SAND2007-0558C

Title: Nanostructural Engineering of Nitride Nucleation Layers for GaN Substrate Dislocation Reduction

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Project Team and Roles

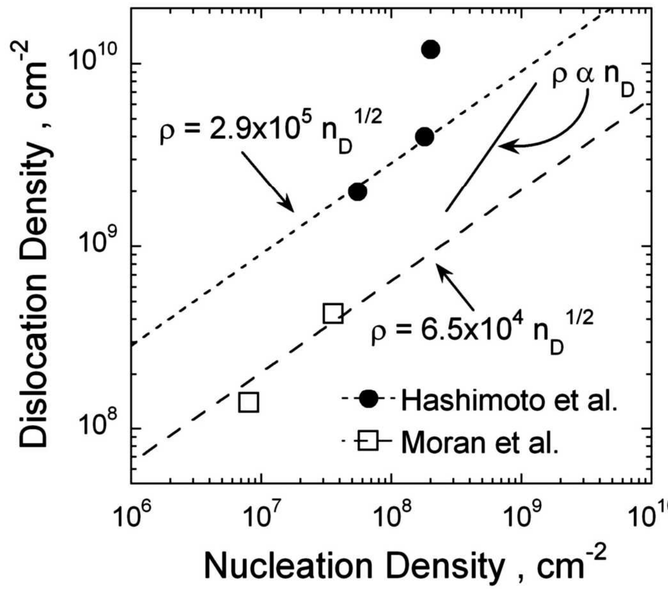
Name	Role	Responsibilities	Fraction of time*
Robert M. Biefeld	P.M.	Project Manager	
Daniel D. Koleske*	P.I.	MOCVD growth and reports	0.50
Michael E. Coltrin	I.	Growth modeling & morphology evolution	0.30
Stephen R. Lee	I.	XRD analysis of films	0.20

*Fraction of time includes any technical-support personnel allocated to each investigator.

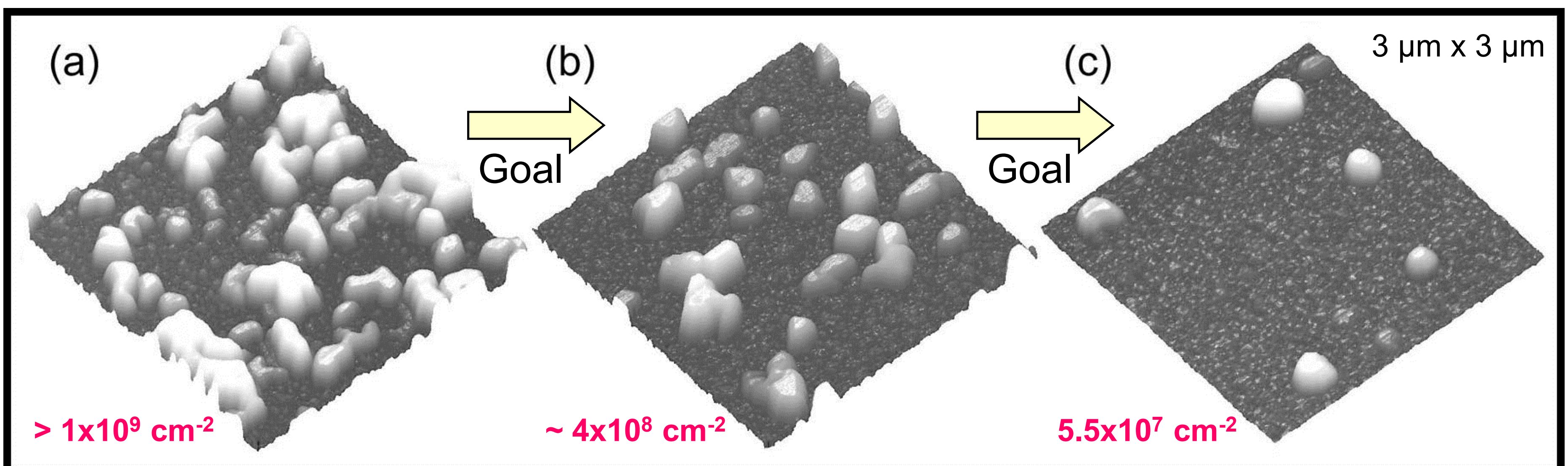
Project Objective

- If dislocations form to accommodate grain twist and tilt, then the GaN nuclei density, n_D, should correlate with the dislocation density, ρ.

$$\rho = \text{const} \times n_D^{1/2} \rightarrow$$



- Goal is to reduce the dislocation density of GaN films on sapphire from $5\times10^{8}\ cm^{-2}$ to $1\times10^{8}\ cm^{-2}$ by limiting the nuclei density while maintaining high lateral growth rate.

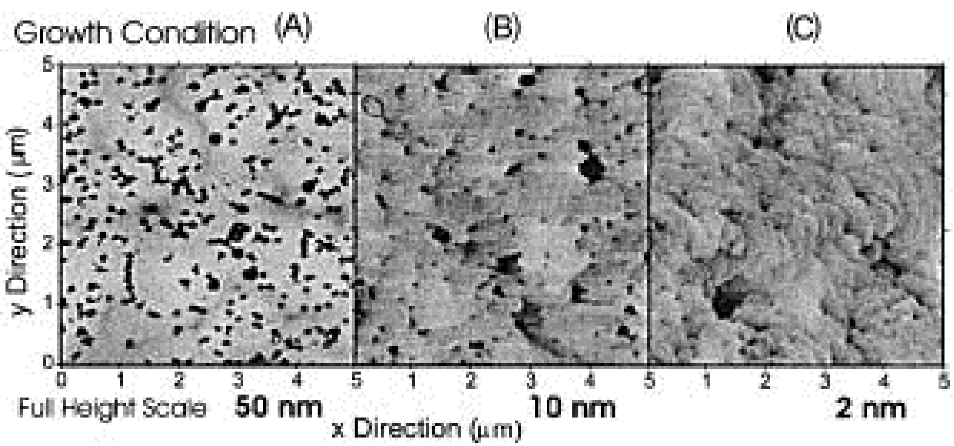


Potential Benefits to SSL – Improved Green LEDs

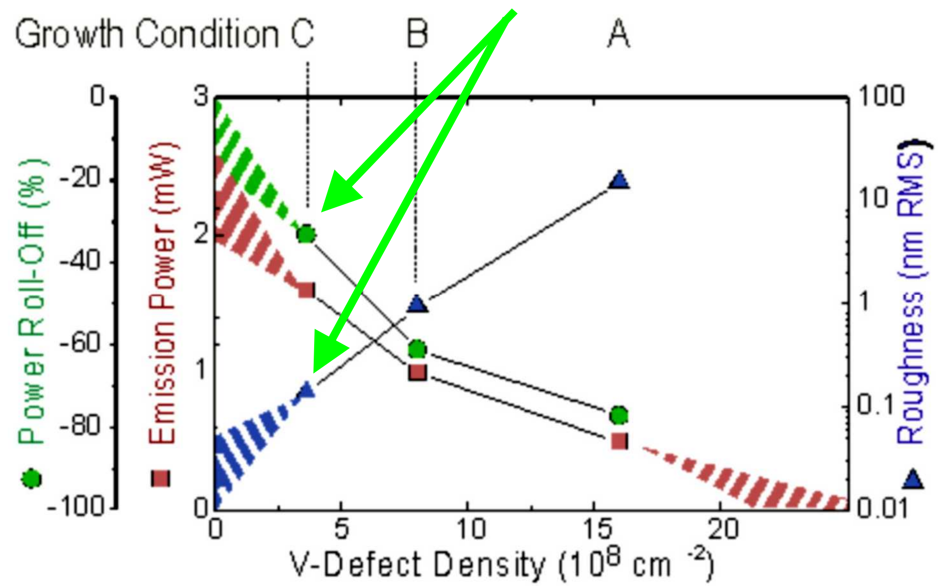
Red-Green-Blue SSL approach should be most energy efficient, however green LEDs efficacy is substantially lower than red or blue LEDs.

Possible correlation between reduced V-defect formation, smoother surface morphology, and brighter green LEDs.

Rougher morphology → Smoother morphology



Condition C = brighter green LED, lower RMS roughness

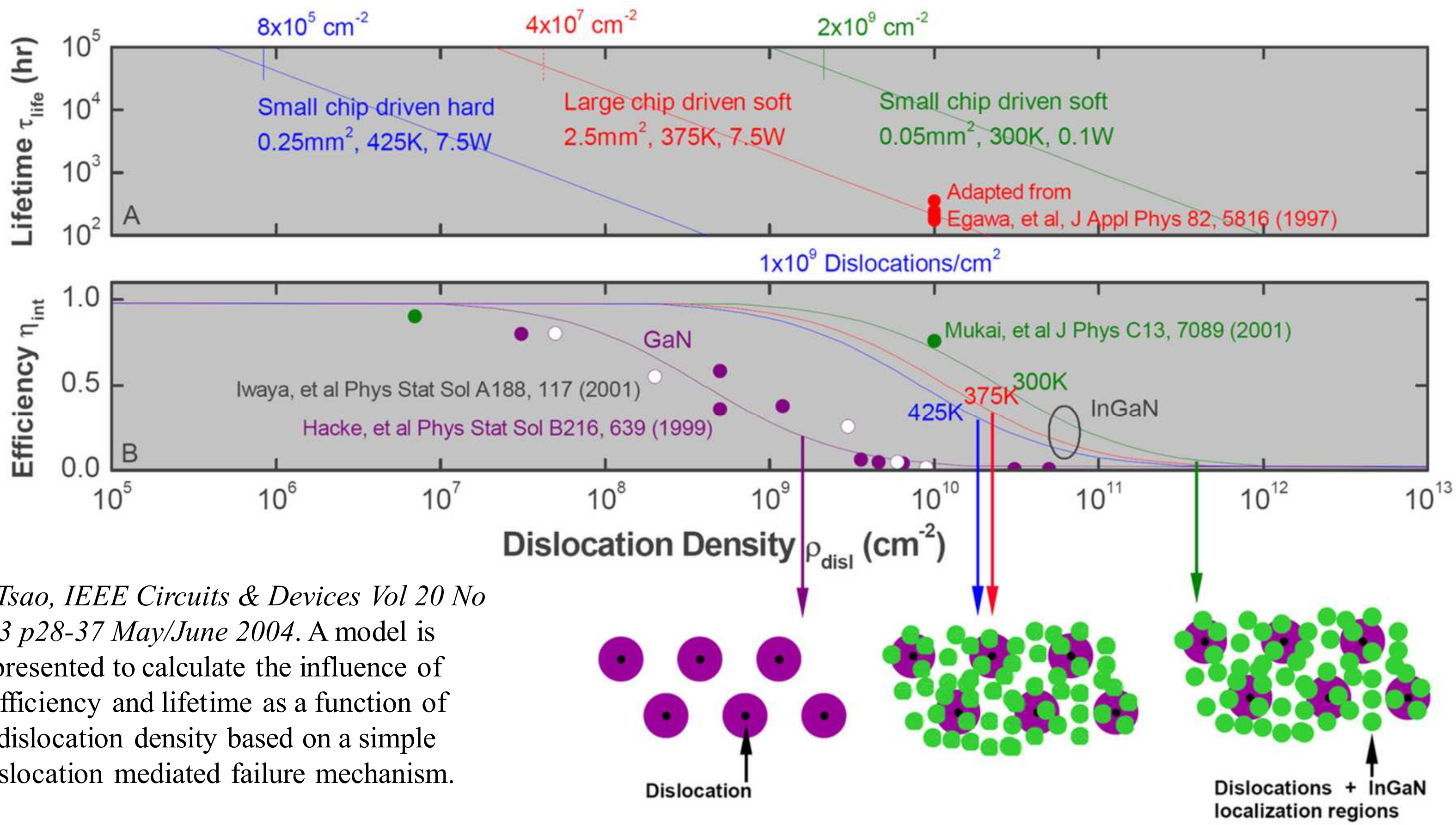


Wetzel, et al., Appl. Phys. Lett. 85, 866 (2004).

Brighter green LEDs when grown on lower dislocation density GaN.

Potential Benefits to SSL – Improved LED lifetime

For high current opto-electronic applications, devices might degrade through common dislocation induced failure mechanism observed in other III-V semiconductor devices.



J.Y. Tsao, IEEE Circuits & Devices Vol 20 No 3 p28-37 May/June 2004. A model is presented to calculate the influence of efficiency and lifetime as a function of dislocation density based on a simple dislocation mediated failure mechanism.

Device lifetime increased on lower dislocation density GaN.

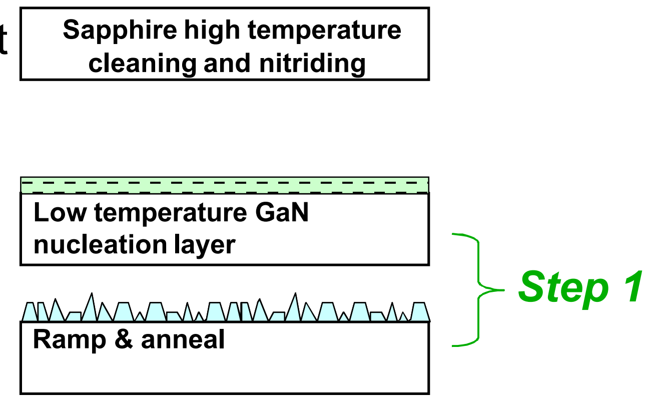
Typical "two step" heteroepitaxy of GaN on sapphire

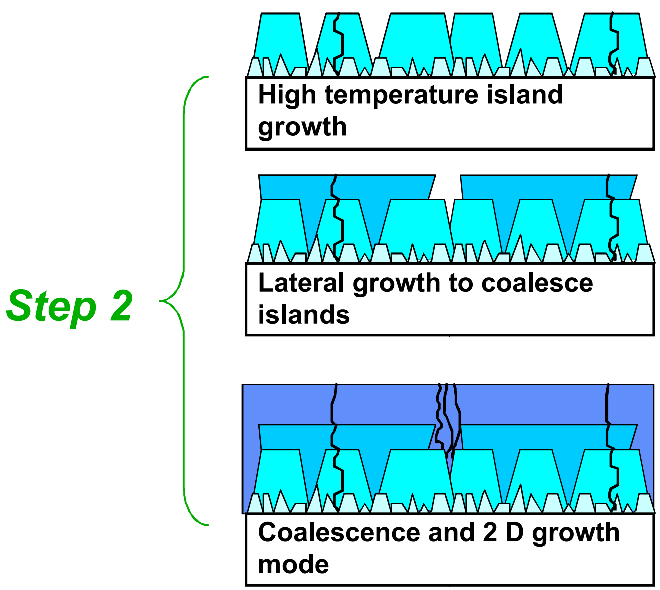
Based on work from K. Hiramatsu, et al., Journal of Crystal Growth 115, 628 (1991).

1) Sapphire heated to high temperature (1050 – 1100 ºC) in H_2 to "clean" the surface; surface sometimes exposed to NH_3 at high temperature.

2) Grow 20 – 30 Å GaN NL at 500 – 600 ºC; as grown NL contains "cubic" material with stacking faults.

3) Heat GaN NL to 1000 – 1080 ºC in flowing H_2, N_2, and NH_3. Wurtzite GaN nuclei form.





4) At high temperature, Ga source is turned on. Isolated GaN grains grow on the GaN nuclei. Some dislocations propagate up from the GaN grains.

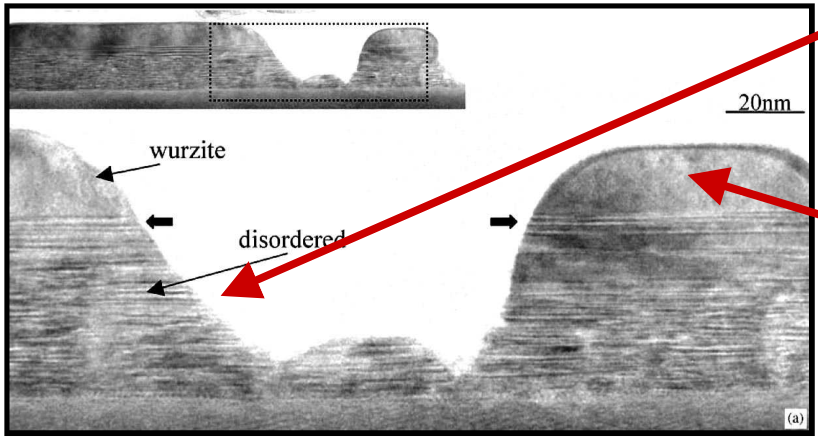
5) Islands grow laterally / vertically; grains begin to coalesce. Growth conditions can be tuned to increase / decrease lateral growth rate.

6) When grains have coalesced, growth becomes 2-D. Dislocations are formed as GaN grains coalesce to accommodate grain twist / tilt.

How many dislocations evolve from grains (4) vs. grain coalescence (6)?

GaN morphology evolution on sapphire

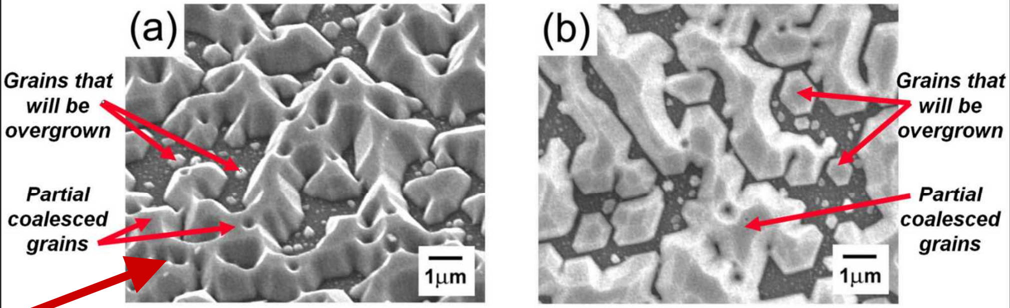
Figure from Lada et al., J. Crystal Growth 258, 89 (2003).



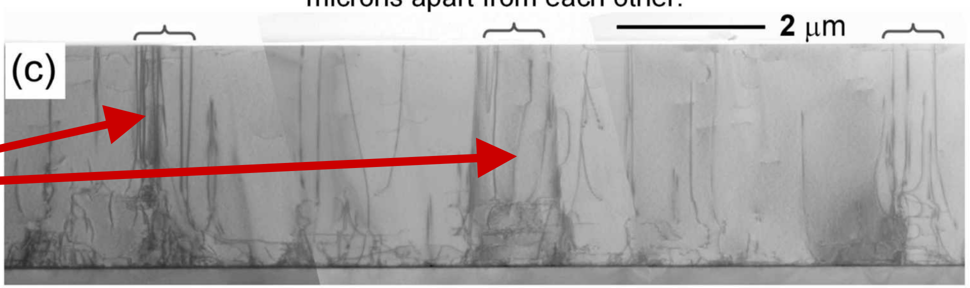
- As grown GaN nucleation layers contain disordered GaN with many stacking faults.
- Once annealed, wurtzite GaN forms on top of disordered GaN NL, forming nano-sized GaN nuclei from which further high temperature GaN growth occurs.

- High temperature growth on the GaN nuclei produces GaN grains.
- Growth conditions can be varied to enhance the pyramidal growth mode or lateral coalescence. Dislocations are bent laterally on pyramidal facets.
- Dislocations are concentrated in bunches located microns apart.

SEM Images of 3D GaN grain growth



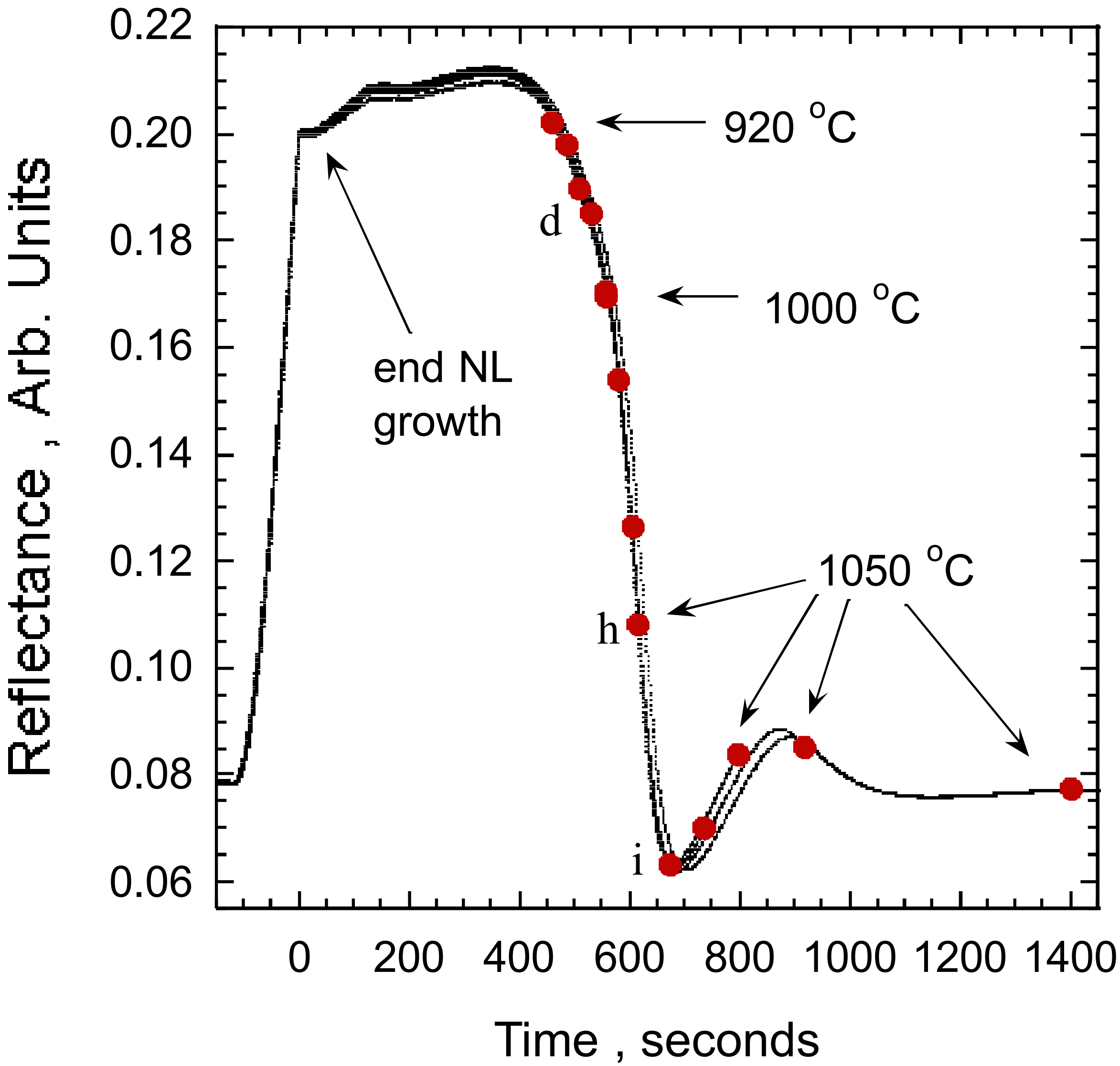
The threading dislocation appear in bunches which are located a few microns apart from each other.



TEM cross section

TEM courtesy of D. M. Follstaedt

Evolution of the reflectance waveform as the GaN NL is annealed



To understand the NL decomposition and morphology, 13 NLs (30 nm thick) were grown and annealed for different times (red circles). Annealed NLs were quenched in N_2 and NH_3 to freeze the morphology.

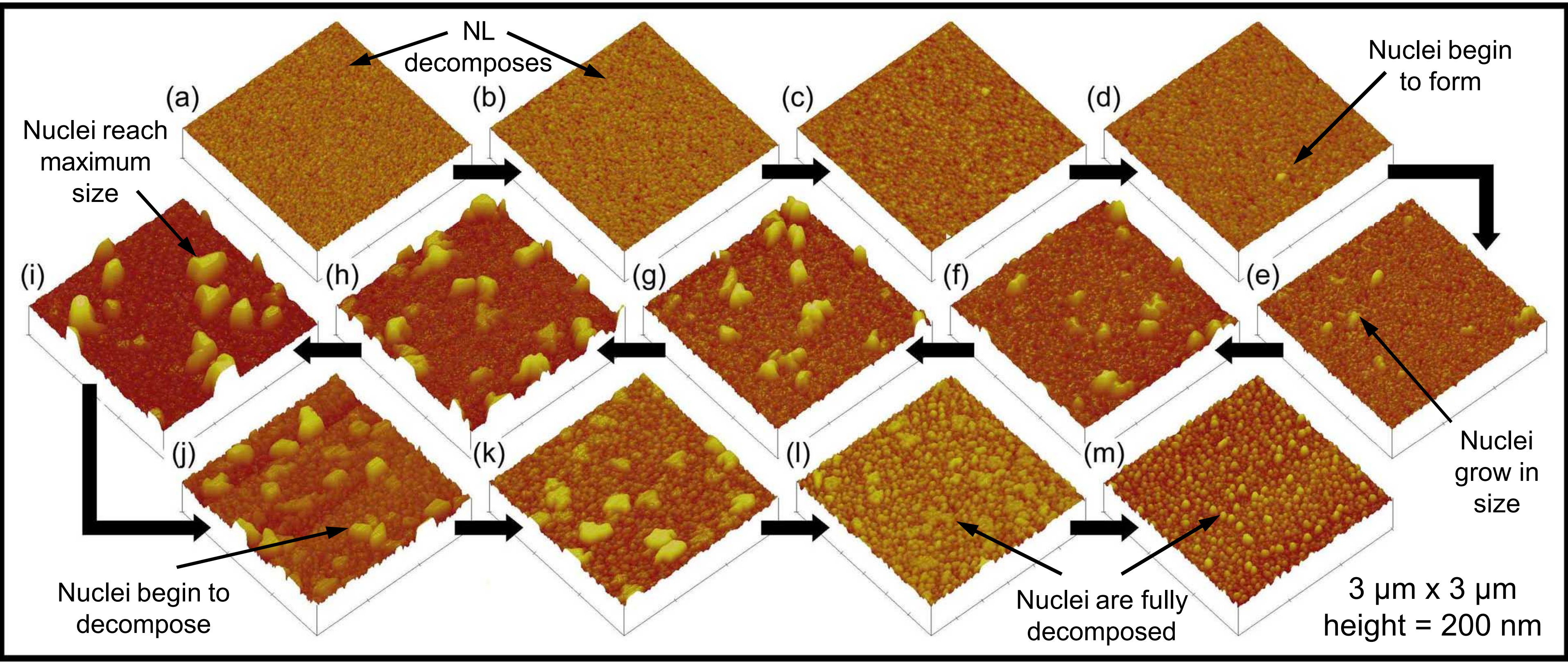
All reflectance waveforms shown on the left are overlaid in the figure. The overlap in waveform shapes indicates reproducibility of the NL evolution.

AFMs of annealed NLs shown next.

Details in Koleske et al., J. Crystal Growth 272, 227 (2004).

Mechanism for GaN nuclei formation as the nucleation layer is annealed.

Arrows indicate increasing annealing temperature + time in H_2, N_2, and NH_3.



Details in Koleske et al., J. Crystal Growth 273, 86 (2004).

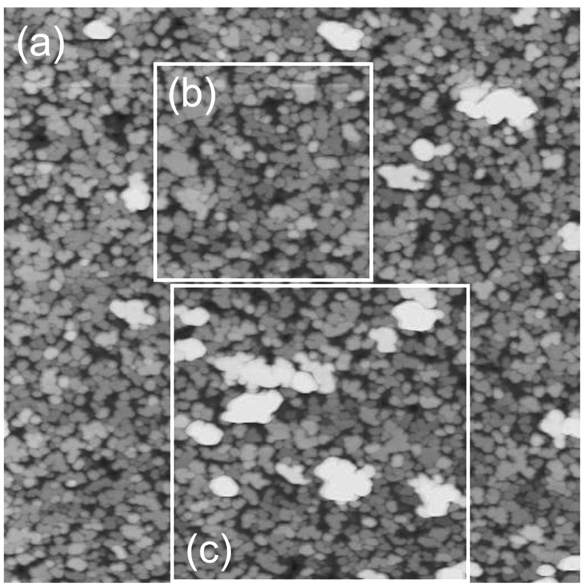
Mechanism for GaN nuclei formation → NL decomposes during annealing, Ga atoms desorb into the gas phase and reincorporate with NH_3 to form GaN nuclei. For this NL thickness, 1/3 of the Ga atoms from the initial NL growth end up in the GaN nuclei.

Key mechanism: Gas phase desorption and reincorporation not surface diffusion.

Nucleation layer evolution mechanism was determined from analysis of AFM power spectral density

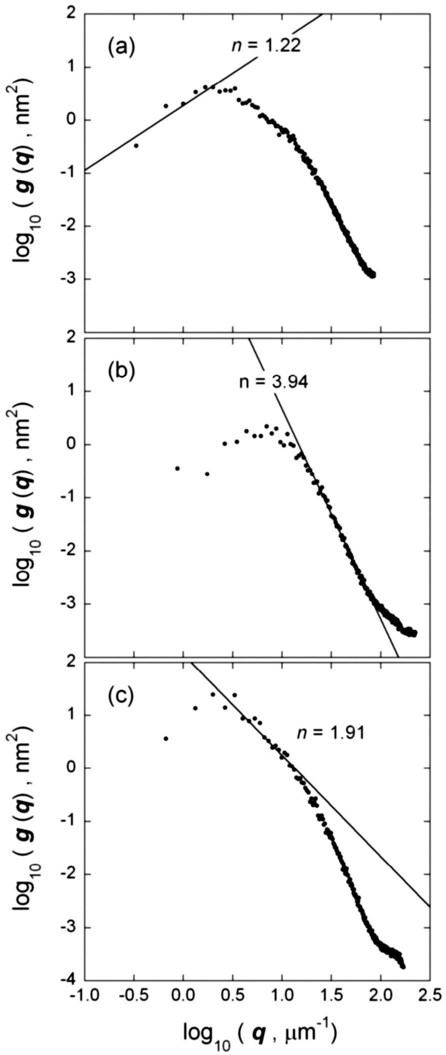
Koleske et al., J. Crystal Growth 273, 86 (2004).

Calculate height-height correlation function = $g(r)$ or $g(|q|)$ from $h(x, y)$



The $g(r)$ is related to the RMS roughness σ_{RMS} by

$$\sigma_{RMS} = (\Sigma\, g(r))^{1/2}$$



Smoothing exponents

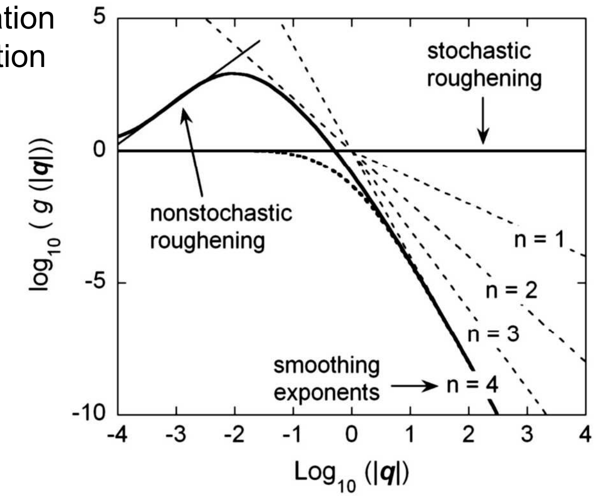
n = 2 → evaporation and recondensation

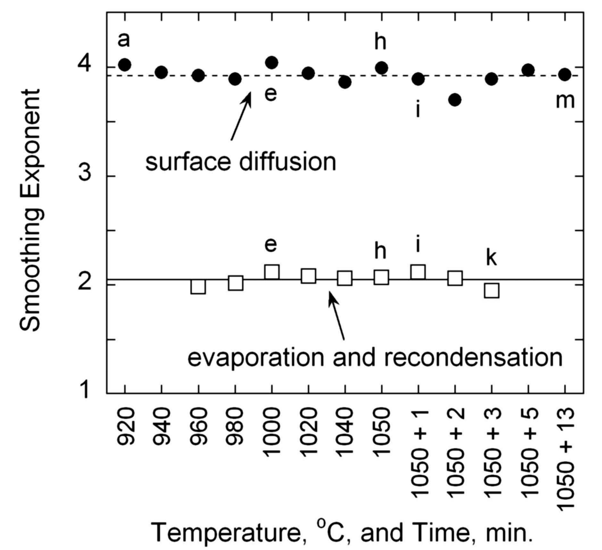
n = 4 → surface diffusion

and other mechanisms for other values for n

Conclusion: as grown NL is smoothed by surface diffusion; GaN nuclei are smoothed by evaporation / recondensation mechanism.

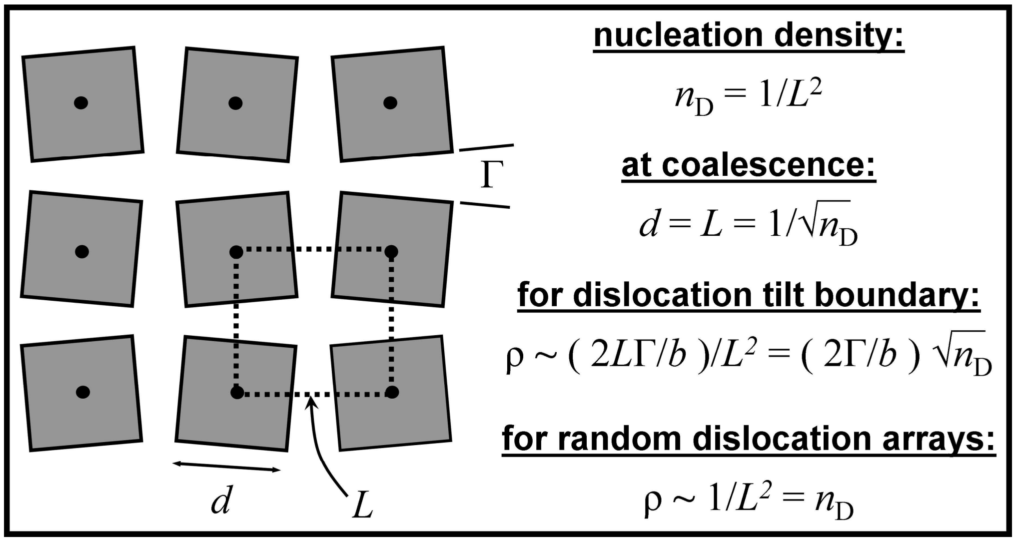
Tong and Williams, Ann.Rev. Phys. Chem. 45, 401 (1994).



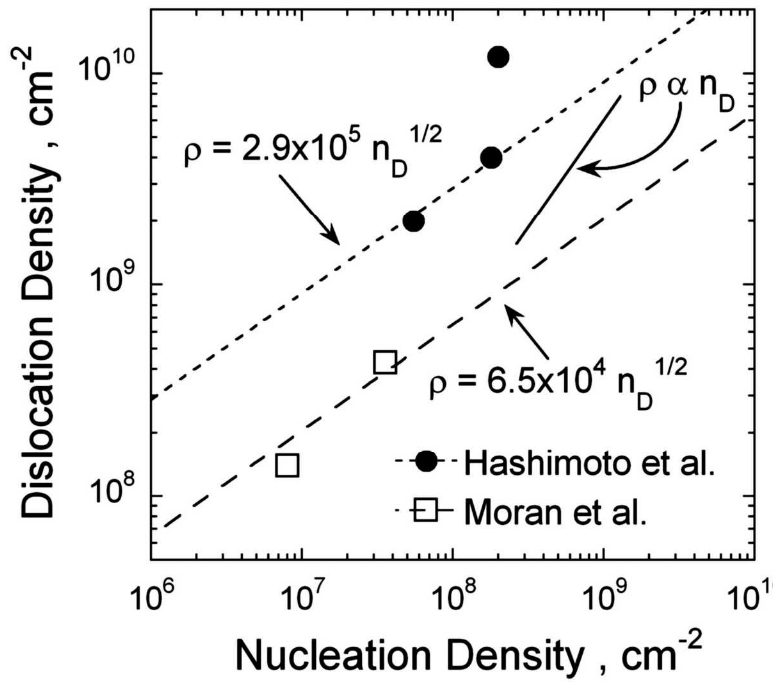


Task 1: Establish correlation between nucleation density and GaN dislocation density

Goal: Determine specific power law dependence between the nuclei density, n_D, and the dislocation density, ρ, test $\rho \propto n_D^{1/2}$ or $\rho \propto n_D$.



Γ is angle between grains, b is the Burgers vector, and L is the distance between grains.



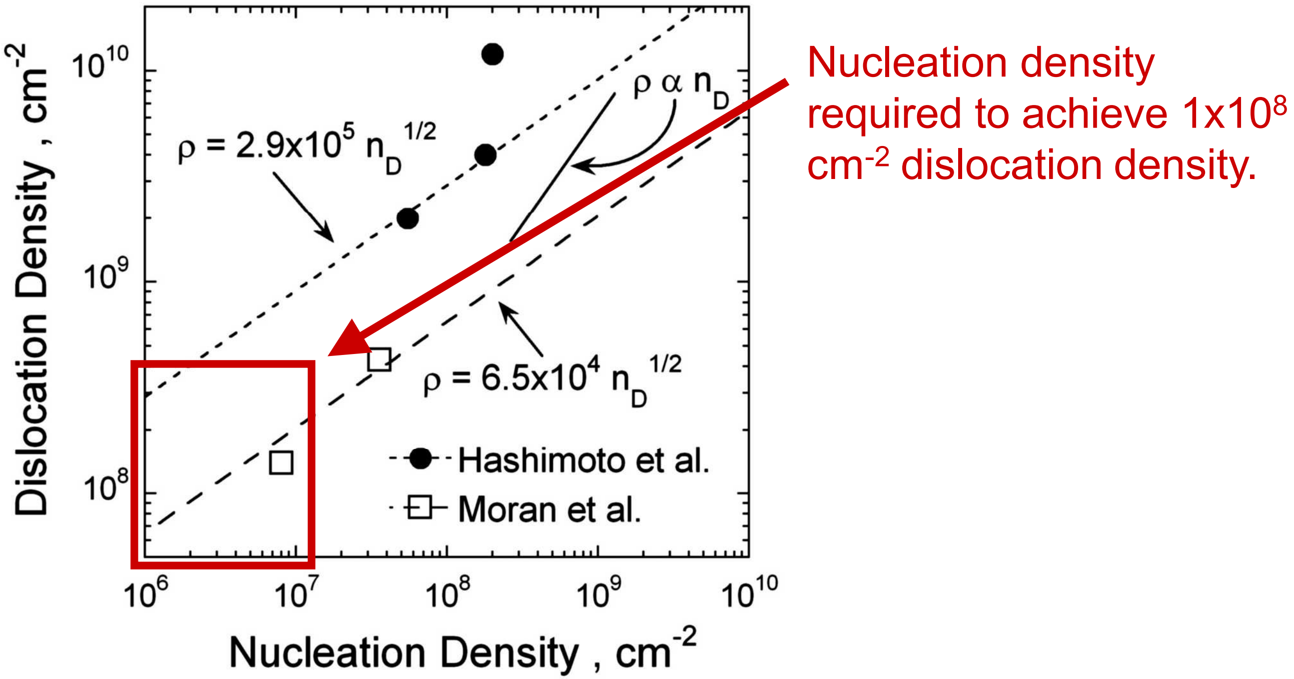
Simple geometric model for dislocation generation suggests two possibilities:

1). Dislocations generated at coalesced tilt boundaries – then $\rho \propto n_D^{1/2}$.

2). Dislocations generated as random arrays within each grain – then $\rho \propto n_D$.

Task 2: Develop growth methods that limit the GaN nuclei density, preventing growth between nuclei

Goal: control the GaN nuclei density in the range 10^6 to 10^7 cm^{-2}; should allow us to achieve dislocation densities in the low 10^8 cm^{-2}.



1). Want to controllably decrease GaN nuclei density in the range: 10^6 to 10^7 cm^{-2}.

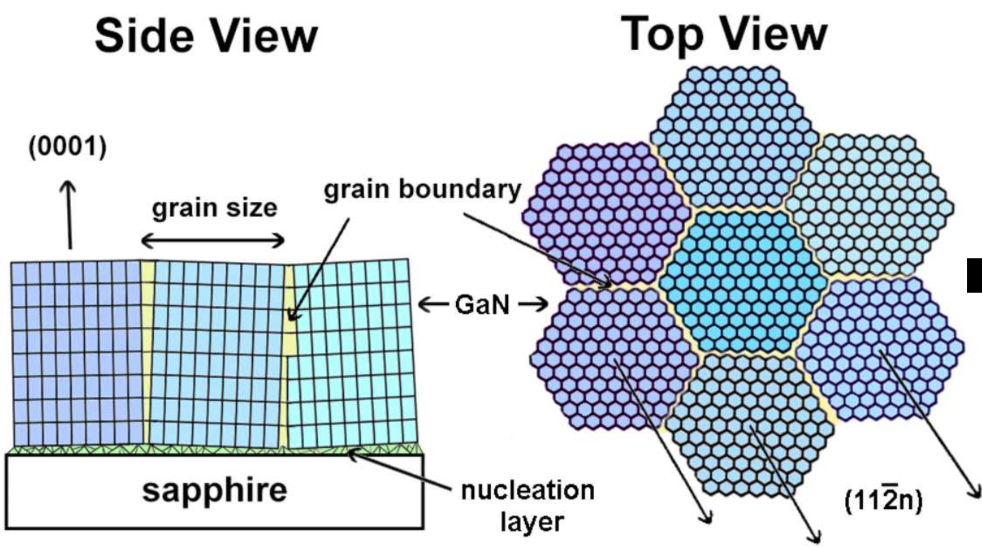
2). Prevent additional nuclei formation as GaN growth continues on top of the established nuclei to prevent dislocation formation as grains overgrow one another.

Task 3: Condition sapphire substrates to improve GaN nuclei orientation

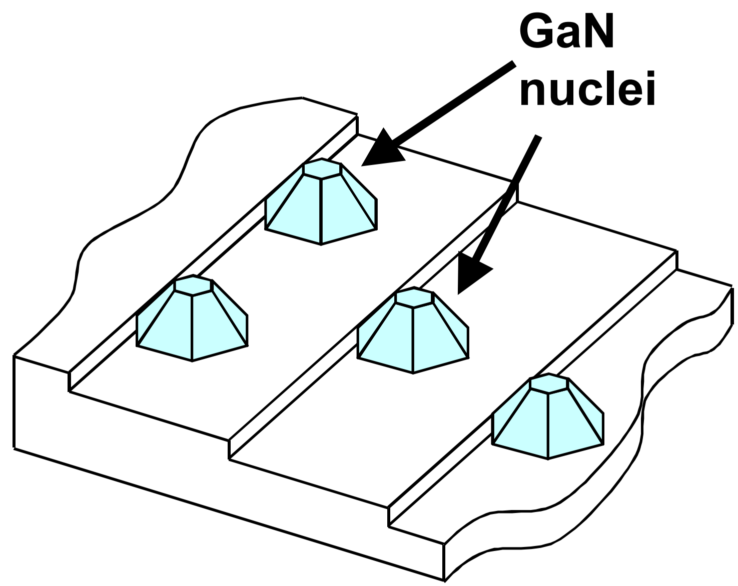
Goal: improve GaN nuclei orientation and decrease degree of misfit that must be accommodated by dislocation generation during coalescence.

GaN grows on sapphire as an oriented poly-crystal with both tilt and twist components. Initial sapphire smoothness / polishing damage may play a role in the degree to which the GaN grains are oriented.

By improving sapphire smoothness and decreasing polishing damage to create regular, smooth steps, GaN orientation might be improved.



GaN: Oriented poly-crystal on sapphire



Annealed sapphire

Task 4: Develop full growth model to fit the optical reflectance waveforms during growth

Goal: develop a full GaN growth model and use it to simulate reflectance waveforms to obtain useful information on the GaN NL evolution, GaN nuclei formation, and coalescence of the films.

Measured reflectance, R, is given by $|r(t)^2|$ where $r(t)$, the complex reflectance amplitude within the virtual interface approximation is,

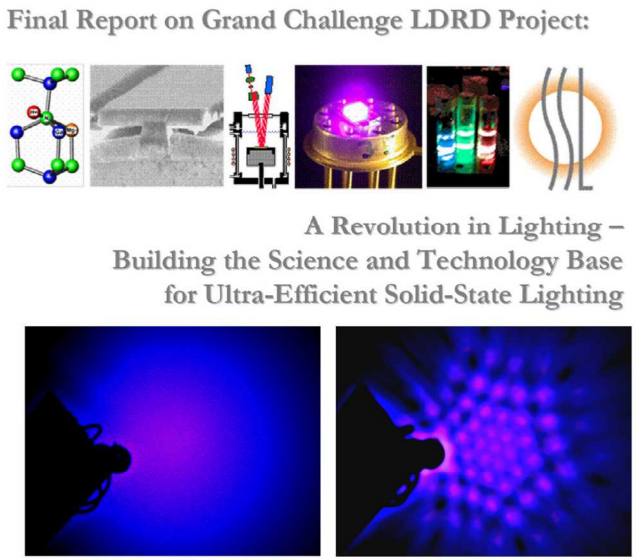
$$r(t) = \frac{r_{12} + r_{23}\exp(-i4\pi Nd/\lambda)}{1 + r_{12}r_{23}\exp(-i4\pi Nd/\lambda)}, \quad r_{12} = \frac{1 - N_{\mathrm{GaN}}}{1 + N_{\mathrm{GaN}}}, \quad r_{23} = \frac{N_{\mathrm{GaN}} - N_{\mathrm{sapphire}}}{N_{\mathrm{GaN}} + N_{\mathrm{sapphire}}}$$

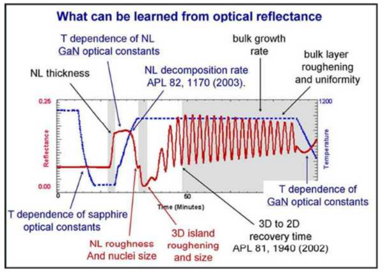
And N_i is the complex index of refraction of the ith layer, given by $n_i + ik_i$.

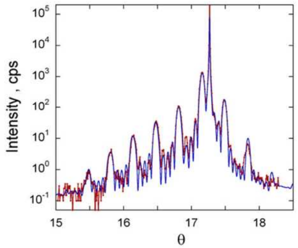
Some of the terms to be included in the simulation of reflectance are:

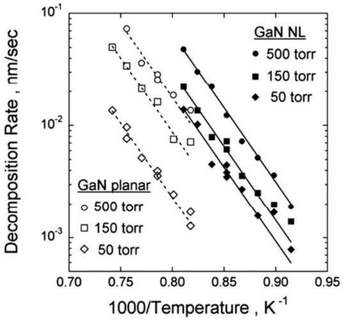
1) Nucleation layer and main layer growth,
2) Roughening of the NL and main layer
3) Nucleation layer decomposition
4) Temperature dependence of the optical constants
5) Thickness non-uniformity.

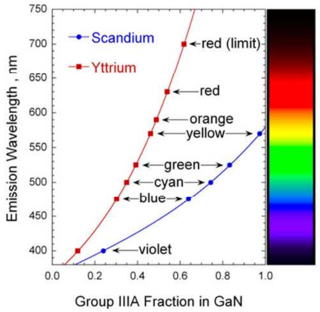
Indirect Cost Benefit from Ongoing Programs

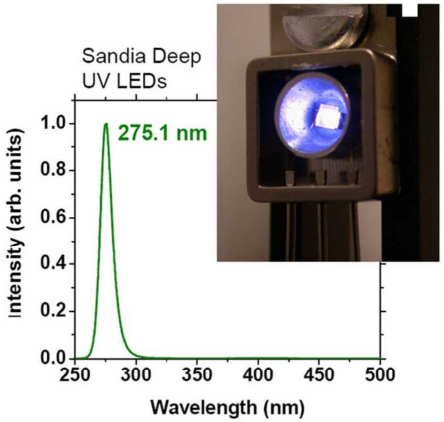


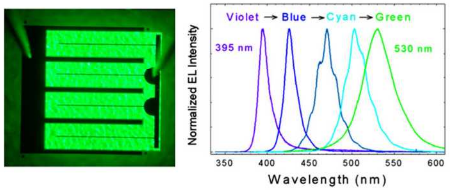












- Sandia has been involved in group III nitride research since 1997.
- This work has been supported both internally (LDRD) and externally (BES, NETL, and DARPA) for many years. From 2001 to 2004 it was supported by a 8 M$ grand challenge LDRD at Sandia. More recently, support has been provided by DOE basic energy sciences (BES) and additional LDRDs to study luminescence properties.
- In several publications PI and colleagues investigated nucleation layer evolution and optical reflectance interpretation. This work is now accepted by nitride community.
- Complementary to work on other NETL funded programs such as “Innovative Strain-Engineered InGaN Materials for High-Efficiency Deep-Green Light Emission”.

R&D 100 Research Award in 2004

U.S. Department of Energy
Energy Efficiency and Renewable Energy
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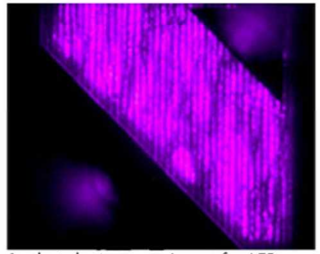
Building Technologies Program

Solid-State Lighting

Cantilever Epitaxy Process Wins R&D 100 Award

Sandia National Laboratories received an R&D 100 Award from *R&D Magazine* for development of a new process for growing gallium nitride on an etched sapphire substrate. The process, called cantilever epitaxy, promises to make brighter and more efficient green, blue, and white LEDs.

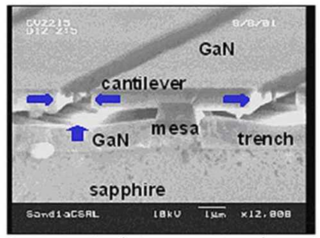


An electroluminescence image of an LED fabricated using the cantilever epitaxy process shows uniform LED intensity over multiple regions.

The cantilever epitaxy process eliminates many of the problems that limit the performance of LEDs grown on sapphire/gallium nitride substrates. In the past few years, LEDs have been grown with various combinations of gallium nitride alloys on sapphire substrates. In the process, regions of imperfections – called dislocations – are formed, which limit LED brightness and performance. The cantilever epitaxy process reduces the number of dislocations, offering the potential for longer-lived and better performing LEDs.

Reducing Dislocation Density Through GaN Cantilever Growth

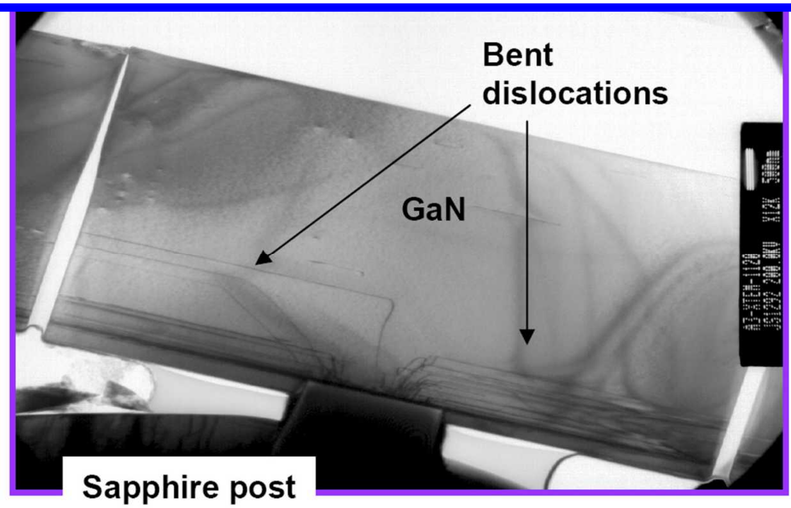
Sandia's cantilever epitaxy growth process begins with etching trenches into the sapphire substrate, leaving stripes of mesas in the surface. Vertical growth of the GaN overlayer is then initiated on the mesas. After some vertical growth, the conditions of the growth reactor are adjusted to produce lateral growth over the trenches. This lateral cantilever material – suspended by the mesas – does not contain dislocations because it is not in contact with the substrate. After adjacent cantilevers are grown together, the material is grown vertically to produce the desired thickness. In the end, dislocations produced by contact with the substrates are confined to the mesa areas, and the cantilever regions over the trenches have very low dislocation densities.



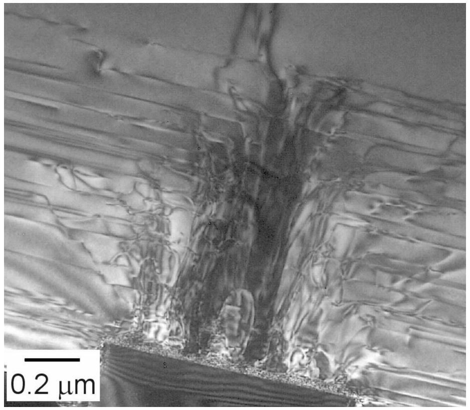
A cross-sectional microscope image shows GaN cantilevers growing toward each other with GaN growing upward in the trenches.

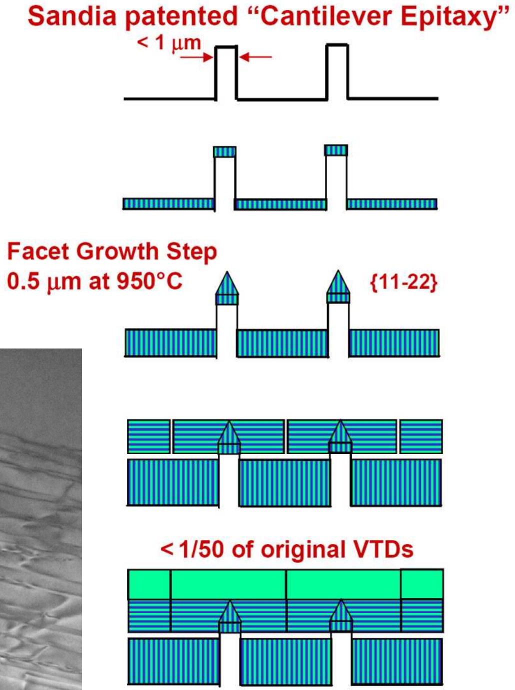
The cantilever epitaxy research conducted at Sandia was supported in part by an internal Laboratory Directed Research and Development (LDRD) Grand Challenge, and in part by a cooperative agreement from DOE (Office of Energy Efficiency and Renewable Energy, Building Technologies Program) for a collaborative project with Lumileds Lighting.

For more information on cantilever epitaxy, see the Sandia/Lumileds Research Highlights and the Sandia National Laboratories News Release.



Koleske and Coltrin previously worked on this project.



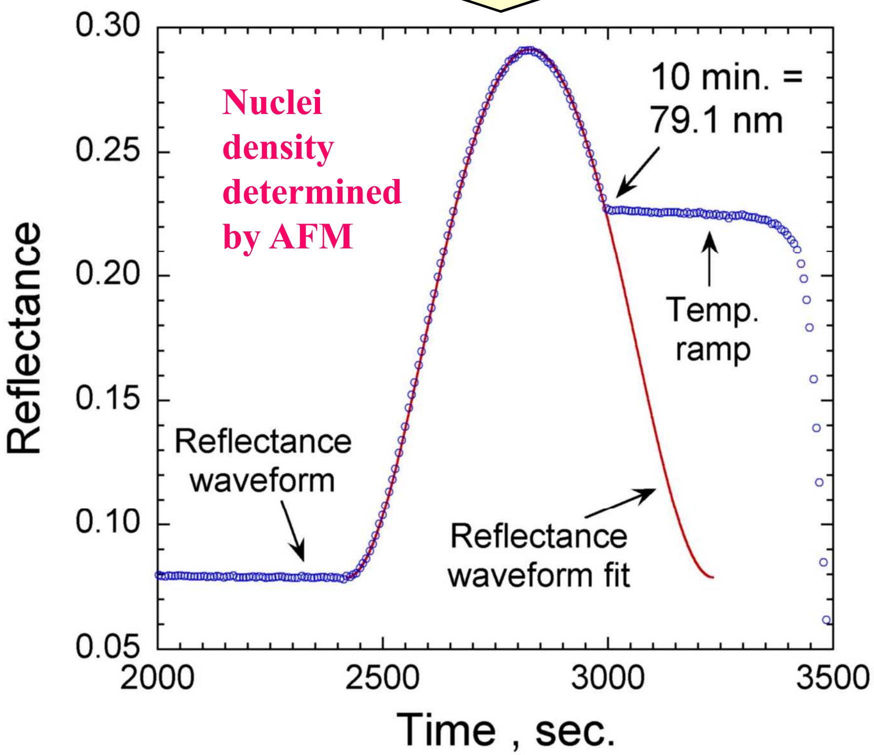


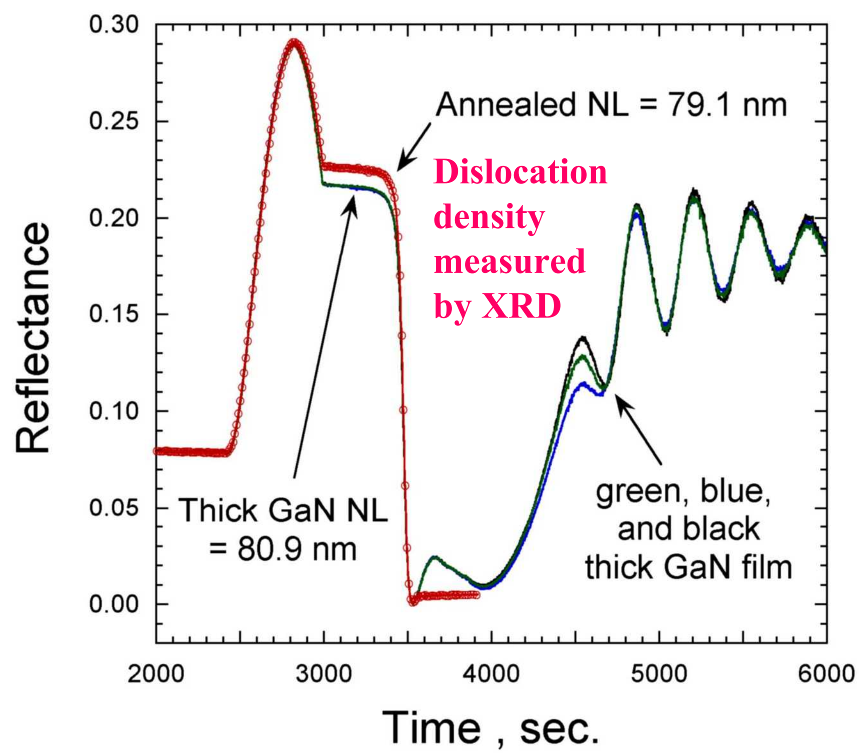
R&D 100 Award, 2004

SNL: Follstaedt et al., APL, 2002

Reflectance control of initial NL thickness

The nucleation layer (NL) thickness can be determined from the measured reflectance waveform (shown in blue) by simulating the reflectance as the NL thickness increases (shown in red).



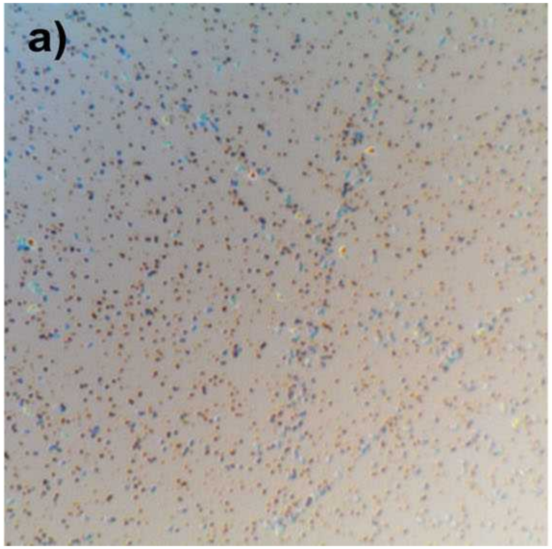


The reflectance waveform for the companion bulk GaN film grown on a NL with a similar initial thickness. Note that there is a slight and measurable thickness difference between these two films.

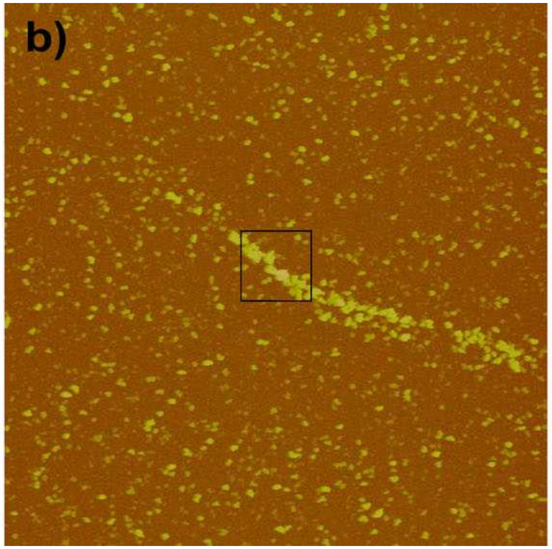
Images of annealed nucleation layers

Initial NL thickness is 15.9 nm

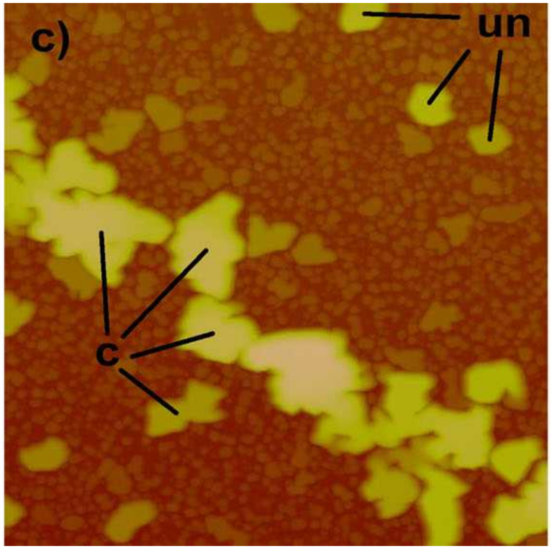
x 150 magnification



40 x 40 μm

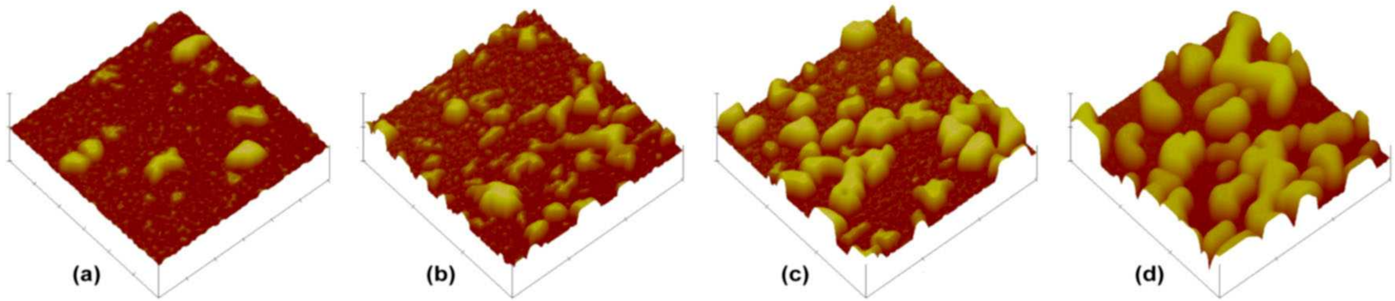


5 x 5 μm



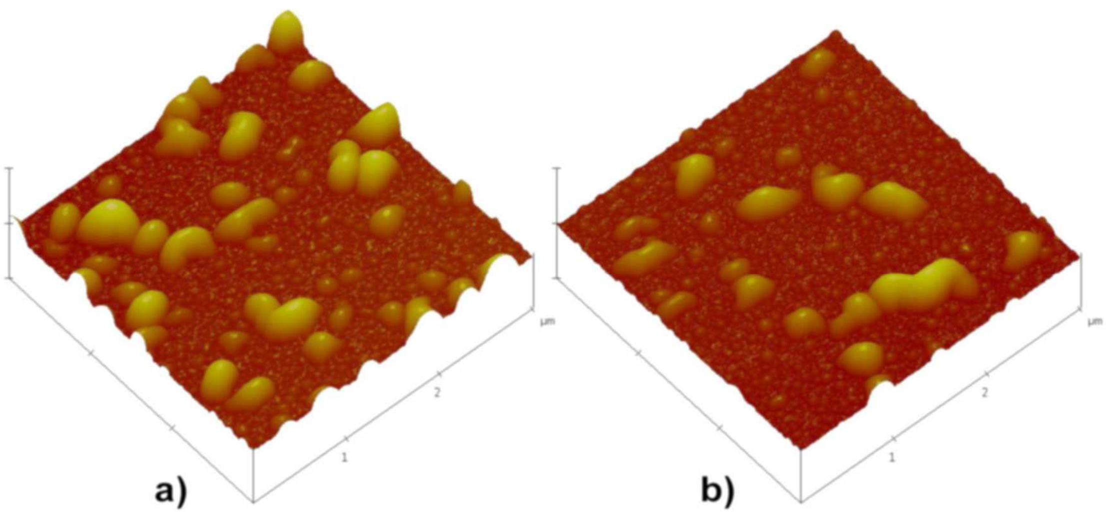
In a) GaN nuclei are visible using Nomarski phase contrast microscopy. Note that in some regions the GaN nuclei are bunched together along what are likely polishing scratches on the sapphire surface. In b) and c) the increased nucleation near the polishing scratches are better observed. In image c) coalesced nuclei denoted by the letter c are shown along with individual uncoalesced nuclei denoted by uc. The groups of coalesced nuclei produce a non-uniform distribution of initial nuclei and may result in a higher density of dislocations in this region.

Two ways to control initial GaN nuclei density



Initial NL thickness

AFM images of annealed nucleation layers (NLs) with initial thicknesses of a) 15.9 nm, b) 33.5 nm, c) 51.4 nm and d) 79.1 nm. As the NL thickness increases the amount of material that is reincorporated into GaN nuclei increases along with an increase in the number of partly coalesced nuclei.

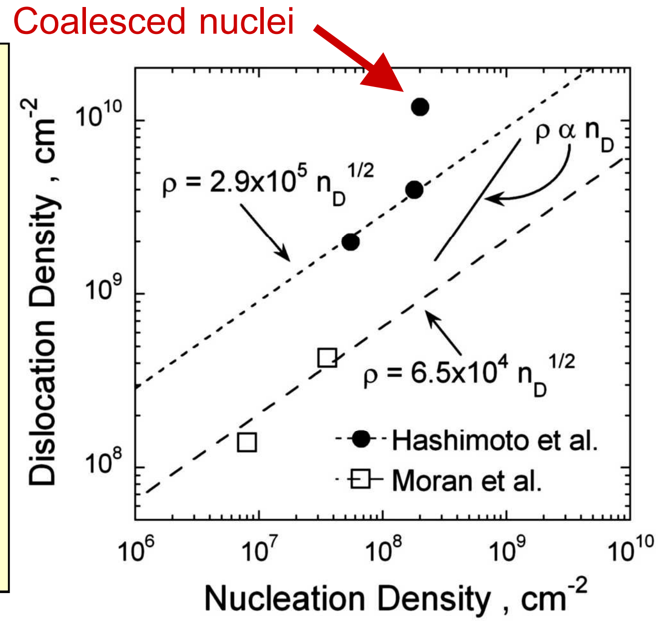


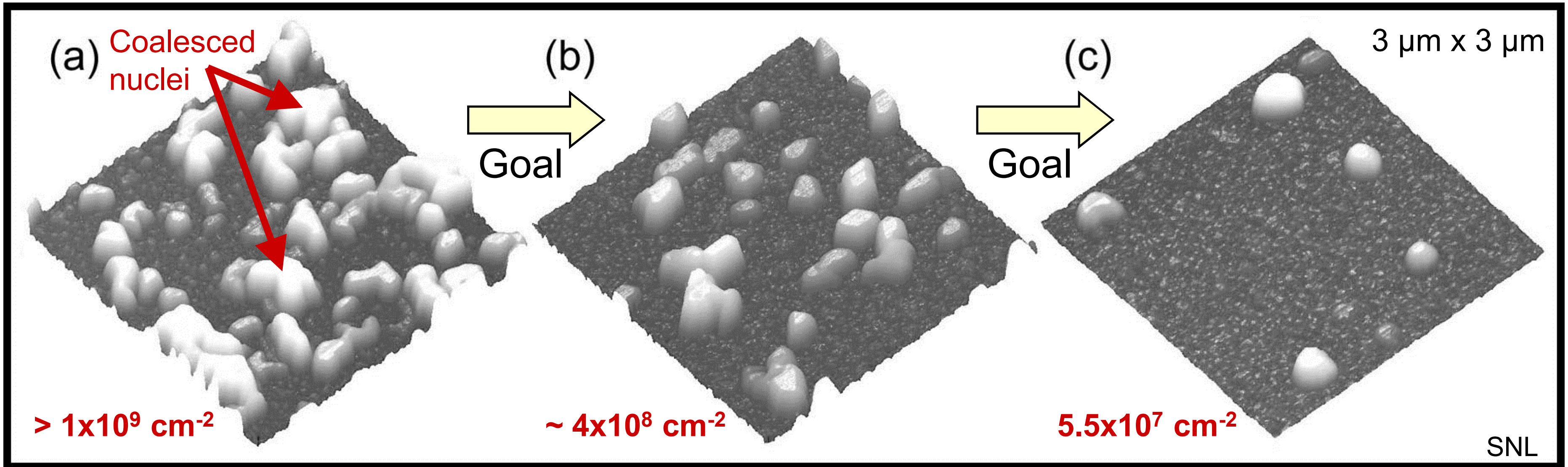
Total gas flow through the reactor

AFM images of annealed NLs using the same initial NL thickness and a) flow rates of 15 SLM H_2, 11 SLM N_2, and 2 SLM NH_3 and b) flow rates of 23 SLM H_2, 15 SLM N_2, and 2 SLM NH_3. Note the decreased GaN nuclei density in b) with the higher total flow rates compared to a) with the lower total flow rate.

Subtask 1.1: Develop templates that have evolved nuclei densities ranging from 10^7 to 10^9 cm^{-2}

- Vary nucleation layer (NL) thickness and other annealing parameters to establish different GaN nuclei densities.
- Prevent nuclei coalescence at high density, see (a) below
- As NL is annealed, quench sample temperature once maximum NL roughness is achieved (determined by optical reflectance).
- Nuclei distributions will be captured in time; then nuclei density will be determined by AFM. Nuclei densities from partially coalesced nuclei will be estimated (see (a) below) so as not to undercount nuclei density.

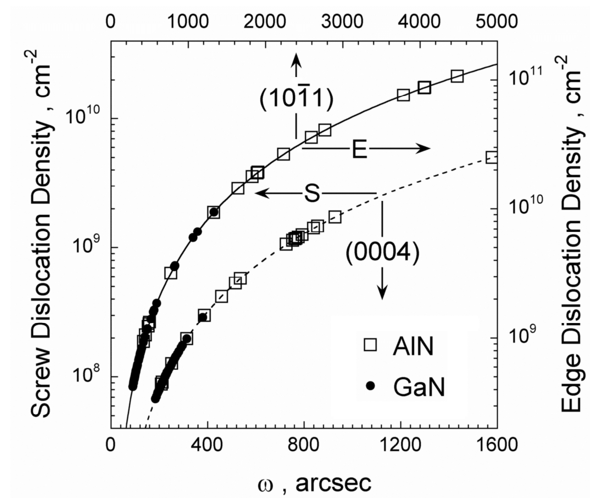


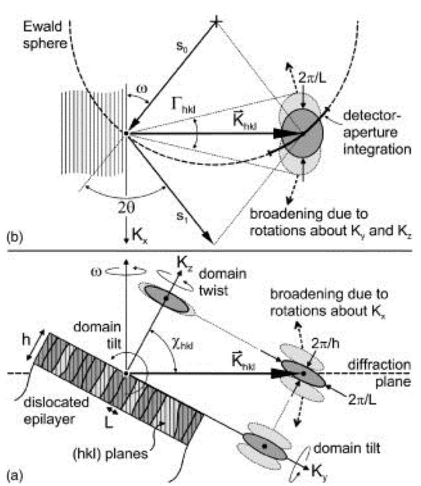


Subtask 1.2: Determine the dislocation density in fully coalesced GaN films on templates with variable GaN nuclei densities

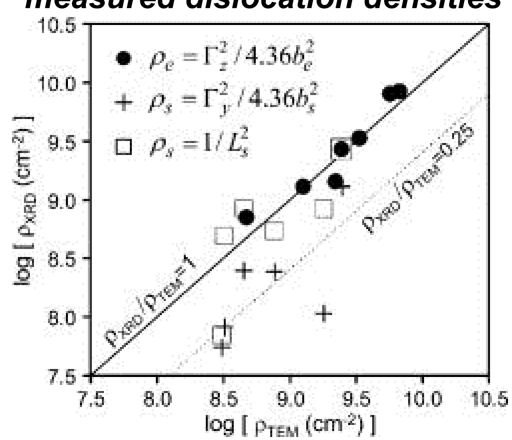
- Using films obtained in Subtask 1.1, full GaN films will be grown on top to thicknesses of 5 µm.
- Dislocation densities will be determined from XRD peakwidths of the (0004) and (1011) reflections; Ref: Lee (APL 86, 241904 (2005)).
- After calibration with TEM, the Lee XRD method provides an accurate accounting of the edge component dislocation density but under-estimates screw-dislocation density by a factor of ~4.
- Method based on reciprocal-space model of Bragg peak width that describes dependence on coherence length, tilt variance, and twist variance of a dislocated epitaxial layer.

Correspondence between XRD peak width and dislocation density



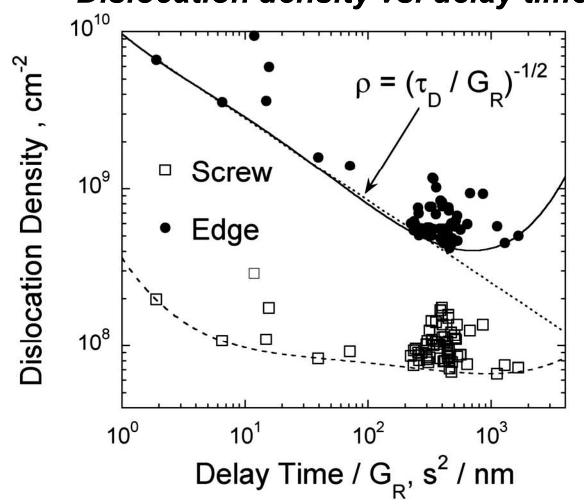


Comparison between XRD and TEM measured dislocation densities



S. R. Lee, *et al.*, Appl. Phys. Lett. 86, 241904 (2005).

Dislocation density vs. delay time

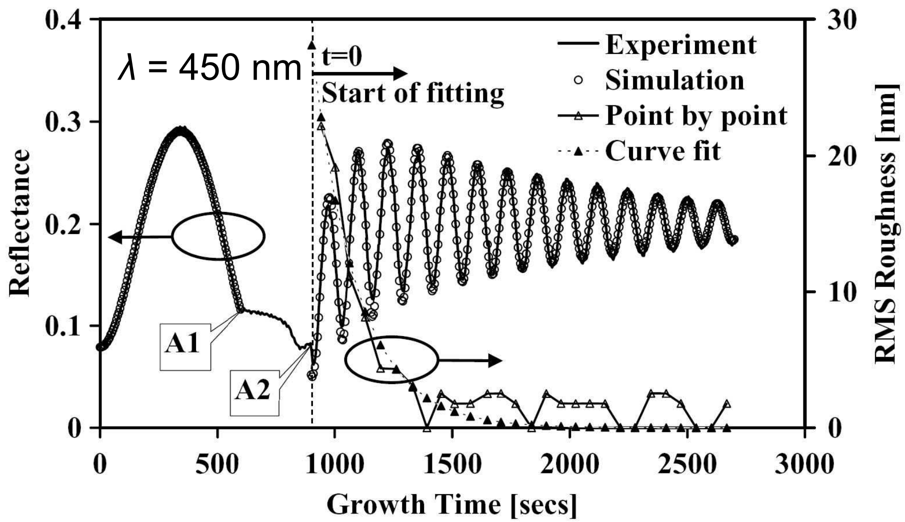


Subtask 4.1: *Develop model and reflectance waveform simulator to model GaN growth on sapphire*

- **A reflectance waveform simulator will be developed accounting for all aspects of GaN growth, including: done (blue), need to work on (red)**
  - **1). sapphire annealing (changes in optical constants)**
  - **2). GaN NL growth**
  - **3). GaN NL annealing and decomposition,**
  - **4). GaN nuclei formation,**
  - **5). initial growth on the GaN nuclei,**
  - **6). roughening as the GaN nuclei grow,**
  - **7). GaN grain coalescence and smoothing of the surface**
  - **8). surface thickness non-uniformity.**

First attempt at modeling optical reflectance

Optical reflectance measured during growth by R. S. Balmer, et al., J. Crystal Growth 245, 198 (2002).



NL thickness = 84 nm, d = 20 nm, α = 0.8, A_0 = 5x10⁸ nm/s, σ = 26 nm