SAND2008-4906P

SSL Peer Review, July 22, 2008

"Improved InGaN Epitaxial Quality by Optimizing Growth Chemistry"

Sandia National Laboratories
Albuquerque, NM 87185

M6743230
(Inter-Entity Work Order Number)

Joel Chaddock
(NETL Project Manager)

Sandia National Laboratories

PI and Point of Contact:
J. Randall Creighton
Sandia National Laboratories, MS 1086
Albuquerque, NM 87185-1086
jrcreig@sandia.gov
phone: (505) 844-3955, fax: (505) 844-3211

Project Team Member/Presenter:
Michael E. Coltrin
Sandia National Laboratories, MS 1086
Albuquerque, NM 87185-1086
mecoltr@sandia.gov
phone: (505) 844-7843; fax: (505) 844-3211

Other Team Members:
Sandia National Labs is the sole performer

Technology Focus:
Core

Relevant Subtask Priority Area:
"High-Efficiency Semiconductor Materials, 1.1.2"
(Improve IQE across the visible spectrum and in the near UV – down to 360 nm)

Project Schedule / Budget

	Start Date	End Date	Government Share	Performer Share	Total
Budget Period 1	08/01/07	07/31/08	$385,000	$0	$385,000
Budget Period 2	08/01/08	07/31/09	$400,000	$0	$400,000
Total	**08/01/07**	**07/31/09**	**$785,000**	**$0**	**$785 ,000**

Note: The funding for this Project was received in early August 2007, but because of manpower and administrative issues we did not begin work until September. Budget Period 1 will be extended by 1 month, to 8/31/08.

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Project Objective

Relevant Subtask 1.1.2 “High-Efficiency Semiconductor Materials”

Goal: Achieve a 2X improvement in IQE for green InGaN emitters (~ 530 nm) by optimization of the growth chemistry*

The critical problems that we will address are:

- The generally poor InGaN material quality (defect formation, metallic inclusions, impurity incorporation) due to low growth temperatures currently necessary to incorporate sufficient indium
- Inefficient and poorly controlled growth process, which are potential barriers for cost and manufacturability

*Note: the current IQE of our 530 nm test structure is 5.2%. While this is not “state-of-the-art”, the methods we discover that yield IQE improvements should be universally applicable

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Task 1: Determine Role of Parasitic Gas-Phase Chemistry in InGaN MOCVD

1) Background:

Our earlier research clearly demonstrated that parasitic gas-phase reactions lead to nanoparticle formation and pathological MOCVD behavior for the AlGaN system

Preliminary results also strongly suggest that nanoparticle formation is significant at InGaN MOCVD conditions

Task 1 Goals – Answer two questions:

Do gas-phase nanoparticles significantly impact our ability to grow InGaN?
What is the role (if any) of H_2 carrier gas in the decomposition of TMIn and TMGa?

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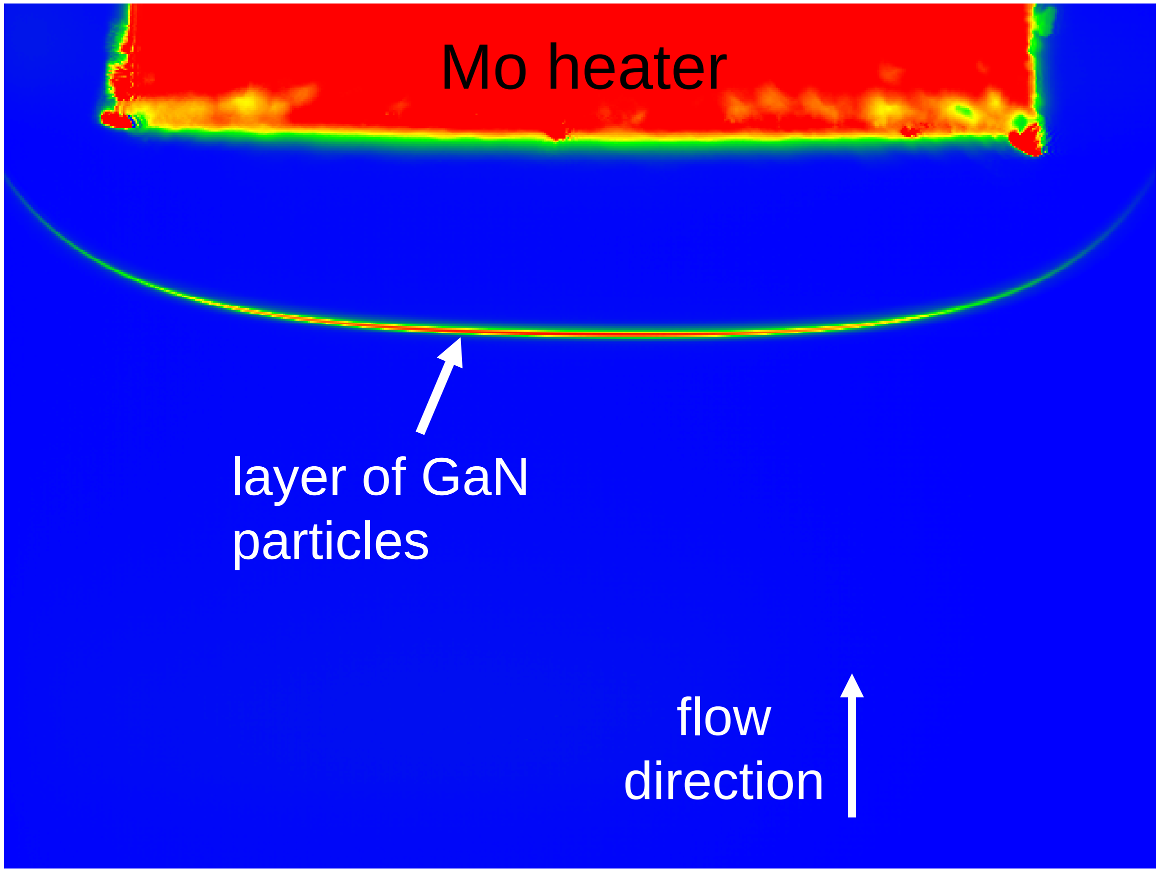
Nanoparticles are detected for GaN, AlN, and InN MOCVD. They reside in the thermal boundary layer at a gas temperature of ~600°C



GaN conditions;

P = 140 Torr

T ~1000°C

F_t = 6.5 slm

vel = 23 cm/sec

NH_3 = 16%

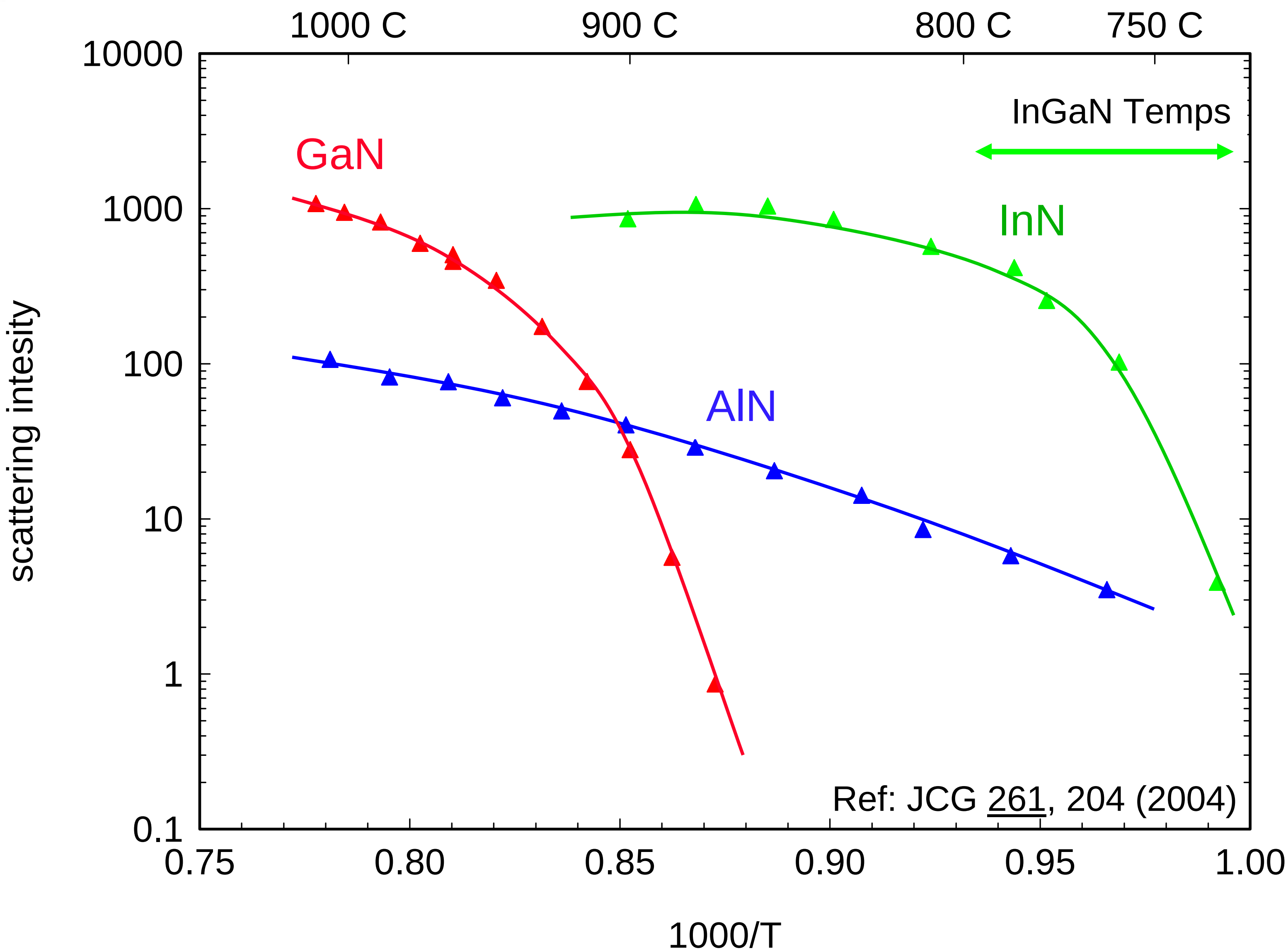
TMGa = 3 sccm

Reference:

APL 81, 2626 (2002)

Mie scattering yields AlN particle size of ~ 50 nm, with 10-80% precursor consumption. GaN nanoparticles are non-spherical, size not determined.

Onset of particle formation occurs in temperature range where drop in grow rate (or %In) is observed



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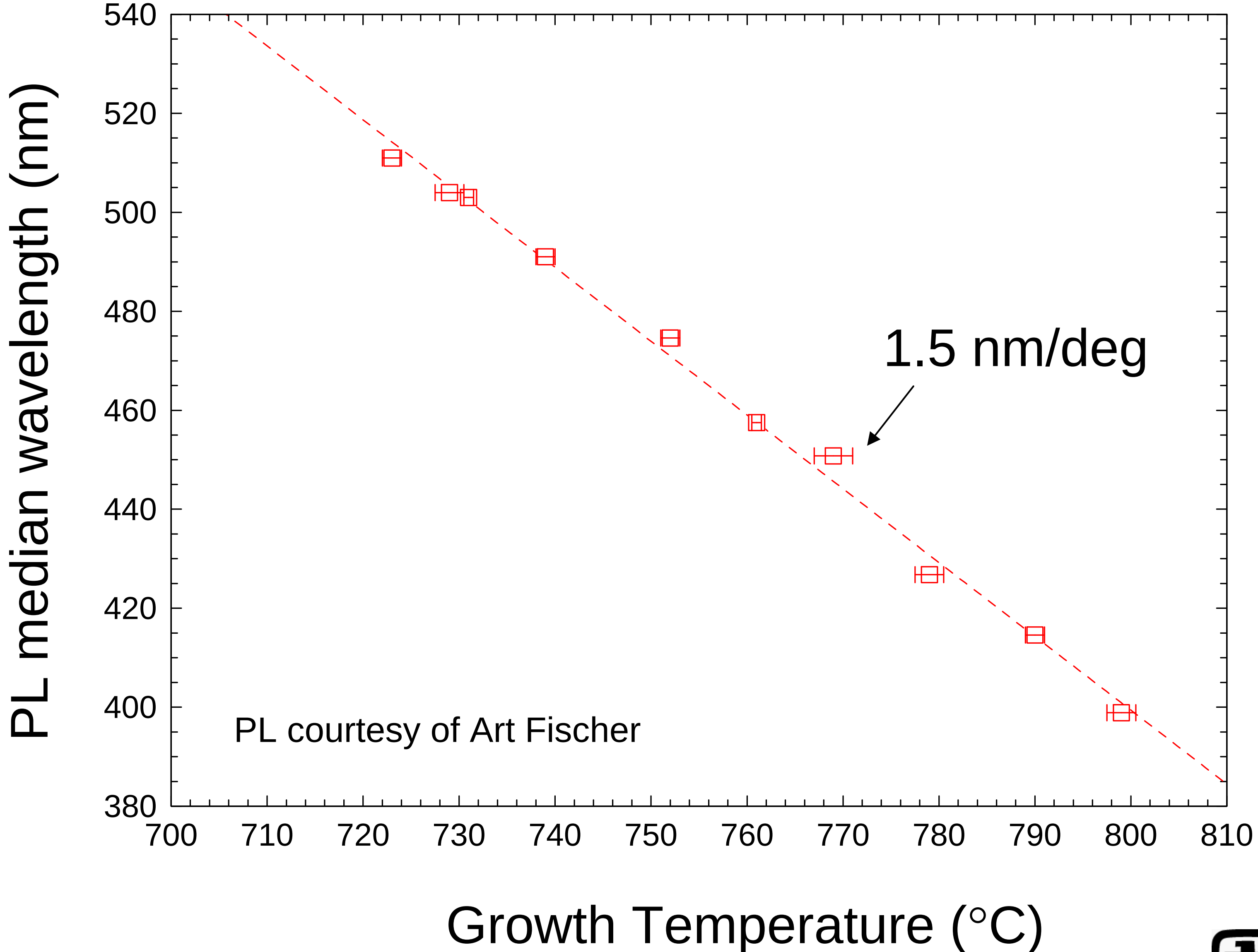
In-content drops with increasing temperature in 700-800°C range



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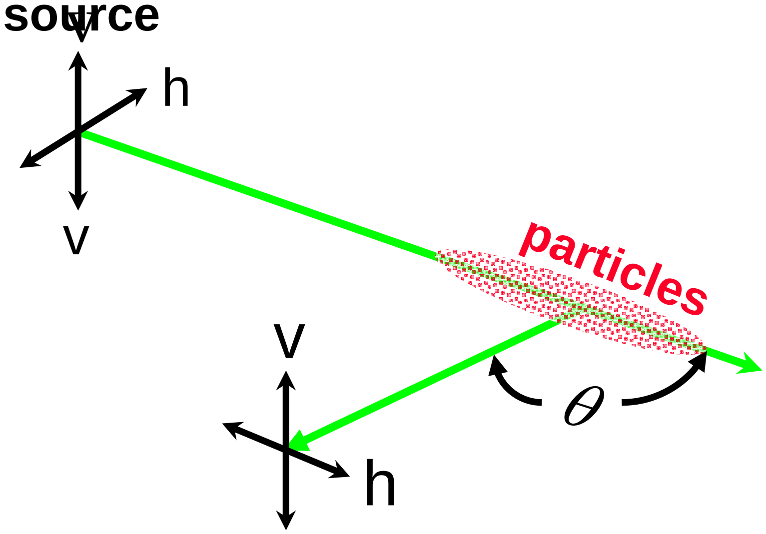
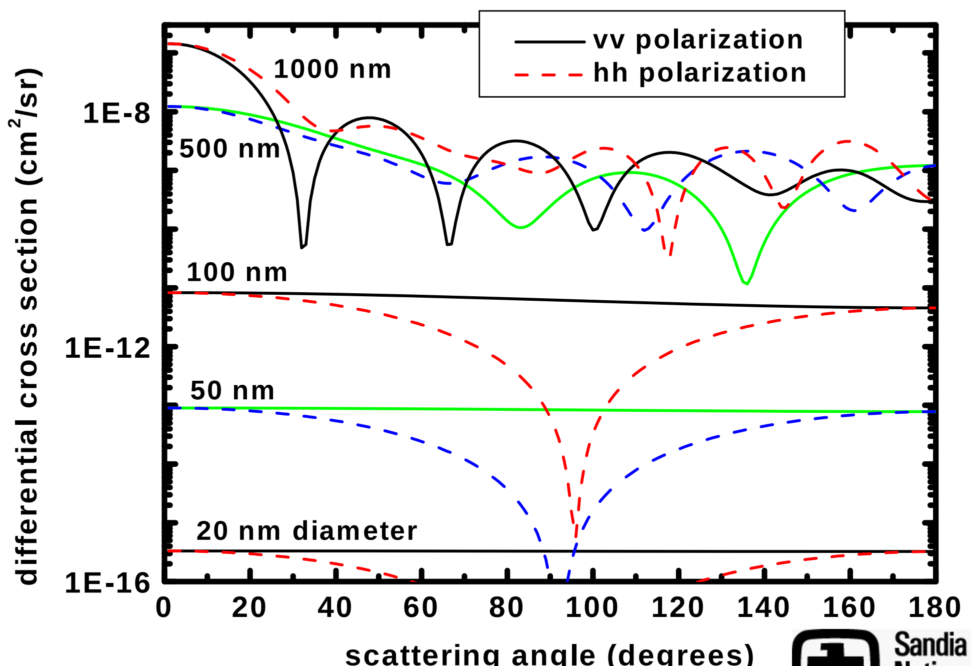
Subtask 1.1: Laser light scattering measurement of gas-phase nanoparticles during InGaN MOCVD

1) Measure the nanoparticle light scattering intensity over a wide range of InGaN MOCVD conditions (Temperature, total pressure, residence time, group-III partial pressure, NH_3 partial pressure, carrier gas type, etc.)

   Measure angular and polarization dependence of light scattering signal in order to extract particle size and number density (if spherical).





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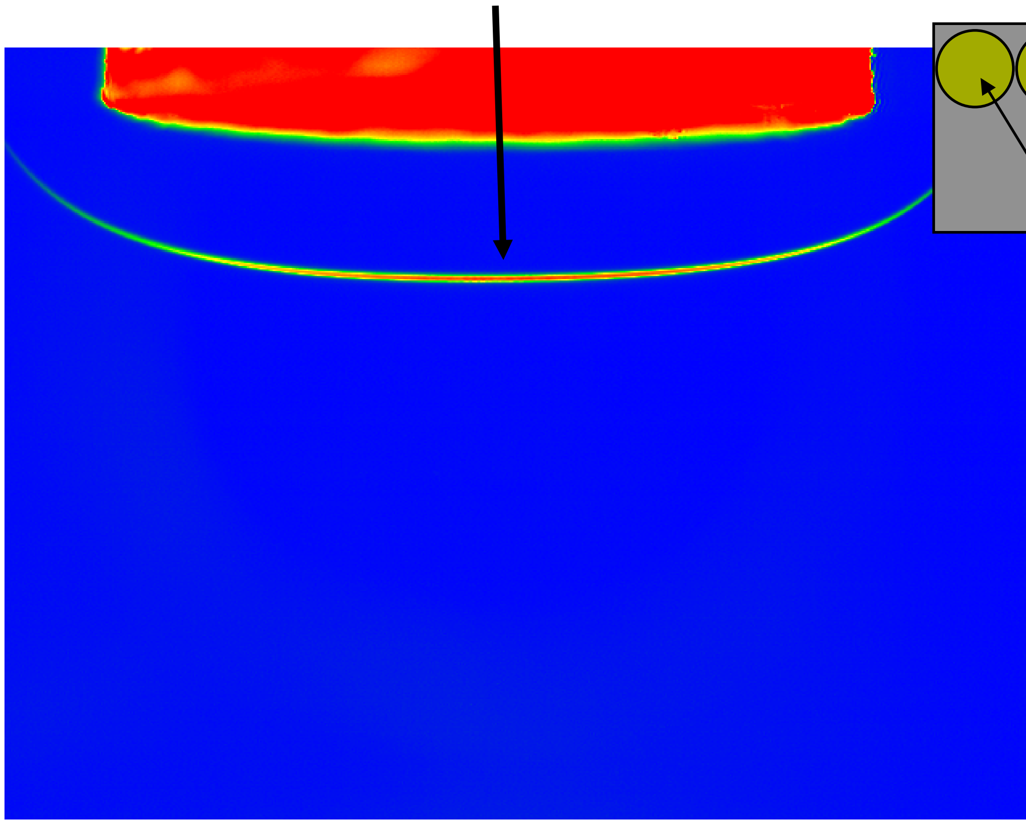
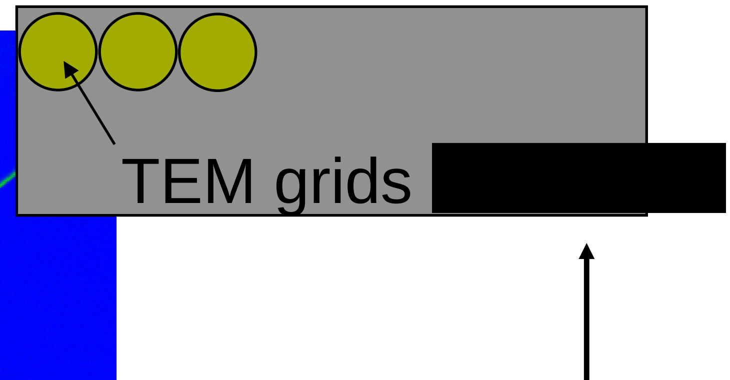
Subtask 1.2: Determine gas-phase nanoparticle structure, size, and composition (ex-situ TEM)

Our First Generation Particle Grabber "thermophoretic sampler" was too perturbative, sampled near centerline

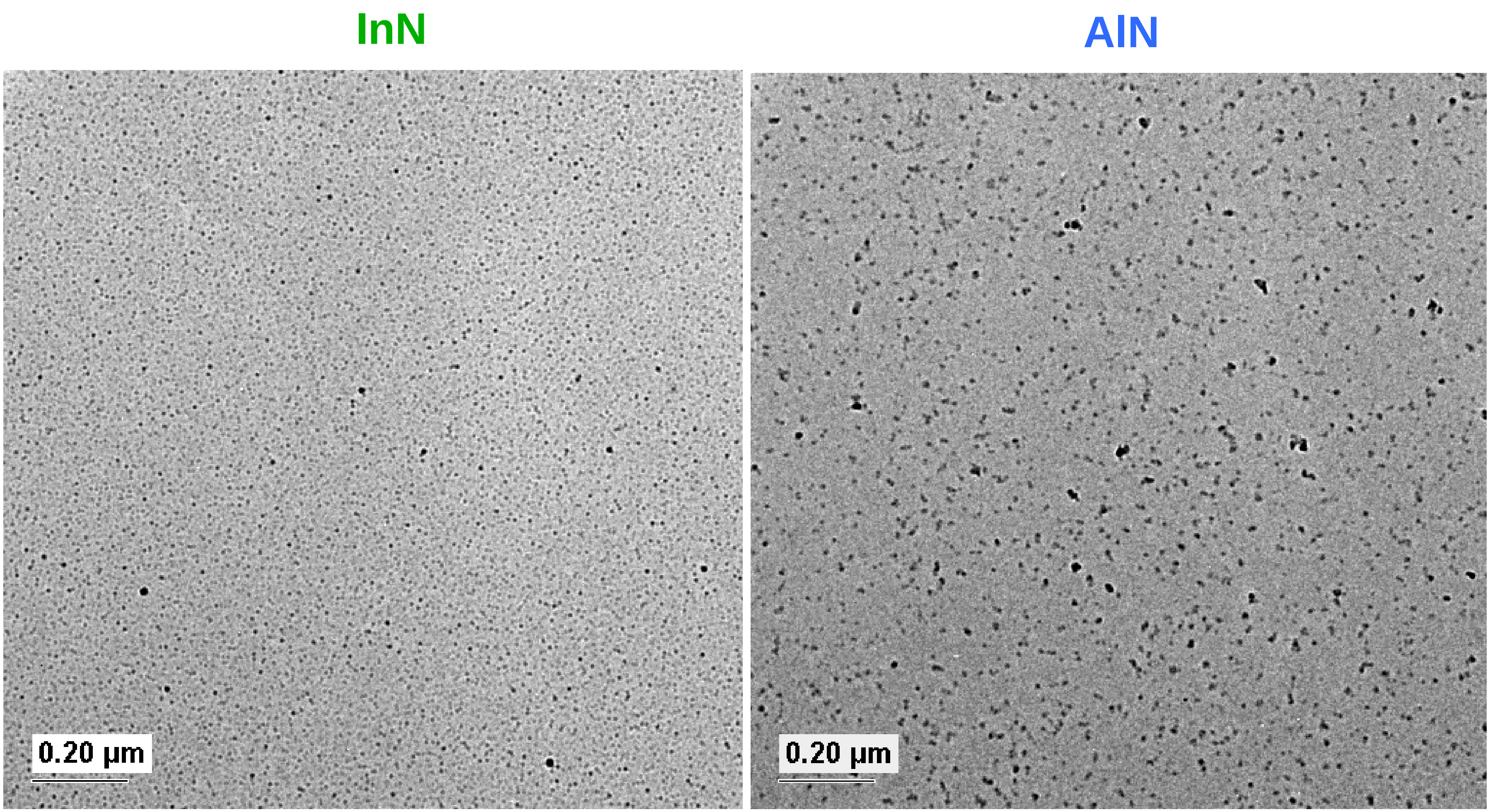
Moving the probe further downstream should greatly decrease the sampling perturbation





exposure time
~1/2 - 1 s

AlN and InN nanoparticles captured on particle grabber

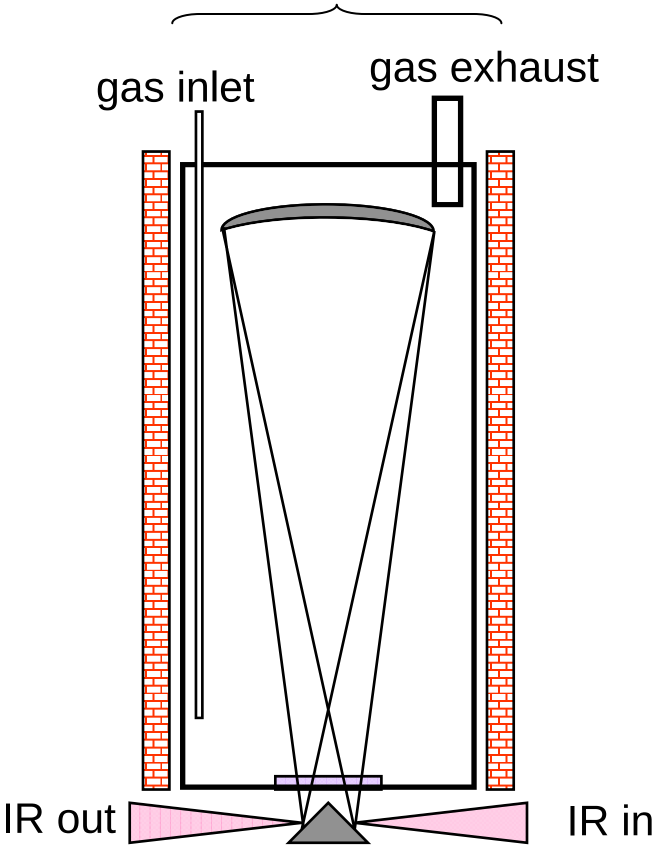


Ref: JCG 298, 2 (2007)

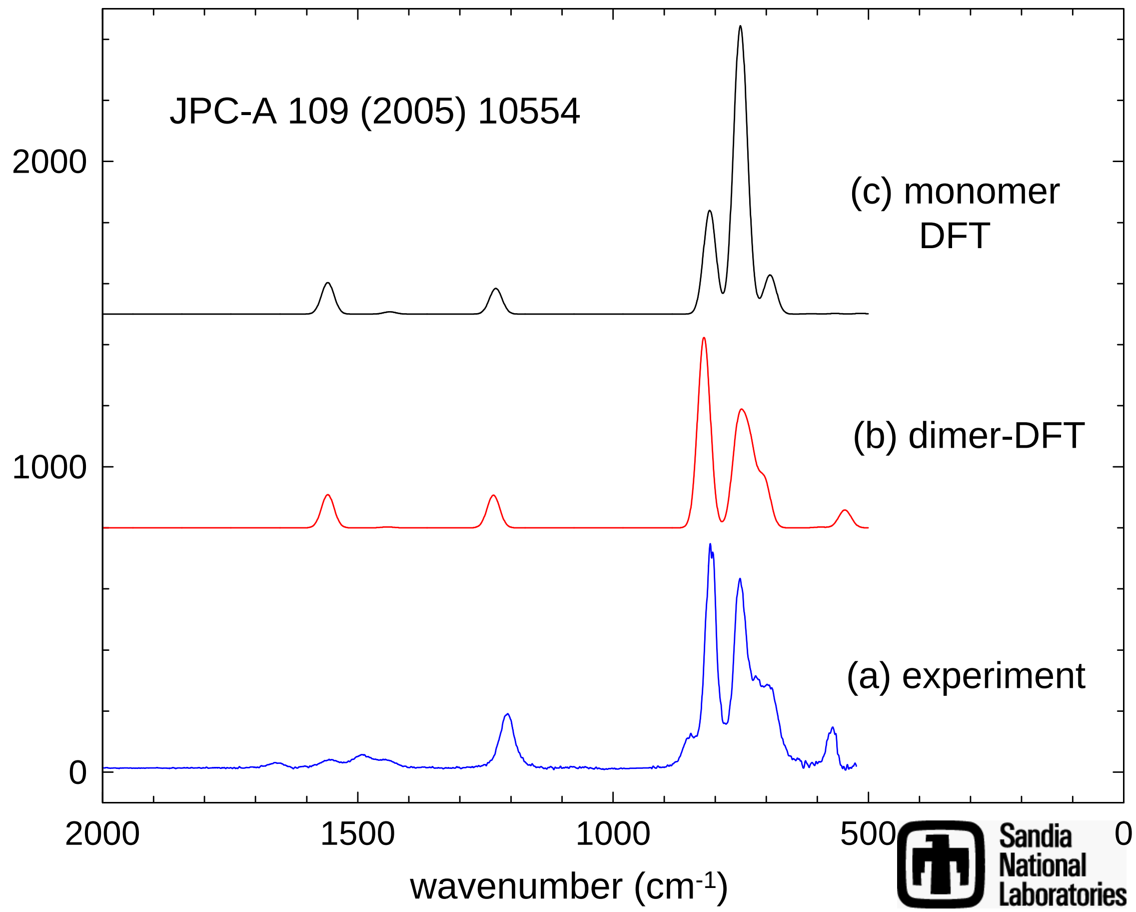
Subtask 1.3: Determine role of hydrogen in TMIn and TMGa gas-phase reaction pathways

Primary experimental method will be FTIR, possibly supplemented with quantum chemical calculations (DFT). Other experimental methods may be explored.

heated FTIR gas cell



Example: $[(Me)_2Al\text{-}NH_2]_2$ identification



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Task 2: Determine Role of Surface Chemistry in InGaN MOCVD

Background:

Thermodynamic (e.g. In evaporation) and/or surface kinetic effects (e.g. etching by H_2) are generally thought to be major factors that limit In-incorporation.

These effects necessitate:

1) lower deposition temperature (700-800°C vs. 1050°C for GaN)
2) replacement of H_2 with N_2 carrier gas

Both of these requirements adversely affect the InGaN material quality and negatively impact IQE

Task 2 Goals – Answer these questions:

1) Is the thermodynamic stability of InGaN a major reason why the temperature must be lowered so much?
2) How does strain affect the In desorption rate?
3) Does H_2 really "etch" InGaN, and if so, then how?

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SubTask 2.1: Characterize InGaN Growth Rate and Composition as a function of MOCVD conditions

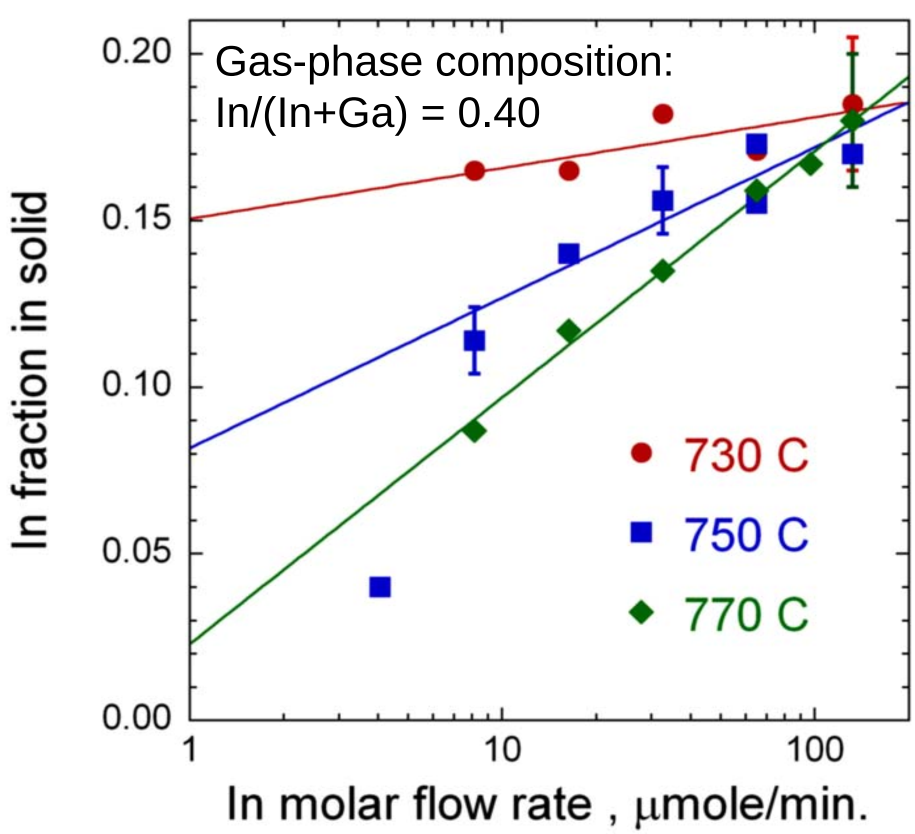
An extensive database of InGaN growth rate and composition measured over a wide range of well defined conditions is needed as a baseline to develop a thorough understanding and model of the InGaN MOCVD process

We will extend our earlier work to include the effects of:

- Spin rate (affects residence time)
- Total pressure (affects residence time and concentrations)
- Total flow rate (mainly affects residence time)
- Ammonia partial pressure (may affect InGaN stability, gas-phase parasitic mechanisms)
- Small amounts of H_2 carrier gas (potentially improve material quality)

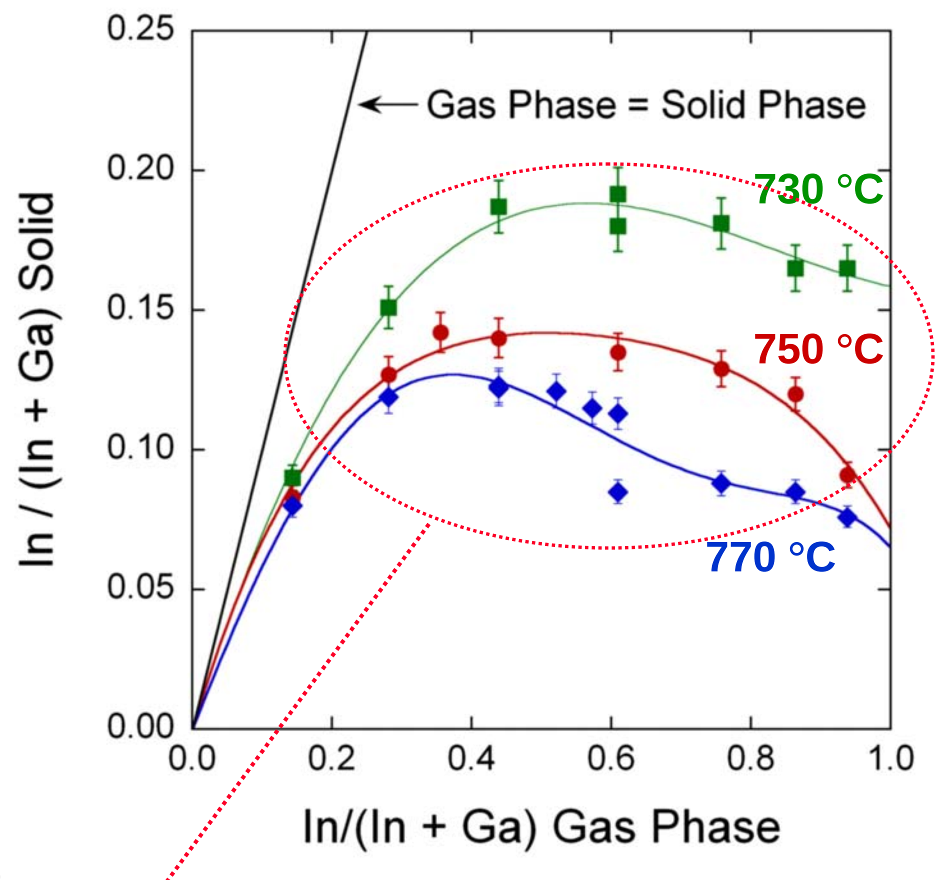
Example results from Koleske demonstrate the complex and non-ideal nature of the InGaN MOCVD process

Growth-Rate Dependence



(Here, growth rate ∝ TMGa flow ∝ TMIn flow)

Gas-Phase-Composition Dependence



In incorporation does not follow gas-phase composition and is very temperature dependent

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SubTask 2.2: Measure InGaN Desorption Rate as a function of MOCVD conditions

We will use *in situ* reflectometry (or other optical methods) to measure the InGaN desorption rate as a function of temperature and gas composition (NH_3, H_2 partial pressures)

Optical contrast issues will determine the minimum InGaN thickness we can work with. Experiments may require shorter wavelength reflectance or alternative optical methods

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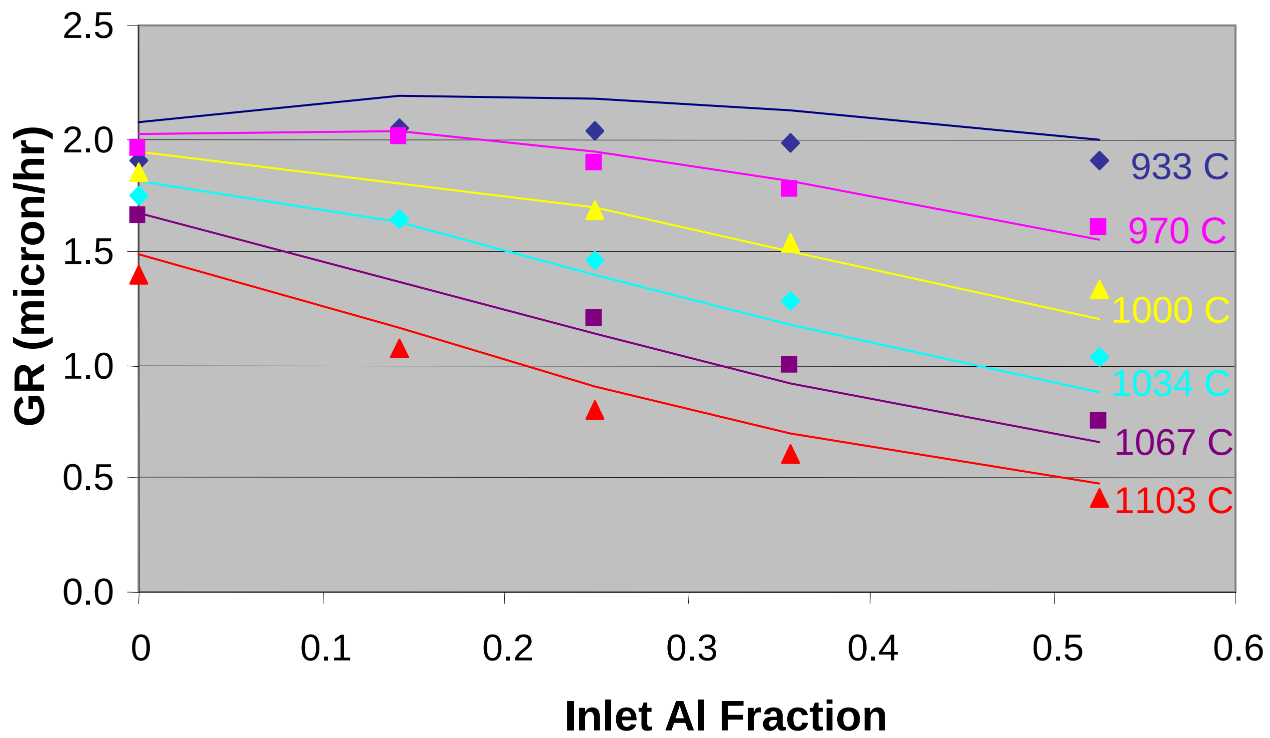
Task 3: Demonstrate Optimal Growth Conditions for InGaN

We will use the results from Task 1 and 2 to develop a quantitative and predictive reactor-scale model of the combined (parasitic) gas-phase chemistry and film growth mechanism in order to optimize In-incorporation at conditions that lead to improved material quality, and therefore increased IQE

Task 3 Goal: 2X improvement in IQE for our baseline 530 nm MQW structure

Example comparison of earlier AlGaN model with experiment



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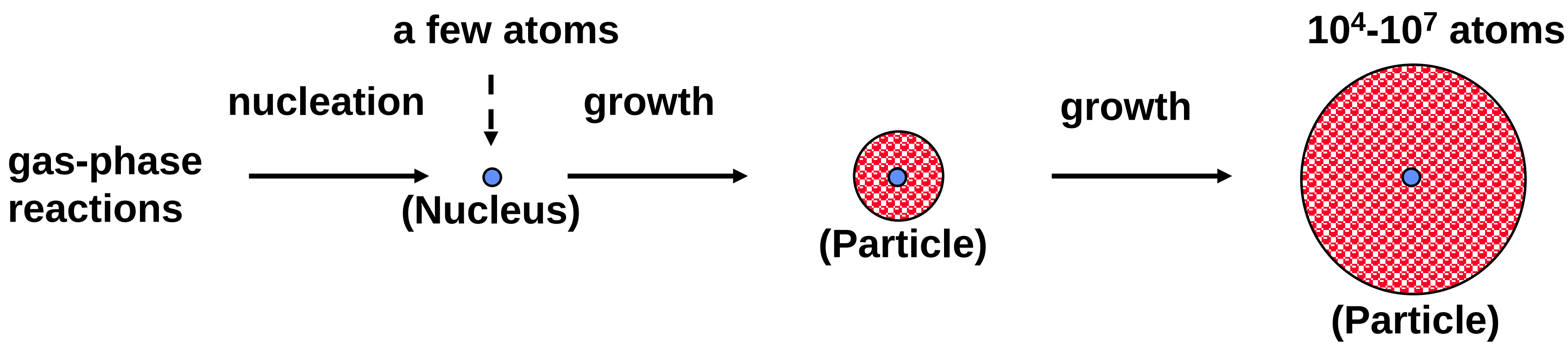
We have developed a simple approach for modeling particle growth using existing Chemkin / Spin software (Coltrin JCG 2006)



$$\frac{d[\#\,\text{atoms in Particles}]}{dt} \equiv \frac{d[\text{Part}]}{dt} = Z_w \cdot \gamma \cdot A_{tot}$$

$$A_{tot} = [\#\,\text{of Particles}]^{1/3}[\#\,\text{of atoms in Particles}]^{2/3} \cdot 4\pi \cdot \left(\frac{1}{\rho_P}\frac{3}{4\pi}\right)^{2/3}$$

$$A_{tot} = [\text{Nuc}]^{1/3}[\text{Part}]^{2/3} \cdot 4\pi \cdot \left(\frac{1}{\rho_P}\frac{3}{4\pi}\right)^{2/3}$$

Simple approach produces the expected autocatalytic effect

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SubTask 3.1: Extend upper temperature limit for growth of high In-content films

Higher deposition temperatures will improve material quality by improving morphology and by lowering impurity (C,O) concentrations

Unfortunately, increasing deposition temperature (while holding other parameters fixed) always reduces the amount of In incorporation

From a thorough quantitative understanding of all of the tradeoffs involved, we will increase the deposition temperature of our baseline 20% In MQW structure (530±5 nm) by at least 30°C

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SubTask 3.2: Demonstrate Improved InGaN IQE at 530 nm

1) In addition to growing films at higher temperatures, we expect to discover modifications to process conditions that lead to improved material properties

These may include:

High spin rates and/or total flow rates (reduced parasitic reactions)
Addition of small amount of H_2 (decreased C, O)
High NH_3 partial pressures, and/or V/III ratios (decreased C)
(Something we haven't thought of yet)

Using our optimized growth conditions we will demonstrate a $\geq$ 2X improvement in IQE (currently at 5.2%) for our baseline green InGaN MQW structure (emission at 530 $\pm$ 5 nm)

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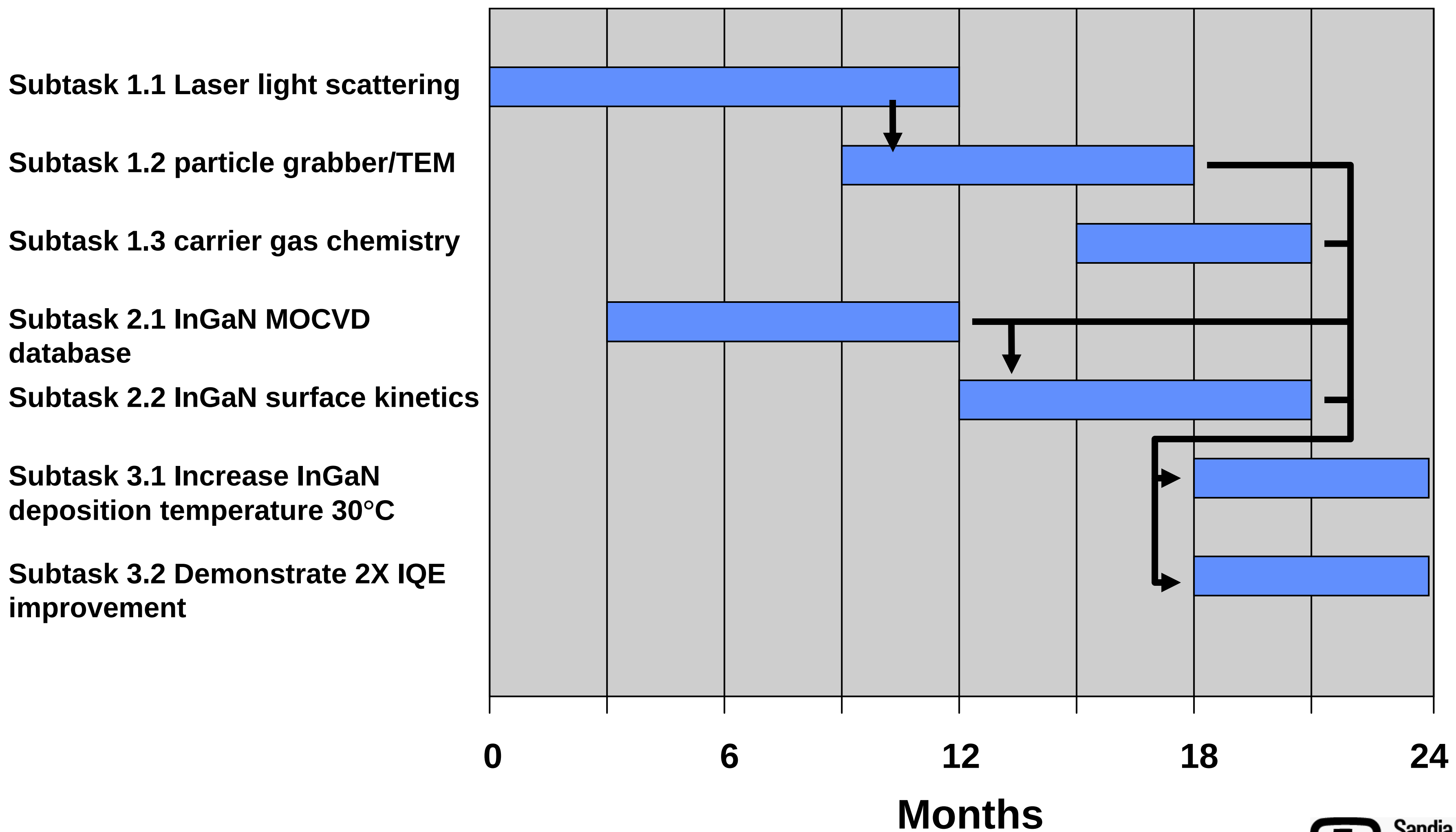
Project Gantt-like Chart



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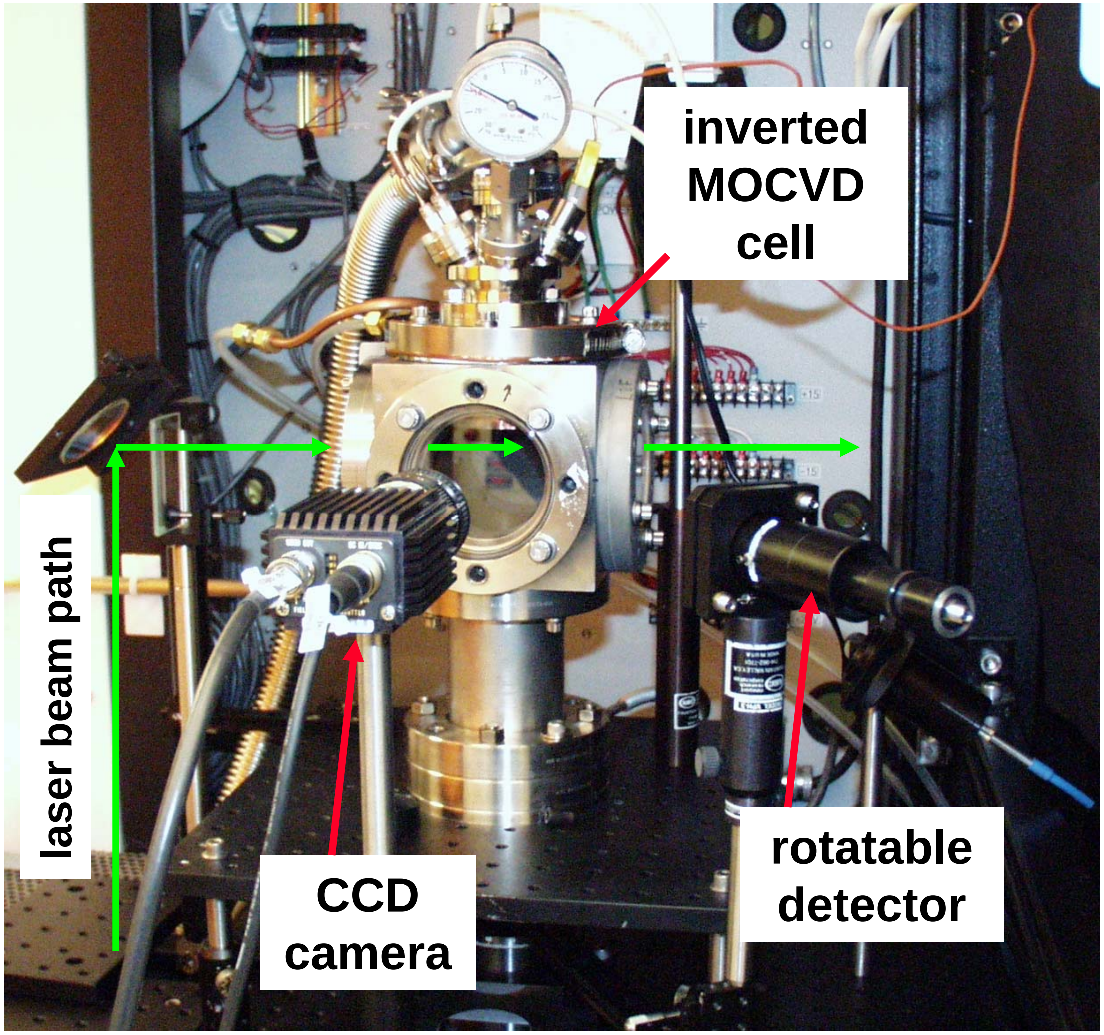
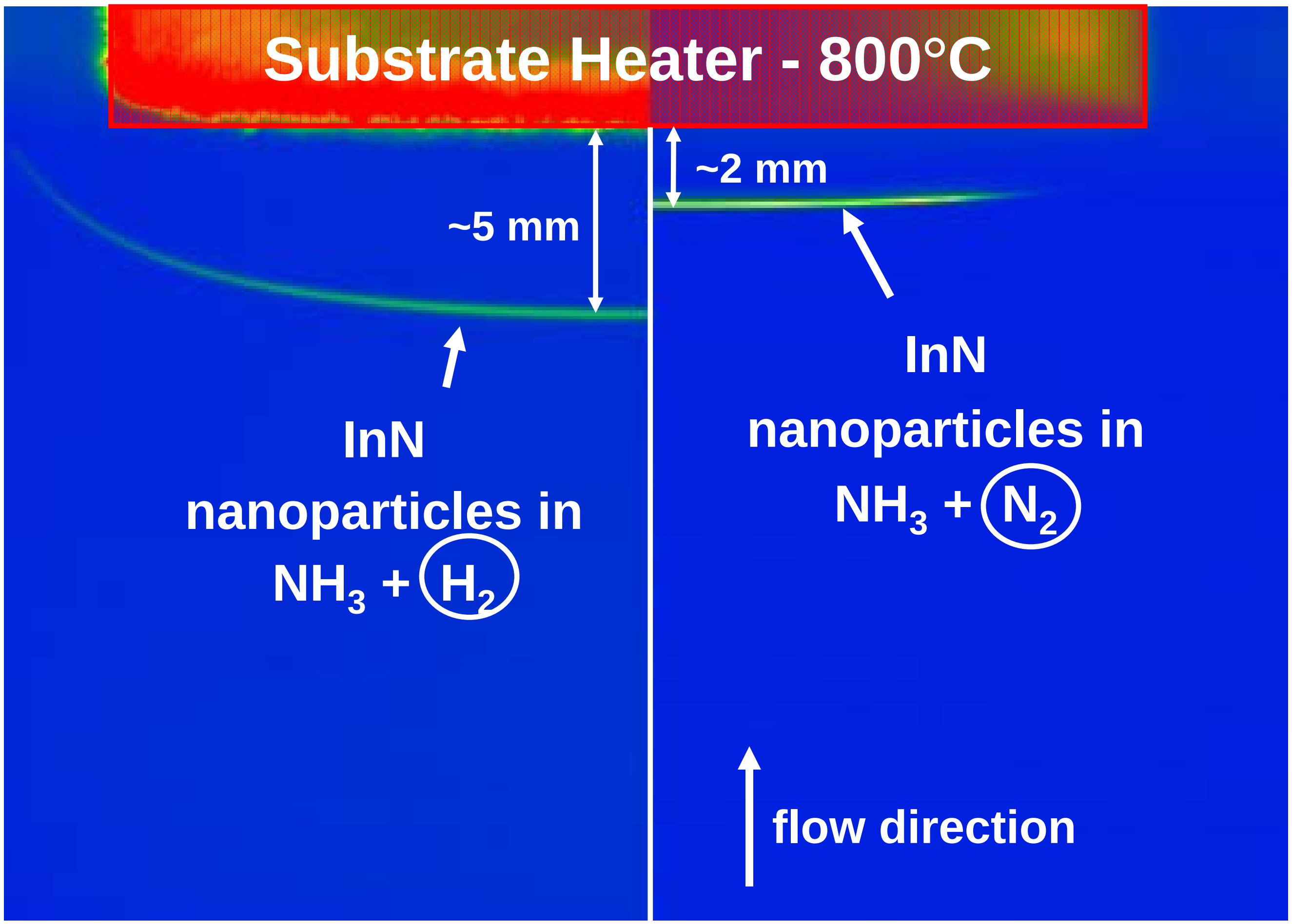
Task 1 Progress-to-Date

- **laser-light scattering chamber and detectors were added to one of our Veeco D-125 MOCVD systems**



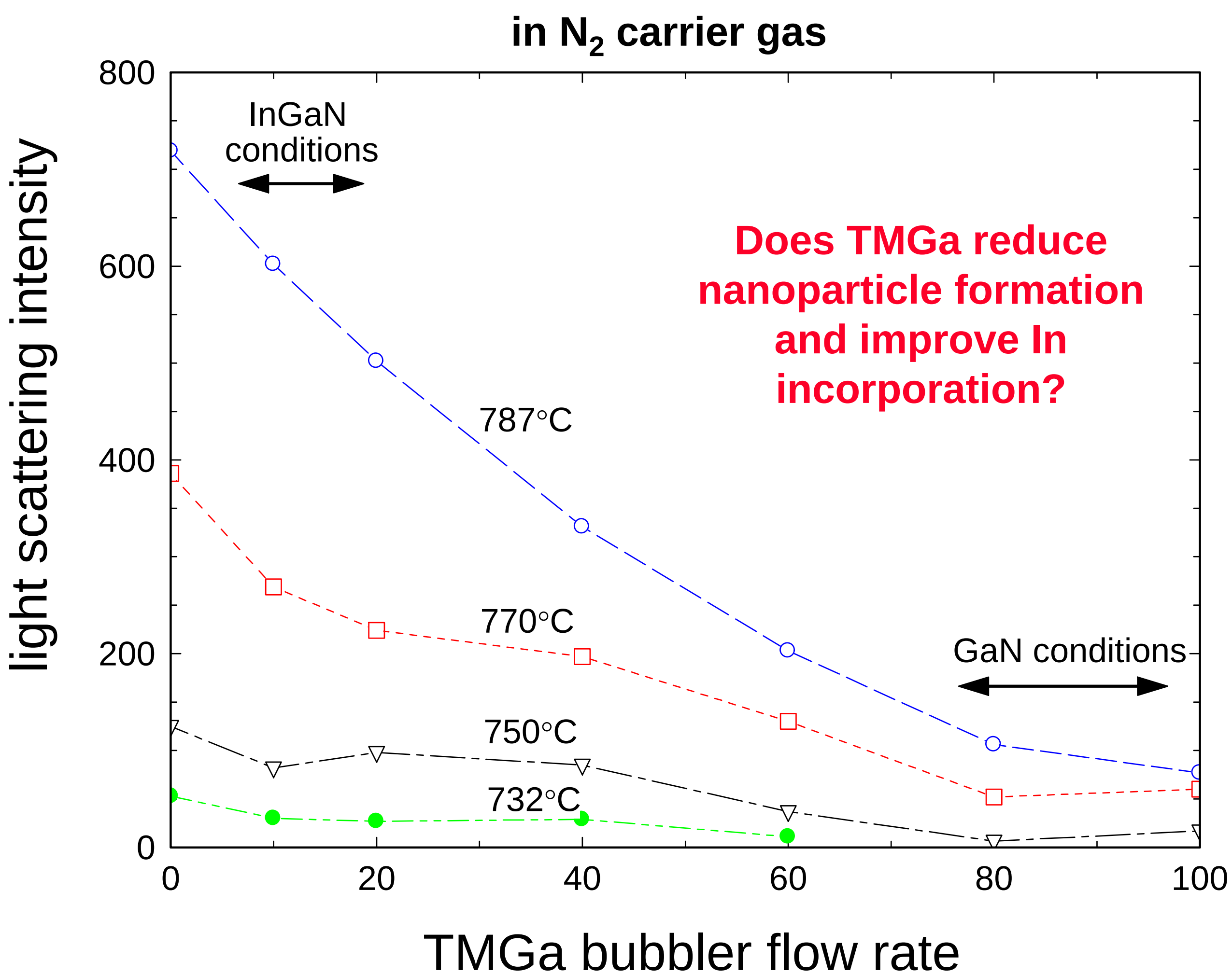
Task 1 Progress-to-Date

- At InN and InGaN MOCVD conditions gas-phase nanoparticles are observed in both H_2 and N_2 carrier gases, with position determined by physical properties of gas mixtures



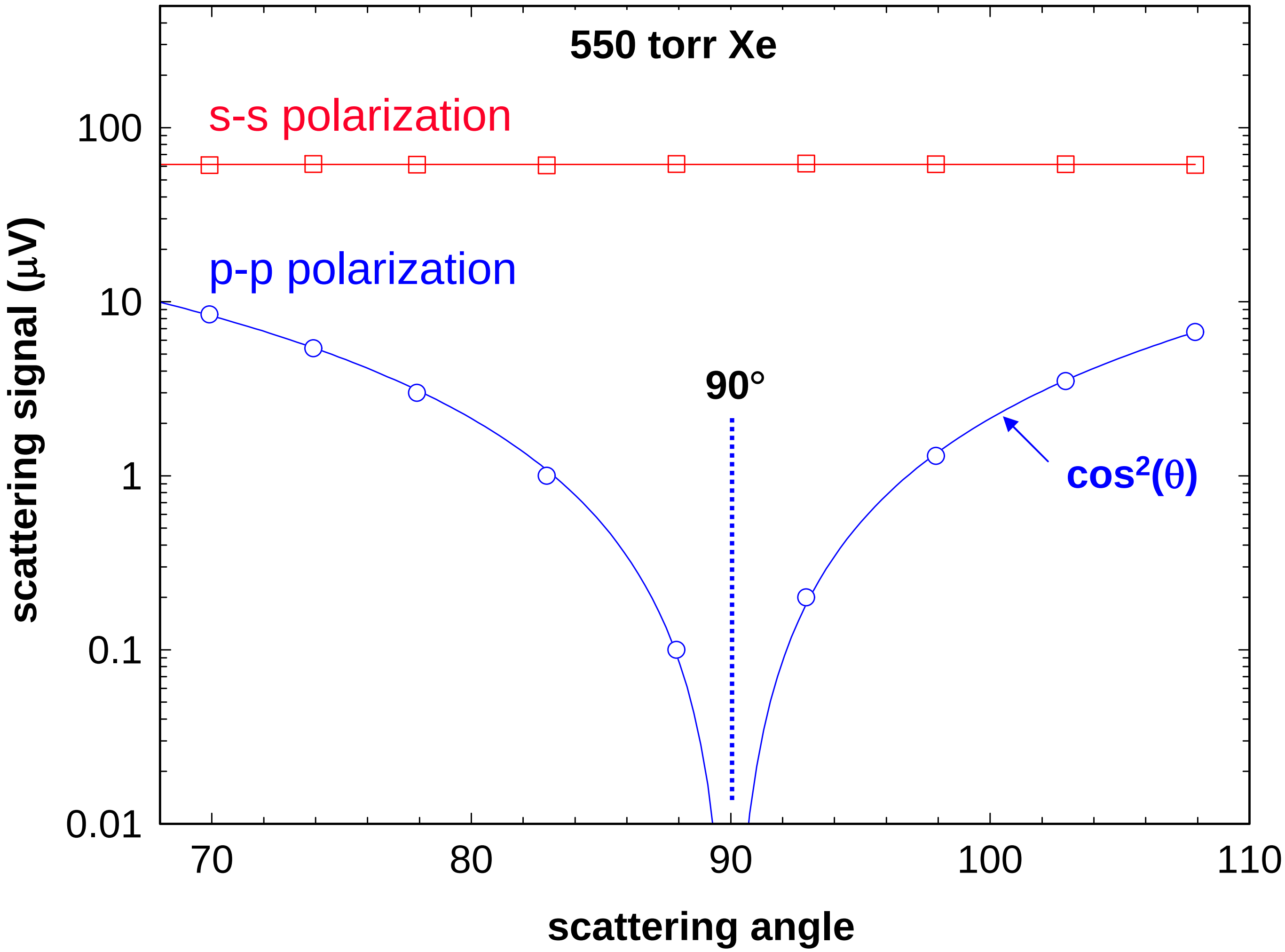
Task 1 Progress-to-Date

- **Nanoparticle scattering increases rapidly with temperature and decreases with added TMGa flow**



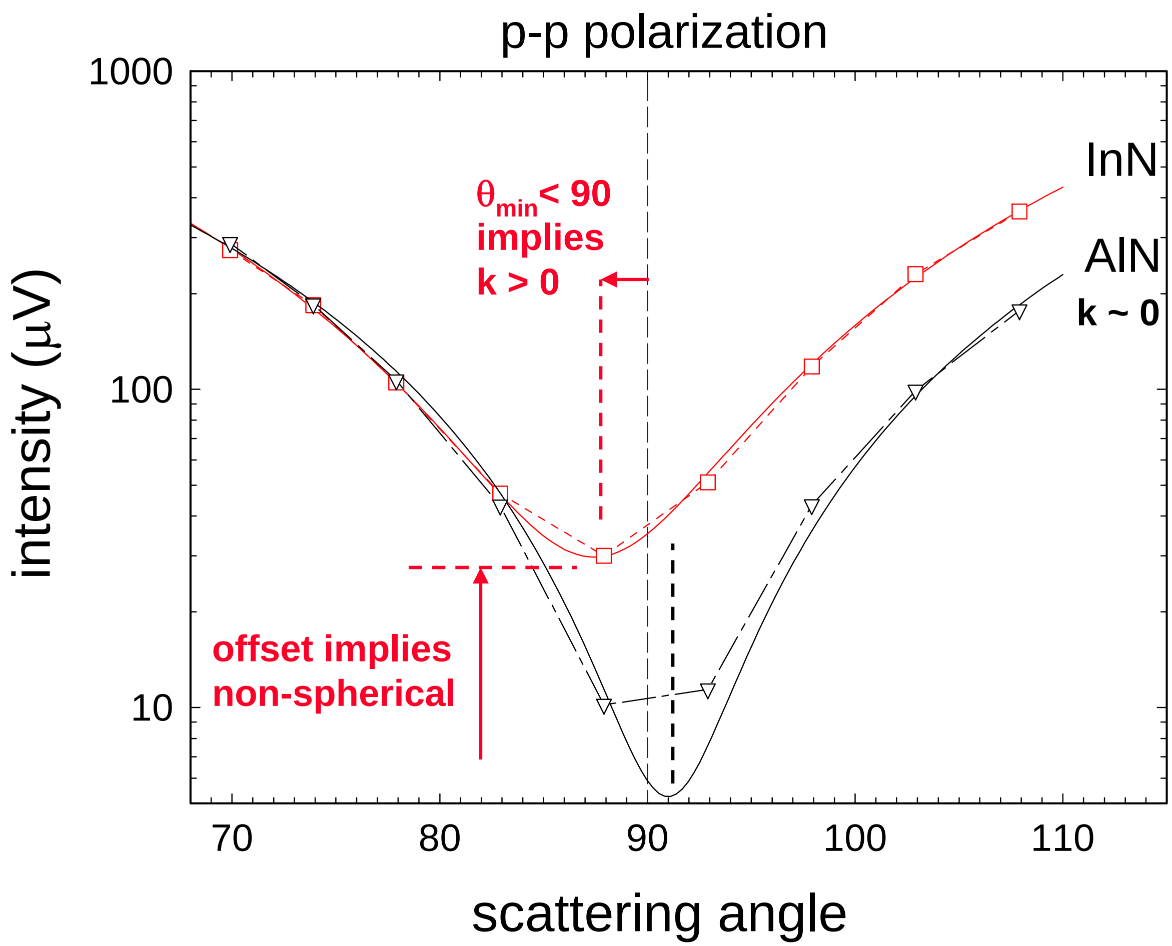
Task 1 Progress-to-Date

- **Rayleigh scattering from Xenon is used to calibrate the scattering angle and absolute intensity**



Task 1 Progress-to-Date

- **Under InN and InGaN MOCVD conditions the nanoparticles are absorbing (k > 0) and perhaps metallic. In most cases the particles display some non-spherical characteristics.**



Progress Towards BP1 Milestones

Milestone 1.1

We have measured qualitative and quantitative aspects of nanoparticle formation during InGaN MOCVD.

Determing particle size is complicated by absorbing (k>0) and possible non-spherical shapes

Added capability to calculate Mie scattering cross sections for absorbing particles (previous capabilities were for k = 0 only)

Results indicate the nanoparticles are metallic (k ~ 5), and not InN or InGaN (k ~ 0.5)

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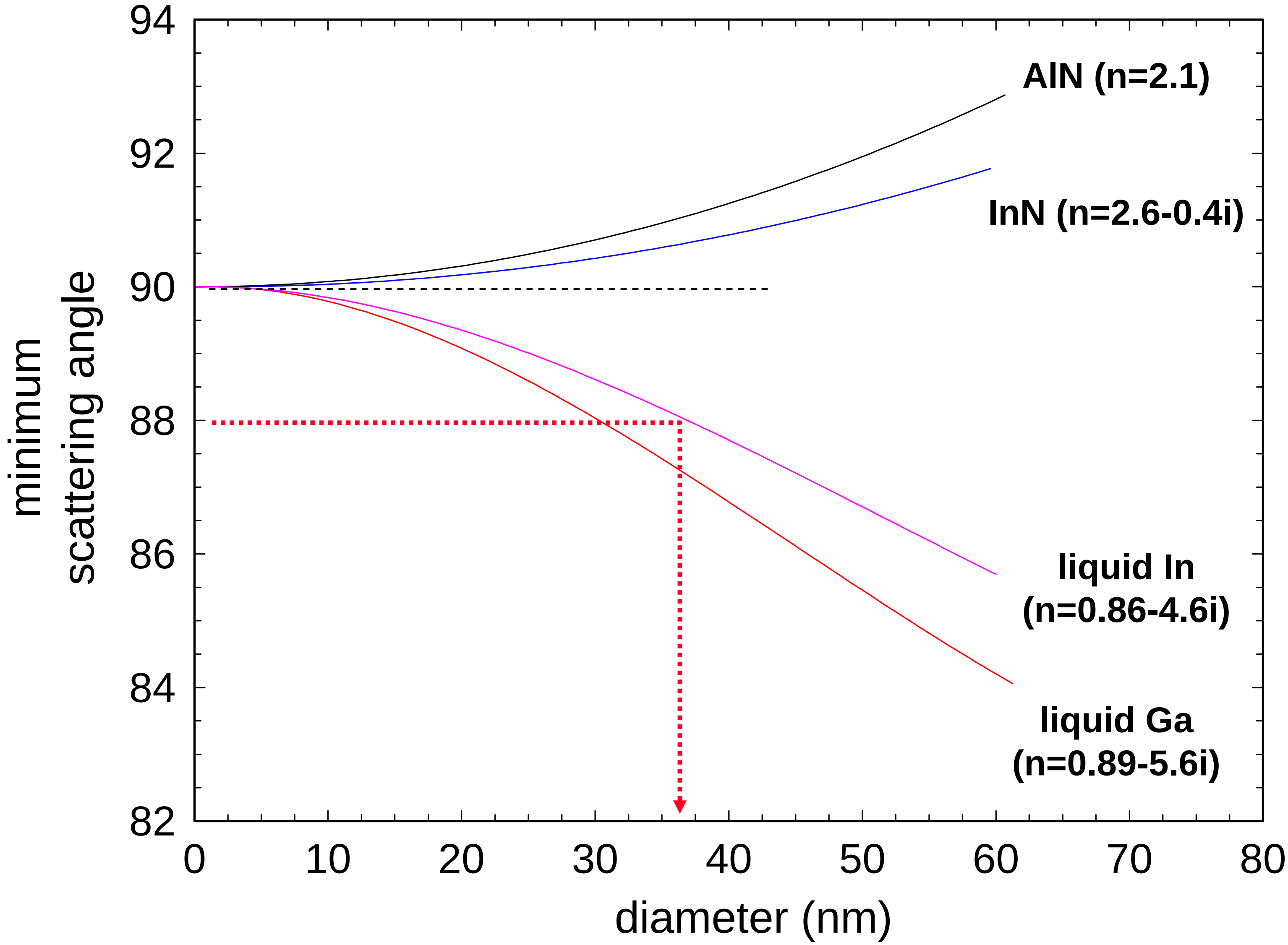
Scattering curve shift below 90° indicates metallic nanoparticles, θ_{min} yields size



Progress Towards BP1 Milestones (continued)

Milestone 1.1 Measure size and density of gas-phase nanoparticles using laser light scattering. Determine mass fraction of indium converted into nanoparticles (to order-of-magnitude accuracy)

From the particle size, and absolute scattering signal (referenced to Xe) we can determine the particle number density and fraction of In converted into nanoparticles (f_c).

Early results from 9 InN & InGaN experiments (750-880°, N_2):

d = 22-45 nm, $\langle d \rangle$ = 32 nm

f_c = 6-167%, $\langle f_c \rangle$ = 65%

Progress Towards BP1 Milestones (continued)

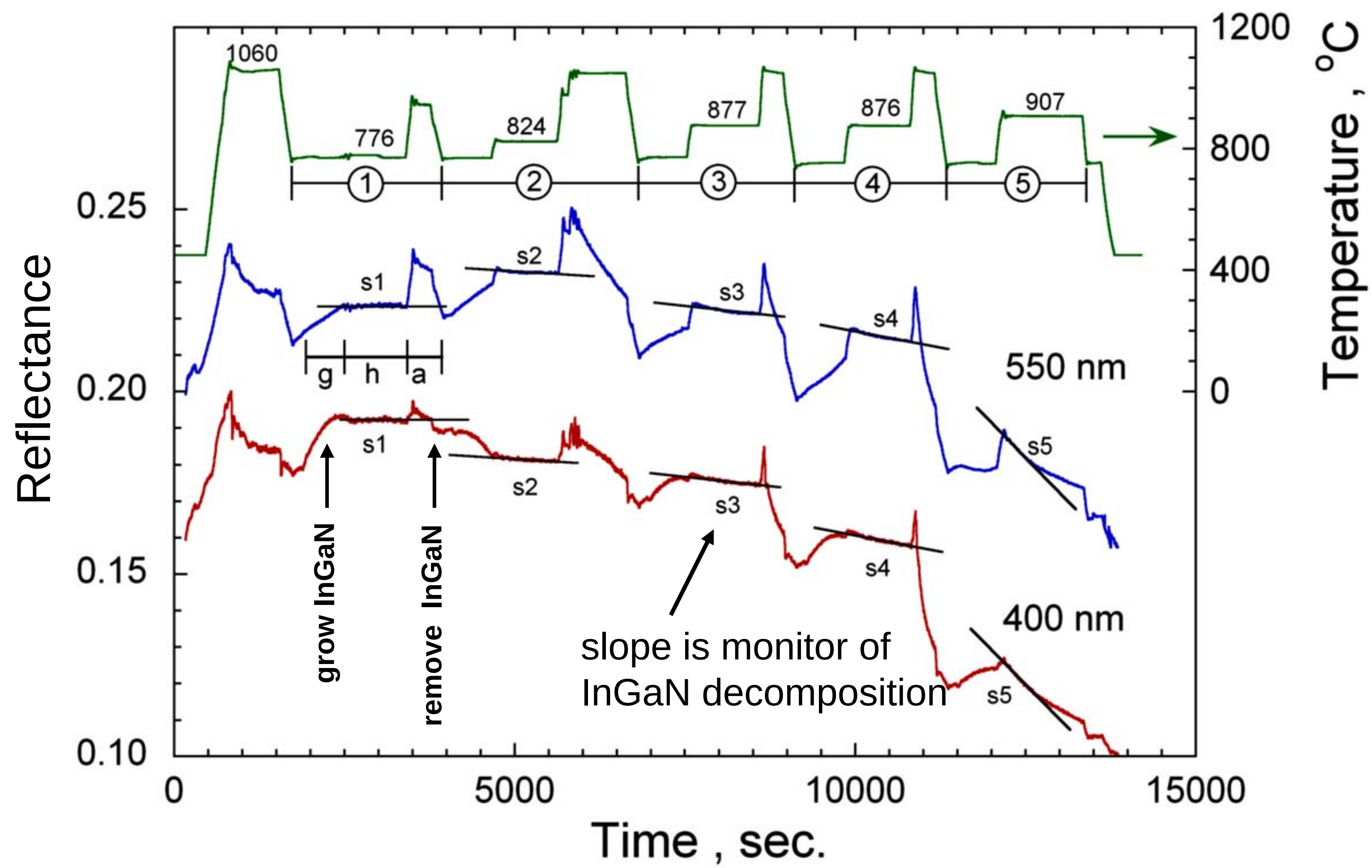
We plan to add a few more InGaN measurements and mop up a few details, but we have essentially achieved Milestone 1.1

Take home message:

Measurements of f_c (10-100%) indicate that nanoparticle formation significantly affect our ability to deliver indium to the surface

Task 2 Progress-to-Date

- **A "proof-of-concept" set of experiments were performed to determine if reflectometry was capable of monitoring InGaN thermal stability (Task 2.2).** **Results are very encouraging.**



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Progress Towards BP1 Milestones

Milestone 2.1

We are currently measuring the MOCVD platen spin rate and total pressure dependence of the InGaN quantum well composition and thickness for our otherwise standard InGaN conditions.

These experiments provide a measure of the reactor residence time dependence, which particularly highlights the presence of a gas-phase particle formation mechanism, and complements our existing database. We expect to achieve this Milestone by the completion date.

Task 3 Progress-to-Date

- Modeled the gas-phase temperature fields when using H_2 carrier gas (normally used for GaN growth) versus N_2 carrier gas (required for InGaN growth)
- Updated our nanoparticle formation mechanism for InGaN chemistry

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Project Team and Roles

Name	Role	Responsibilities
Randy Creighton	P.I.	Gas-phase and surface chemistry
Michael E. Coltrin	I.	Growth modeling/Mie theory
Daniel D. Koleske	I.	MOCVD growth/surface chemistry
Robert M. Biefeld	Manager	