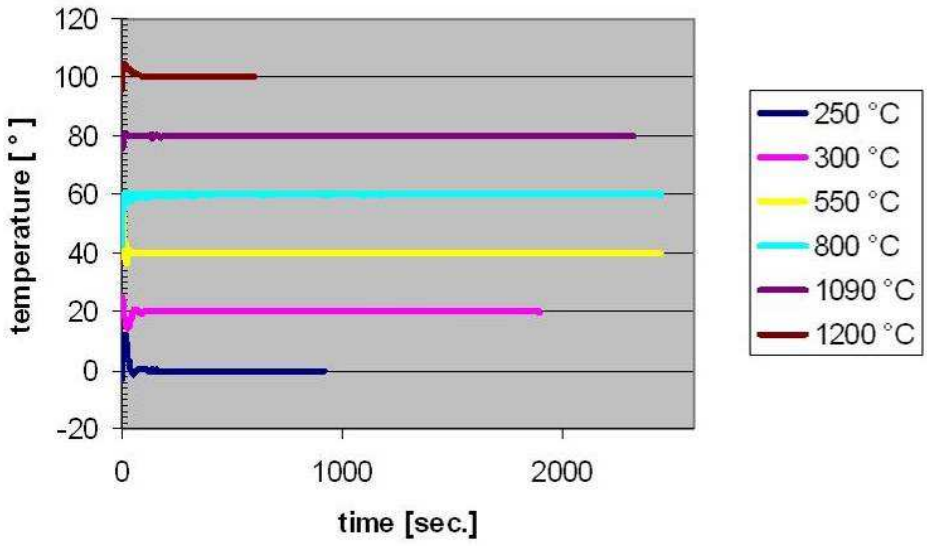


Fig. 18: Long term temperature measurement for temperatures between 250 °C and 1200 °C using the new TCS. Temperature deviation is less than ± 0.5 °C after short stabilization phase.

Basis for all optimizations in Montpellier was the bottom temperature measured on a single spot in the middle of the susceptor. As shown, this temperature was very stable after the TCS optimization and the daily work with the system in Montpellier showed also an excellent run to run reproducibility. But also the temperature homogeneity across the whole wafer will be a key factor for the later production of nanophotonic devices. The "on wafer" temperature homogeneity influences directly the material uniformity across the wafer and thus the yield of the production. Mainly kinetically driven growth processes, like the QD deposition, are influenced by smallest temperature deviations. Therefore a similar MOCVD system (AIX 200/4 RF-S) as the one in Montpellier was used at AIXTRON to optimize also the "on wafer" temperature homogeneity. Responsible for the homogeneous temperature distribution across the wafer is the design and the materials of the susceptor (cup, center disk, cover ring) shown in fig. 19. The whole set was iteratively optimized to ensure a uniform temperature distribution at high as well as at low temperatures. The low temperature measurement across the half wafer area with the optimized set-up can be seen in fig. 20. The temperature deviation (max-

min) across the wafer is < 0,25 °C.

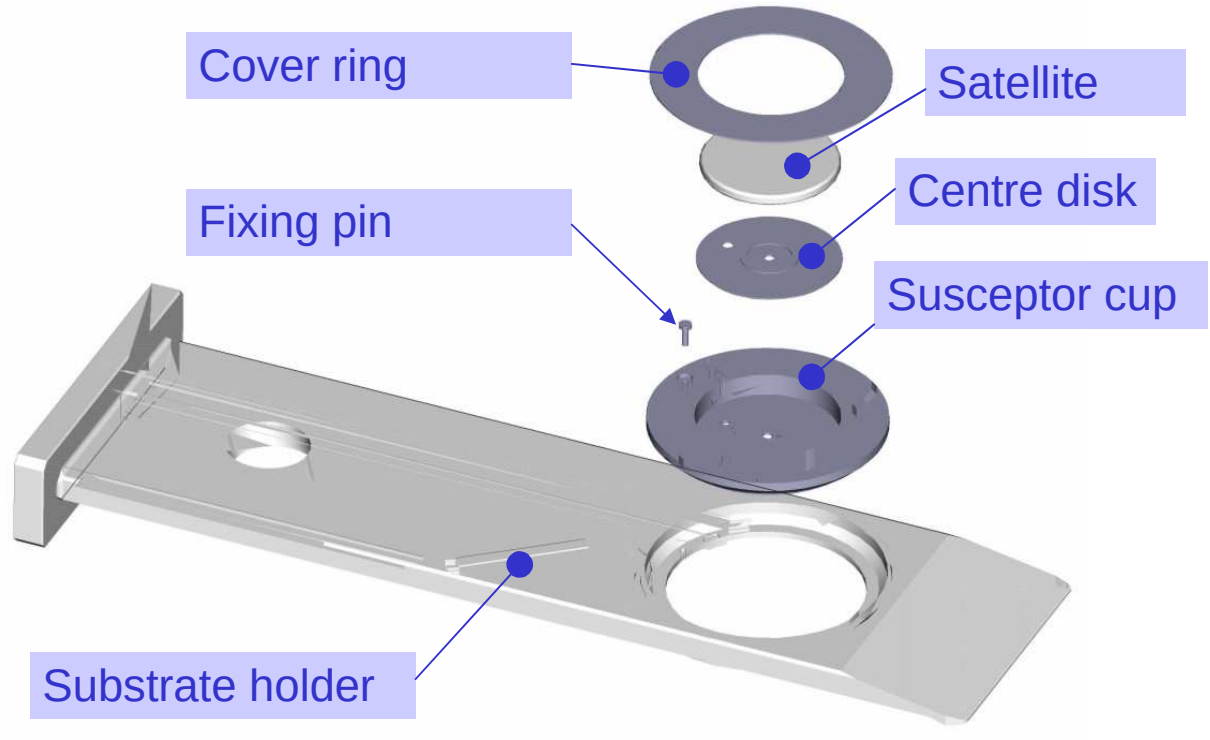


Fig. 19: Substrate holder and susceptor parts of an AIX200/4RF-S MOCVD reactor.

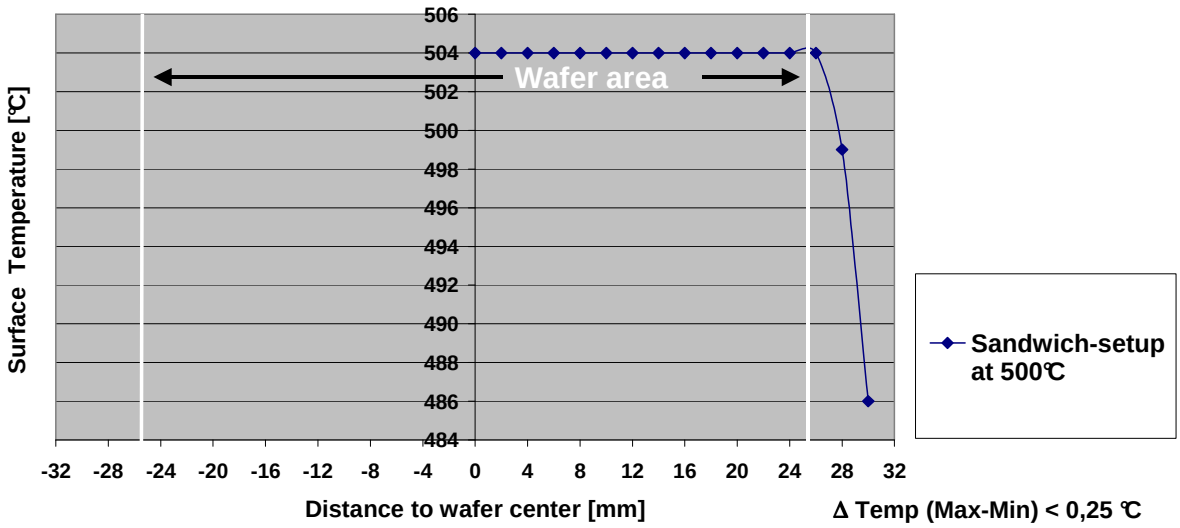


Fig. 20: AIX200/4RF-S on wafer temperature homogeneity measured from top site using a pyrometer.

Final goal of InDot was to have production type MOCVD equipment available for the deposition of InN based materials. Therefore AIXTRON transferred the InDot results into the optimization of its commercial production MOCVD technology. AIXTRON's state of the art portfolio of commercial multi wafer reactors consist of horizontal flow Planetary Reactors® and vertical flow Closed Couple Showerhead (CCS) Reactors. Both technologies had to be adapted to the special needs for the growth of InN-based materials to exploit the InDot results. First a Planetary® Reactor was adapted with respect to the low temperature growth of InN based materials. According to the InDot results the TCS

of a Planetary® reactor was improved to allow the precise control of the required low growth temperatures. Also the reactor hardware, mainly the susceptor, was improved to achieve sufficient temperature homogeneity on large areas. Current state of the art multiwafer Planetary® Reactors for the production of GaN-based materials on 2-inch substrates have a capacity of 42 2-inch wafers, which are arranged on six 6-inch satellites - see fig. 21. Thus, the homogeneous material deposition requires a very uniform temperature distribution across the whole 6-inch satellites.

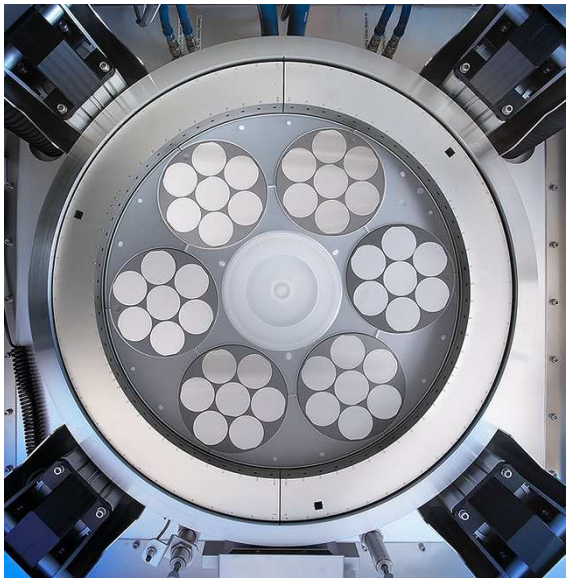


Fig. 21: Planetary Reactor® in its 42 x 2-inch configuration. The Temperature Control System as well as the reactor hardware was optimized for the low temperature deposition of InN-based materials.

To evaluate the improved TCS and the adapted hardware (mainly susceptor, gas inlet) AIXTRON performed numerous heating tests and measurements. Fig. 22 shows the temperature distribution across all six 6-inch satellites for a mean temperature of 491°C. The temperature deviation across one satellite is as low as ±0,5 °C, from satellite to satellite only ±1,4°C.

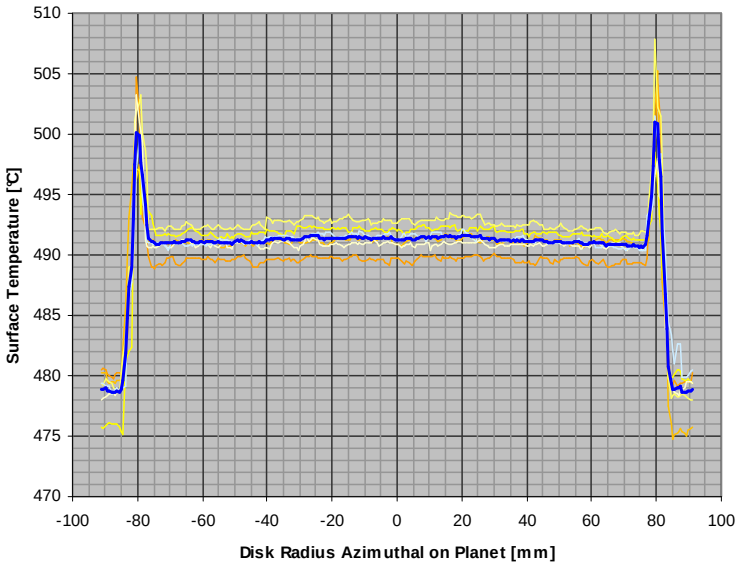


Fig. 22: Temperature distribution across all six 6-inch satellites for a mean temperature of 491°C

2.1.7. WP8 Adaptation/optimization of gas lines and reactor design

Leader: AIXTRON

Objectives

- Development and test of MOCVD equipment for the epitaxial growth of InN based materials
- Specific gas lines for new precursors and alternative carrier gas
- Gas injection and reactor optimization

Description of WP activities and progress towards objections, deliverables and milestones (devided by tasks)

Task 8.1: Design of the 2 lines optimized for precursors #1 and #2 provided by SAFC

In the frame of task 8.1 AIXTRON has designed and realized two new lines for alternative nitrogen precursors. AIXTRON service engineers have installed the new lines in the MOCVD system in Montpellier (fig. 23). To save travel costs and time AIXTRON decided in accordance with CNRS to up-grade the system at the same time with a new dilution line for Cp_2Mg to be used as p-type dopant later in the project. The first line was equipped with mass flow controllers (MFC) and special seals for the new nitrogen precursors DMHz and TBHz. The second line for precursor #3, the single source, was first delivered and installed without MFCs due to the fact that the nature of precursor #3 was not fixed at that time. The dimension and sealing of the MFCs depends strongly on the chemical properties of the precursors. After the single precursors have been defined by SAFC and CNRS, AIXTRON delivered and installed suitable MFCs.

Beside the installation of the hardware (tubing, MFCs, pressure controller (PC), diverse valves, thermo bathes, etc.) the work included modifications on the control and safety software of the MOCVD equipment.

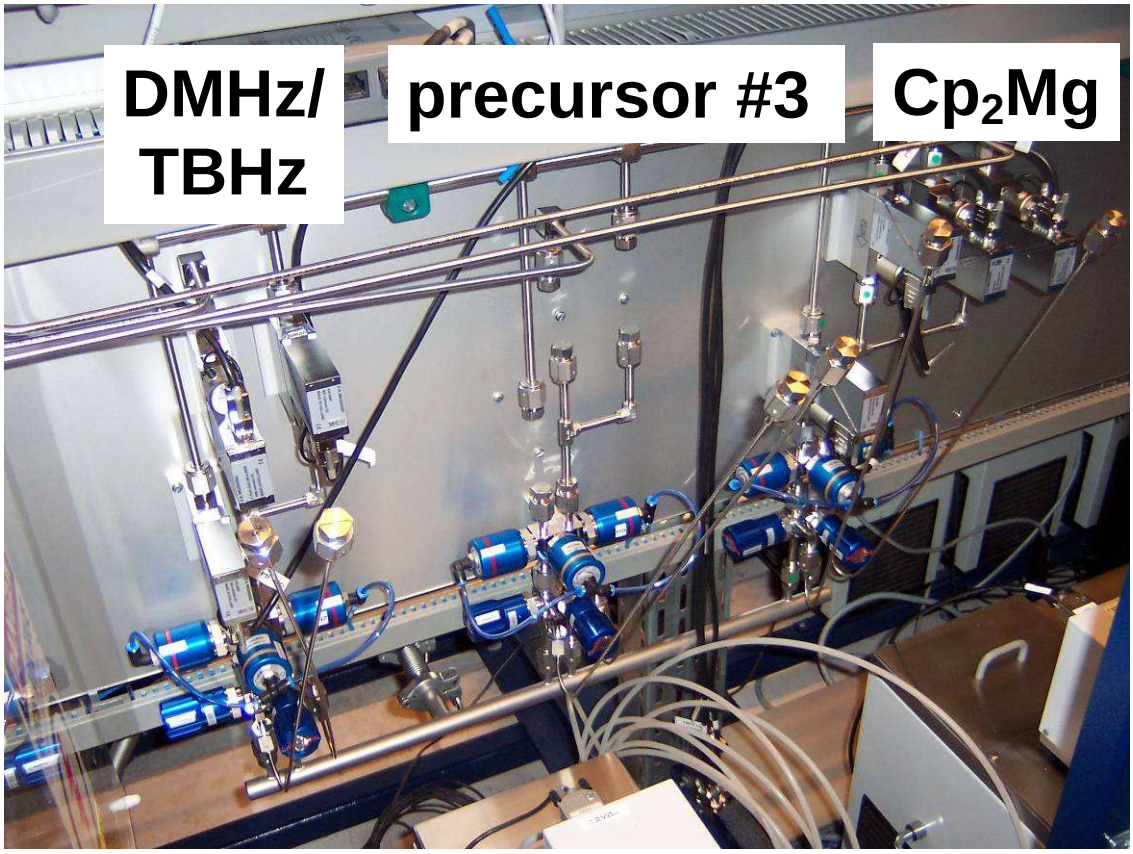


Fig. 23: Two new lines for alternative N-precursors and a dilution line for Cp_2Mg. All lines were installed into the AIX200/4RF-S reactor in Montpellier.

Task 8.2: Continuous optimization of the lines for precursor and carrier gas

Initial experiments at CNRS have shown that an alternative carrier gas might be necessary. Therefore AIXTRON has designed an additional carrier gas line for Ar just at the beginning of the project. The new design allows to use only one of the three gases (H2, N2, Ar) or to use mixtures of H_2 + Ar or N_2 + Ar, see fig. 24. The new carrier gas system was installed at the same time as the three new precursor lines.

Fig. 24: Installation of third carrier gas line (Ar) into the AIX200/4RF-S reactor in Montpellier. The three carrier gases can be switched individually or can be mixed.

At the beginning of the second year the new single precursor was defined by SAFC and CNRS. Due to its large legants this precursor had a very low vapor pressure which makes the mass transport into the reactor difficult. One possible solution to overcome this problem was to heat the line between source and reactor inlet. But this would have required an additional temperature control system and special heat resistant MFCs, PC and valves. Thus, the realization would have been time and cost consuming. The second possibility was to use MFCs with high mass flow capacity. The drawback of this simple solution is, that it might be, that the carrier gas will not saturate with the precursor. Nevertheless all partners agreed to start with the second approach to investigate the general suitability of the single precursor. If necessary the growth results would have been promising, it was planned to up-grade the MOCVD system with the line heating to increase the growth rates. But finally the results using the single precursors were not as good as with the individual precursors. Thus, it was the right decision, to perform first the basic studies without the expensive reactor up-grade.

Task 8.3: Gas injection and reactor optimization

During the whole project duration AIXTRON and CNRS have continuously monitored and analyzed the growth experiments with respect to further optimization potential of the reactor hardware and software.

In the 2nd half of the project many reactor optimizations have been developed by AIXTRON to improve the reliability of the reactor and to increase the reproducibility of the growth experiments. In detail the following reactor parts have been improved:

- The susceptor design was optimized to improve the temperature homogeneity across the wafer and to solve rotation problems.
- The design of the separation plate in the gas inlet has been optimized to improve the exact and reproducible positioning of the plate. The separation plate influences significantly the gas flow behavior in the reactor and thus, the deposition homogeneity.
- The Liner tube design was changed to allow the integration of a quartz ceiling, which significantly reduces the reproducibility and maintenance efforts.

The complete set of up-grades and optimizations was successfully tested at CNRS. The reliability of the MOCVD equipment and the reproducibility of the experiments were significantly improved. Also the time, spend for maintenance could be reduced. All these were important aspects regarding the later production potential of the technology.

Task 8.4: Final configuration of the MOCVD growth equipment

All reactor modifications developed during the InDot project have been successfully tested at CNRS. Finally the remaining process challenges concerning the p-type doping were not related to the MOCVD reactor design of the CNRS equipment. Thus, the existing MOCVD reactor state of the art at CNRS at the end of the project has been defined as “final MOCVD system design for InN / InGaN quantum dot structures growth” which was a milestone of the project. Using the new equipment CNRS was able to handle all new precursors in an efficient manner, all experiments were reproducible and the reliability of the MOCVD system under the extreme conditions given by the InN growth process was significantly reduced.

As far as adaptable, the MOCVD equipment related InDot results have been transferred into Planetray and CCS production reactors. This concerns so far mainly the improved TCS. In future the InDot results will be used to further improve the production type MOCVD equipment with respect to the growth of diverse compound materials requiring low growth temperatures. The optimized production equipment will not be limited to the growth of InN-based materials.

2.1.8. WP9 Mapping of characterizations

Leader: AIXTRON

Objectives

- Qualifying the equipment design through the determination of the sample uniformity
- Verification of the reproducibility of the growth processes

Description of WP activities and progress towards objections, deliverables and milestones (divided by tasks)

Task 9.1: Photoluminescence and sheet resistance mapping on 2 inch wafers

To verify the improved susceptor design - see tasks 7.2/8.3 – CNRS has grown thick GaN, InGaN and InN layers on 2-inch sapphire substrates using the old susceptor set-up and the new set-up, respectively. All wafers delivered by CNRS have been characterized in detail using sheet resistance mapping, room temperature (RT) PL, white light interference and X-ray diffraction. The experiments at CNRS have been performed without special uniformity tuning for the process. This was true for the new as well as for the old susceptor set-up because the priority for uniformity studies was low compared to the challenge to achieve the p-type doping before the end of the project.

The sheet resistance of all samples was comparable for the old and the new susceptor set-up. The uniformity values for all samples, independent of the material and the set-up were between 3 and 5% across the 2-inch wafers. For tuned processes and optimized equipment uniformity values below 2% are possible.

Only the GaN samples showed RT-PL activity. With both set-ups state of the art material could be grown in terms of PL intensity and line width (FWHW ~ 7eV for both samples).

The uniformity of the layer thickness was determined using white light interference measurements. Fig. 25 shows as an example the measurement on the InGaN samples grown with the old (a) and new (b) set-up.

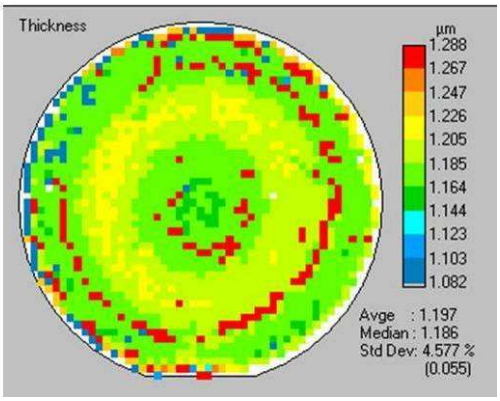


Fig. 25a: Thickness mapping on a thick InGaN layer grown with the old susceptor set-up.

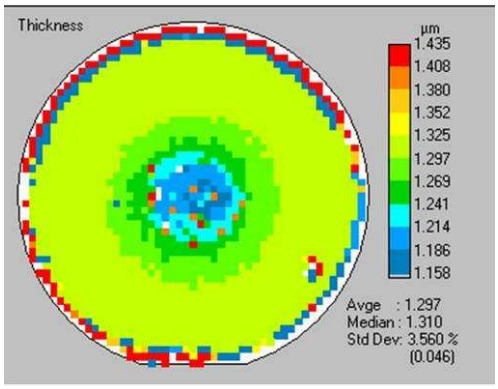


Fig. 25b: Thickness mapping on a thick InGaN layer grown with the old susceptor set-up.

The InGaN sample grown with the new set-up has a slightly more homogeneous thickness distribution. This is due to the fact, that the growth rate of the ternary compound is more sensitive on temperature deviations than the binary materials InN and GaN. For GaN the thickness uniformity was the same, for InN the sample grown with the new set up was much better compared to the one grown with the old set-up. But this result could be explained by the inaccuracy of the measurement for the InN. Due to the low refractive index of the InN the approximately 1,2 µm thick layers showed only half of an oscillation which could causes a huge failure for the thickness determination from this whit light reflection measurement.

In summary, the layer properties of the materials deposited with the new susceptor set-up were not significantly better than the properties of the layers grown with the old set-up. But this was more due to the not tuned deposition process than due to not optimized equipment. The temperature uniformity measurements performed on the new set-up in the AIXTRON laboratory demonstrated the potential of the improved equipment to enhance the material homogeneity and process reproducibility.

To evaluate the improved TCS and the adapted hardware in the 42x2-inch Planetary Reactor® (fig. 26) as well as in the 30x2-inch Close Coupled Showerhead (CCS) reactor (fig. 27) AIXTRON has investigated the growth of InGaN MQW structures containing In-rich material. The experiments at CNRS have shown that the increased Ga-content in the InGaN has only a minor influence on the material quality. Therefore AIXTRON decided to test the reactor hardware and the new TCS in the production type reactors using InGaN material emitting in the green spectral range. This gave AIXTRON the opportunity to embed the material into existing LED structures which are easy to characterize using PL mappings. In addition, the ternary material is much more sensitive against temperature inhomogeneities than the binary InN. Thus, AIXTRON has performed several full loaded runs for the deposition of InGaN MQW structures in both types of production reactors and has characterized all wafers by RT PL mappings.

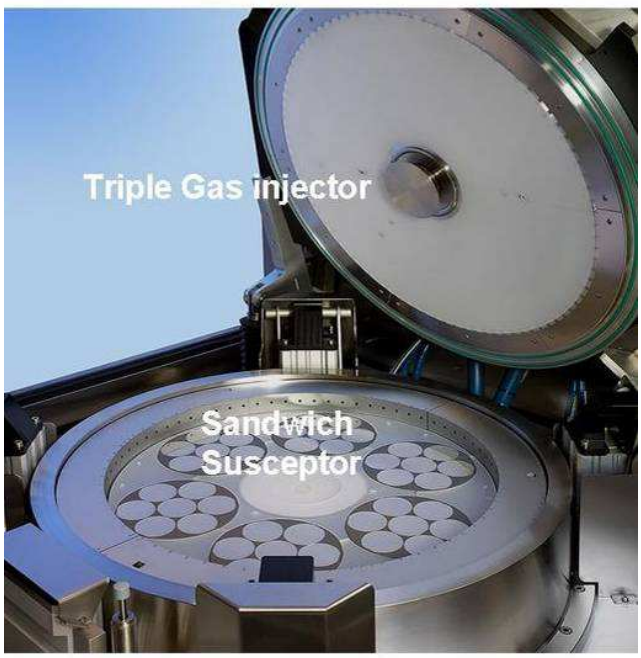


Fig. 26: Production type Planetray® MOCVD Reactor G4 HT in its 42x2-inch configuration.

Fig. 27: Production type CCS MOCVD Reactor CRIUS in its 30x2-inch configuration.

Fig. 28 shows the InGaN MQW wave lengths uniformity on one single wafer taken from the 42x2-inch Planetary reactor. The average wavelength is 527 nm, the standard deviation across the wafer only 1,2 nm which fulfills the material requirements of M16 but in a material with higher Ga-content. The wave length spread (maximum to minimum) from run to run for 3 executive runs was only 4,4 nm.

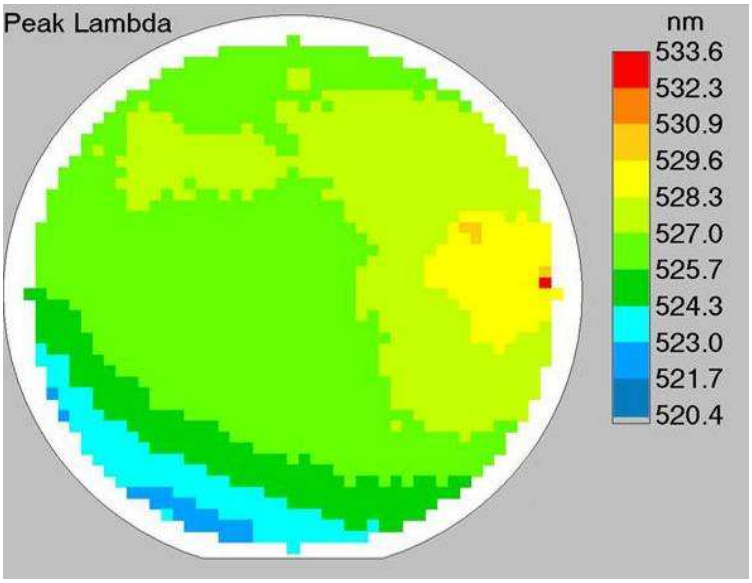


Fig. 28: RT PL mapping from an InGaN MQW structure. The single wafer has been taken from a full loaded run in an 42x2-inch Planetray Reactor. Average wavelength is 527 nm, the standard deviation across the wafer 1,2 nm.

The same InGaN MQW structures have been grown in the modified 30x2 inch CCS reactor. In the 30x2-inch reactor the wafers are arranged on three rings - see fig. 27 - 4 on the center ring, 10 on the middle ring and 16 on the outer ring. Fig shows the PL mapping from one wafer of each ring. The average wave length for all wafers is 509 nm. The standard deveations on the sngle wafers are about 2 nm, the wave length spread between maximum and minimum value only 4,6 nm. These are excellent values for the ternary InGaN material emitting in the green spectral range.

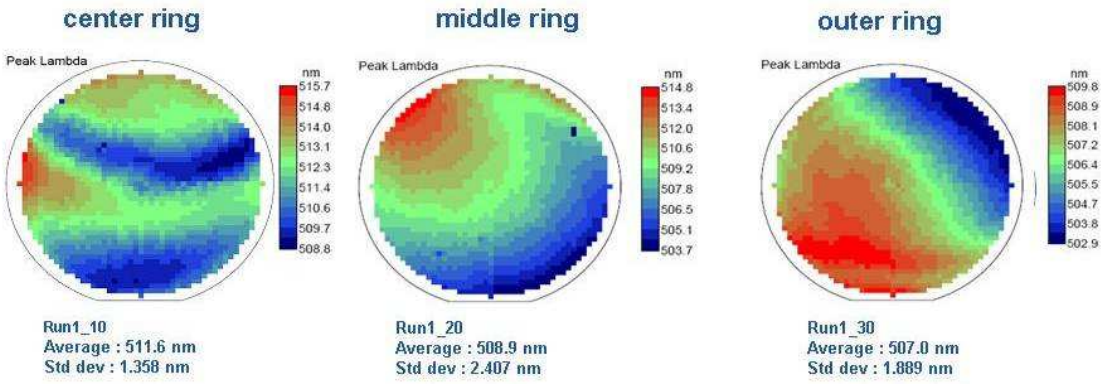


Fig. 29: 3 wafers with InGaN MQW structures of a full loaded run in an 30x2 inch CCS production MOCVD reactor.

The experiments in the different production type reactors verified the reproducibility of the growth processes and thus qualified the equipment design through the determination of the sample uniformity which was the objective of this WP.

2.1.9. Purifier design

Leader: SAES

Objectives

- Development of specific purifying package for InN, InGaN and quantum dots MOCVD growth:
- In- process qualification and validation (purity, lifetime, …)
- Ammonia purification
- Organometallic precursors
- Carrier gases (standard : N2 and alternative :Ar, He)

Description of WP activities and progress towards objections, deliverables and milestones (divided by tasks)

This Work Package was focused on providing reliable sub-ppb gas quality for the process gases used in the growth of InN and other thin films. On site tests to monitor the gas purity were carried out during the project by means of trace gas analyzers or a new off-line batch analysis method.

At CNRS, the process gases come from high pressure cylinders with a degree of purity not adequate for the purpose of the research; considering the flow rate during film growth, gas specifications and the duty cycle, the right set of purifiers was identified and supplied to guarantee a content of oxygen and water vapour consistently below 1 ppb.
The figure below shows the set of bulk purifiers installed at CNRS and used throughout the duration of the project. The purifiers are mounted on the wall next to the Aixtron reactor; from left to right it is possible to identify the hydrogen, the argon and the nitrogen purifiers.

The ammonia purifier, in the picture below, has been mounted inside the Aixtron reactor.

The gas purity at the outlet of the hydrogen and nitrogen purifiers was checked with the highly advanced Delta F DF-760 suitable for the continuous monitoring of oxygen and water vapour in bulk gases down to concentrations below 1 ppb.
The results confirmed the efficiency of the purifiers to remove the impurities of interest.
Since the above instrument or others with equivalent specifications are highly sophisticated and expensive, their use for the monitoring of gas purity at the point of use

is not practical; thus the development of a method for off-line batch analysis has been a target of the project. A sensitivity of 10 ppb for the contribution of oxygen and water vapour has been considered a reasonable target.
A dedicated study was carried out in the laboratory to develop a device capable to concentrate oxygen and water vapour from a sample gas and then release both impurities in controlled conditions in order to be able to make their quantification.
The method was first developed and tested in the laboratory and proved to be very solid with sensitivity in the very low ppb range, depending on the quantity of sample gas passed through the concentration device.
The method was then validated by testing the nitrogen purity upstream and downstream the getter purifier at CNRS. Four collection devices, previously used for the laboratory testing, were mounted at CNRS, two in parallel before the purifier and two in parallel after the purifier.
Since SAES personnel were on site for the sample collection, it lasted about 24 hours; longer collection time can be applied to increase the sensitivity of the method.
The following table summarises the gas specifications at purifier inlet and outlet together with the results obtained in the laboratory after the release of the oxygen containing impurities from the collection devices.

GAS SPECIFICATIONS	SAES RESULTS
☐ Inlet: 5N	☐ Inlet: O2 equivalent
☐ O2: <2 ppm	☐ 1.7 ppm
☐ H2O: <3 ppm	☐ 1.8 ppm
☐ Outlet: purifier specifications	☐ Outlet:
☐ O2< 1 ppb	☐ <2 (1.4) ppb
☐ H2O< 1 ppb	☐ <2 (1.5) ppb

The results are given in oxygen equivalent because the method cannot distinguish between water vapour and oxygen.
It can be observed that the reproducibility of the results, even if limited to 4 analyses, is quite good and the estimated oxygen content is in very good agreement with the specifications.

To summarize, the results in the field confirmed the ones obtained in the laboratory; the main features of this new off-line batch analyses are:

- excellent dynamic range: the method allows to adjust over a very broad range of gas purity changing the collection conditions, mainly time and sample flow rate
- excellent sensitivity: 1 ppb is doable allowing 1 week of sample collection or with flow rates higher than 1 l/min
- long shelf life: the impurities desorption from the collection devices has been carried out about 20 days after sample collection
- no analytical expertise is required for sample collection
- the collection device is compact and light

2.2. Summary of main achievements

Precursor development

Objectives of the development of new precursors which are suitable for the growth of high quality InN QD and In-rich InGaN layers were to ensure a reliable fabrication process and to guarantee the potential for scale up synthesis and purification procedures to production level.

The first series of compounds developed in the project were alternative N sources to access lower growth temperatures followed by compounds containing both In and N to enhance stoichiometry control and finally improved In compounds to fully optimise the deposition parameters accessible. Having determined the best source combinations for the matrix deposition a range of dopant materials was developed to enable device structures to be targeted. The progress in identification, synthesis, characterisation, purification and supply of samples followed the planned sub task schedule with all milestones and deliverables met in a timely fashion. The experimental processes employed have been refined and proven to yield ultra-high purity materials in a reliable and scaleable fashion. This new combination of precursors is now ready for launch as suitable for InN based device fabrication to the highest standard.

MOCVD equipment development

The objective of the equipment development was to improve the MOCVD equipment for the low temperature growth of InN and InN-based compounds. The final equipment should allow the growth of InN-based materials under production conditions. Thus, the optimized equipment had to enable stable, reproducible and efficient MOCVD processes. In a first step the R&D MOCVD reactor at CNRS was up-graded accordingly. A new temperature control system has been developed, to allow the low temperature growth on the InN-based materials and new precursor lines have been implemented to handle the new precursors provided by SAFC. In a second step the MOCVD equipment was optimized to enhance the process stability, reproducibility and efficiency. Main components which have been optimized were the gas inlet, the design of the inner quartz tube (liner) and the susceptor set-up regarding design and used materials. After the successful testing of the new equipment at CNRS, two different production type reactors in the AIXTRON laboratory have been adapted accordingly to test the new equipment and processes under production aspects. In both reactors, a 42x2-inch Planetary® Reactor as well as a 30x2-inch Close Coupled Showerhead (CCS) Reactor InGaN MQW structures have been grown with excellent uniformity values for the material quality. In full loaded runs the MOCVD equipment was validated by excellent homogeneity values on all wafers of the same run as well as on all wafers of three consecutive runs with the same process recipe. All deliverable and milestones related to the equipment development have been fulfilled. The main InDot achievement related to the MOCVD equipment development is the availability MOCVD prototype equipment, for R&D as well as for industry, which can be used for the production of advanced InN or In-rich InGaN based devices. But the new technology is not limited to these materials and can also be used for the deposition of other compound materials requiring low deposition temperatures like chalcogenides (e.g. GeSbTe) which have a huge marked potential as basis for phase change memories.

Gas purification and analysis equipment

Objective of this task was the development of a specific purifying package for InN, InGaN and quantum dots MOCVD growth. SAES has developed and delivered several gas purifying systems for bulk gases. In particular advanced purifiers for H_2, Ar and NH_3

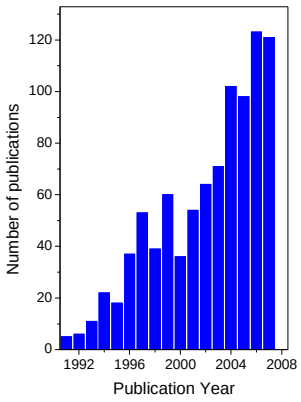
were installed into the MOCVD system in Montpellier. The purifier package has been tested for the growth of the nitrides thin films and with off-line batch analysis method. The off-line batch analysis method has been developed to measure oxygen containing molecules in gas at single ppb detection limit. The procedure was used to validate the Monotorr nitrogen purifier efficiency at CNRS monitoring the purity upstream and downstream. The test demonstrated both the good efficiency of the purifier and the capability of the off-line batch analysis to monitor low ppb impurities concentration.

Status on MOCVD process development for InN and In-rich InGaN layers

Using the new precursors and the optimized equipment CNRS has developed MOCVD processes for the deposition of InN QD and InGaN films at low temperatures. The QD density could be increased up to $1x10^{11}cm^{-2}$ and $In_{1-x}Ga_xN$ alloys have been realized in the whole composition range envisaged in the frame of the project ($x < 0,15$) and in exceed of that up to 0,67. The high temperature encapsulation of InN QD with GaN failed but the alternative approach of using In-rich InGaN grown at moderate temperatures was successful. To achieve this, the reproducible growth process of high quality InGaN, with composition up to 40% was studied. The use of TMGa was preferred for compositions above 15%, while TEGa proved more suitable below this limit. The best crystalline quality was obtained by lowering the growth temperature to 500°C, compared to the standard growth temperature of 550°C used before. N-type doping of these alloys with silicon was successfully achieved. For p-type doping, Mg was used, and the incorporation of Mg into InN was calibrated. Annealing procedures for activating the magnesium dopant were established, and the effectiveness of p-type doping was demonstrated by photoluminescence. However parasitic n-type conduction prevented the determination of the p-type doping level in Hall effect experiments. The possibility of parasitic conduction channels at grain boundaries was evidenced, and a breakthrough was made in improving the lateral growth of InN, by using the $CBrCl_3$ precursor developed by SAFC to modify the growth mechanism of InN in MOCVD. Extremely flat surfaces were obtained, which pave the way to strong improvements of the grain structure of InN (seen in all samples worldwide). This should enable CNRS to get rid of the parasitic conduction, but necessitates further studies to be combined with the use of low temperature buffer layers to overcome the lattice mismatch problem.

The InDot consortium has launched a new FET Open proposal to further investigate the potential of improving the lateral growth of InN, by using the $CBrCl_3$ or equivalent compounds to improve the structural properties of the InN and to achieve electrically active p-type doping.

3. Dissemination and Use



Indium nitride and Indium nitride nanostructures will most probably take an important place on the nitride semiconductor business and science. The partners of this project are directly involved in the design, realization and marketing of MOCVD related technologies and the use of the results of this project place them ahead of competitors.

The figure on the left shows the evolution of the bibliography about InN semiconductor during the last decades. One clearly sees an exponential increase (Data extracted from Web Of Science, for the search "InN and nitride").

The development of a MOCVD technology for the production of InN-based devices will expand the market for multiwafer epitaxial systems manufactured by AIXTRON that expects a significant increase in demand for epi-systems designed for nitrides with high In-content, developed and tested in the frame of the Project. AIXTRON will use the project outcome to improve its CVD equipment with respect to the production of InN-based new devices. This will directly strengthen AIXTRON's position as European world leading manufacturer of CVD equipment and will result in the creation of new jobs at AIXTRON as well as on the end user site.

With regards to the actual production of the source materials in large scale SAFC Hitech has experience in-house for taking lab scale processes up to multi tonne capacity plants without compromise of purity. Investment in appropriately sized equipment will be performed as the market-need increases after the project has been completed. Due to the large number of areas the technology could be used in, it is difficult to estimate the volumes that could be needed but a target is to upscale to multi kg pa capacity equipment within 5 years of the end of a successful project.

SAES purifiers, standard or specifically developed for the application, have been qualified as an essential part of the process equipment to reliably grow InN films. Especially in a production environment where sources of contamination are numerous (backdiffusion, virtual leaks, outgassing, permeation...) point of use purifiers will allow to deliver consistent oxygen free process gases.

The statutory CNRS goals are: the advancement of fundamental knowledge with the aim of economic, social and cultural progress as well as to take care of result's valorization and application. This is exactly what CNRS does in the context of InDot: InN, related alloys and dots are quite an unknown system and most of their fundamental properties still have to be measured thoroughly. However, for the few which is known, this system is extremely promising in terms of practical applications. InDot will allow to develop the growth knowledge and to establish the required resources in order to be able to supply industrial and scientific community with appropriate samples. This should impulse a European dynamic toward this new promising technology, to be able to compete with USA and Asia similar efforts.

Exploitable knowledge and its Use

Overview table

Exploitable Knowledge (description)	**Exploitable product(s) or measure(s)**	**Sector(s)** of application	Timetable for commercial use	Patents or other IPR protection	**Owner** & Other Partner(s) involved
Advanced temperature control system for low temperatures	*MOCVD equipment*	*Compound semiconductor industry/Compound semicondiuctor based research*	*2008 onwards*		*AIXTRON*
Gas mixing system for the simultaneous use of different carrier gases	*MOCVD equipment*	*Compound semiconductor industry/Compound semicondiuctor based research*	*2008 onwards*		*AIXTRON*
Ceiling for tube reactors	*MOCVD equipment*	*Compound semiconductor industry/Compound semicondiuctor based research*	*2008 onwards*		*AIXTRON*
Improved Hardware for MOCVD R&D reactors	*MOCVD equipment*	*Compound semiconductor industry/Compound semicondiuctor based research*	*2008 onwards*		*AIXTRON*
Improved Hardware for industrial MOCVD reactors	*MOCVD equipment*	*Compound semiconductor industry*	*2008 onwards*		*AIXTRON*
InN nucleation/dots densities using rare gases	*MOCVD process parameters*	*Compound semiconductor industry*	*About 2010*	*Patented in July 2006*	*CNRS*
New precursors for InN QD fabrication by MOCVD	Novel source(s) combinations and increased purity	Compound Semiconductor	2008 onwards	Secret know how	SAFC Hitech
Ar, N2 and H2 purifiers qualified for MOCVD	Gas purifiers	Compound semiconductor and silicon industry	2008 onwards		SAES
Development of an off-line	Analytical Certifications	Compound semiconductor	2008 onwards		SAES

Exploitable Knowledge (description)	**Exploitable product(s) or measure(s)**	**Sector(s)** of application	Timetable for commercial use	Patents or other IPR protection	**Owner** & Other Partner(s) involved
method to monitor O2+H2O		and silicon industry			

Usually, the MOCVD equipment for the deposition of Group-III-N-based materials is optimized for a high temperature growth regime but for the InN deposition low temperatures are required. The temperature in the reactor chamber is measured with a light pipe (pyrometer). The commonly used Si detector operates at temperatures between 400°C and 1900°C. The output of the Si detector is fed into the Eurotherm controller and is used to control the susceptor temperature. To allow the control of temperatures below 400 °C the the temperature control system was upgraded with an additional low band gap detector made from InGaAs. The InGaAs detector operates in the lower temperature range between 100°C and 1000°C. In the new developed equipment the output of the light pipe is split and connected to the two detectors to cover the temperature range between 100 °C and 1900 °C. The control software was modified in a way that for the low temperature range the signal coming from the InGaAs detector is used by the Eurotherm controller. For the high temperature range the Si detector output is used.
The new temperature control system can be exploited in all up-coming MOCVD systems for the deposition of InN based materials, but also for MOCVD equipment for all other kind of materials requiring growth processes running at extremely low and high temperatures within one deposition process. Examples are the MOCVD deposition of high quality ZnO or chalcogenide materials like GeSbTe.
Recent R&D results have shown that a very low growth temperature at the substrate ZnO interface significantly improves the material quality and the same is true for the deposition of GeSbTe for applications based on the phase change behavior of this material.

Today MOCVD systems are equipped with one or two carrier gasses, which are used separately for different deposition processes. The new gas mixing system allows the use of three carrier gasses and the use of a mixture of two of them at the same time. The new gas mixing system offers much more flexibility compared to the standard equipment which is of particular importance for the development of new material systems and thus, will be exploited in AIXTRON R&D MOCVD reactors.

To improve the temperature homogeneity across the substrate the materials as well as the design of the wafer carrier was significantly improved. The improved design will be exploited in all AIXTRON R&D MOCVD reactors for the growth of Group-III-N based materials.

Currently the Liners of tube reactors must be etched from time to time to remove depositions. Usually the Liner is only coated above the wafer position but, due to practical reasons, the whole Liner has to be etched, which results in significant maintenance effort. In contrary AIXTRON has profound experience in the use of “ceilings” as the top reactor wall in production Planetary Reactors®. These ceilings can easily be exchanged, which improves the reproducibility and reduces the

maintenance time. Therefore AIXTRON worked on an improved Liner design for tube reactors like the AIX200/4 RFS to adapt the ceiling-concept.

All new equipment has been qualified in the frame of the projects and prototype equipment is running on CNRS site (R&D) reactor as well as in the AIXTRON laboratory (industrial multiwafer reactors). AIXTRON sees the direct exploitation for the new equipment for the production of InN and In-rich InGaN based devises only on a mid to long-term timescale because the final prove of p-type doping is missing and this is a prerequisite for the realization of optoelectronic devices. But the last years have shown, that there is a world wide increasing interest in research on these kinds of materials which gives AIXTRON the opportunity to exploit the improved R&D MOCVD reactors from now on. The breakthrough in the process development at CNRS at the end of the project and the world wide increasing research activities make AIXTRON sure, that the last process related problems will be solved within the next 5 years and first InN-based devises will be produced on an industrial scale.

With GeSbTe (GST) a second compound material is close to jump from R&D to production for the realization of phase change memories (PCM). Today this material is already used for the production of PCMs. But current devices consist of a simple structures and bases on sputtered GST. The next generation of these devices will require more sophisticated deposition techniques and MOCVD has been proven to be suitable. The deposition of GST requires comparable equipment properties as for InN-based materials. Therefore the InDot results can be exploited also for this new class of materials, too. This exploitation path was not foreseen at the start of InDot but has much even higher potential for mid term commercial exploitation of the new MOCVD equipment optimized for the low temperature growth.

One patent application has been deposited on July 2006, by CNRS. It deals with the improvement of InN nucleation/dots densities using rare gases. This application has been extended to Europe, USA and Japan according to the standard CNRS procedure, on July 2007.
The main exploitation foreseen by CNRS for this result will be to sell an exploitation licence to an industrial interested in producing devices using a process based on the patented results.
Further work is still ongoing within the Indot project. Appropriate IPR protection measures will be taken when and if necessary by the involved partners.

To date a number of sophisticated analytical techniques have been optimised in-house by HITECH to allow good sensitivity to be achieved for the new compounds developed. In-house methods have been used to purify sources to ensure that impurity levels are low and do not affect electronic performance. As the chemicals themselves are know patent protection can only be sought for their special use in the developed processes. The results on the project have highlighted the process improvements that can be achieved using different chemicals hence it is hoped to submit applications in the future.

A new hydrogen purifier has been proposed to replace the commonly used Pd purifier; the analytical results have demonstrated that this new purifier has improved performance at least for water vapour removal when compared to the traditionally

used Pd purifier. In addition other advantages of the SAES regenerable purifier compared to the palladium membrane technology are:
- power failure does not damage the on going process and the purifier system itself
- full automation increases the reliability with no downtime and lower cost of ownership
- low pressure drop
The qualification of the purifier in the frame of the project will help in the commercialization. CNRS activity has been essential for the qualification of the hydrogen purifier as well as qualification of the ammonia, argon/helium and nitrogen purifiers.
Thanks to the InDot study, it is expected a benefit in the sales of purifies also in the more traditional application of GaN thin films. A potential new business in the range of a few hundreds of thousands euro is expected if the InN film technology will be used in the future.

The off-line approach for monitoring gas purity will allow SAES to further support its customers to issues related to gas purity. In order to propose to the market this new approach, it will be necessary to engineer the collection device optimised during the research; an initial revenue in the range of a few tens of thousands euro can be expected.

Dissemination of knowledge

Overview table

Planned/actual Dates	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
05/2006	*AIXTRON User meeting*	*Research/Industry*	*Global*	*100*	*AIXTRON*
09/2006	*AIXTRON User meeting*	*Research/Industry*	*Global*	*150*	*AIXTRON*
06/2007	*AIXTRON User meeting*	*Research/Industry*	*Europe/Global*	*150*	*AIXTRON*
08/2007	*AIXTRON User meeting*	*Research/Industry*	*US/Global*	*150*	*AIXTRON*
11/2006	*Workshop*	*Research/Industry*	*Europe*	*100*	*AIXTRON/CNRS/SAFC HITECH/SAES*
06/2008	*AIXTRON User meeting*	*Research/Industry*	*Global*	*150*	*AIXTRON*
09/2008	*AIXTRON User meeting*	*Research/Industry*	*Europe/Global*	*100*	*AIXTRON*
Ongoing	*Costumer information*	*Research/Industry*	*Global*	*50*	*AIXTRON / CNRS*
12/2006	*Project web-site*	*General public*	*Global*		*CNRS / all*
Q1/2006	*Company newsletter*	*Compound semiconductor*	**Global**	*5000*	*SAFC Hitech*
Q3/2007	*Company newsletter*	*Compound*	**Global**	*5000*	*SAFC Hitech*

Planned/actual Dates	Type	Type of audience	Countries addressed	Size of audience	Partner responsible /involved
		semiconductor			
when more results available (2008)	*Company newsletter Direct mailing New product launch*	*Compound semiconductor*	**Global**	*5000*	*SAFC Hitech*
when results available (2008)	*Direct mailing Exhibitions*	*Compound semiconductor and silicon industry*	**Global**		*SAES*
ongoing	*Customer information*	*Compound semiconductor and silicon industry*	**Global**	*50*	*SAES*

AIXTRON contributed on 4 user meetings to the dissemination and exploitation of the MOCVD equipment related results. Usually the AIXTRON user meetings are held in conjunction with important MOCVD conferences and exhibitions to address the key audience. In 2006 two user meetings were held. In Miyazaki, Japan on 22nd May at the occasion of the International Conference on Metal Organic Vapor Phase Deposition as well as in Hsinchu and Tainan, Taiwan on 28th and 29th September, respectively. The two user meetings in 2007 were held in conjunction with the 12th European Workshop on Metalorganic Vapour Phase Epitaxy (EW-MOVPE) in Bratislava (03 - 06 June), Slovakia and with 15th International Conference on Crystal Growth + 13th International Conference on Vapor Growth and Epitaxy in Salt Lake City, Utah, USA (12 - 17 August).
The two user meetings in 2008 were held in conjunction with the international conference on MOVPE (IC MOVPE) in Metz, France (01.-06. June 2008) and with the 7th European Conference on Silicon Carbide and Related Materials (ECSCRM 208) in Barcelona, Spain (07.-11. September 2008).

In November 2006 Dr. Giesen has presented the InDot project and first project results on the MONA (SSA, Contract No 017255) Symposium & Roadmapping Workshop on Nanophotonics Processes, Materials and Devices. Further information and the symposium report can be found on the MONA web page: http://www.ist-mona.org/documents/grenoble.asp.

CNRS has provided process information which can be used by AIXTRON for the commercialization of the new MOCVD equipment in the frame of direct costumer contacts.

An internet/intranet server dedicated to the project was set up to ensure proper circulation of information and results between partners, as well as to present the public information. The server has a part with password protected access, where management information and results are accessible to the partners and the EC. Another part is publicly available, to present the project, the consortium and the key results.
The public part of the website will be accessible and maintained well beyond the lifetime of the project, to ensure a broad dissemination of the results generated by the consortium.

In September 2007, Dr Bernard Gil has presented some results obtained within the Indot project on the 7th International Conference on Nitride Semiconductors (ICNS-7, http://www.tms.org/Meetings/specialty/icns7/Home.html), held in Las Vegas. The slides are available on the Indot website.

From the beginning of the project, 2 publications have been accepted and published:
- Applied Physics Letters Vol. 90, page 153102 (2007)
- Phys.Stat.Sol.RRL 1, vol.6, p.268, 2007)
Since the beginning of the project a lot of work has been done and nice results obtained, although we wanted to keep the know-how developed confidential for a while. In this last period, we will write some joined publications showing these results.

A strong participation to the international symposium on nitride growth, to be held in japan in july 2008 is foreseen, since this is the best place to expose the Indot results to the world wide community.

The launch of the project has been detailed in SAFC Hitech's newsletter that is distributed to a world wide customer base in the Compound Semiconductor industry of around 5000 contacts. Furthermore it is available at exhibitions at conferences and trade shows. The plan to use this medium as the initial method to raise awareness of new products and/or combinations of sources that have achieved improved performance in the area of InN QD fabrication by MOCVD has been followed with a second article dedicated to project results issued in the Q3 newsletter. The chemicals highlighted. It is planned to use this medium as the initial method to raise awareness of new products and/or combinations of sources that have achieved improved performance in the area of InN QD fabrication by MOCVD. These chemicals will be made available to the market place and dedicated customers targeted to generate interest followed by a full product launch if deemed necessary to ensure complete exposure of the project results.
It is also planned to publish joint papers with partners to disseminate the scientific advances of the consortium.

Once the results will be available, dissemination of the information will be through the web site, the participation to conferences and exhibitions like CS ManTech, Semicon and joint papers.