Bulk Single Crystal Gallium Nitride Growth

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LEHIGH UNIVERSITY

Overview

Why (bulk) GaN?

↓

Bulk GaN Growth Methods

↓

Ammonothermal Method

↓

Technology | Crystal Properties | Solvent/Solute

Why GaN?

How to generate light?

Convert **potential energy** of an electron to a **photon**.

Let's say: Electrons = Water Molecules

Waterfall Height: Band Gap Energies

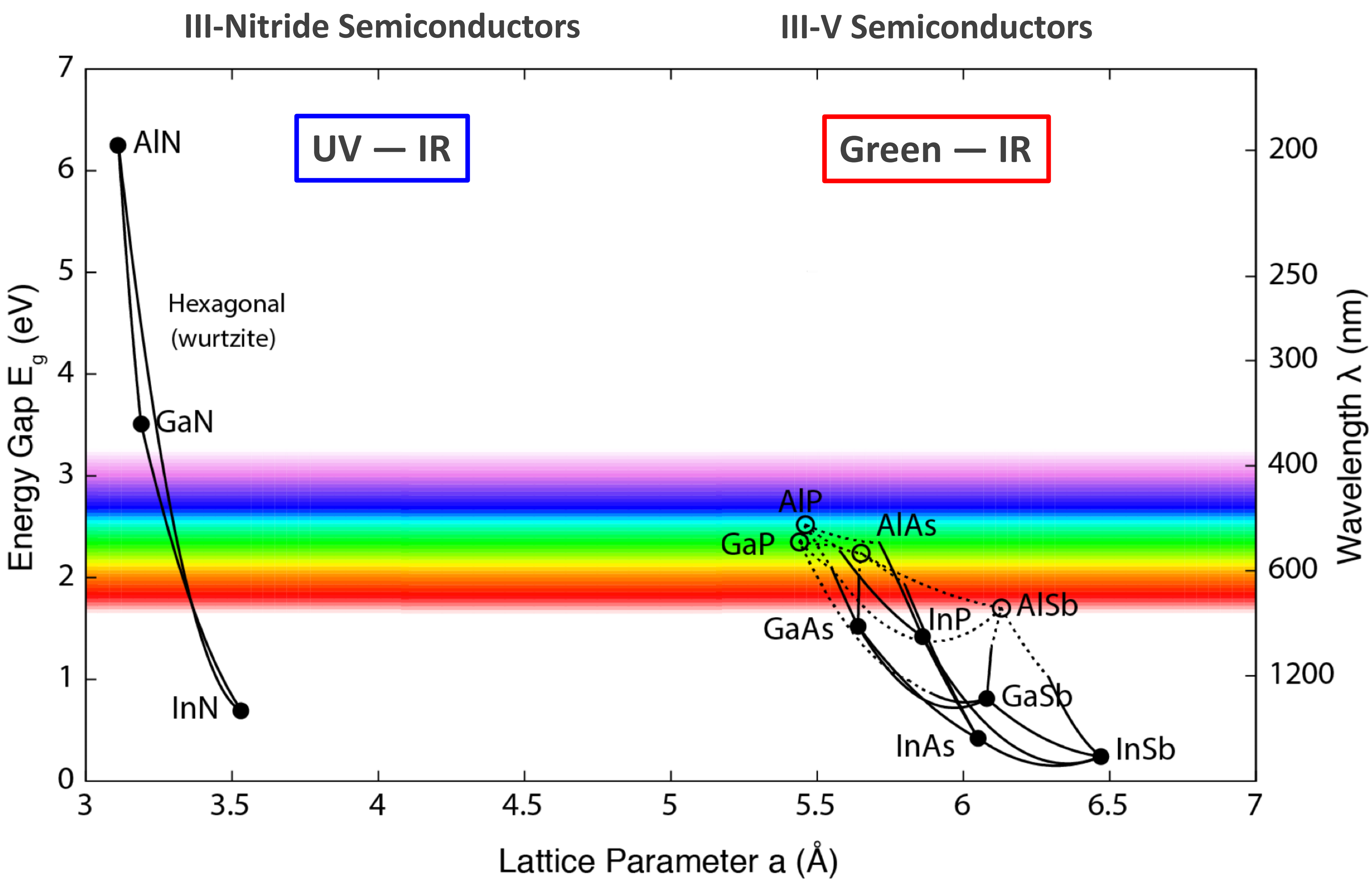
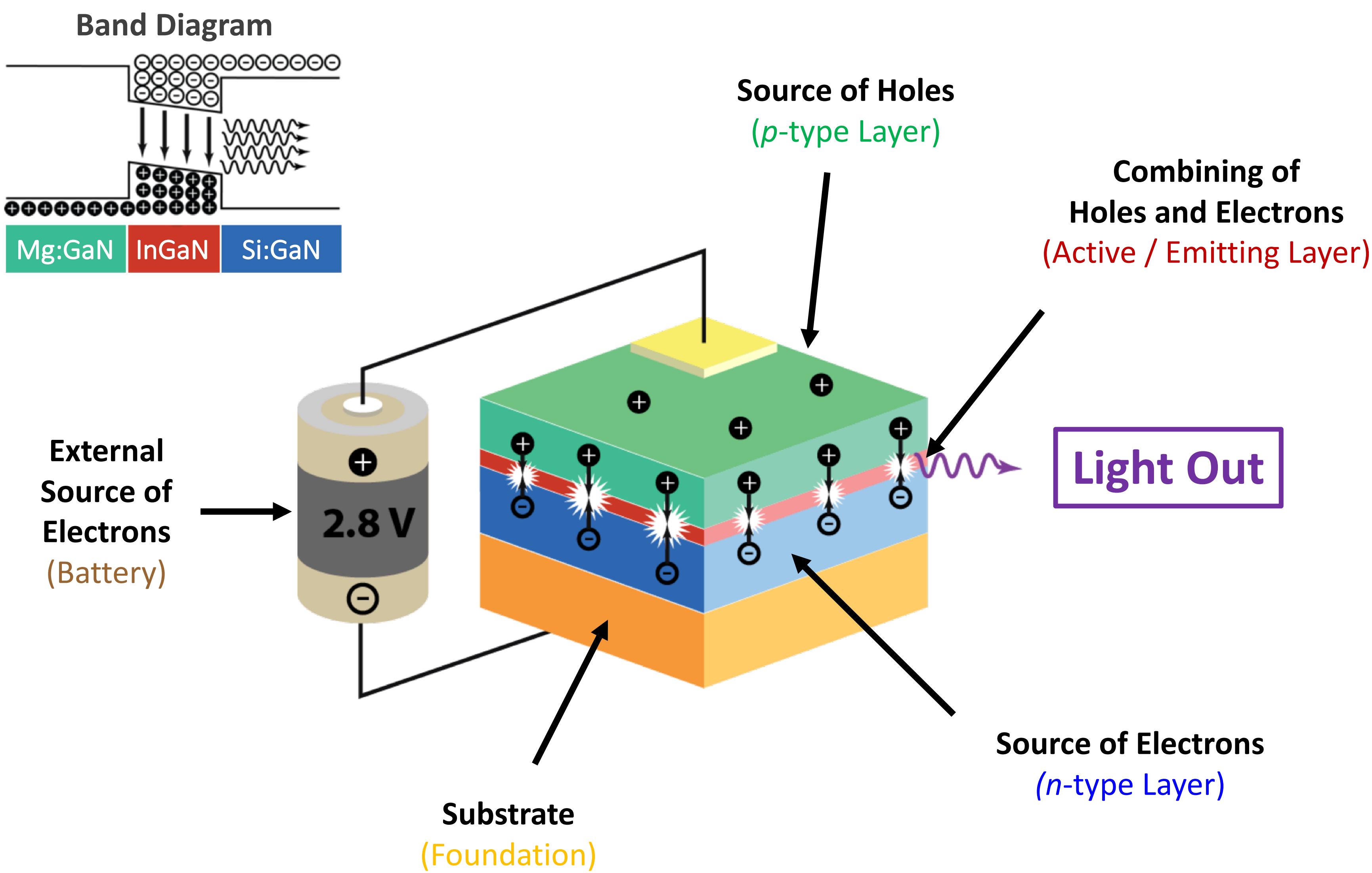


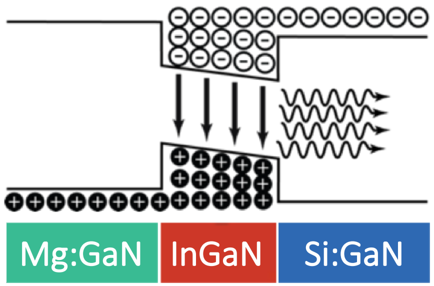
Image after : M. Á. Caro Bayo, Ph.D. Thesis, UCC (2013)

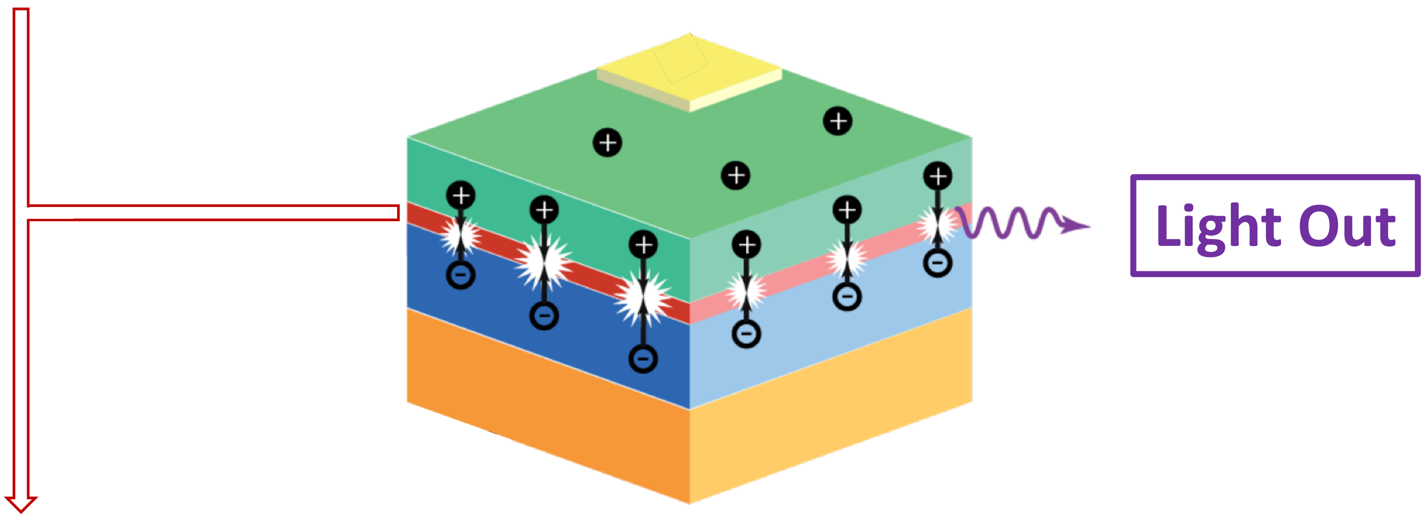
Light Emitting Diode



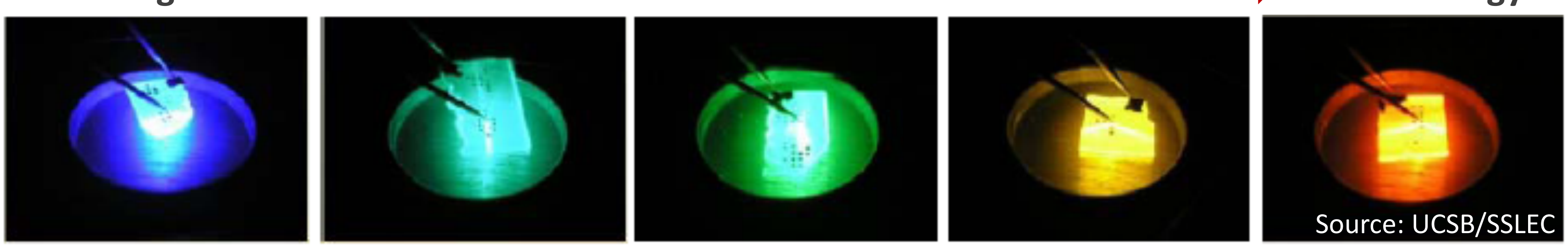
Light Emitting Diode

Band Diagram



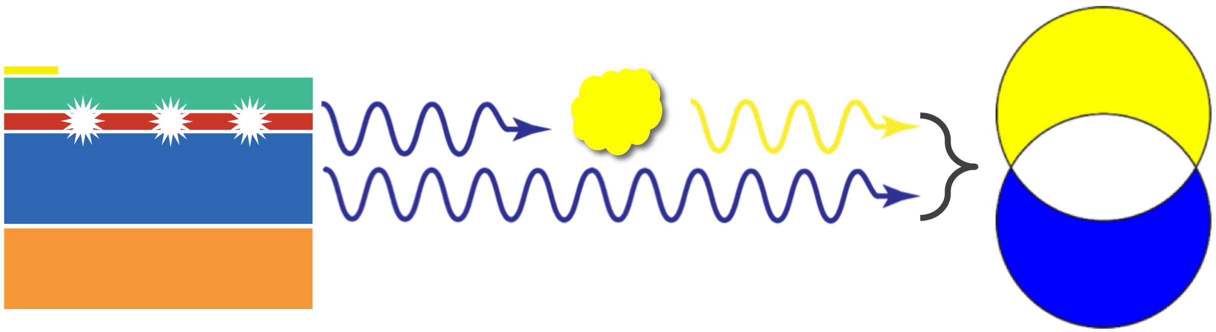


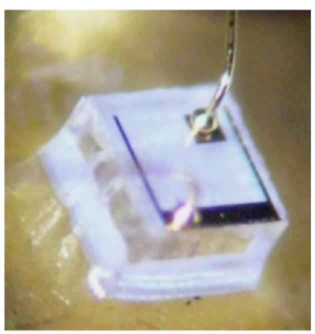
Increasing Indium Content → **Lower Energy**



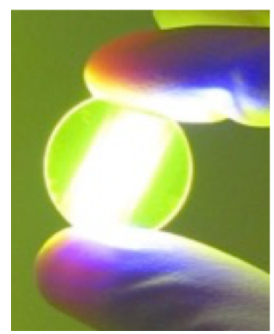
White LEDs: Solid State Lighting

Blue LED	**Phosphor** Convert: Blue → Yellow	**White Light** = Blue + Yellow	**White LED**

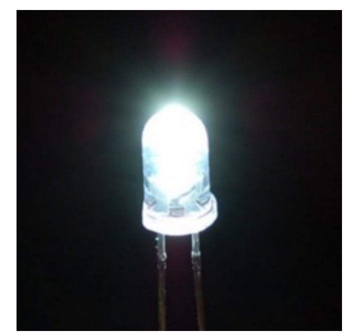




Size: 0.4 mm x 0.4 mm

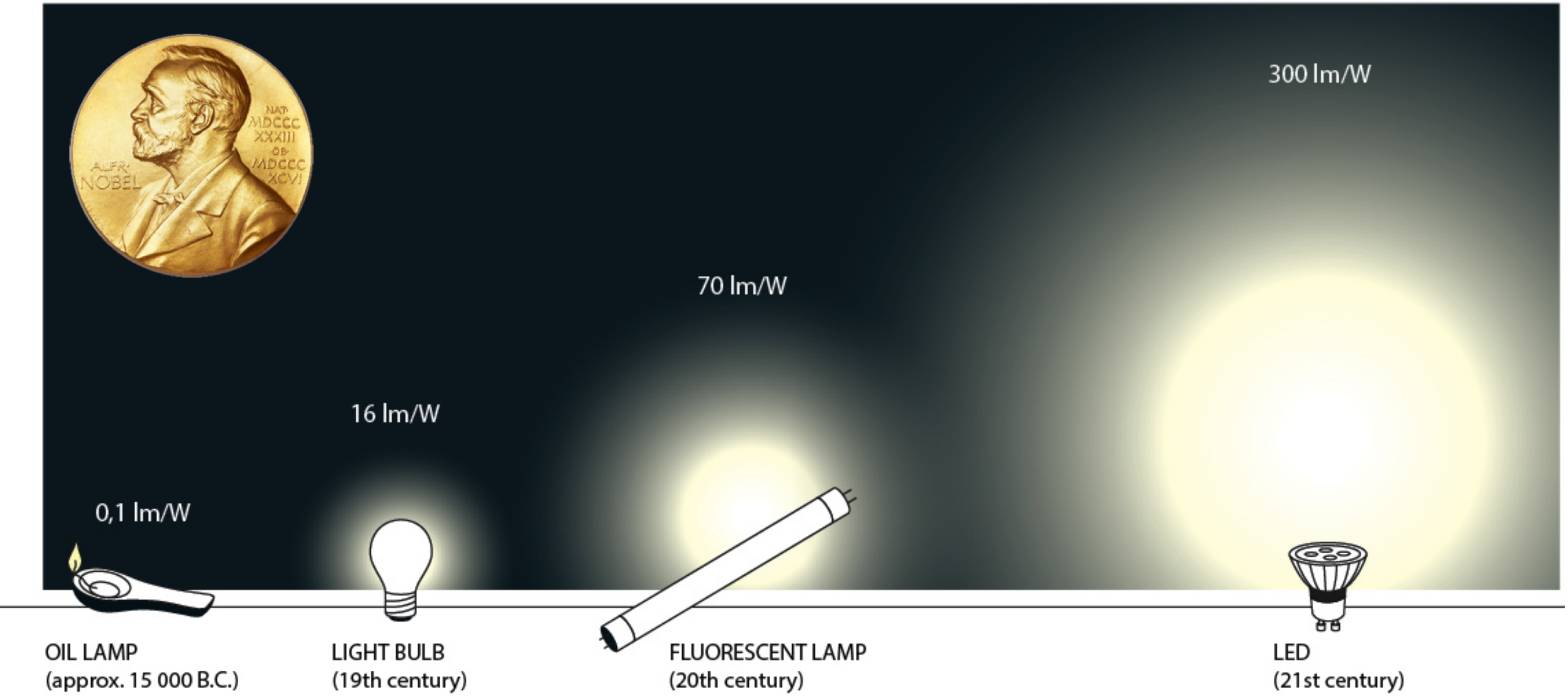


Phosphor Strip



S. Pimputkar et al., *Nature Photonics* **3** (2009) 180—182

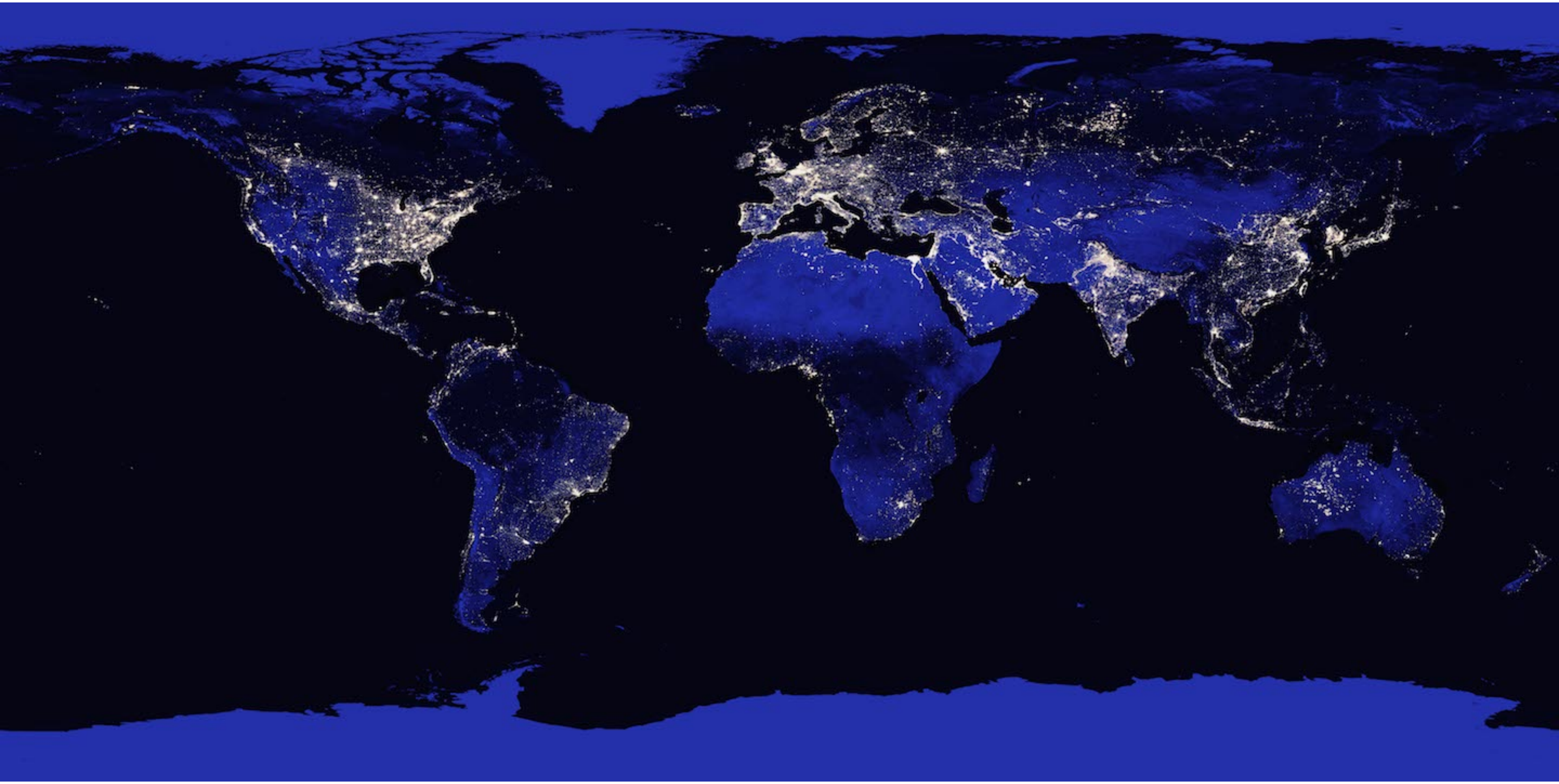
Nobel Prize: Highest Efficiency White Light Source



White LEDs: **20x more efficient than Incandescent**

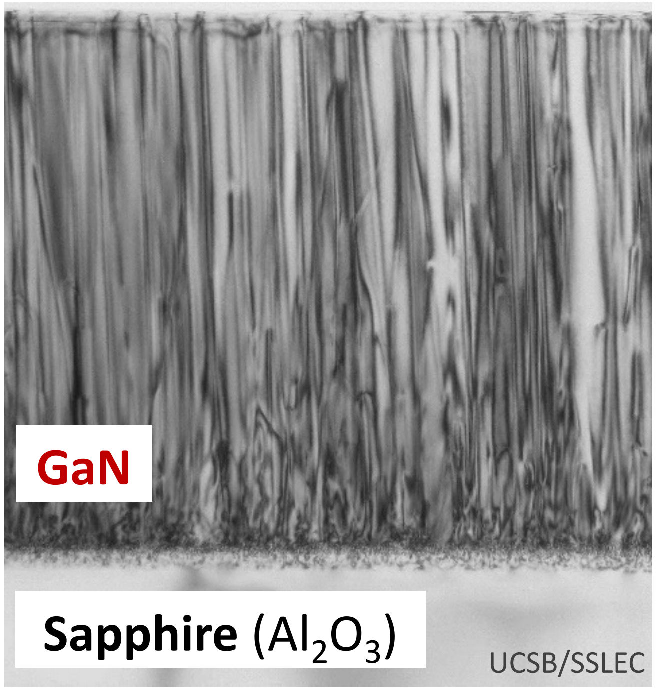
Sources: Nobel Committee, Royal Swedish Academy of Sciences

Huge Savings Potential



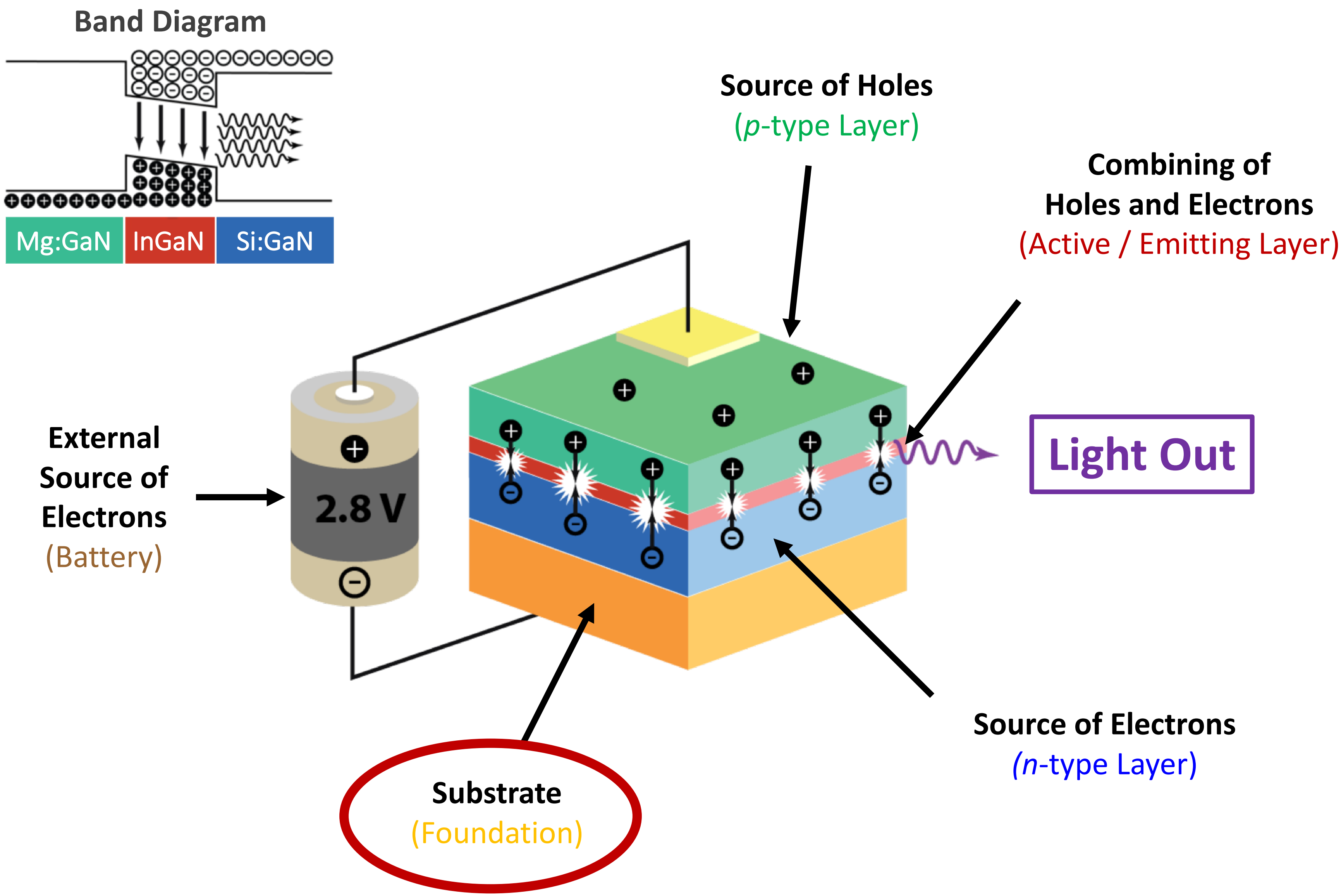
Global Energy Savings: **640 mid-sized Power Plants!**

Source: NASA Earth Observatory / NOAA NGDC, IEA



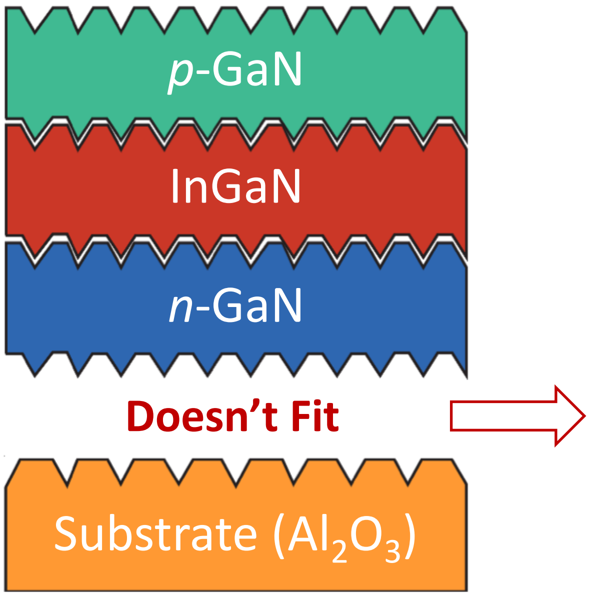
The need for *bulk* GaN

Light Emitting Diode

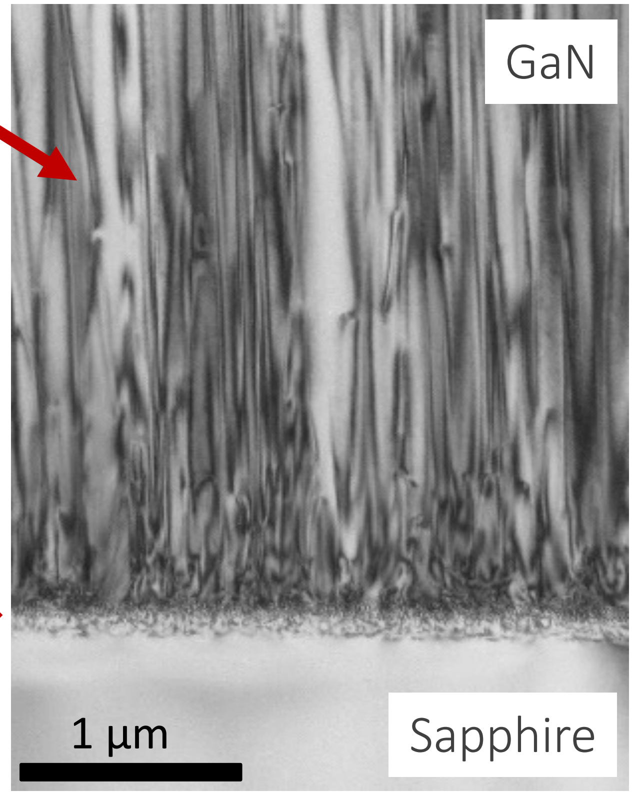


Heteroepitaxy leads to Defects

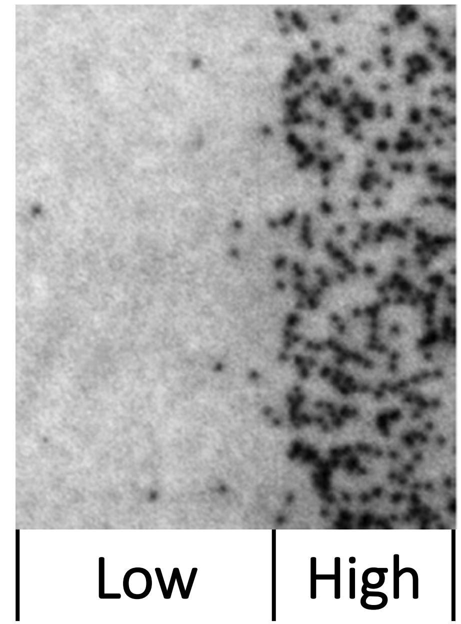
> 10^9 cm^{-2} Dislocations/ Defects



Cross section TEM



Top View CL



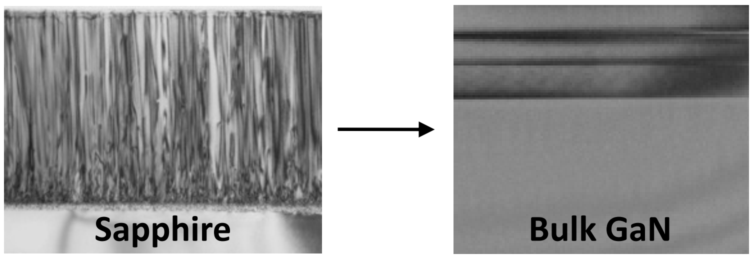
Dislocation Density

Defects: **Non-radiative recombination / diffusion pathways**

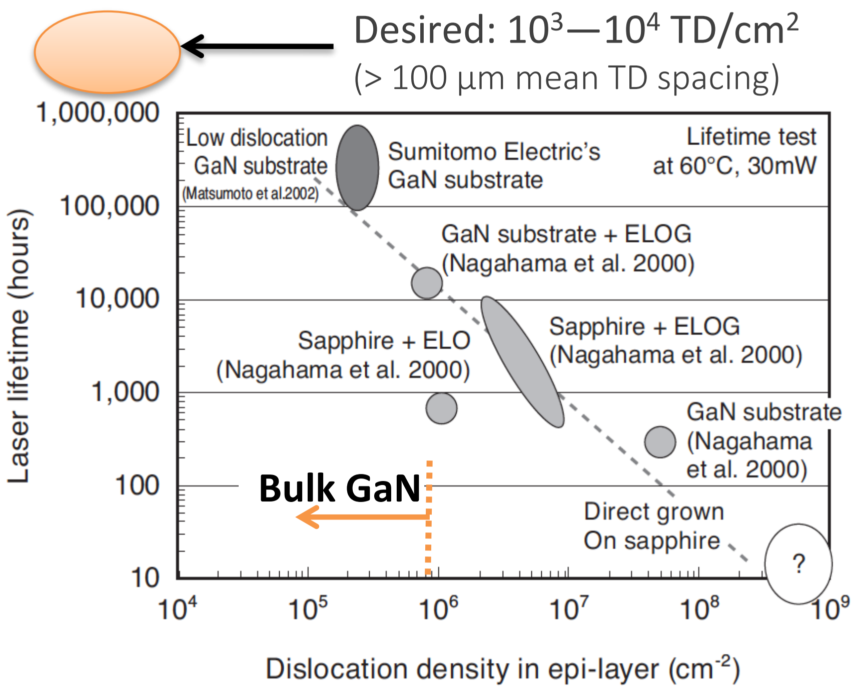
TEM courtesy F. Wu *et al.*, UCSB; CL S. Tomiya et al, *IEEE J. Sel. Top. Quant. Electr.* **10** (2004) 1277

Bulk GaN Substrates Enables …

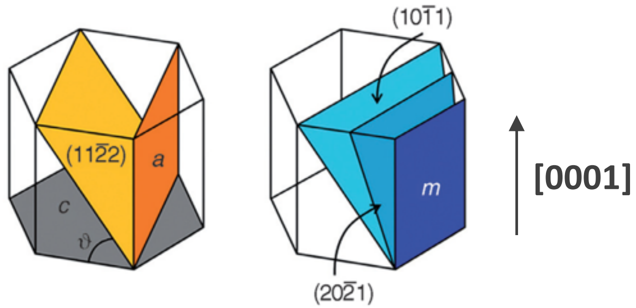
High Efficiency Devices



Desired: 10^3—10^4 TD/cm^2
(> 100 µm mean TD spacing)



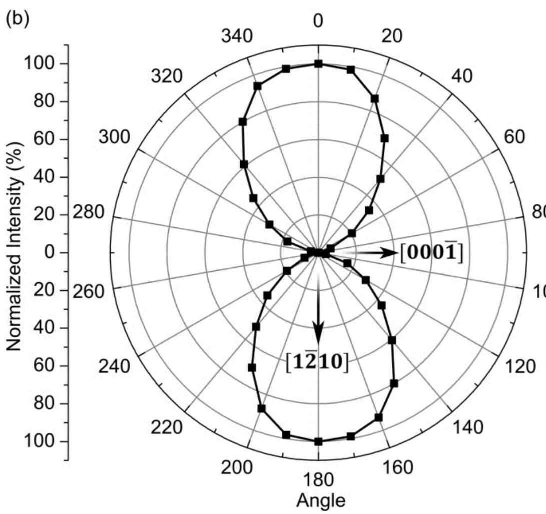
Novel Devices



100% polarized emission

m-plane GaN VCSEL

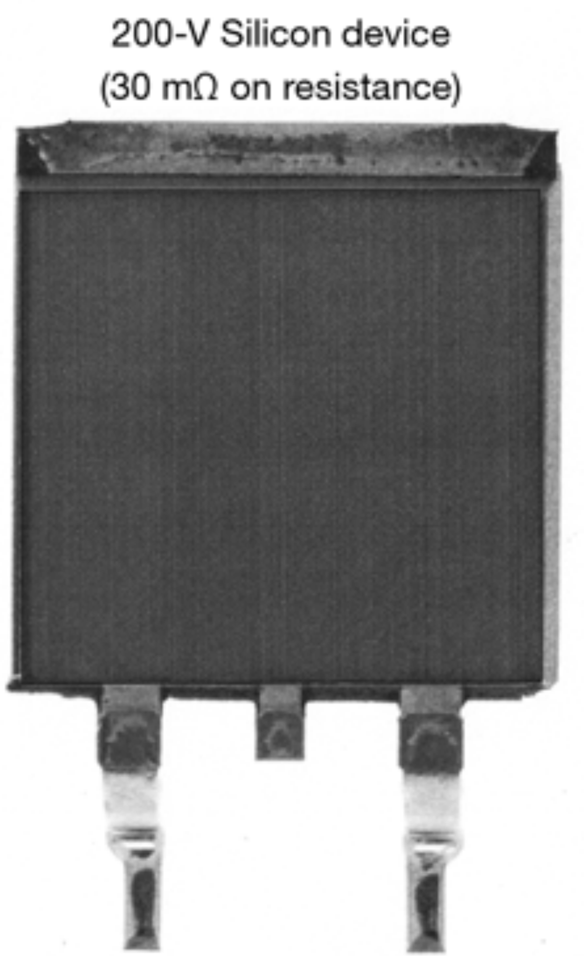
(Vertical-cavity surface-emitting laser)



K. Motoki, *Sei. Tech. Rev*. **70** (2010) 28–35; M.T. Hardy et al., *Mat. Today*. **14** (2011) 408–415; C. O. Holder et al., *Appl. Phys. Lett.* **105** (2014) 031111

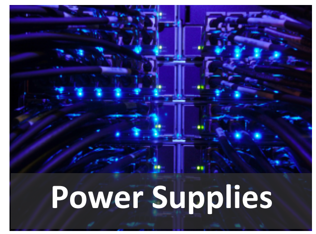
Power Devices

Yesterday
(Silicon)



Today
(Lateral GaN)


Motor Drives


Power Supplies


Solar Inverters


EV Motor Inverters

Tomorrow
(Vertical GaN)


Rail traction

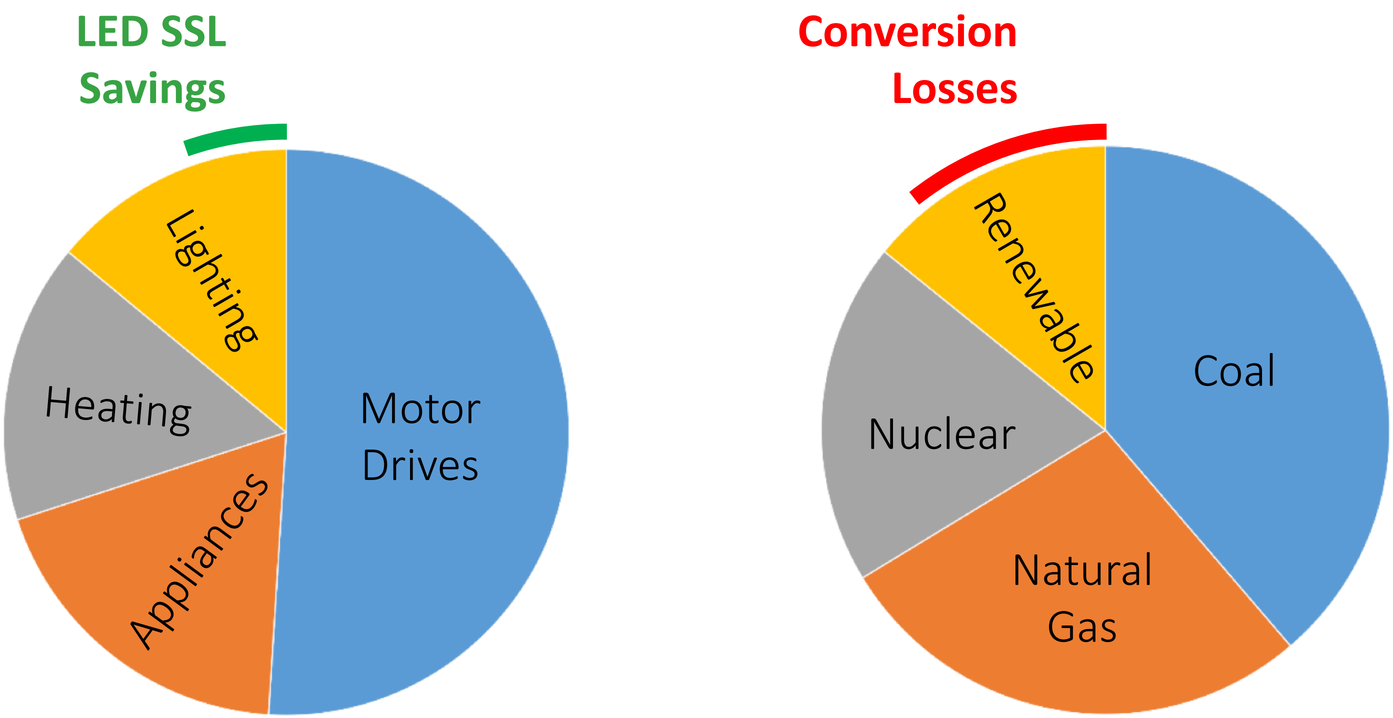

Wind turbine


Grid energy T&D


Ships and vessels

Size Comparison: Efficient Power Conversion Corp.

GaN Power Electronics: Superior Efficiency

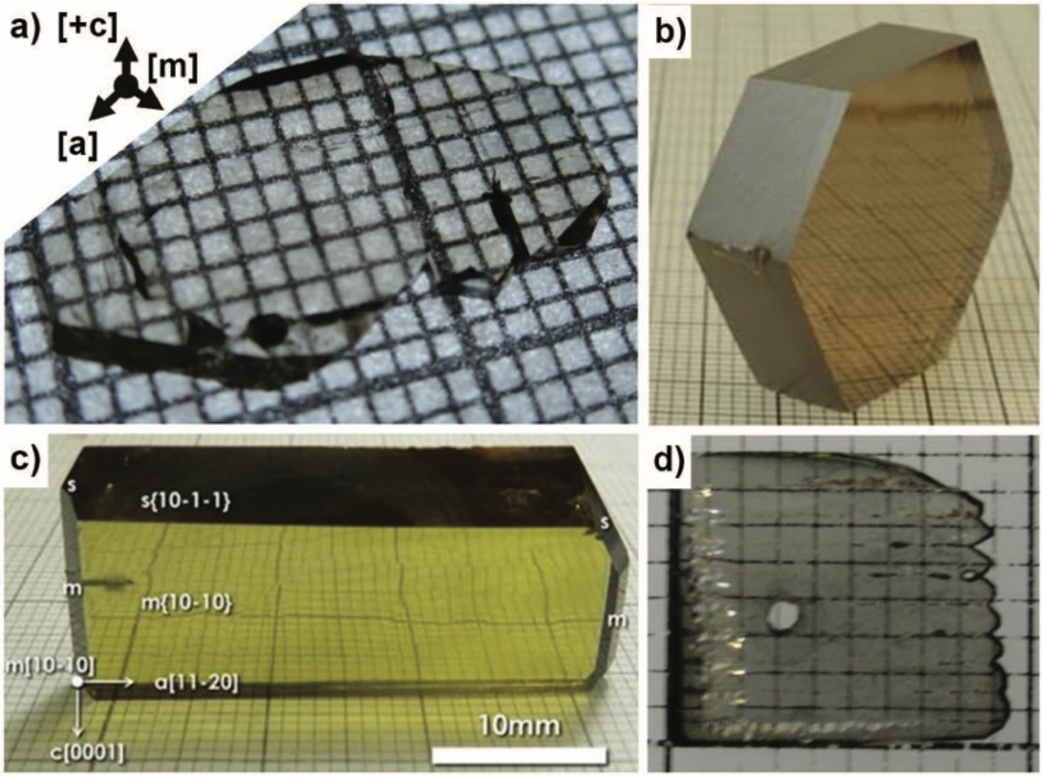


Electricity Consumption
(Global 2011)

Electricity Generation
(U.S. 2014)

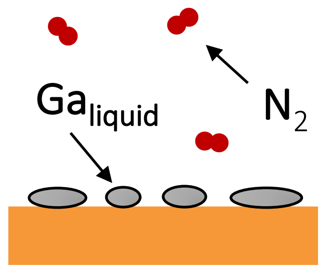
GaN can prevent **15% of all electrical energy** from being wasted.

Sources: EIA, IEA

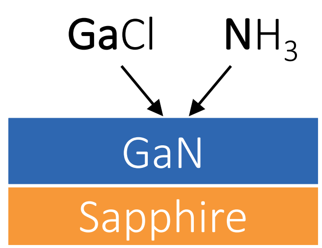


Bulk GaN Growth Techniques

Growth from GaN Melt not Possible

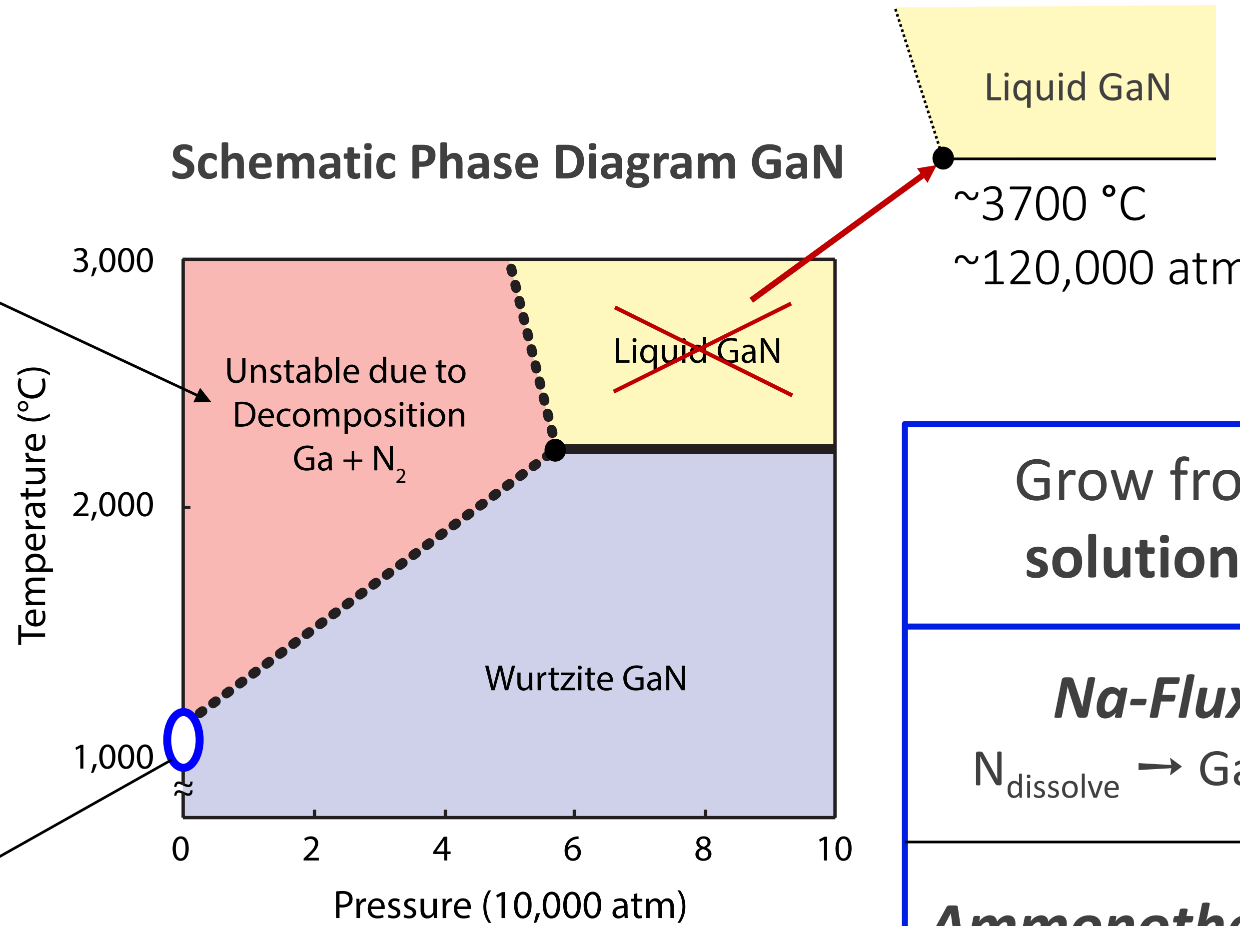


From Gas Phase (HVPE)



~ 1000 °C, 1 atm

Schematic Phase Diagram GaN



GaN **decomposes** readily

Grow from **solutions:**

Na-Flux

$N_{dissolve} \rightarrow Ga_{liquid}$

Ammonothermal

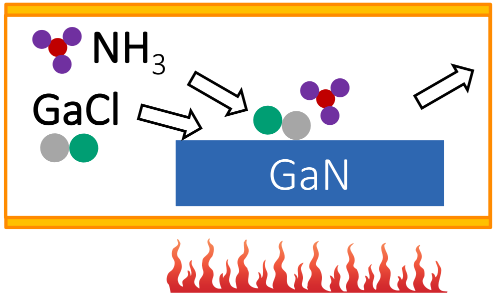
$Ga_{dissolve} \rightarrow N_{gas}$

W. Utsumi et al., *Nature Mater.* **2** (2003) 735–738; S. Porowski et al., *J. Phys. Chem. Solids*. **85** (2015) 138–143

Industrial Growth Methods for Bulk GaN

Option 1:

N and Ga from Gas

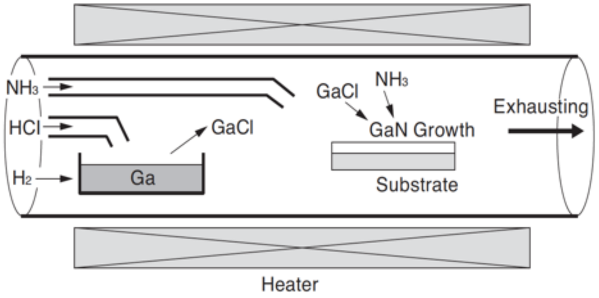


T = 1000—1200 °C

P = 1 atm

HVPE

Growth Techniques for GaN



HVPE

High purity
Seed dependent quality

Growth thickness limited
Strain in boule
No lateral scaling

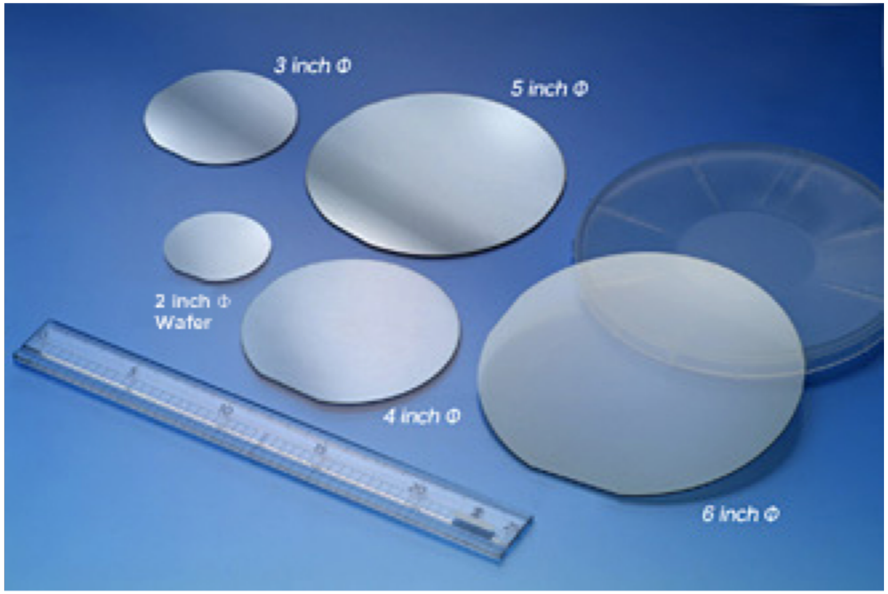
HVPE GaN on *Foreign* Substrate

Four major manufactures

Sumitomo Electric, Mitsubishi Chemical, SCIOCS, Saint-Gobain

Specs

Size: 2—4” available, ***TD***: mid-10^5—high-10^6 cm^{-2}, ***High Purity***



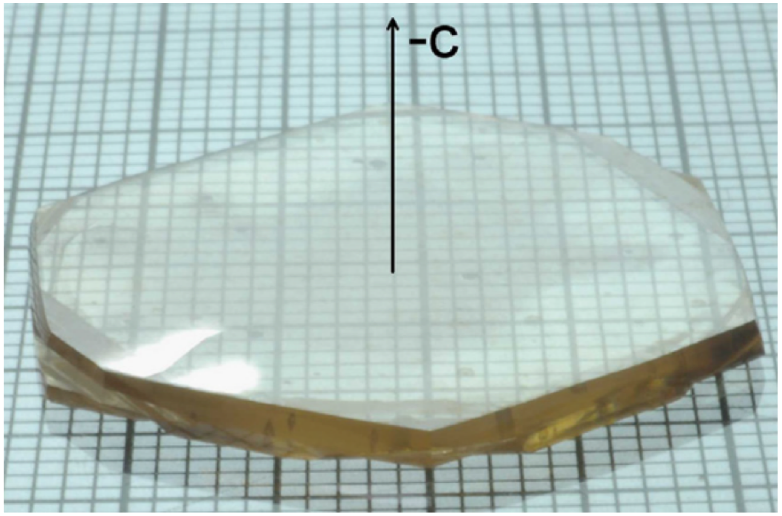
Cost: 500—2000 USD for 2” Wafer

http://global-sei.com/products/compound-semiconductor/

HVPE GaN on *GaN* Substrate

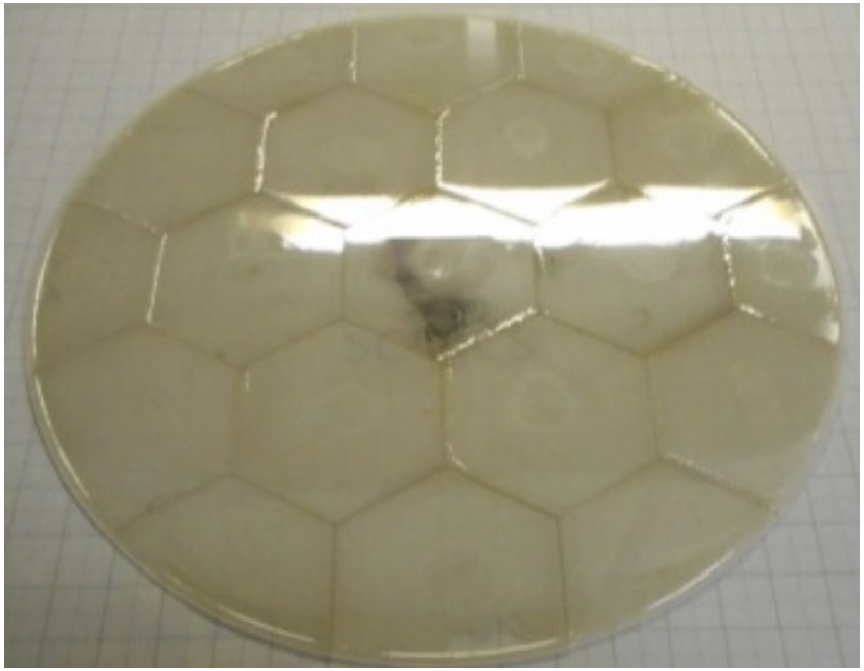
Ammonothermal GaN Seed

TD: mid-10^4 cm^{-2}



1” Seed + HVPE GaN

Na-Flux GaN Seed



7” Tiled Seed + HVPE GaN

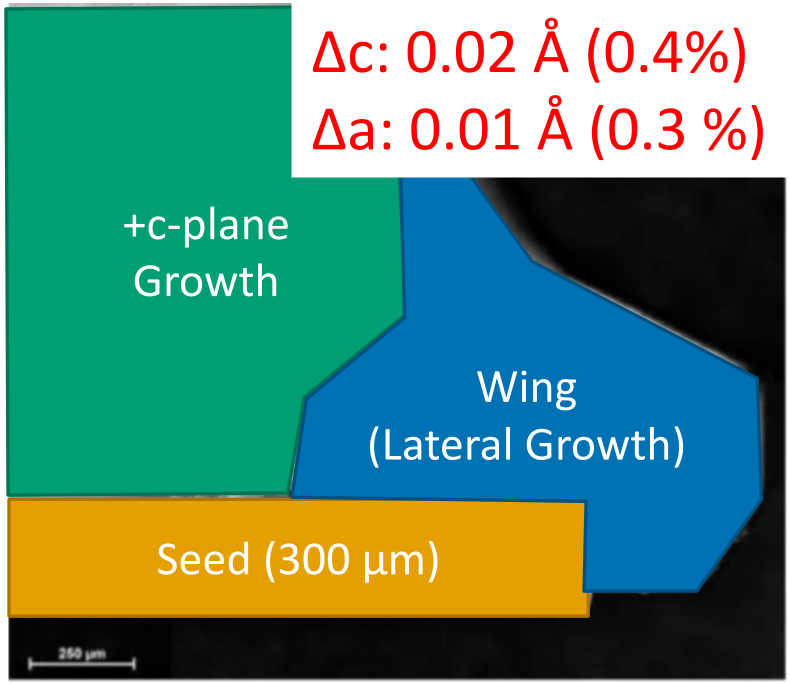
HVPE can **duplicate high quality seed quality**

R. Kucharski, et al., *JCG* **427** (2015) 1–6

T. Yoshida, et al., *PSS (B)* **254** (2017) 1600671

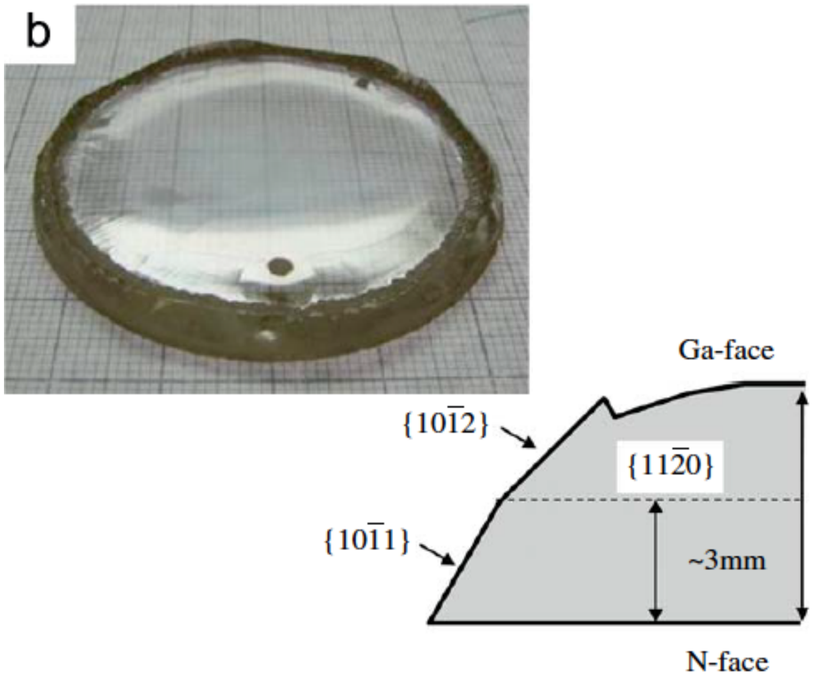
HVPE GaN: Challenges

Growth zone dependent lattice constant (impurities) → **Cracking**



SEM of cross section of **edge** of HVPE boule

$\{10\bar{1}1\}$ Facets → **Diameter reduction**



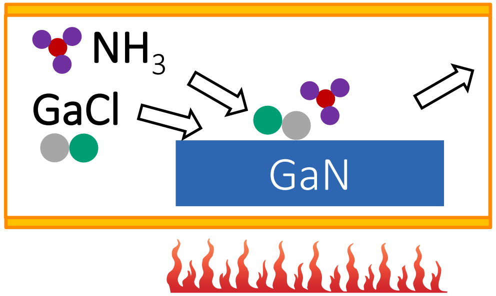
Continued need for *true* bulk GaN growth method

J.Z. Domagala, et al. *JCG* **456** (2016) 80–85

K. Fujito, et al. *JCG* **311** (2009) 3011–3014

Industrial Growth Methods for Bulk GaN

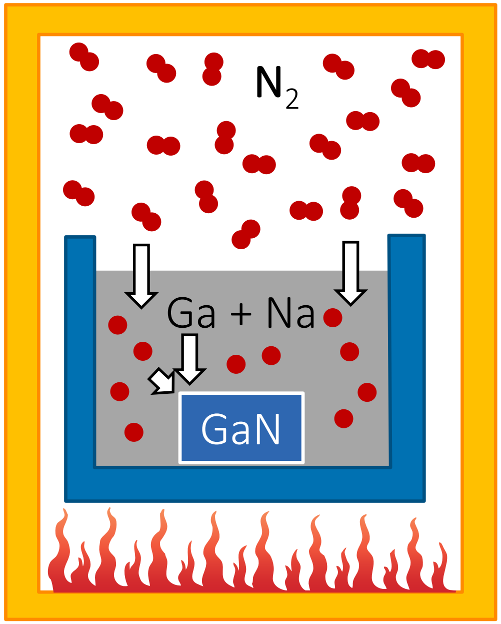
Option 1:
N and Ga from Gas



T = 1000—1200 °C
P = 1 atm

HVPE

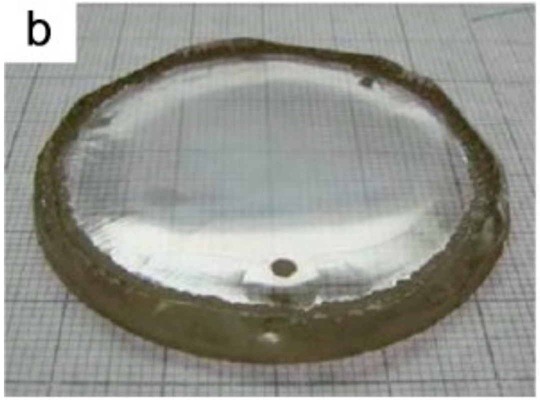
Option 2:
Add N to Ga Melt



T = 800—900 °C
P = 10—100 atm

Na-flux Growth

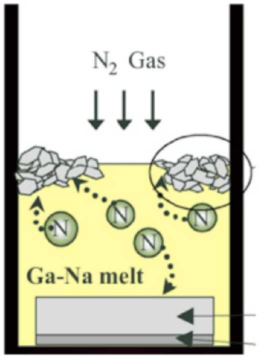
Growth Techniques for GaN



HVPE

High purity
Seed dependent quality

Growth thickness limited
Strain in boule
No lateral scaling



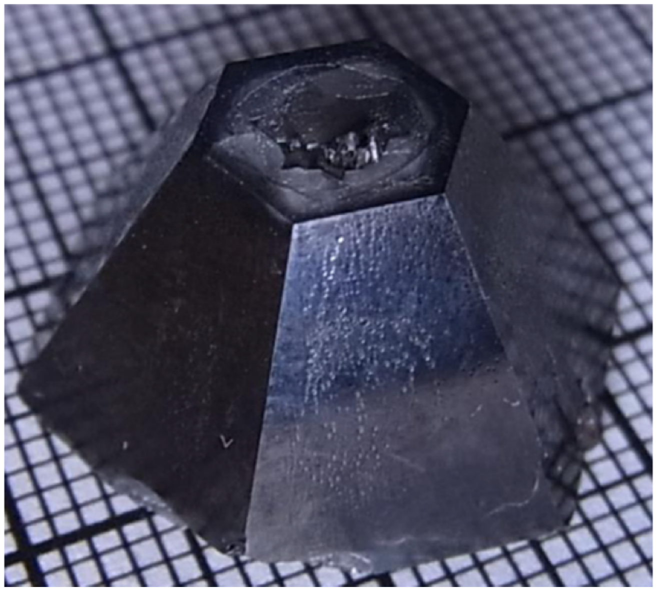
Na-Flux

High purity
Scalable

Doping challenges
Growth thickness

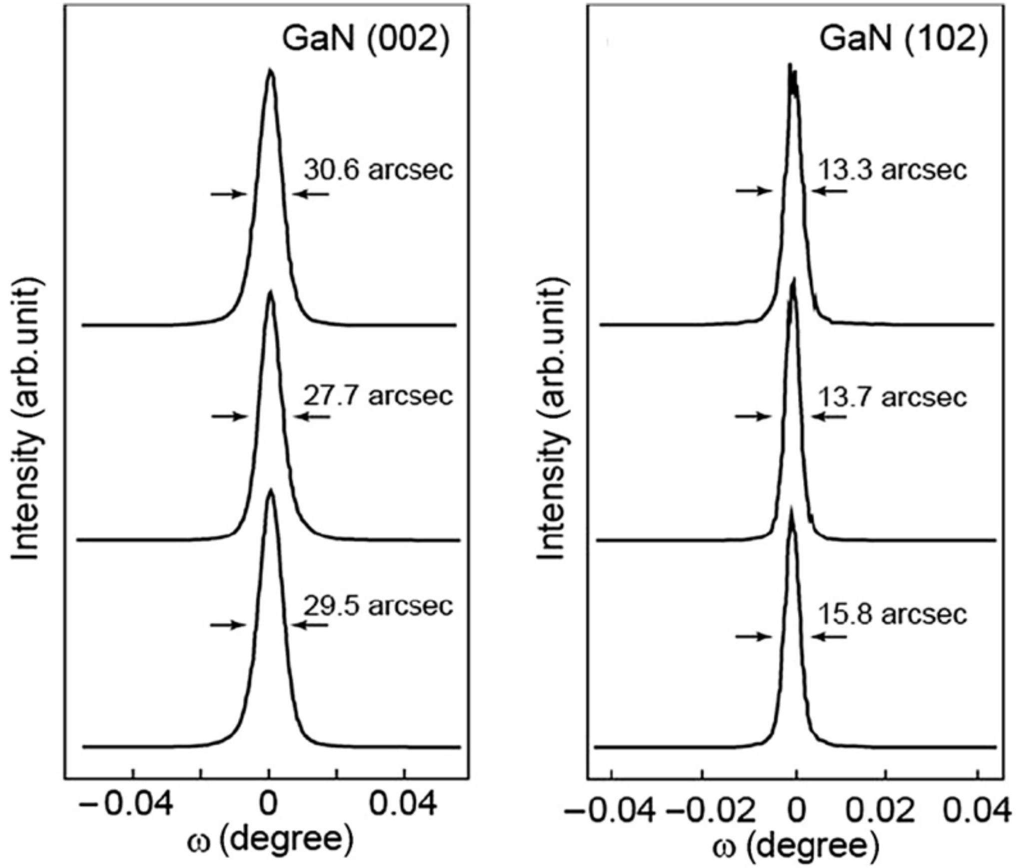
Na-Flux GaN on GaN Templates (Osaka Univ.)

'Point Seed' Growth



400 hr Growth

Coalescence Growth

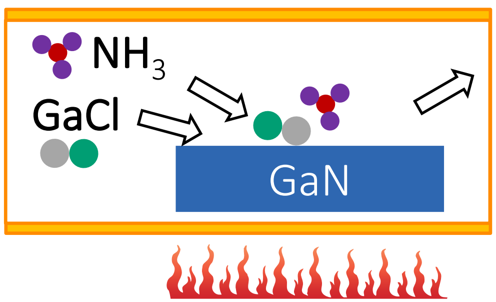


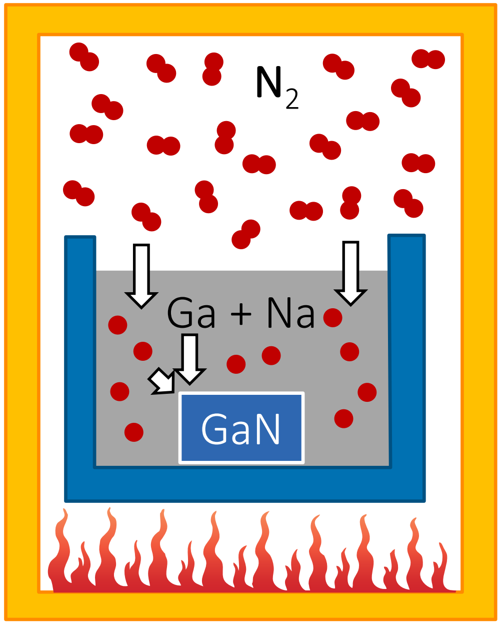
Large-area-seeded, coalesced GaN *thin* crystals possible

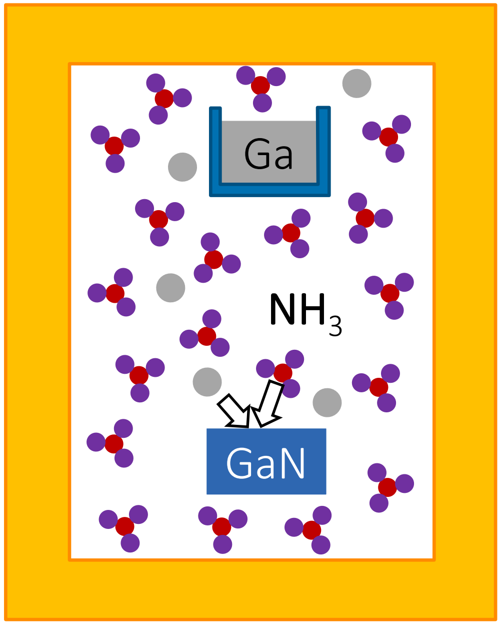
Y. Mori, et al., ECS J. Solid State Sci. Technol. 2 (2013) N3068–N3071.
Y. Mori, et al. Handbook of Crystal Growth - Bulk Crystal Growth, Elsevier, 2015: pp. 505–533.

Industrial Growth Methods for Bulk GaN

Option 1: **N and Ga** from Gas	*Option 2:* **Add N to Ga** Melt	*Option 3:* **Add Ga to N** Solution

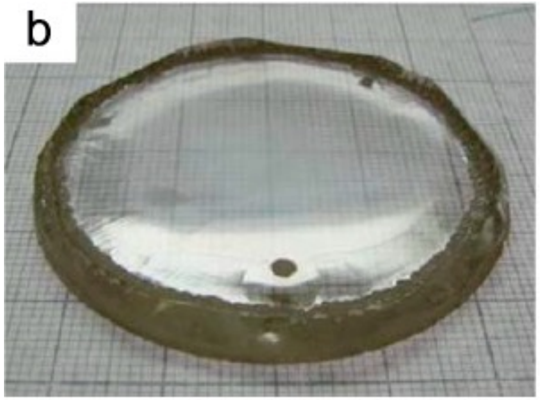






T = 1000—1200 °C	*T = 800—900 °C*	*T = 500—600 °C*
P = 1 atm	*P = 10—100 atm*	*P = 1000—3000 atm*
HVPE	**Na-flux Growth**	**Ammonothermal Method**

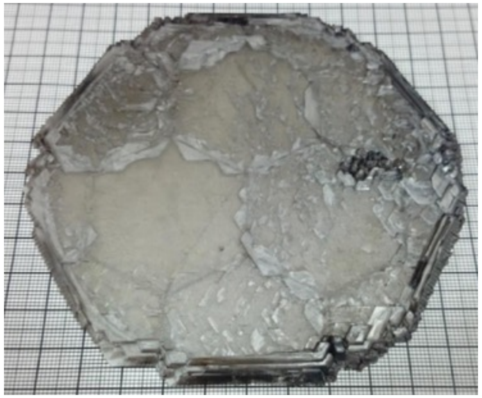
Growth Techniques for GaN



HVPE

High purity
Seed dependent quality

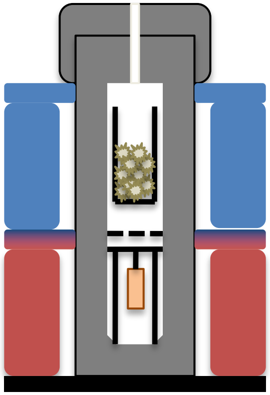
Growth thickness limited
Strain in boule
No lateral scaling



Na-Flux

High purity
Scalable

Doping challenges
Growth thickness



Ammonothermal

High n-type doping
Scalable

Growth rate
Gallium vacancies
Yield/Uniformity

Strategies

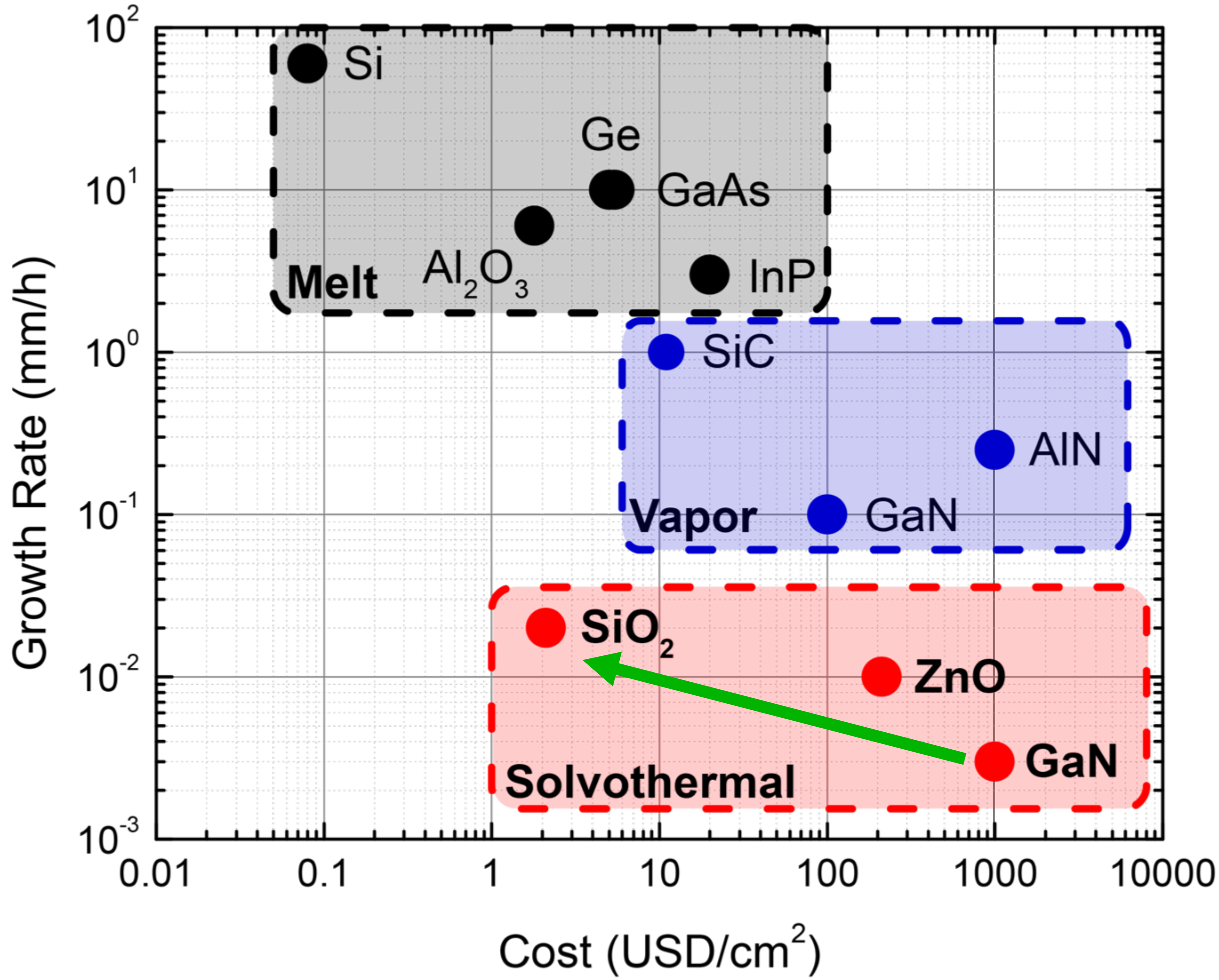
Na-Flux / **Ammonothermal** → (**Large Area Seeds**) → **HVPE** → (**Multiplication**) → ***Wafers***

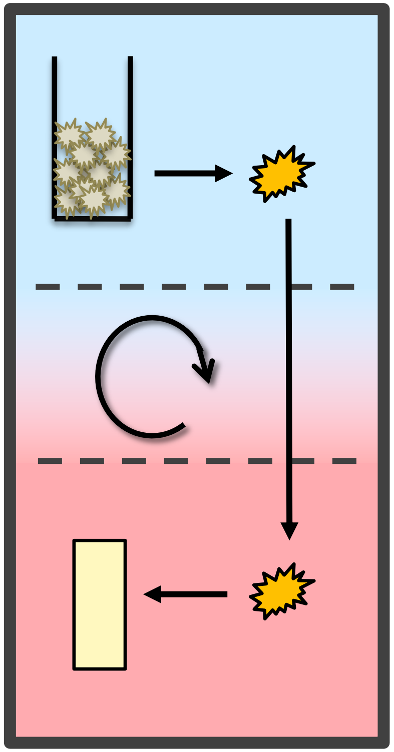
Ammonothermal → (**Large Area, *Thick* Boules**) → ***Wafers***

Need for high growth rate, high quality, high yield ammonothermal GaN

The Path Forward

Target: **High Growth Rate, Large Area Boules**





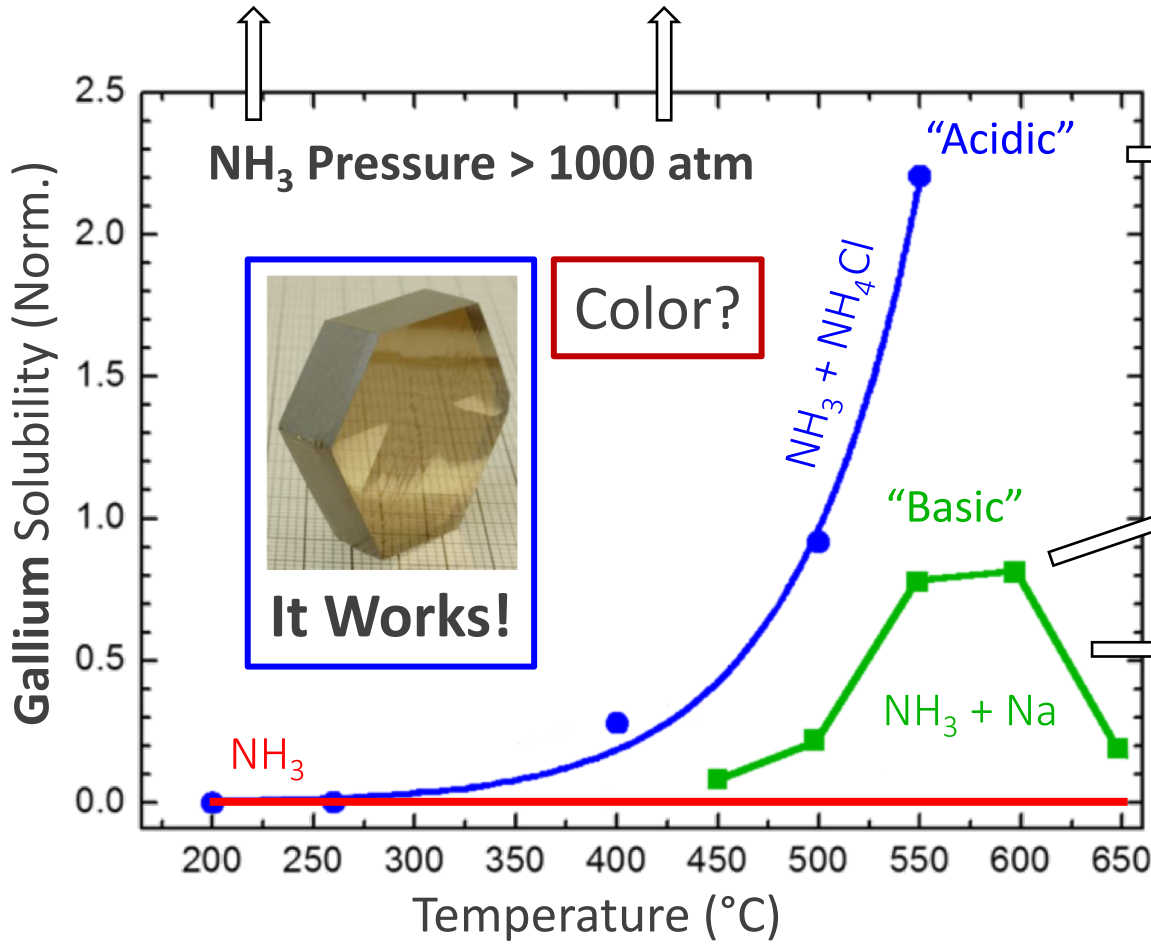
Ammonothermal Method

Solubility GaN in Supercritical NH_3 Solutions

Toxic & Explosive

Challenging, T_{max}

NH_3 Decomposition?



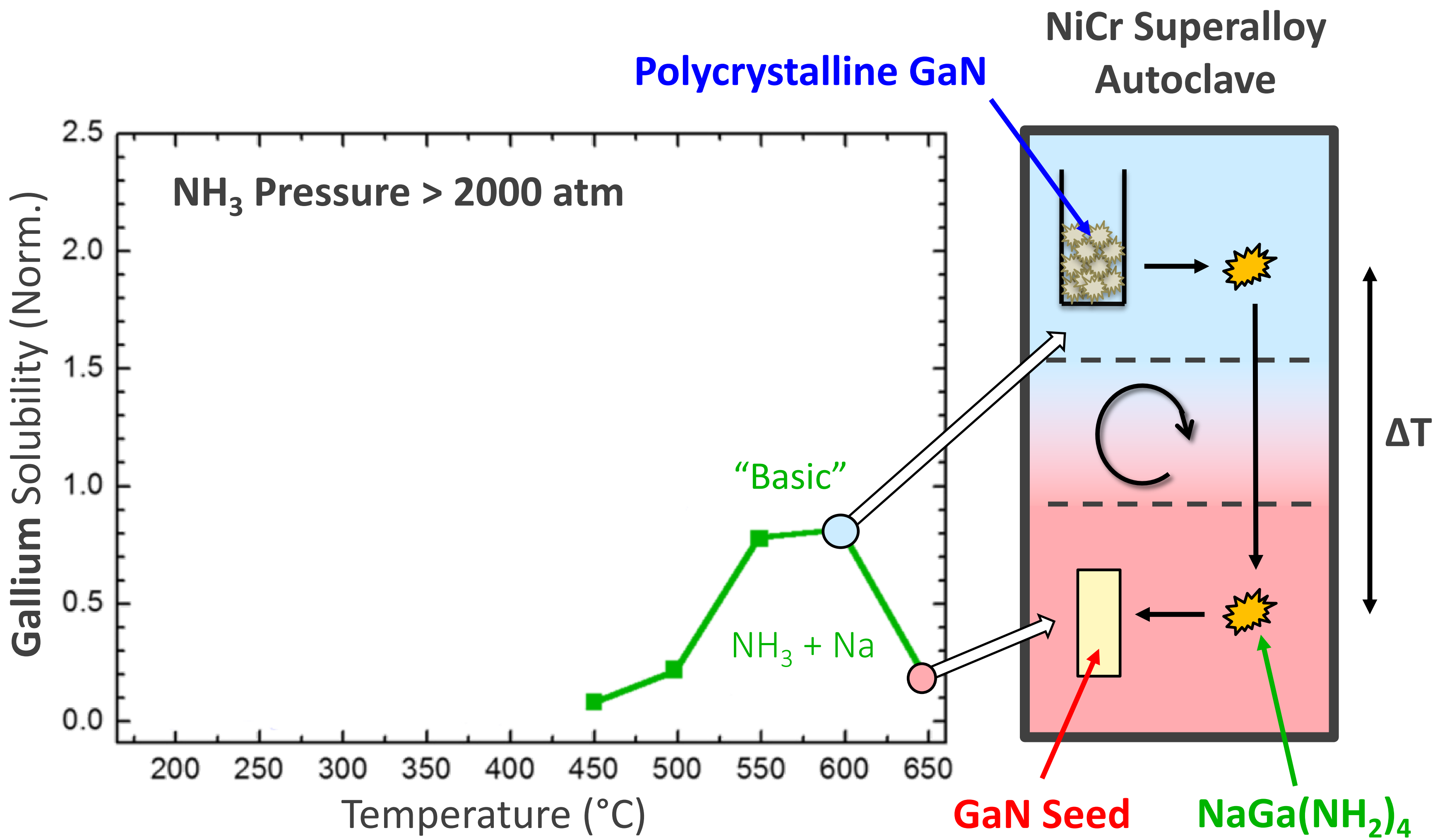
Corrosive

Low Solubility

Origin?

Graph after: D. Ehrentraut and T. Fukuda, *J. Cryst. Growth*. **312** (2010) 2514–2518; Image: R. Kucharski et al., *Semicond. Sci. Tech.* **27** (2012) 024007

Basic Ammonothermal Growth Setup



Graph after: D. Ehrentraut and T. Fukuda, *J. Cryst. Growth* **312** (2010) 2514–2518

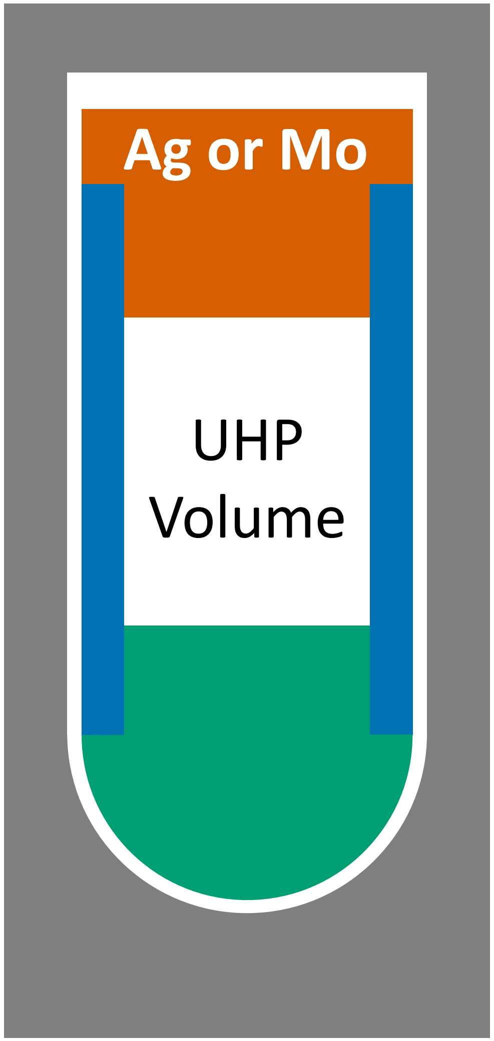
The Path Forward

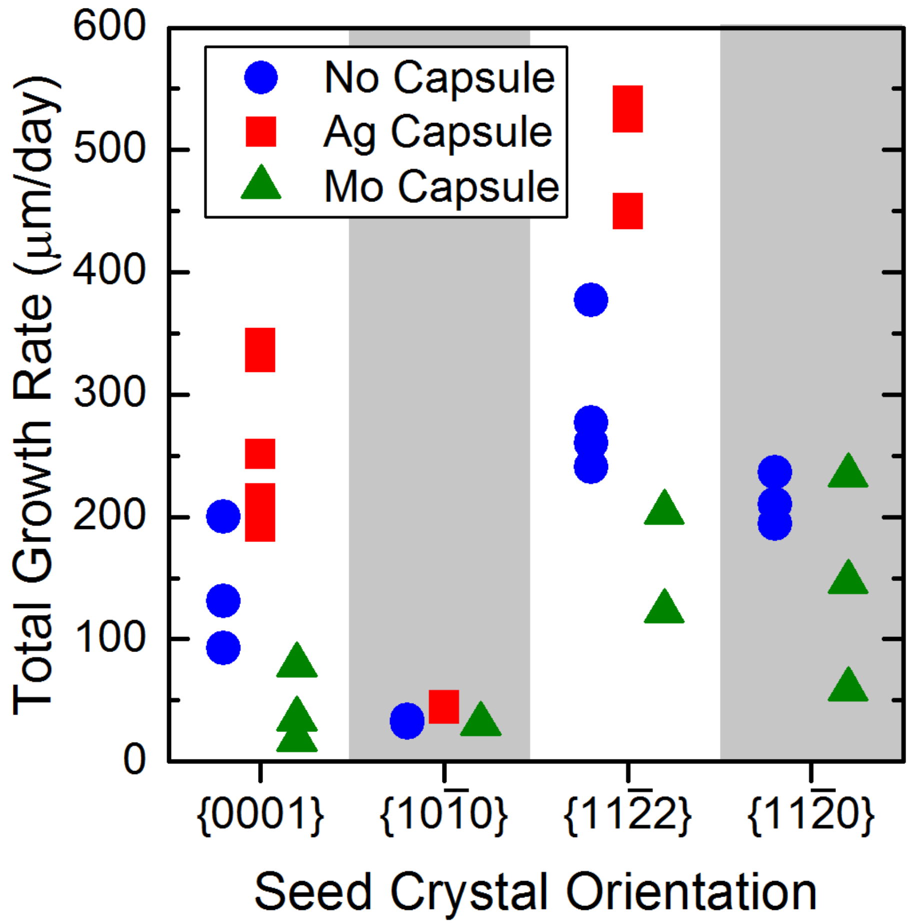
Target: **High Growth Rate, Large Area Boules**

Technology / Engineering	Crystal Properties	Solvent / Solute
Novel Capsule Systems	**Optical Properties**	**Solvent Properties**
UHP Growth Environments	Effect free carrier density	New EOS for NH_3, N_2, H_2
Growth Rates	Point defects	Decomposition NH_3

Technology / Engineering

High Purity Growth Environments: *Capsules*

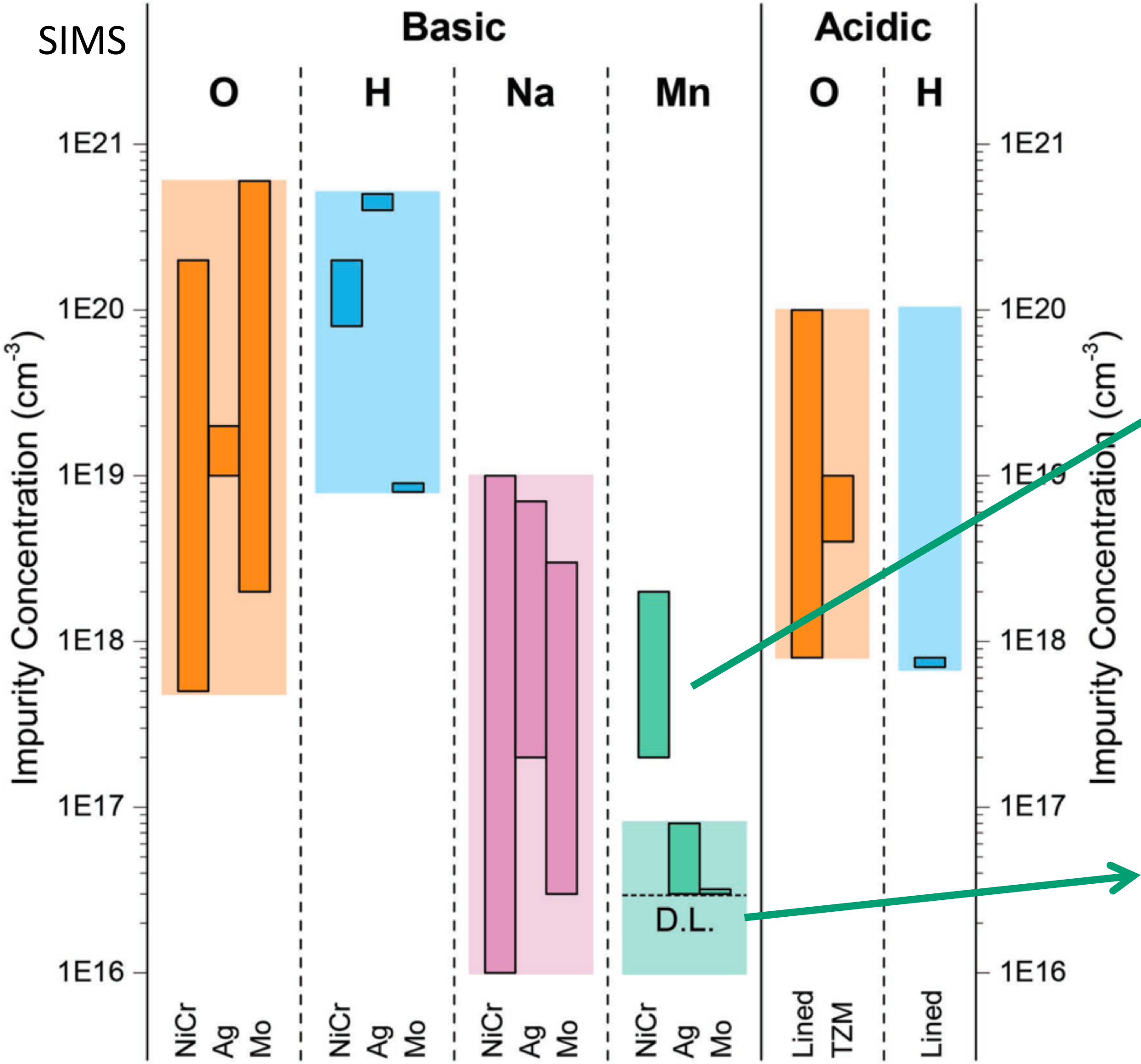




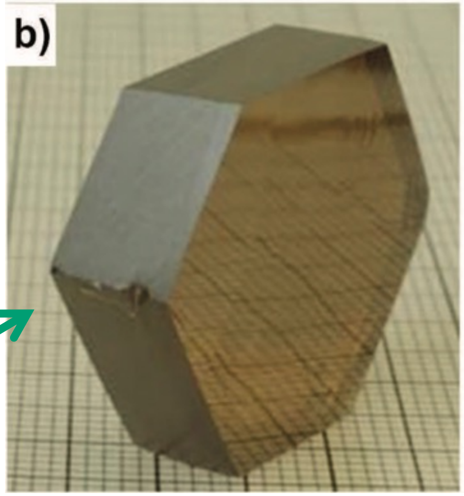
Ag-Capsule: **~ 1.5x Growth rate improvement**

S. Pimputkar, et al., *J. Cryst. Growth* **456** (2016) 15—20

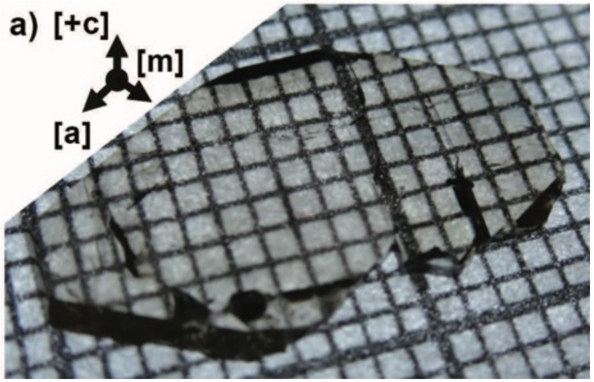
Impurities



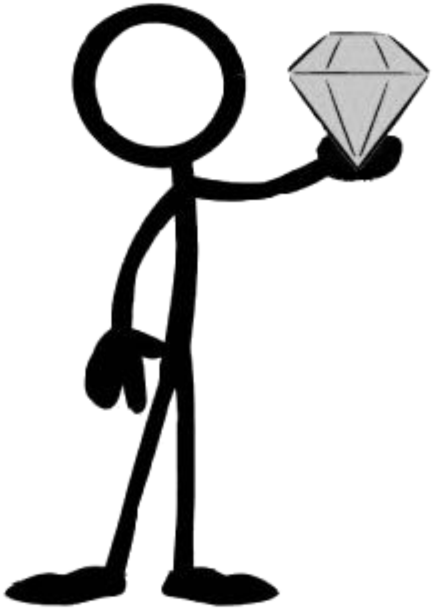
No Capsule



Ag Capsule

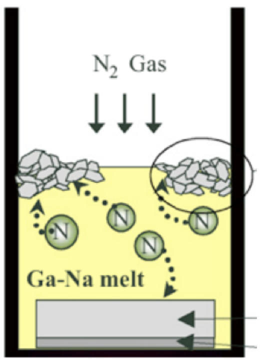


S. Suihkonen, S. Pimputkar, et al., *Adv. Electron. Mater.* **3** (2017) 1600496

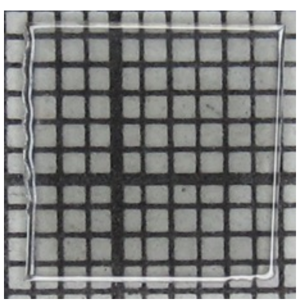


Optical Properties

Study: Optical Absorption on *Bulk* GaN Crystals

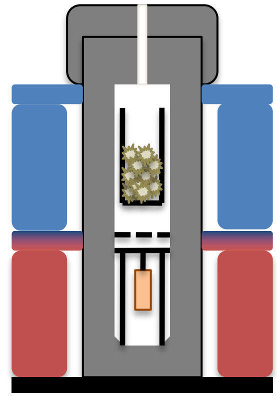


Na-Flux

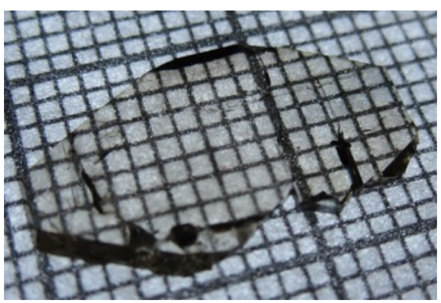


1 sample

490 µm

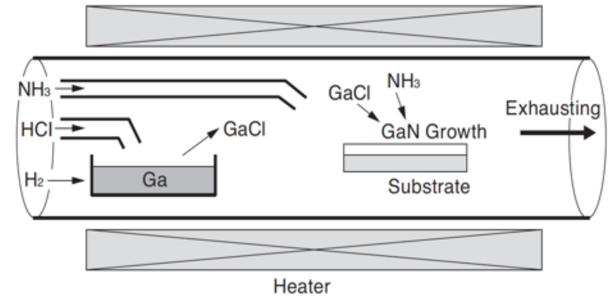


Ammonothermal



2 samples

~ 630 µm



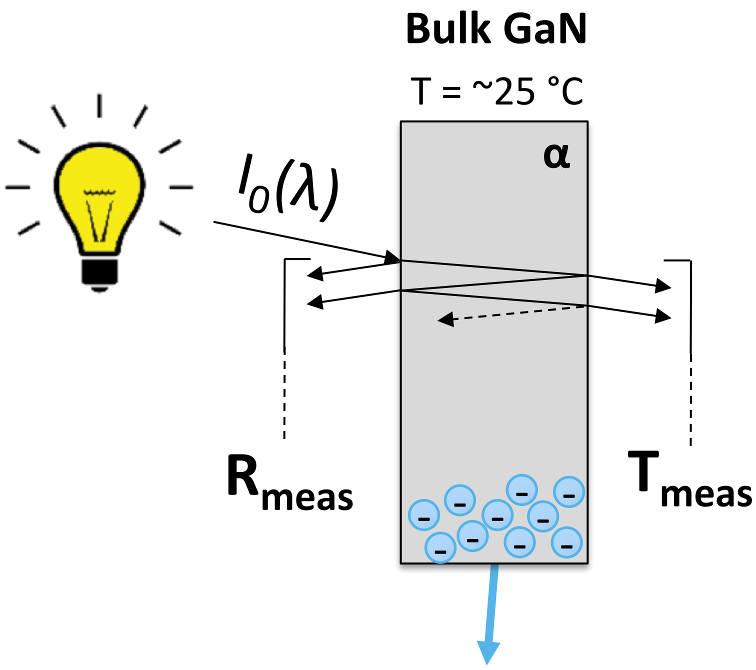
HVPE

5 samples

~ 340 µm

S. Pimputkar, S. Suihkonen, M. Imade, Y. Mori, J.S. Speck, S. Nakamura, *J. Cryst. Growth* **423** (2015) 49—53

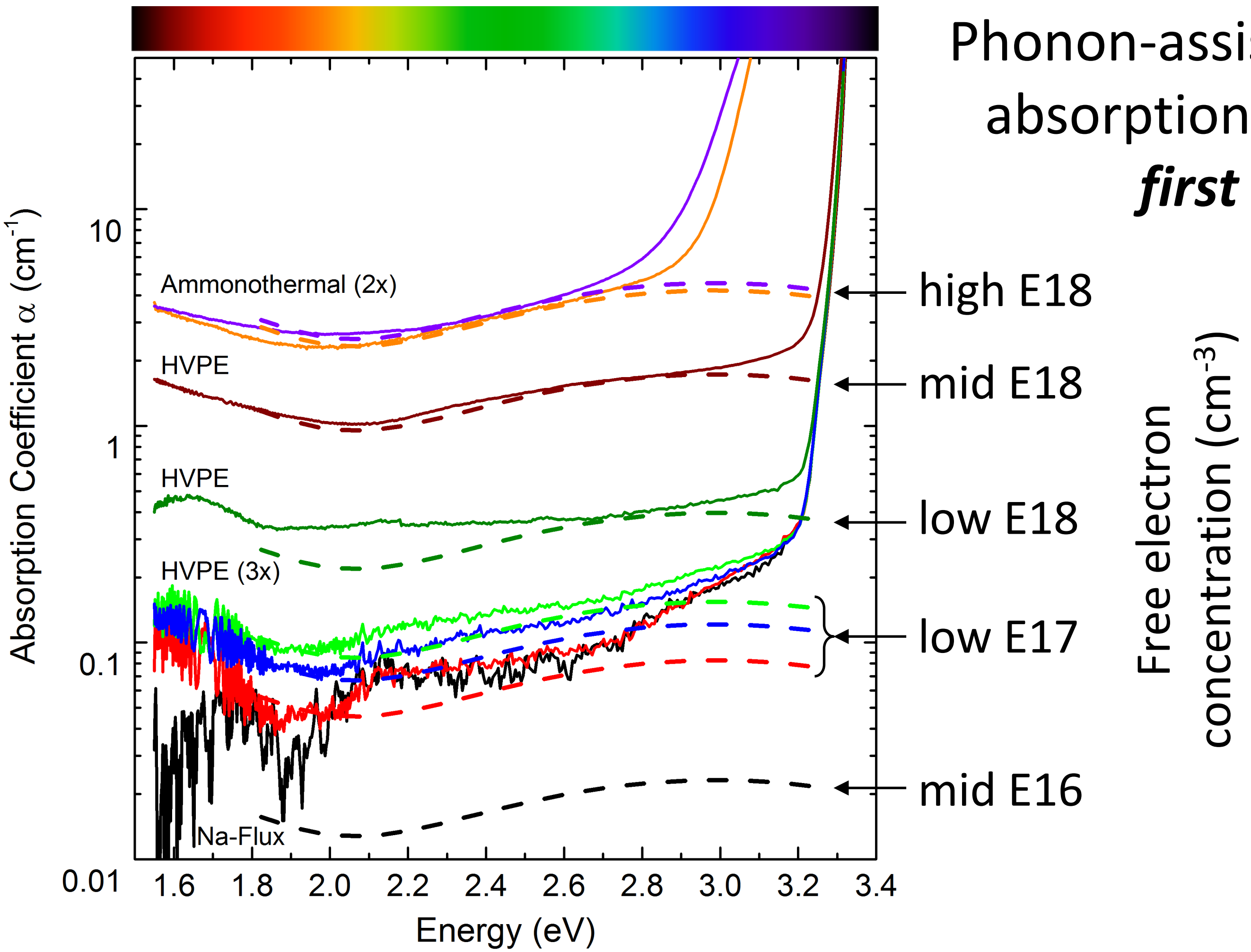
Optical
Transmission Measurements



Free Carriers: 4 x 10^{16} — 9 x 10^{18} cm^{-3}

S. Pimputkar, S. Suihkonen, M. Imade, Y. Mori, J.S. Speck, S. Nakamura, *J. Cryst. Growth* **423** (2015) 49—53

Absorption Coefficient at Varying Doping Levels



Phonon-assisted free electron absorption calculated from ***first principles***

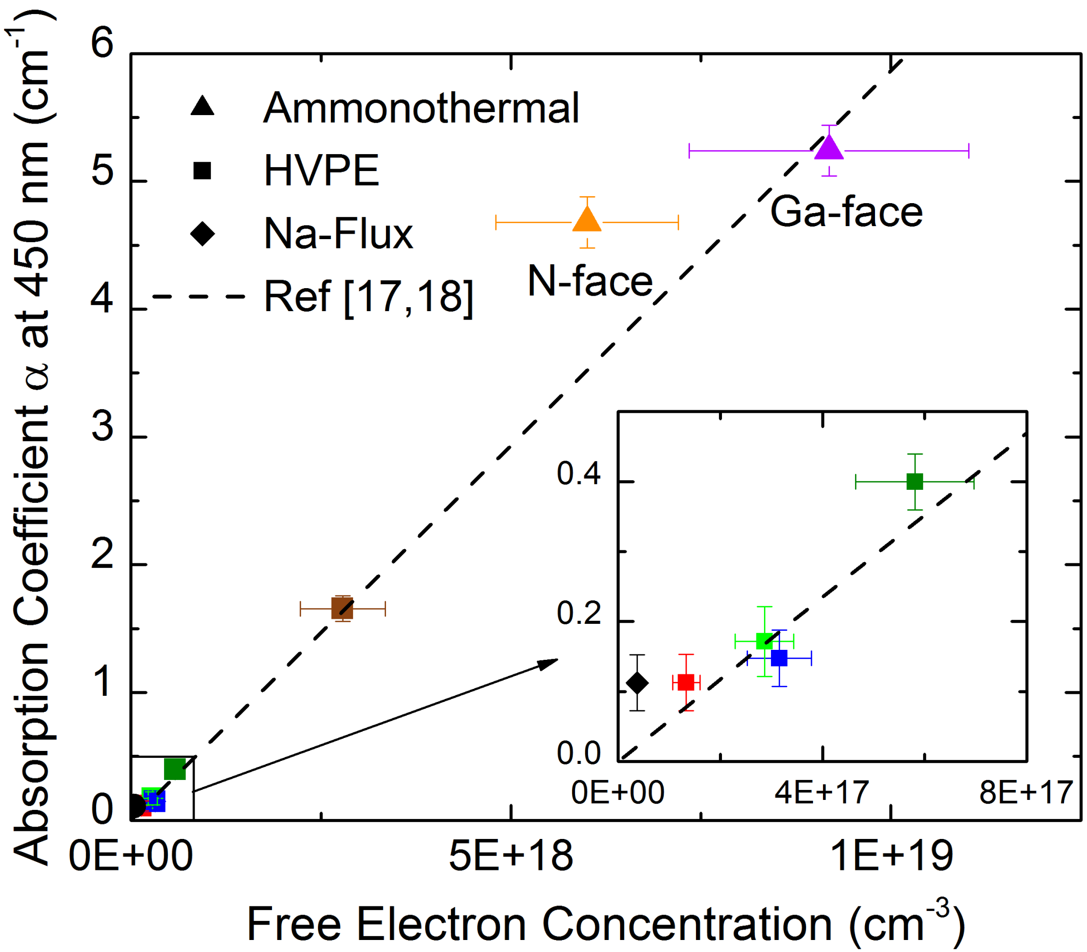
E. Kioupakis et al., PRB 81 (2010) 241201

E. Kioupakis et al., APEX 3 (2010) 082101

Absorption dominated by free electron absorption

S. Pimputkar, et al. , *J. Cryst. Growth* **423** (2015) 49—53

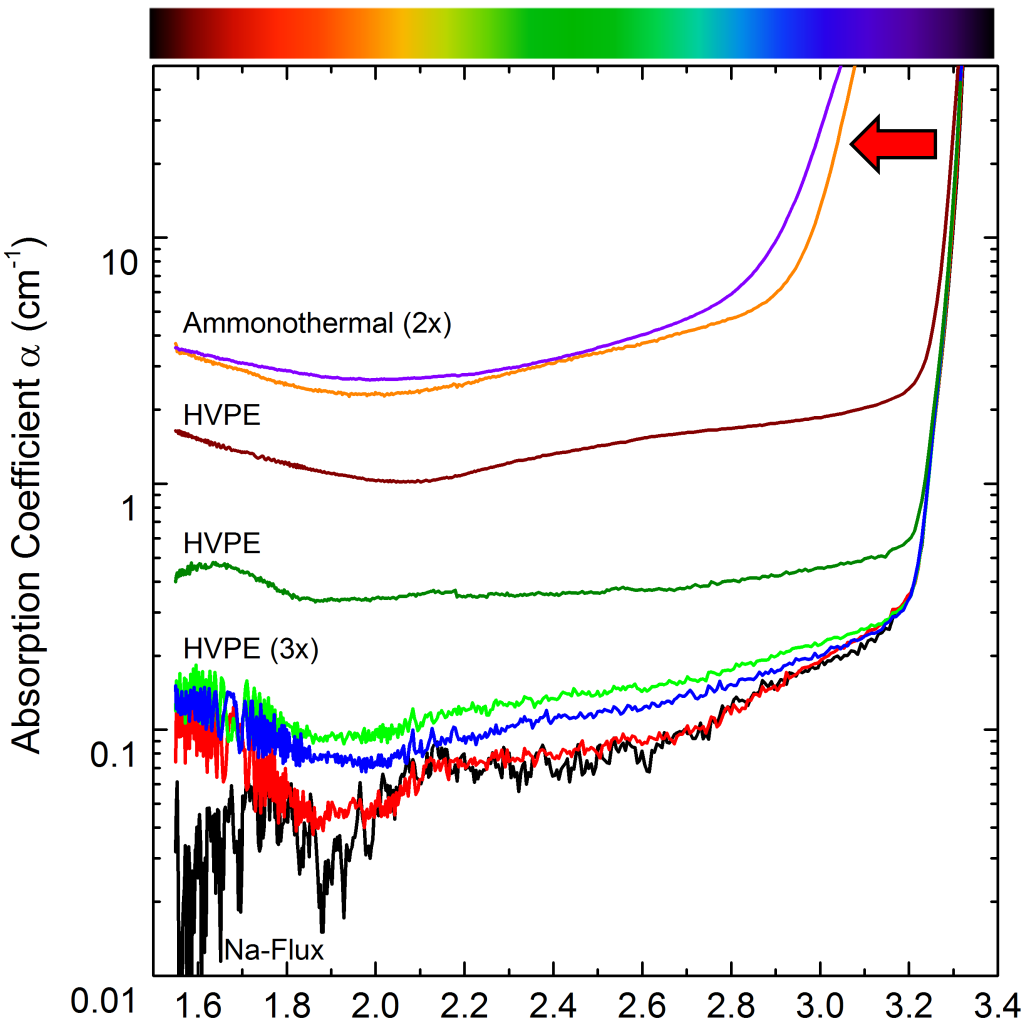
Optical Absorption at 450 nm



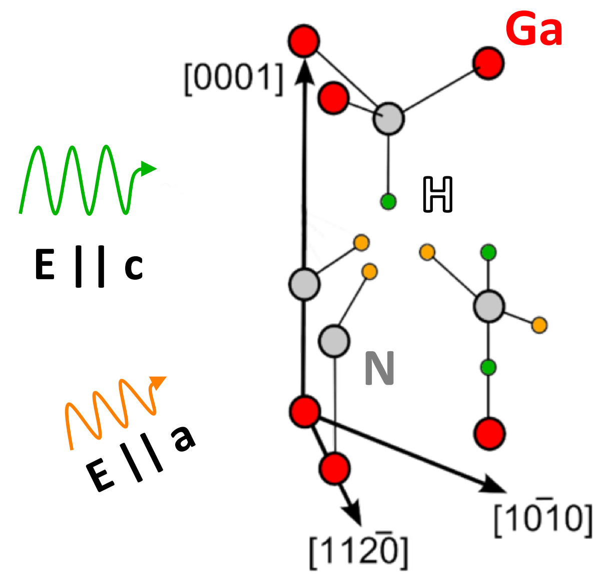
Heavily doped GaN will be absorbing

S. Pimputkar, S. Suihkonen, M. Imade, Y. Mori, J.S. Speck, S. Nakamura, *J. Cryst. Growth* **423** (2015) 49—53

Absorption Coefficient at Varying Doping Levels



Hydrogenated Gallium Vacancy

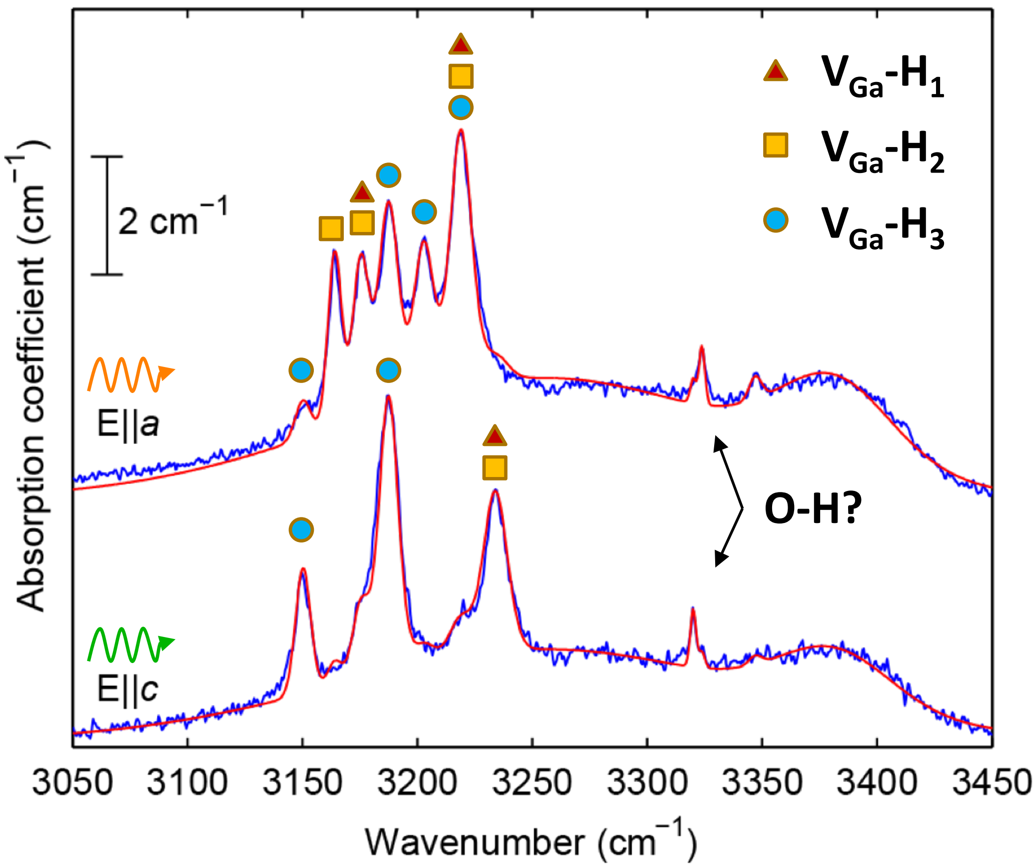


# H (V_{Ga}-H_x)	E_{CB}-E_{defect} (eV)
3	3.3
2	**2.8**
1	**2.7**
0	**2.6**

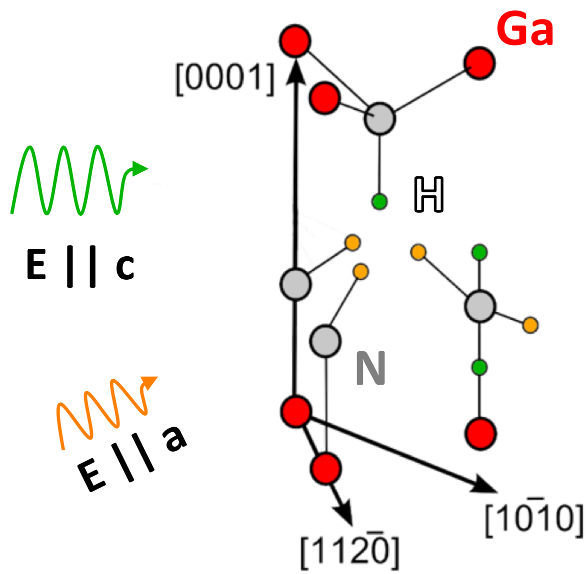
S. Pimputkar, et al., *JCG* **423** (2015) 49—53; S. Suihkonen, S. Pimputkar, et al., *APL.* **108** (2016) 202105

Density of Hydrogenated Gallium Vacancies

Polarized FTIR of ***m*-plane** am-GaN



Hydrogenated Gallium Vacancy



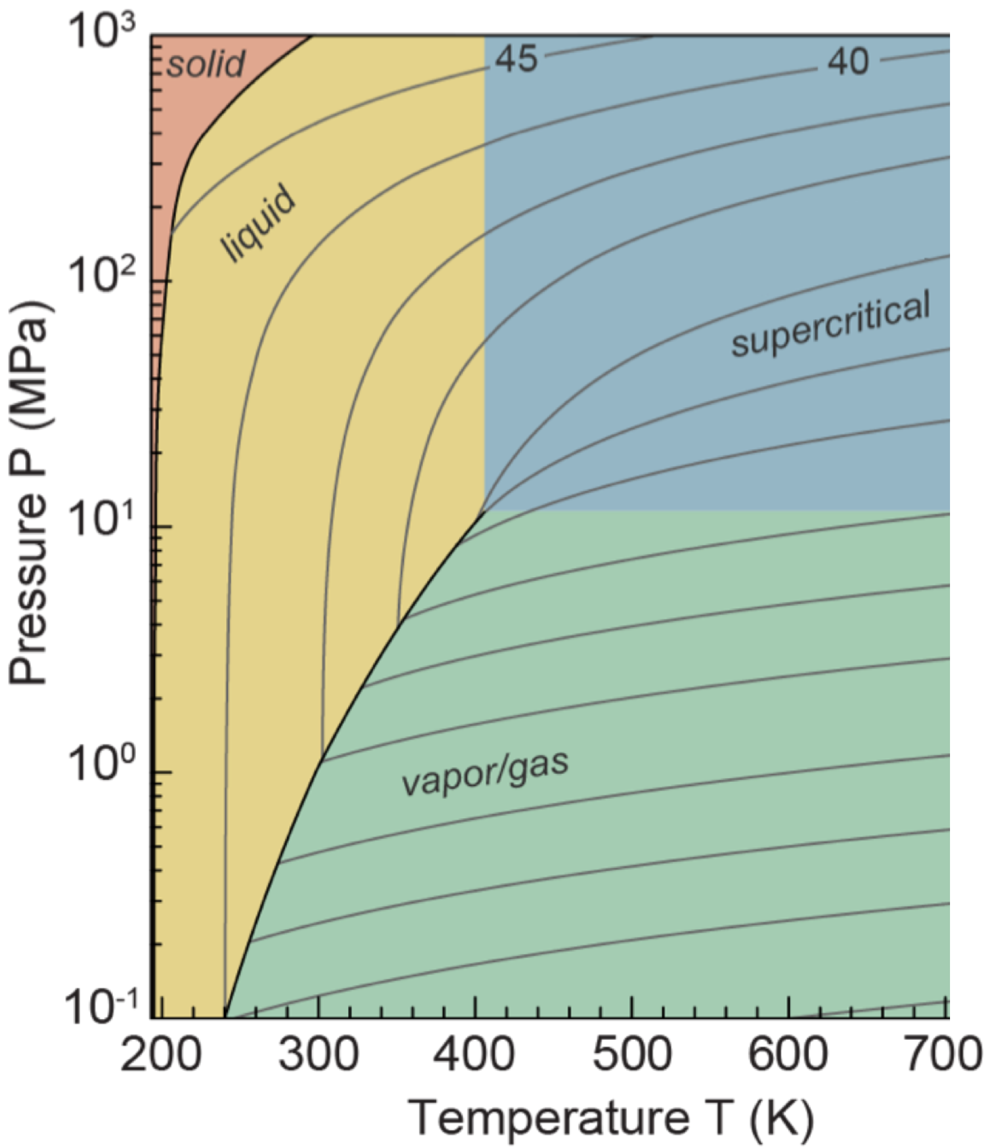
	Density (cm^{-3})
V_{Ga}-$H_{1,2}$	~ 3 x 10^{18}
V_{Ga}-H_3	~ 1 x 10^{18}

V_{Ga}-H_X present (~mid-10^{18} cm^{-3}) and optically absorbing

S. Suihkonen, S. Pimputkar, et al., *Appl. Phys. Lett.* **108** (2016) 202105

Solvent Properties

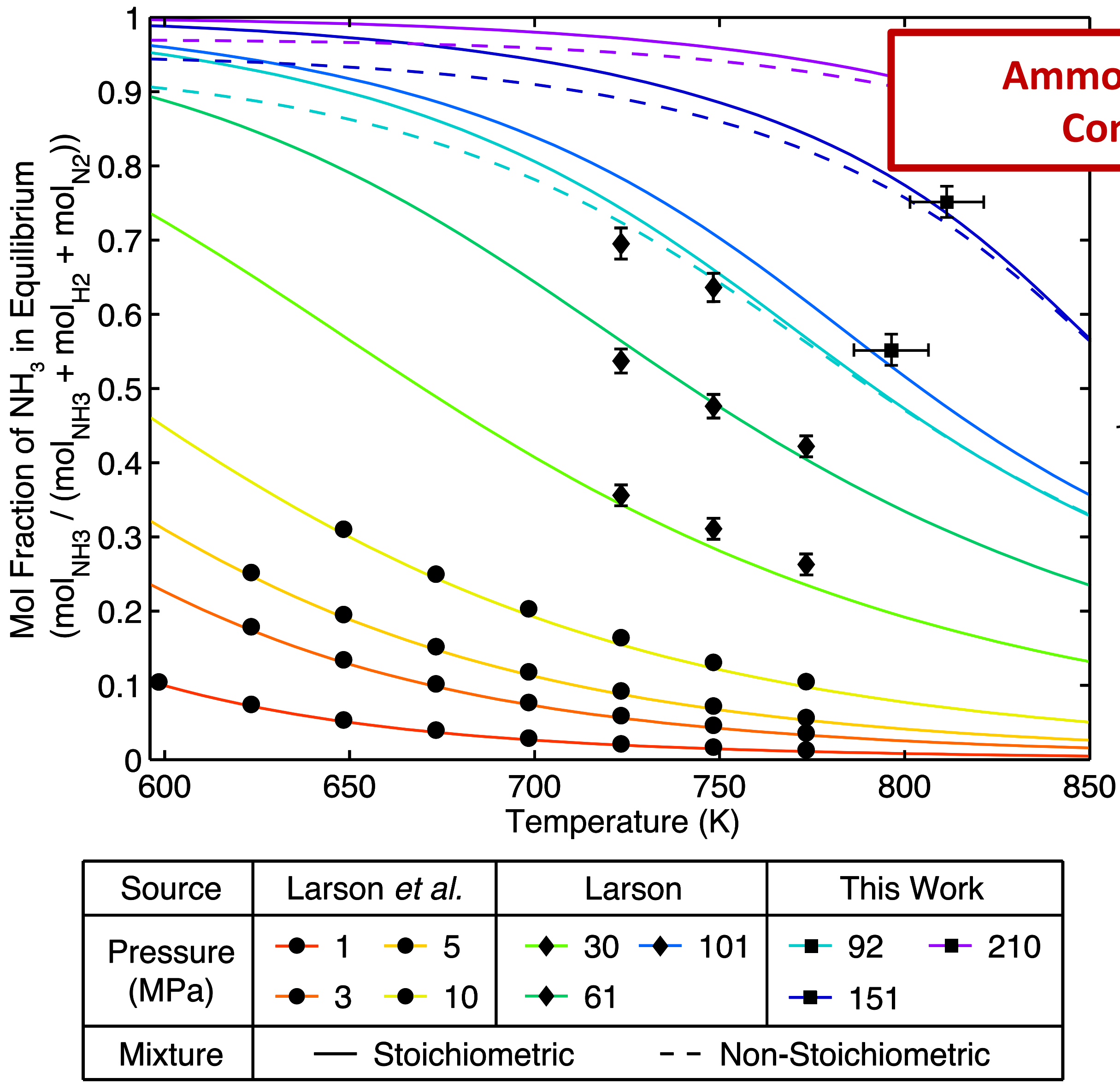
Solvent: Ammonia Phase Diagram



Ammonothermal Conditions

S. Pimputkar and S. Nakamura, *J. Supercrit. Flui.* **107** (2016) 17-30

Ammonia Decomposition



Minimal decomposition at higher P & T

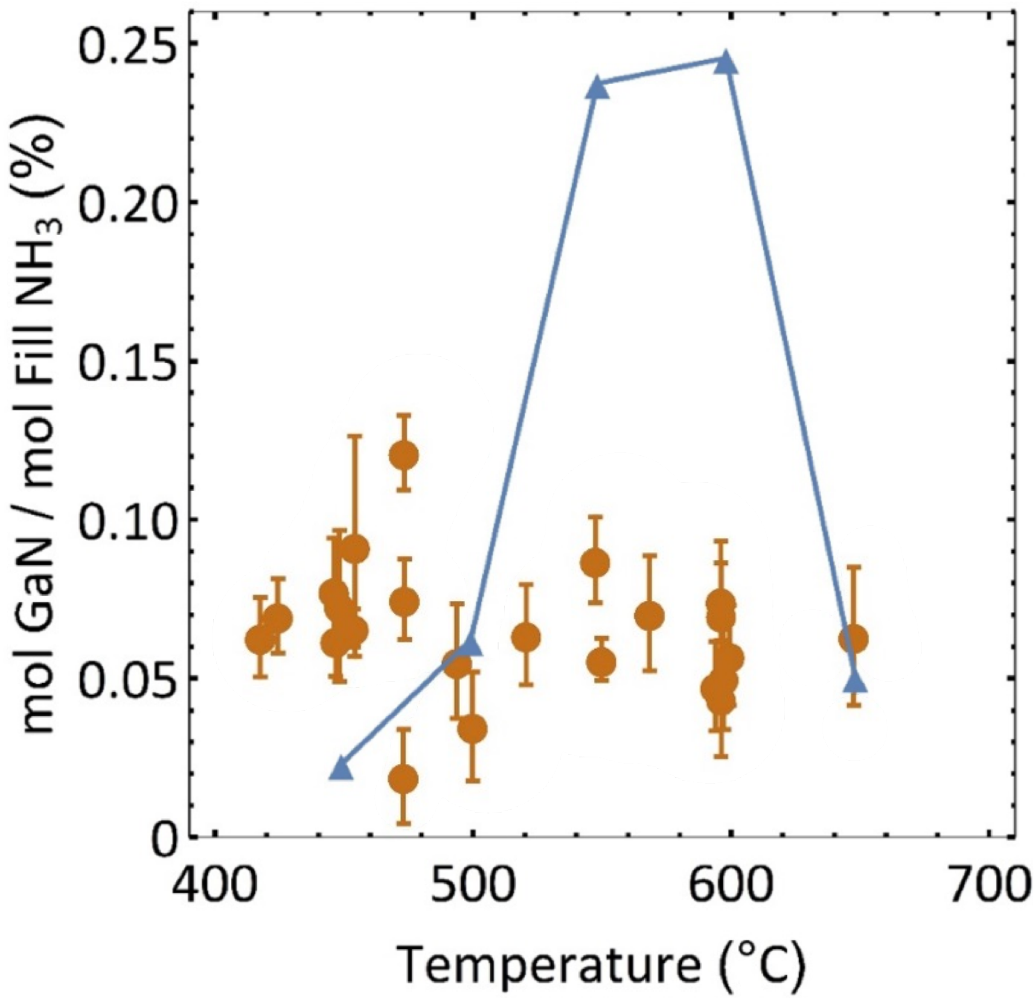
New data points collected

Model for decomposition of NH_3 T < 850 K to < 2 %

S. Pimputkar and S. Nakamura, *J. Supercrit. Flui.* **107** (2016) 17-30

GaN Solubility

GaN Solubility in NH_3-Na Solution



What is the **driving force** for GaN growth?

Retrograde region?

S. Griffiths et al., *J. Cryst. Growth*, **456** (2016) 5—14; T. Hashimoto et al., *J. Cryst. Growth*, **305** (2007) 311—316

Summary

GaN enables ***significant*** **energy savings** and benefits from bulk GaN

Innovative equipment designs opens the door to advances and insight