Presentation 1

Magnetron sputter epitaxy of GaN thin films and nanorods using liquid Ga target

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Magnetron sputter epitaxy of GaN thin films and nanorods using liquid Ga target

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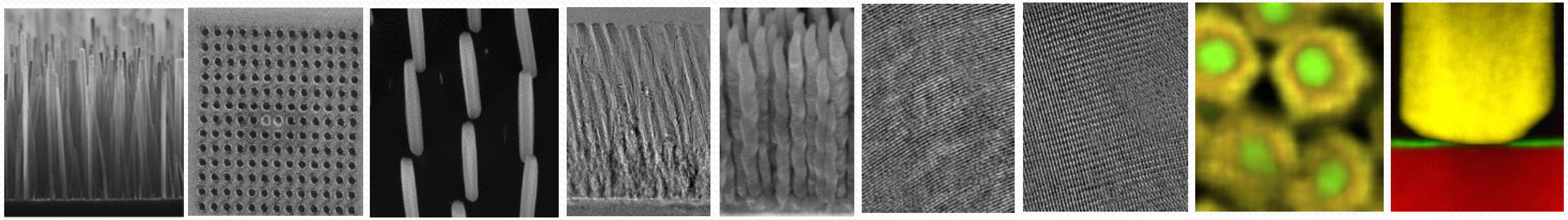
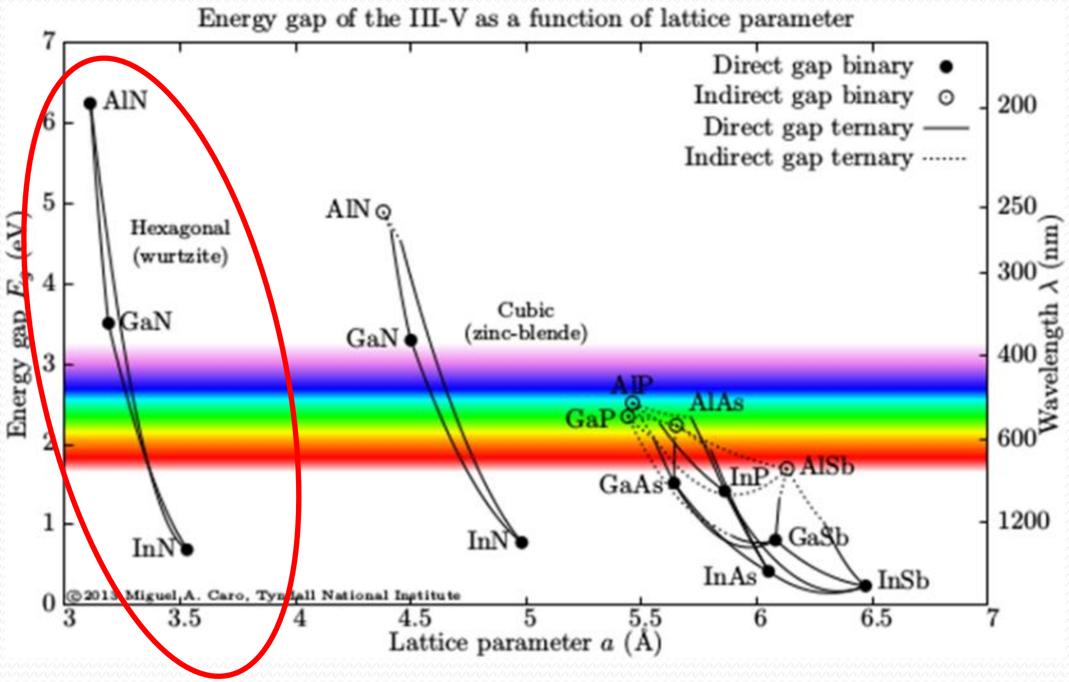


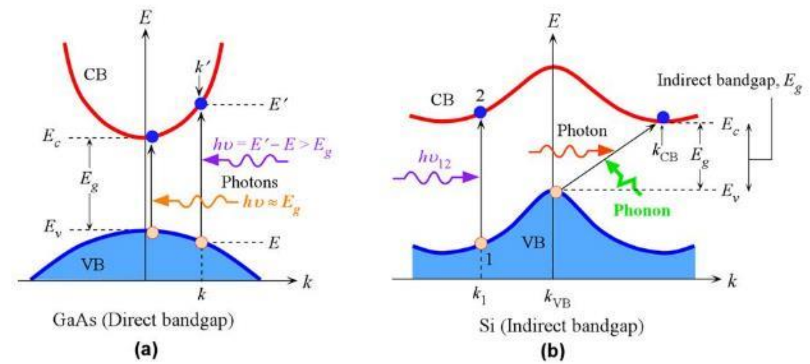
III-Nitride semiconductors

Photonic materials with versatile properties obtainable by band-gap engineering



Caro Bayo, M. Á. 2013. ***Theory of elasticity and electric polarization effects in the group-III nitrides***. PhD Thesis, University College Cork

Absorption and Direct and Indirect Transitions



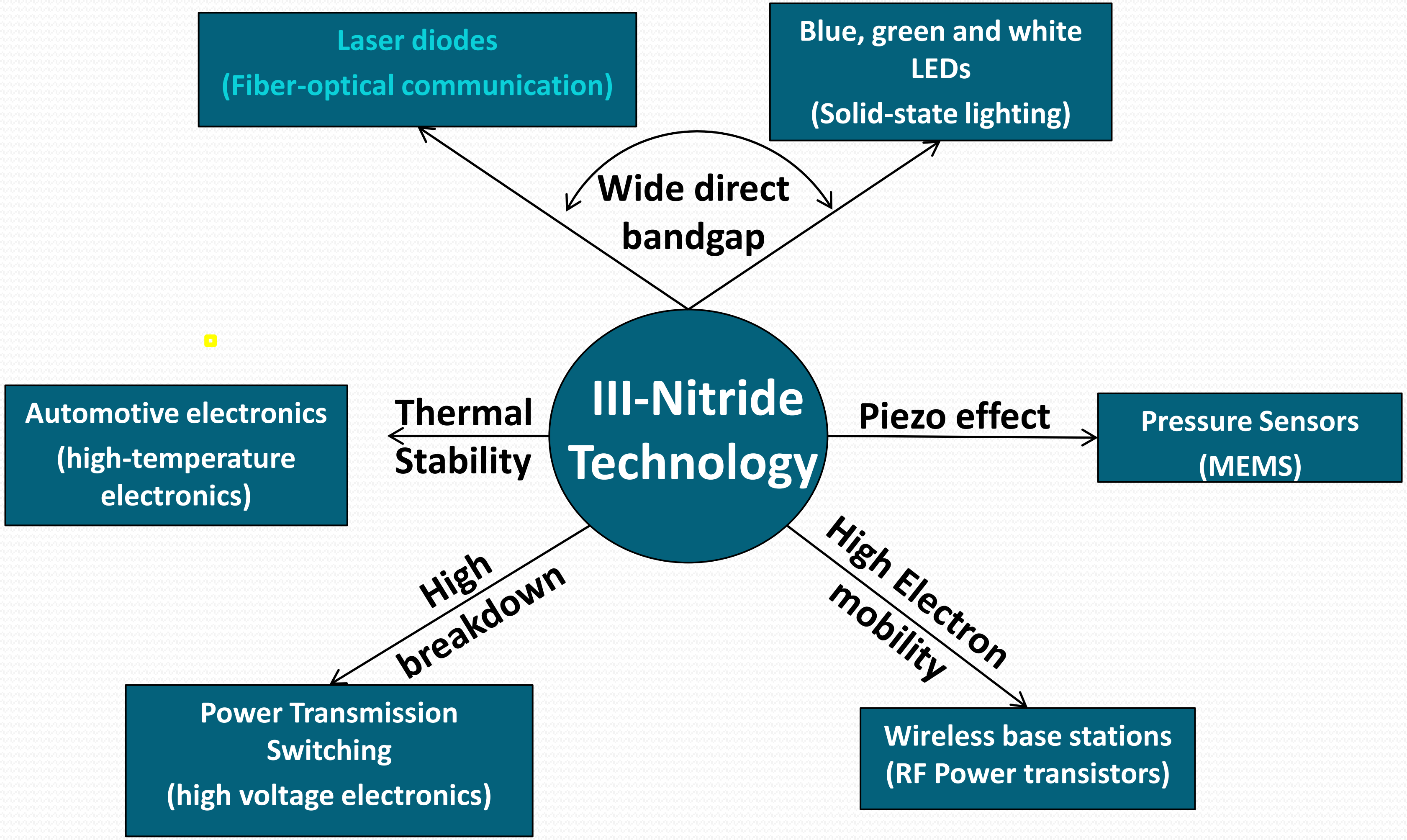
(a) Photon absorption in a direct bandgap semiconductor. (b) Photon absorption in an indirect bandgap semiconductor (VB, valence band; CB, conduction band)

S. O. Kasap, ***Optoelectronics and Photonics: Principles & Practices***, Second Edition, Pearson Education (USA), 2013 Pearson Education

<u>III-nitride semiconducdtors</u>

- Wurtzite structure (Stable phase)
- Direct bandgap: deep UV – near IR
  - AlN: 6.2 eV (200 nm)
  - GaN: 3.4 eV (365 nm)
  - InN : 0.7 eV (1771 nm)
- Tailoring of:
  - band-gap:
    $E_g(x) = xE_g(A)+(1-x)E_g(B)-bx(1-x)$
  - Lattice parameter
    $L(x) = xL_A+(1-x)L_B$

Applications of III-nitride semiconductors

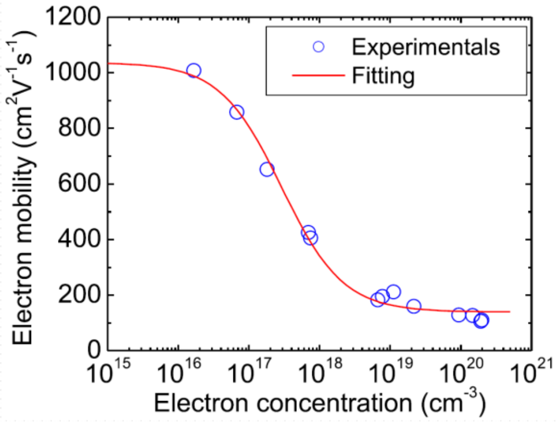


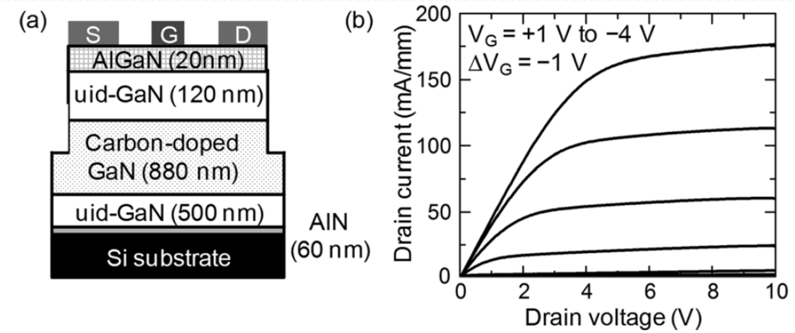
Commercial PVD systems

http://www.pvdproducts.com/

Optoelectronics and Electronics - by magnetron sputtering

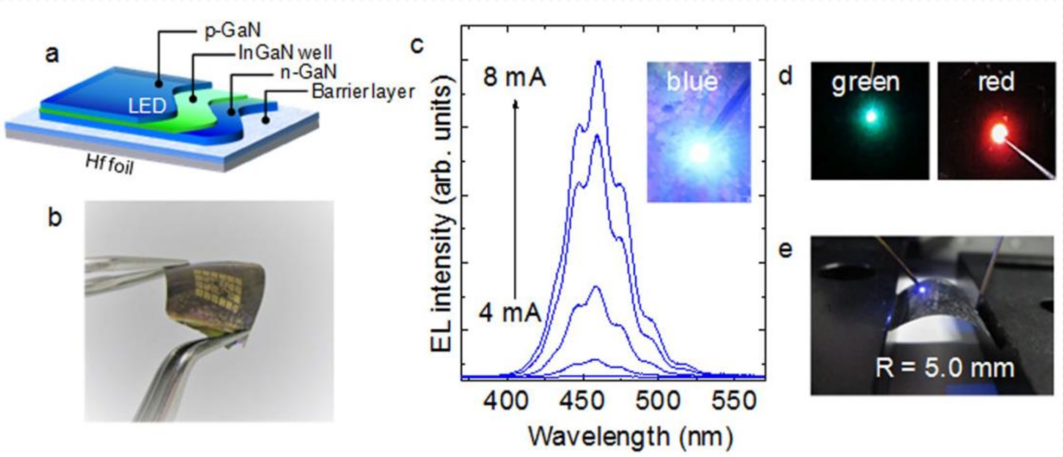
Pulse magnetron sputtering (PSD) grown Si-doped GaN and AlGaN/GaN HEMT





- Si-doped GaN:
  - RT electron mobility (μ_e) >1000 cm²/Vs
- AlGaN/GaN HEMT:
- μ_e :1360 cm²/Vs, sheet carrier density: 1.3 x 10^{13} cm² and a sheet resistance of 386 Ω/sq.

LEDs made on a flexible Hf foil

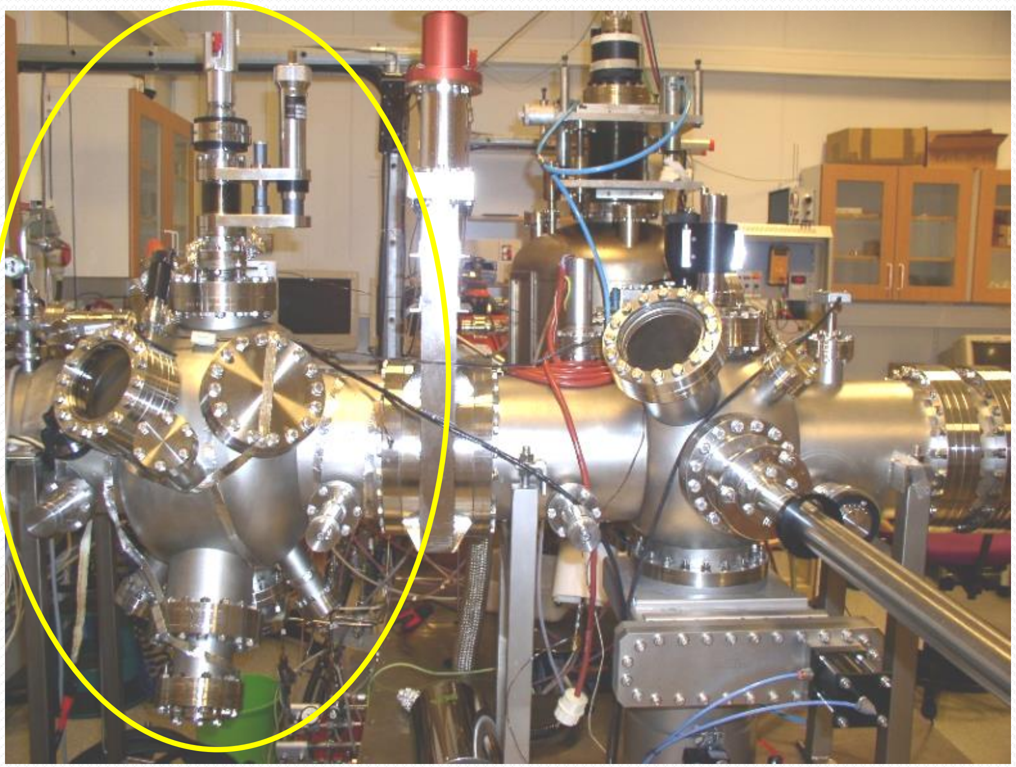


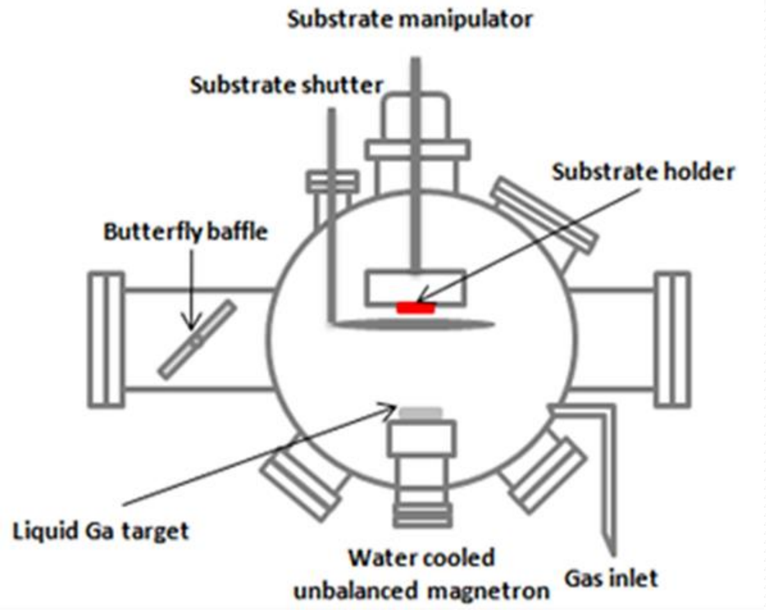
H. Kim … and H. Fujioka et al, *Sci. Rep.*, **7**(2017)2112

- Blue, Green, and Red LEDs
- Electroluminescence (EL) spectra of the LED structure at forward currents ranging from 4 to 8 mA.
- No noticeable degradation upon bending

N. Izyumskaya et al. and H. Fujioka *Semicond. Sci. Technol.* **34** (2019) 093003.

Deposition System for GaN Growth



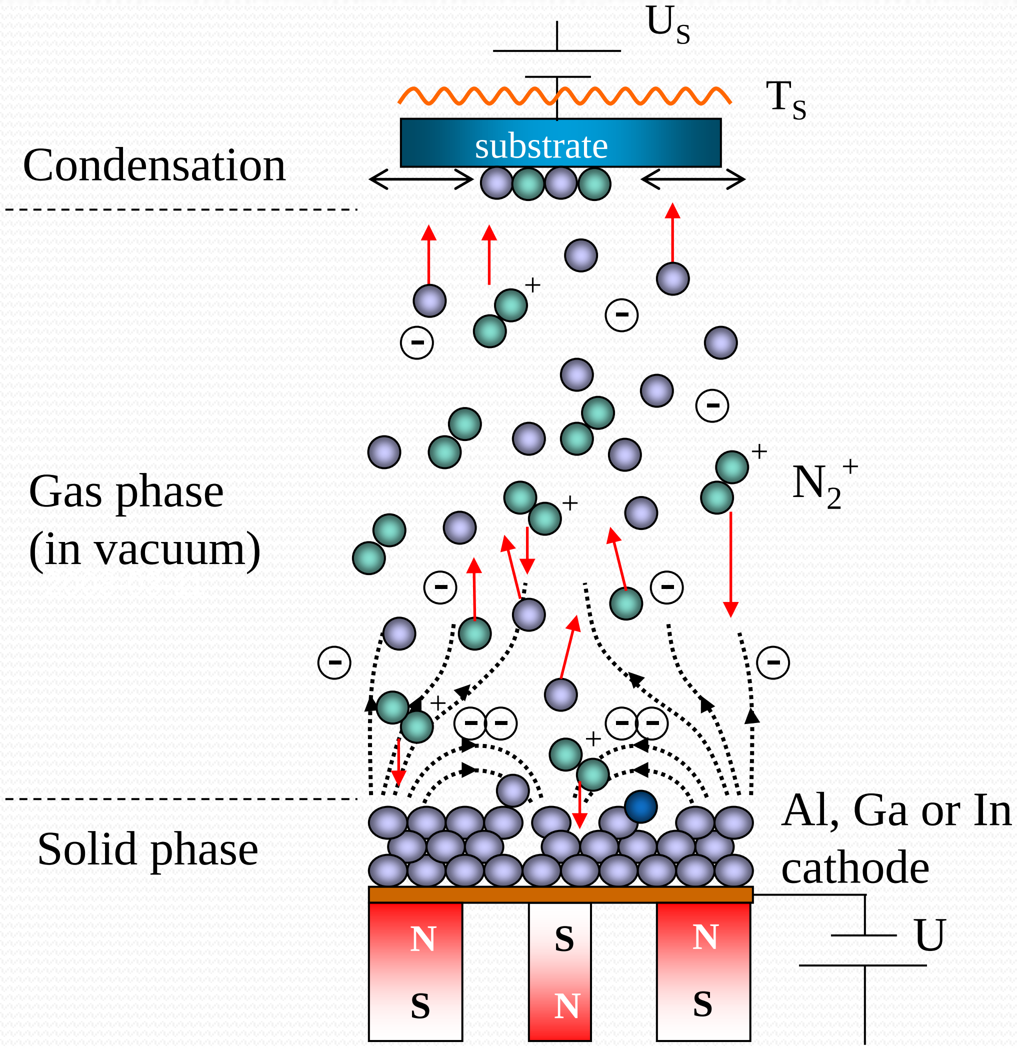


- DC Reactive Magnetron Sputter Epitaxy
- Ultra-high vacuum (UHV) chambers - base pressure < 1×10^{-8} Torr
- Liquid Ga target (purity 99.9999%)
- RT -1000 °C
- N_2 + (Ar)

A. Prabaswara et al. *Appl. Sci.* **10** (2020) 103050.; M. Junaid, *PhD dissertation 2012, Linköping University*

Deposition System for GaN Growth


Sputtering on a Ga Target



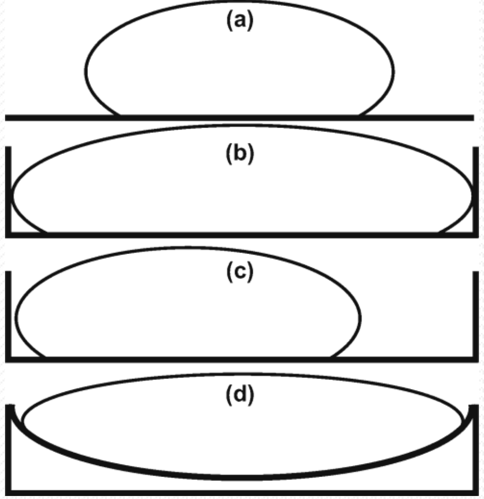
A. Prabaswara et al. *Appl. Sci.* **10** (2020) 103050.; M. Junaid, *PhD dissertation 2012, Linköping University*

Difficulties in sputtering liquid Ga target

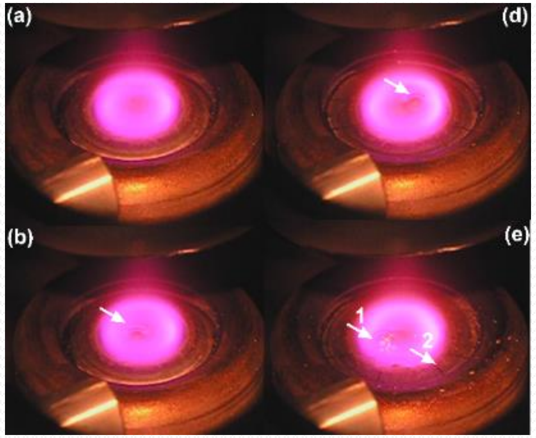
New target-solid

Heating or sputtering - liquid

Proper design for crucible



Formation of bubbles



Poison of target

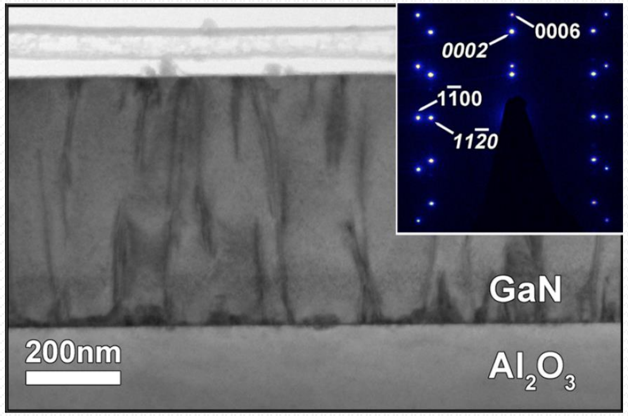
Stabilization of target

- Ga melting point: ~29 ^{o}C
  - Horizontal placement for target
- High Surface tension of liquid Ga
  - Low wetability
  - Proper shape of crucible
- Sputtering: applying target bias
  - Conducting materials
- Stability
  - Proper cooling of target
  - Stabilization process-repeation of nitridation and removing of nitride layer

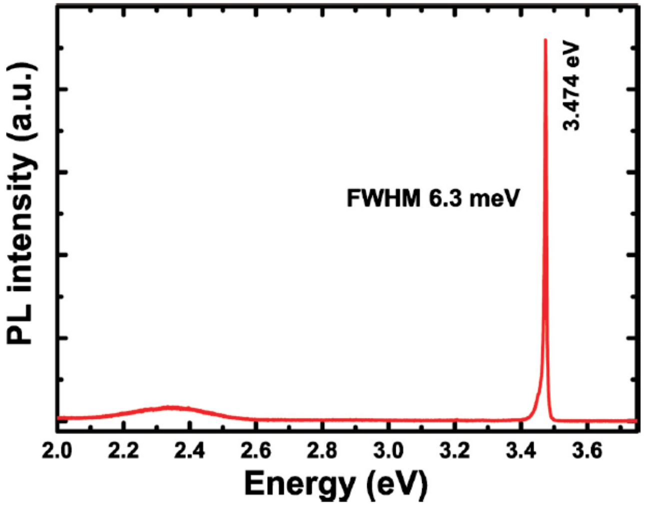
A. Prabaswara et al. Appl. Sci. **10** (2020) 103050.; M. Junaid, *PhD dissertation 2012, Linköping University*

High-quality GaN epitaxial film on sapphire

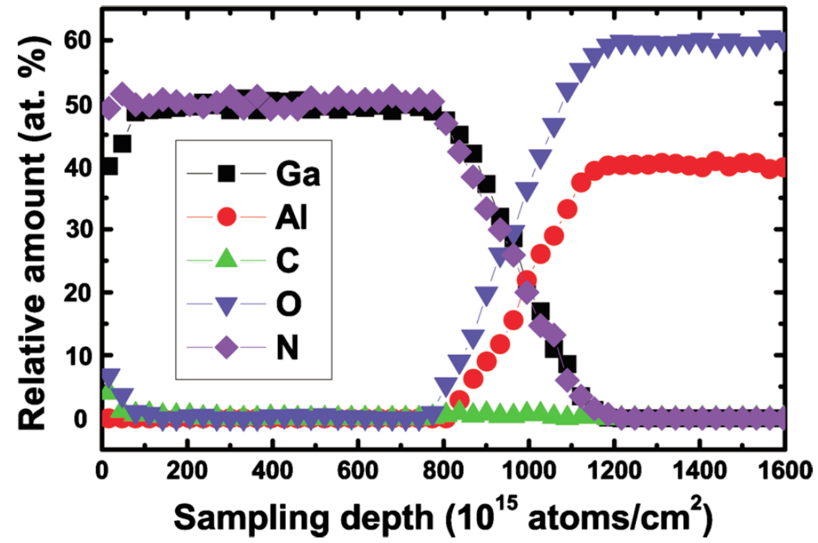
TEM and SAED



4K PL



Tof-ERDA (time-of-flight elastic recoil detection analysis)

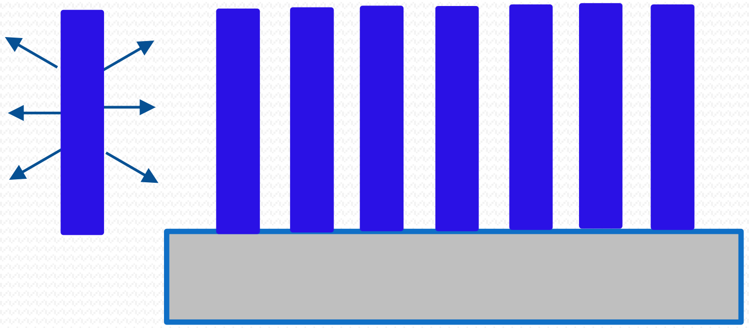


- Film grown at 700 °C
- Epitaxial relationship: [0001]GaN||[0001]Al_2O_3 ; [11-20]GaN||[1-100]Al_2O_3
- Low threading dislocation density ≤10 cm^{-2}

- A sharp band edge emission: 3.474 eV; FWHM of 6.3 meV
- Low yellow band emission
- High quality and purity

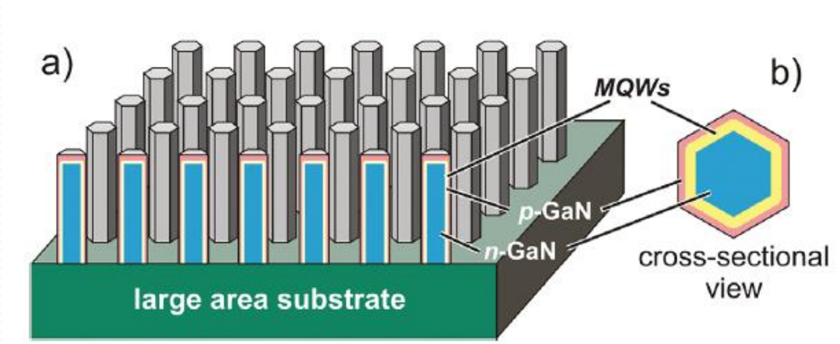
M. Junaid, C.L.Hsiao et al., *Appl. Phy. Lett.* ***98***, 141915 (2011)

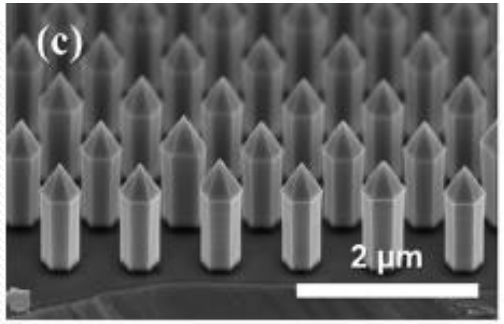
Why vertically aligned nanorods ?



- Vertically aligned nanorods:
  - almost "free-standing" ➔ independent of substrate material
  - low defect concentration
  - negligible mismatch of thermal expansion between GaN and substrate ➔ large area without substrate bending
  - regular periodic array ➔ photonic engineering

Core-shell nanorods





B. O. Jung et al, Nano Energy **11**, 294(2015).

- Core-shell nanorods:
  - n-type core + p-type shell
  - Large active surface area

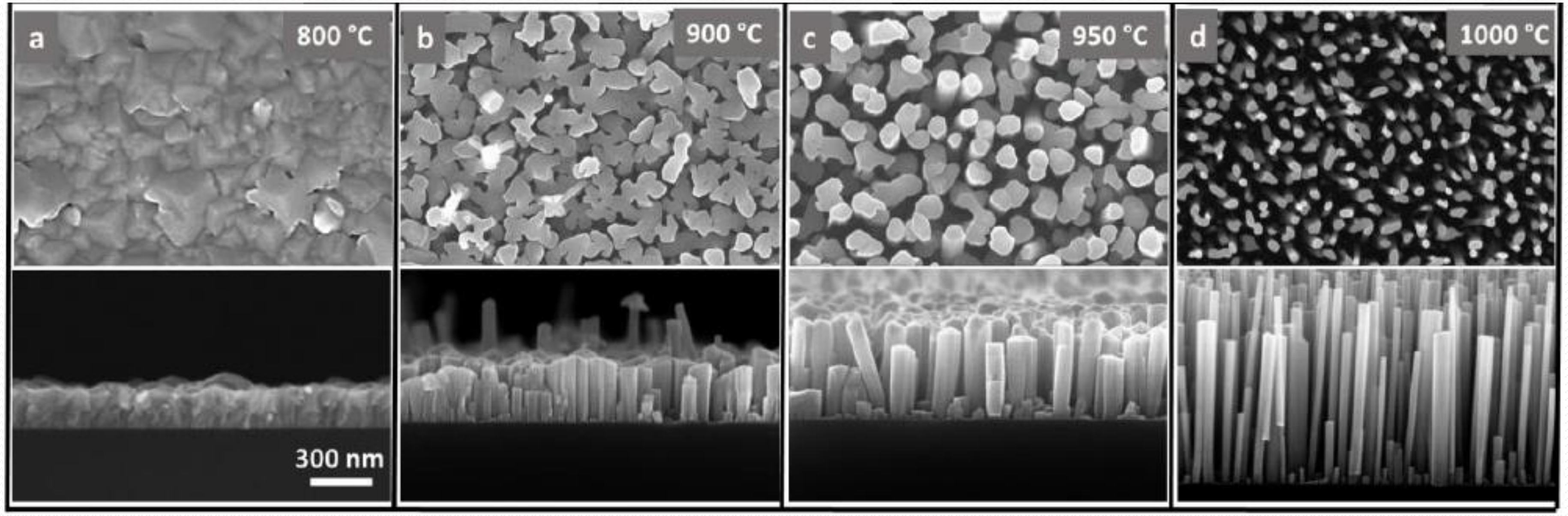
$$\frac{A_{core}}{A_{film}} \quad F = \frac{2\pi r \cdot h}{r^2\pi} \quad F = 4\,(\text{aspect ratio})\,F.$$

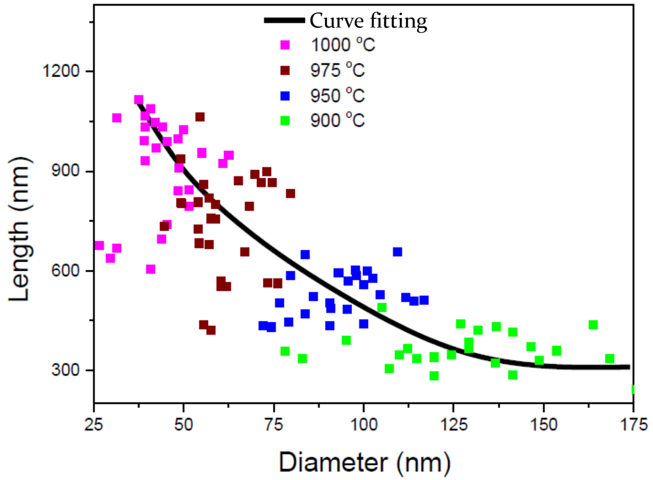
  - r: nanorod radius, h: height, F: filling factor
  - F=0.5, AR~5 ➔ 10 times
- Reduced current densities in the junction at constant total currents ➔ less droop problems
- *c*-oriented wurtzite nanorods ➔ non-polar sidewalls ➔ reduced internal electrical field
- No quantitative comparison between commercial LEDs and Nano-LEDs

S. Li and A. Wagg, *JAP* **111**, 071101(2011).

Self-assembled GaN nanorods on Si substrates

Temperature effect

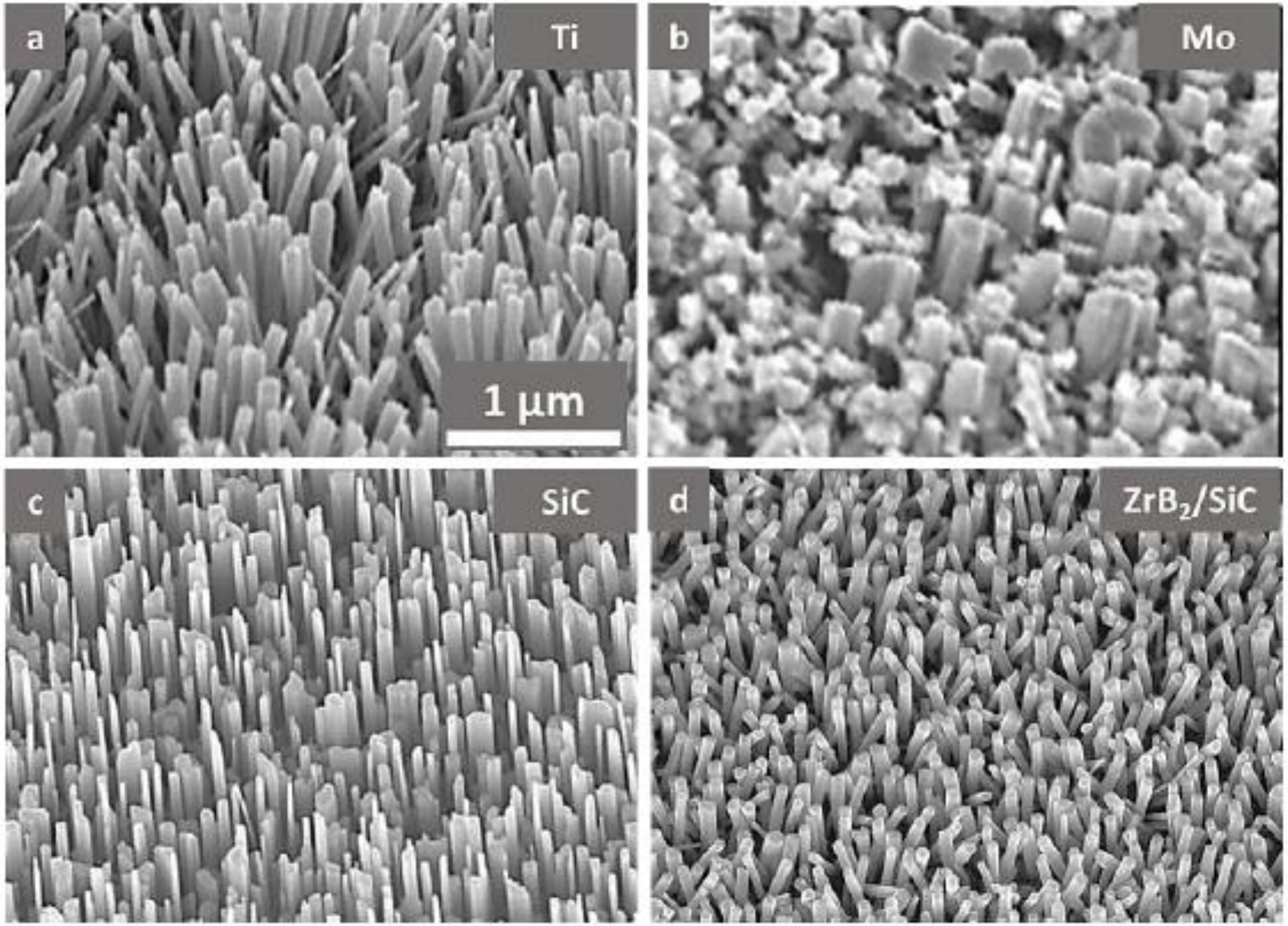




- Increase of axial growth rate with temperature
- linear dependence of the NR length (L) on the inverse diameter (1/d)
    - $L = C_1 (1 + 2C_2/d)$, C_1: film thickness; C_2: diffusion length
    - Diffusion induced growth

Energies ***10***, 1322 (2017)

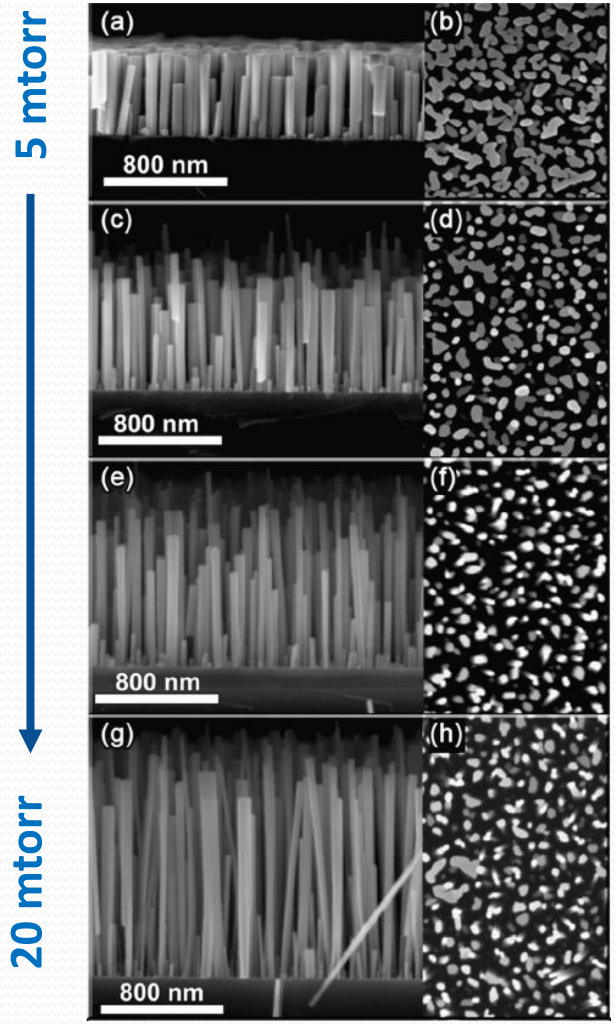
GaN nanorods grown on conducting substrates



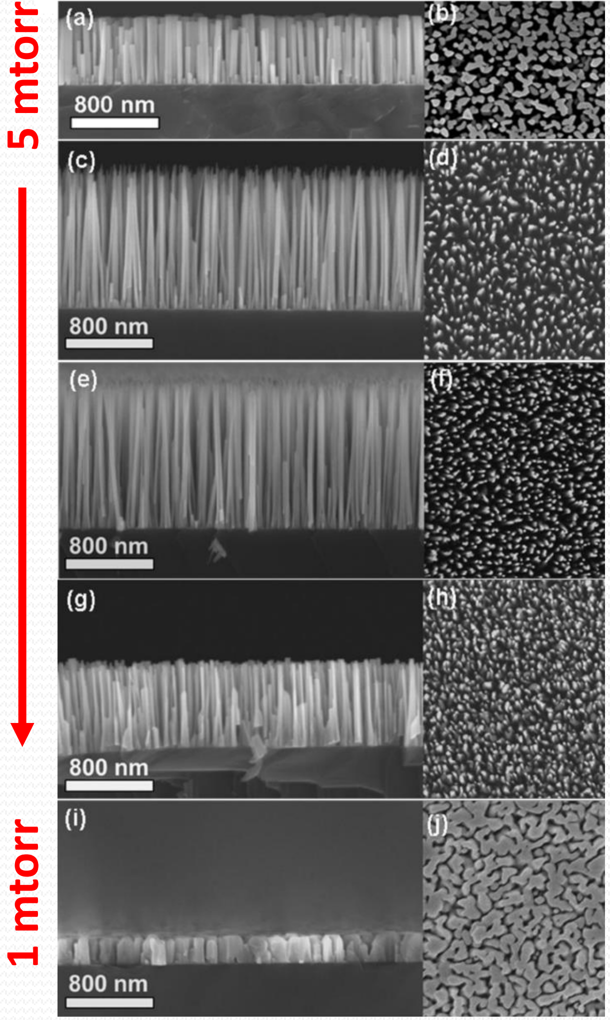
Energies ***10***, 1322 (2017)

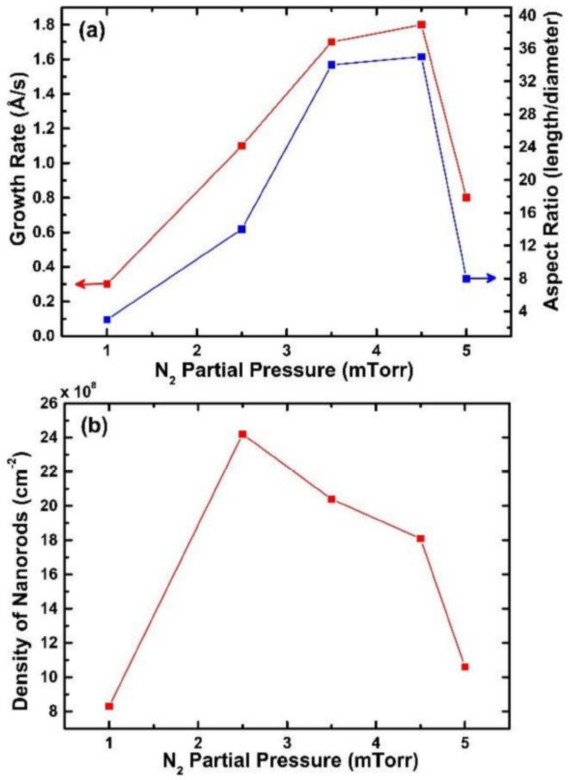
Pressure dependence on nanorod growth

Total working pressure (pure N_2)



Partial pressure (P_{N2}) (N_2+Ar)



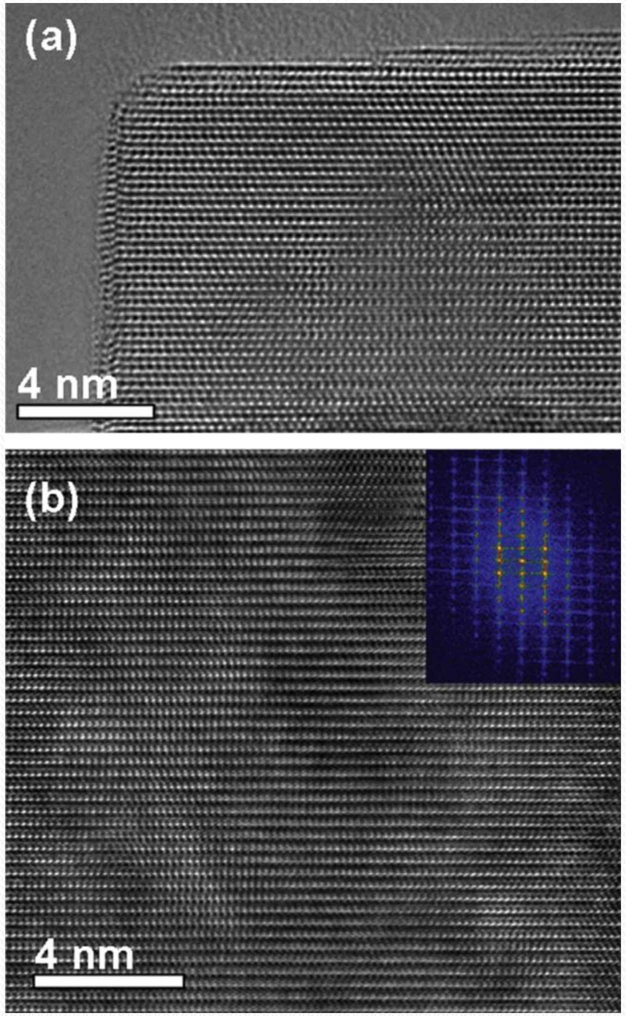


- Increase of axial growth rate with:
  - reactive N2 pressure
  - diluted Ar gas
- Nucleation density and aspect ratio of NR: highly related to P_{Ar}

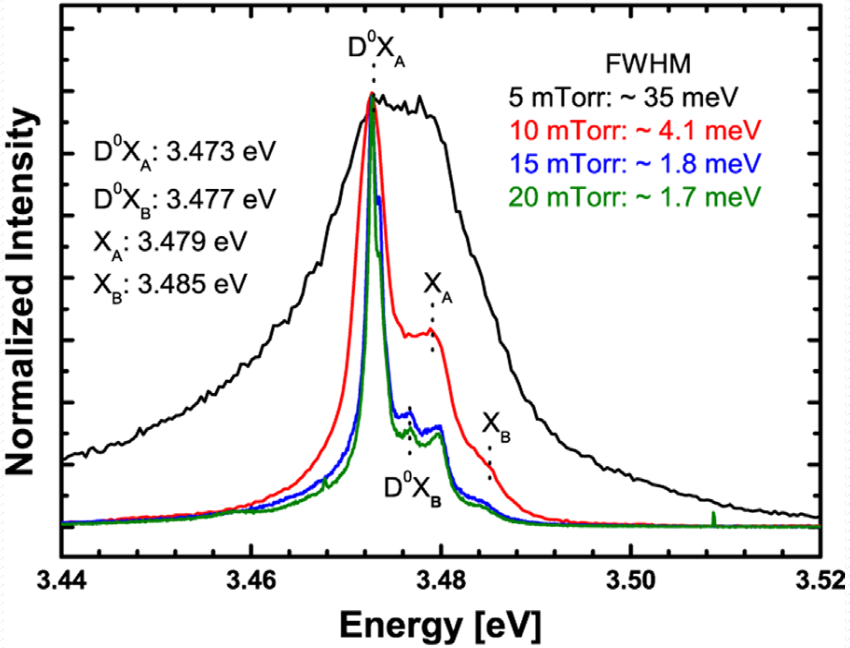
Mater. Sci. Semicon. Proc. ***39***, 702 (2015)
Nanomaterials ***8***, 223 (2018)

Microstructural and optical properties

Transmission electron microscopy (TEM)



Photoluminesence spectroscopy (PL)



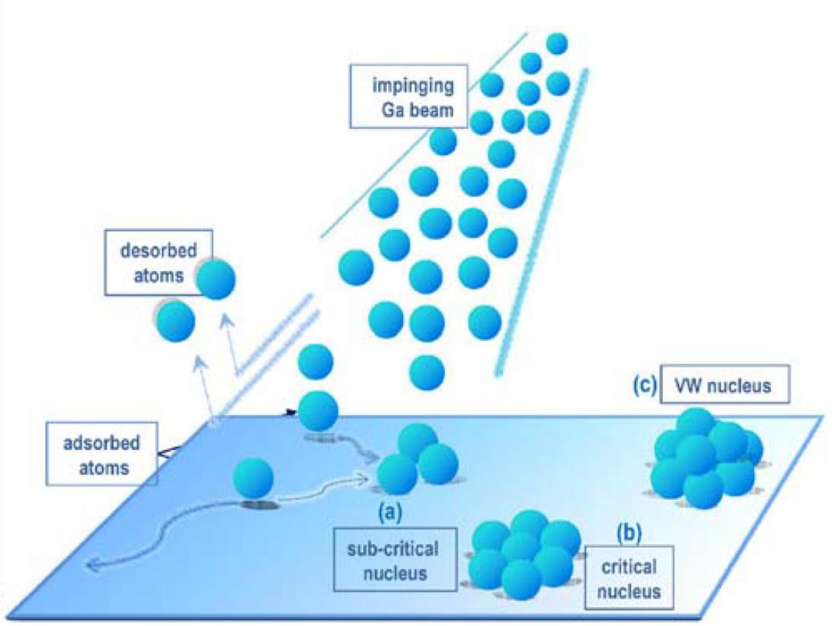
High correlation between optical and structural properties

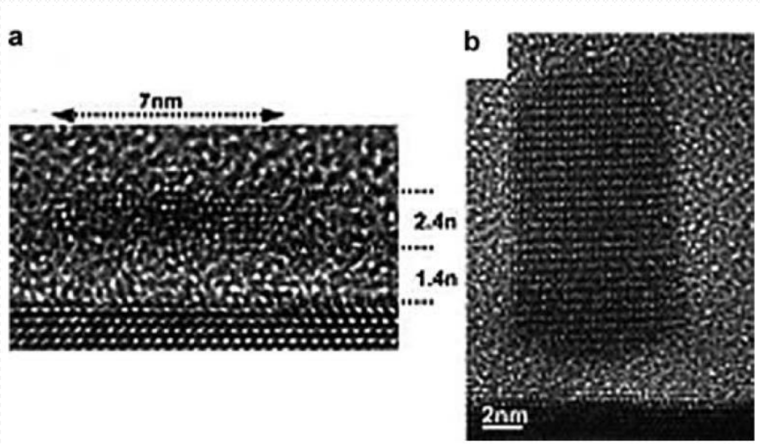
- Single crystal wurtzite structure
- Growth orientation: along *c* axis
- Sharpest emission: ~1.7 meV
- Free exciton: 3.485 eV
- Donor-bounded exciton: 3.479

Mater. Sci. Semicon. Proc. ***39***, 702 (2015)

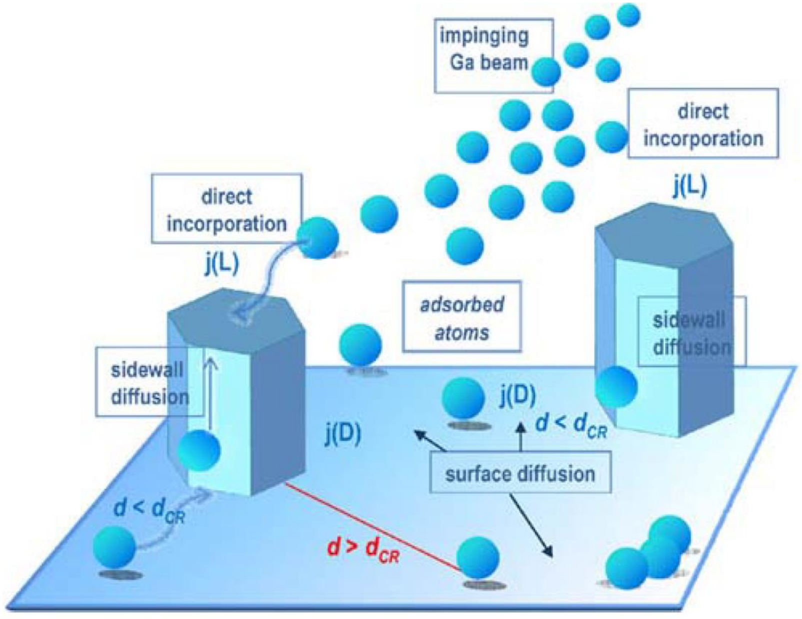
Self-assembled/induced nanorod growth (Bottom up)

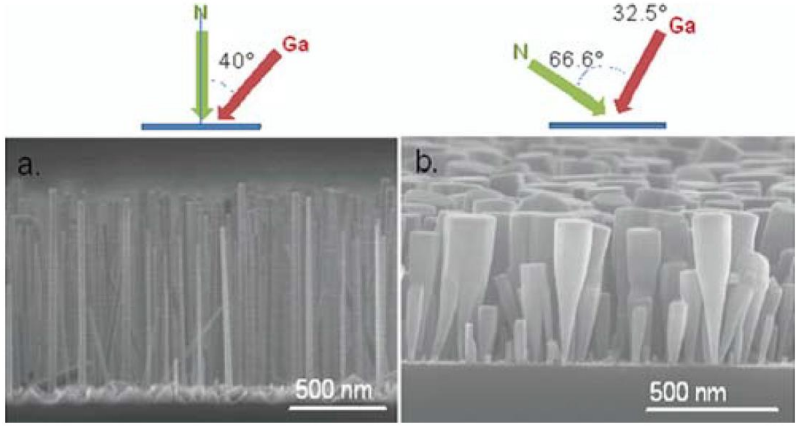
Nucleation





Growth stage

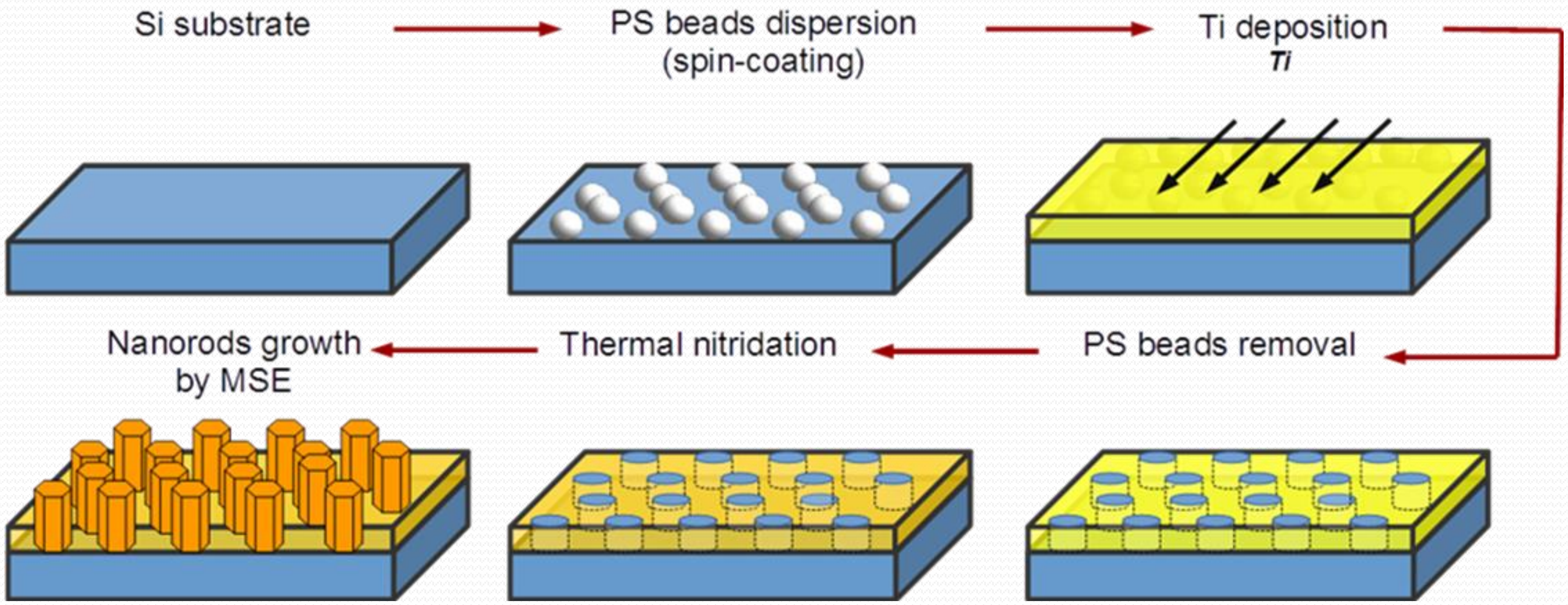




V. Consonni, *Phys. Status Solidi RRL* **7**, 669(2011) ; C. T. Foxon *et al.*, *J. Cryst. Growth* **311**, 3423 (2009).

Selective-area growth of GaN nanorods

Nano-sphere lithography



Si substrate

PS beads dispersion
(spin-coating)

Ti deposition

Nanorods growth
by MSE

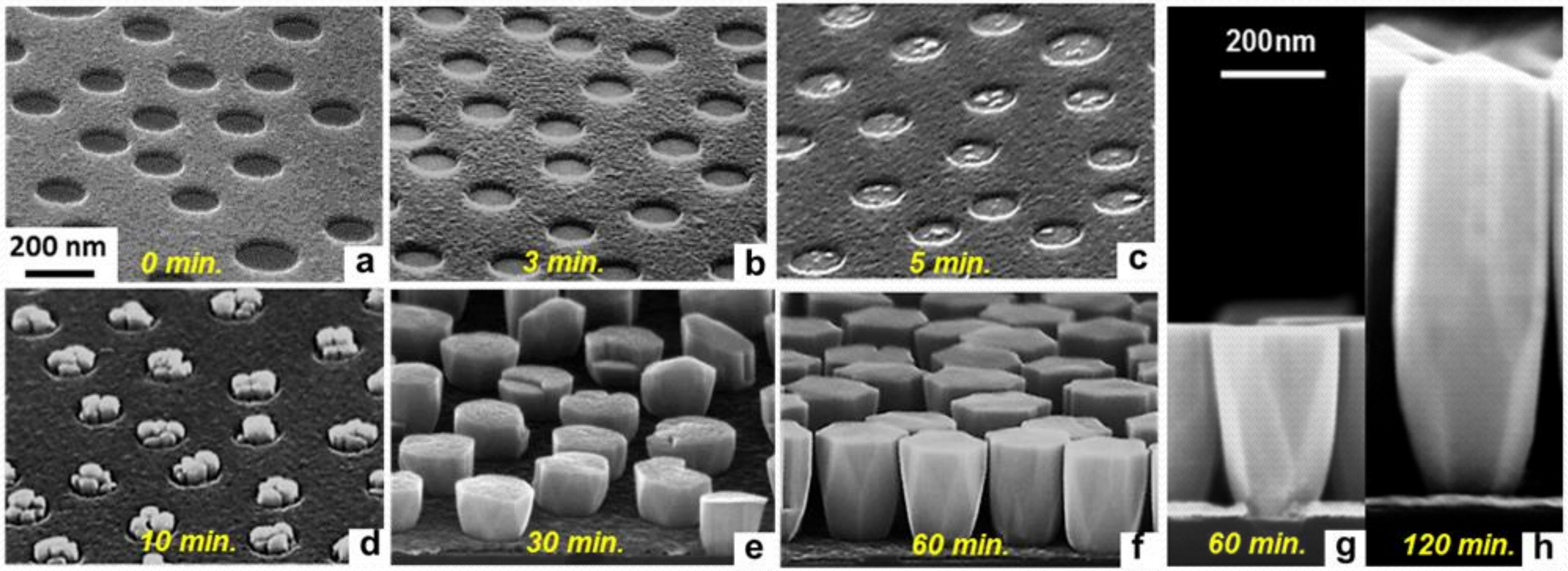
Thermal nitridation

PS beads removal

- Thin TiN mask layer (20 nm).
- Removal of the nanospheres → nanoopenings of ~ 150 nm in diameter.

Sci. Rep. ***7***, 12701 (2017)

Growth evolution with time



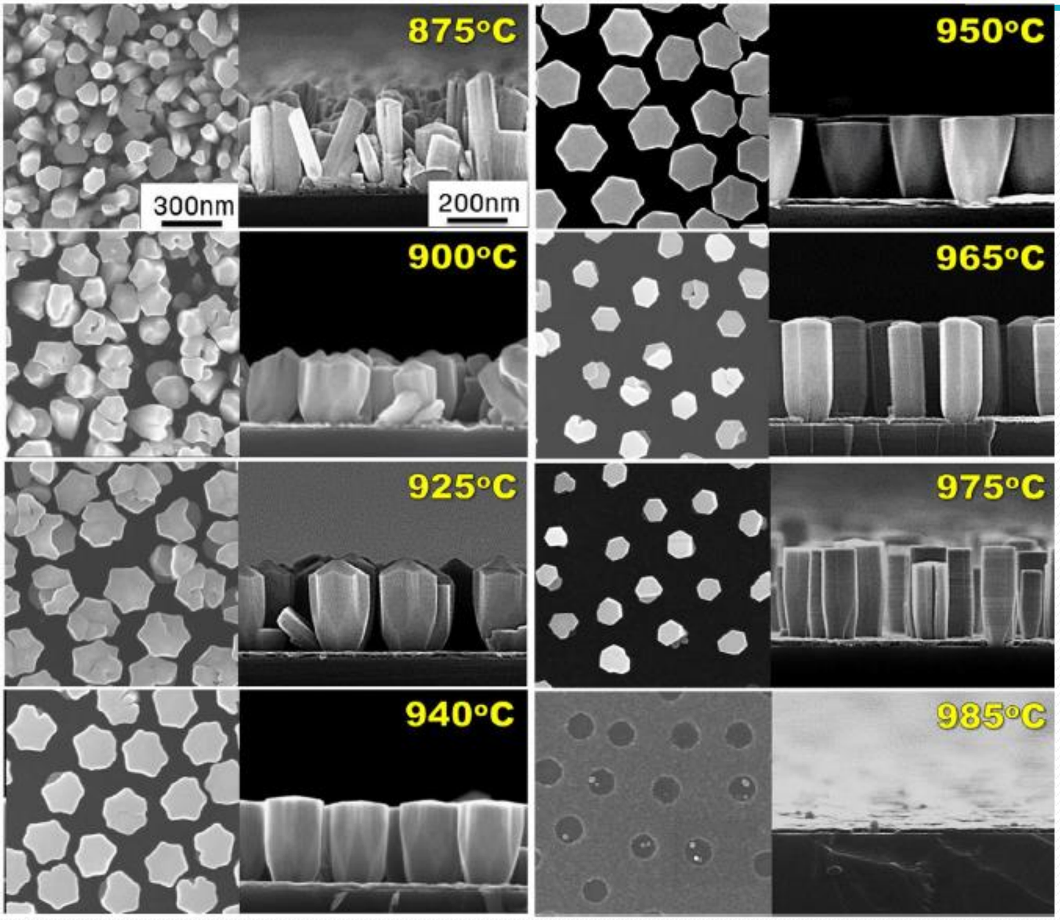
Bird-view (left) and side-view (right) SEM micrographs of the GaN grown for different growth times.

Figures a - e, and g- h have the same scale.

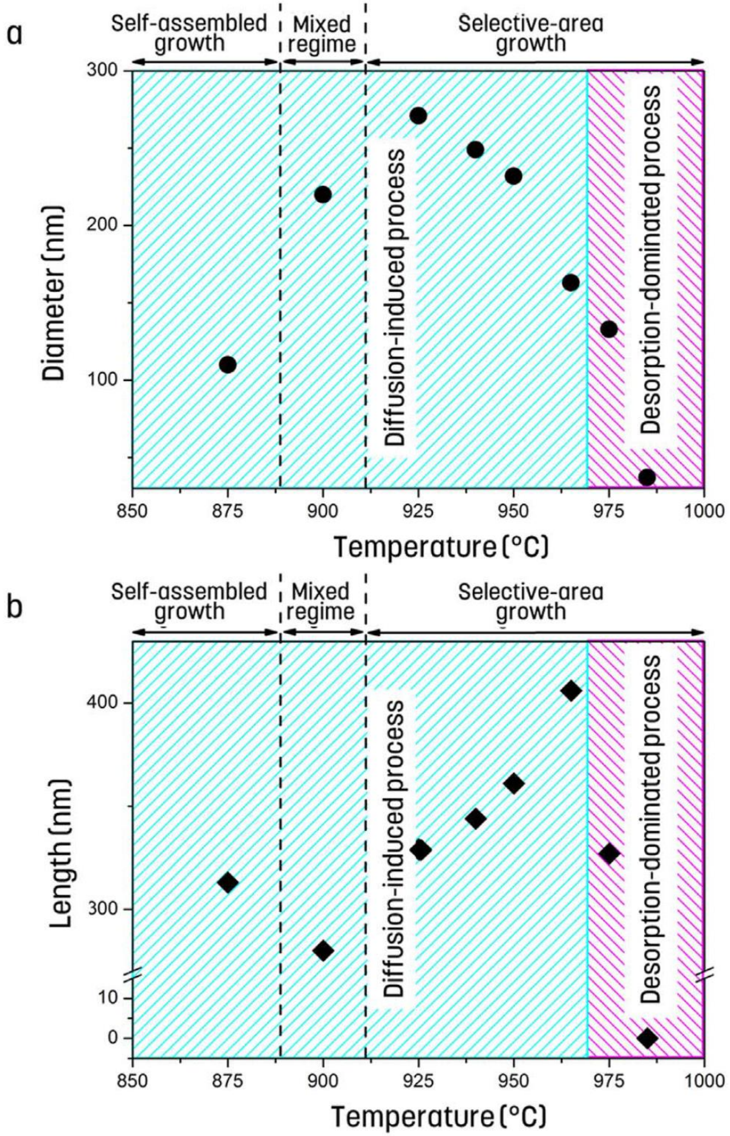
- NRs formed by coalescence of multiple islands.
- After approximately 300 nm, the lateral diffusion is suppressed and the NRs grow along the *c*-direction.
- Longer NRs, grown for 2 hours have a preferential pencil-shaped termination.

Sci. Rep. ***7***, 12701 (2017)

Temperature dependence



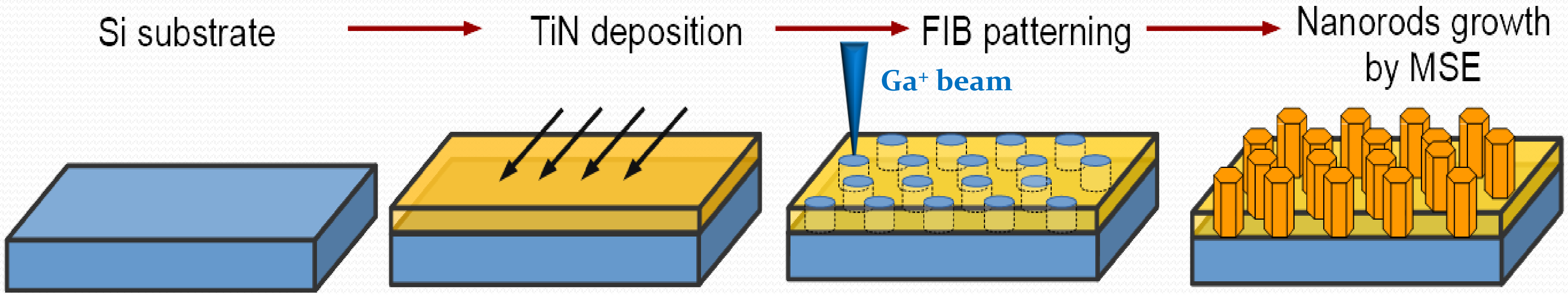
- Equilibrium reshaping of the NRs as a function of growth temperature.
- SAG at temperatures ≥ 925°C – nucleation on the mask at lower temperature
- No growth at 1000°C.



*Thin Solid Films, **660**(2018)950*

Regular-array GaN nanorods

Focused-ion beam (FIB) lithography process



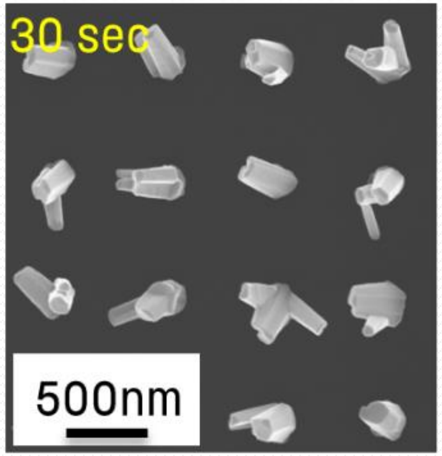
- milling current (2-50 pA)
- milling time (3-50 seconds)
- growth temperature

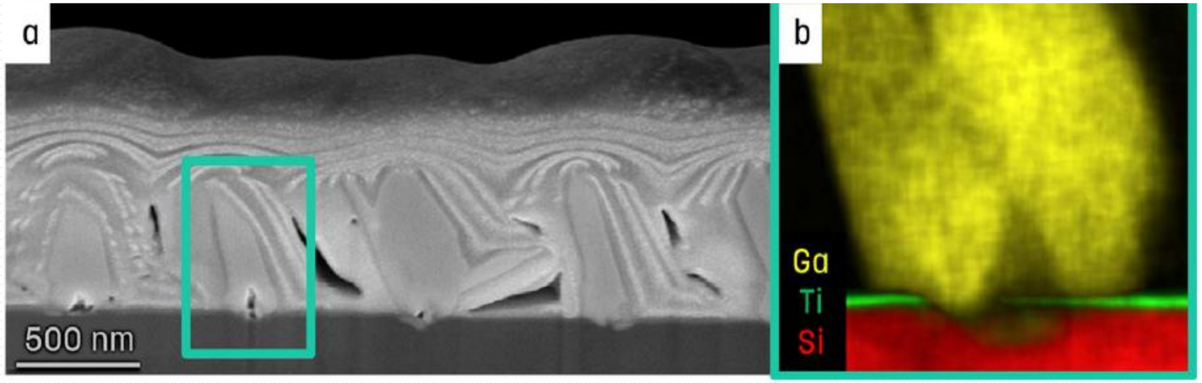
→minimize substrate damage

A. Prabaswara et al. Appl. Sci. **10** (2020) 103050.

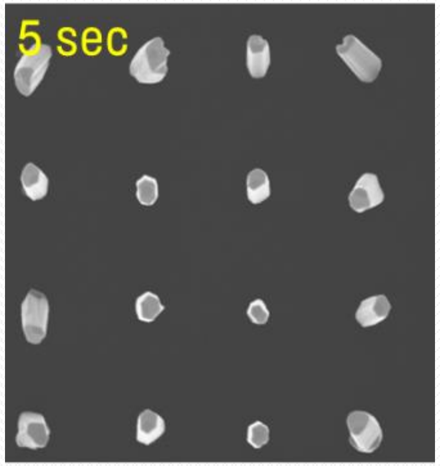
Effect of interface

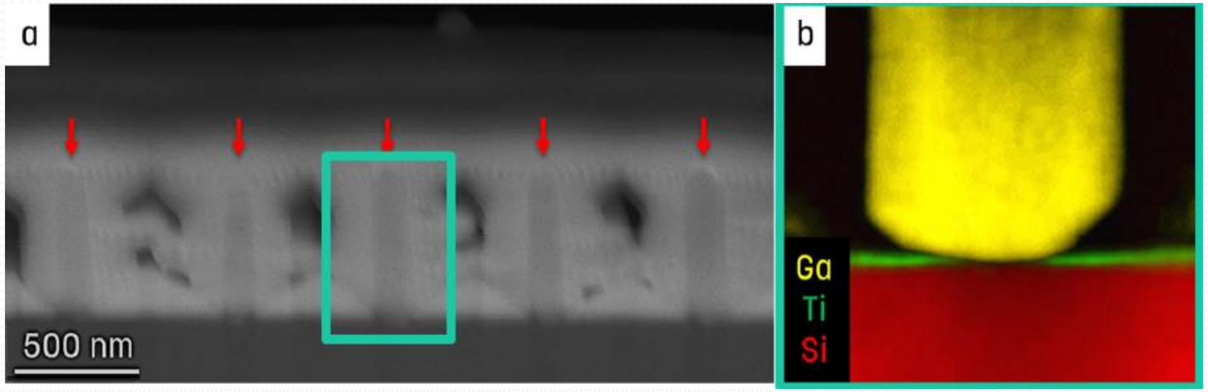
Ion milling time





- Rough surface →multiple tilted nanorods



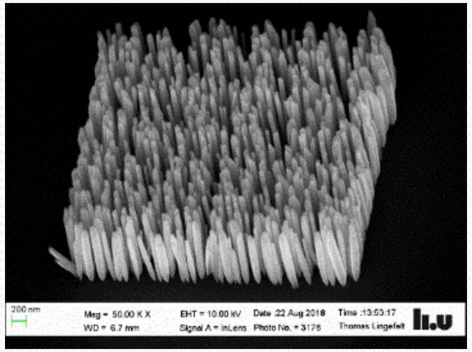


- Smooth surface → Single straight nanorods → minimize substrate damage

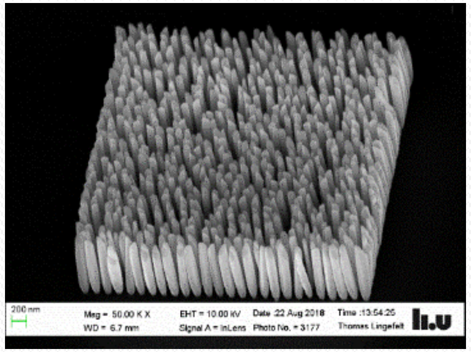
*Thin Solid Films, **660**(2018)950*

Surface diffusion

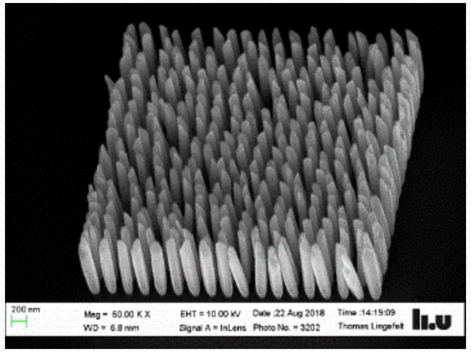
Pitch: 100 nm



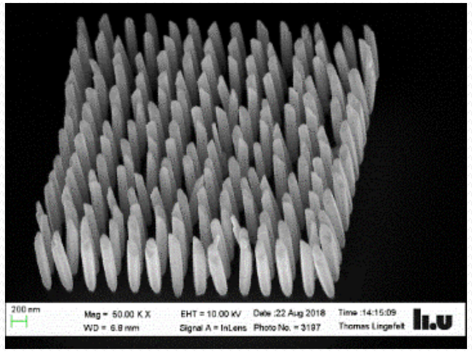
Pitch: 200 nm



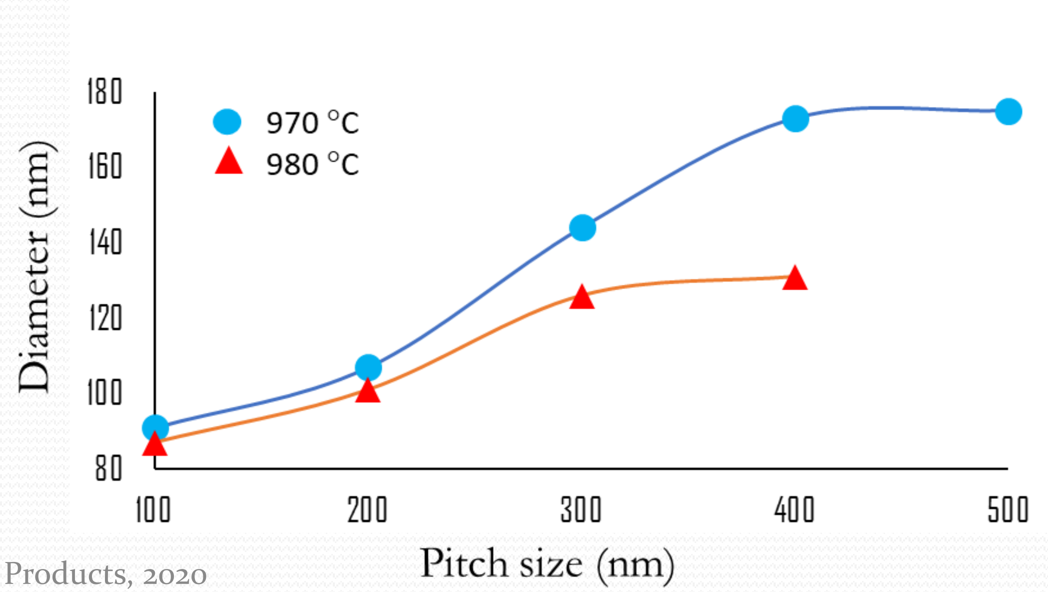
Pitch: 300 nm



Pitch: 400 nm



Temperature dependence of surface diffusion



- Pitch shorter than 200 nm
  - Not very successful
  - Requires well patterning process
- Length and diameter increase with pitch
- Diffusion length decreasing with temperature

E. Serban et al. Appl. Sci. **10** (2020) 719.

Summary

- **Handling of liquid Ga target**
  - Difficult but not impossible
  - Require proper design of crucible and process of target's stabilization
- **Epitaxial growth of GaN thin film on sapphire**
  - Direct growth without buffer, low-dislocation-density film ~ 500 nm, <10^{-10} cm^{-2}
  - Sharp PL emission ~6.7 meV
- **Self-induce growth of GaN nanorods**
  - Dislocation-free, single-crystal wurtzite structure
  - Growth on various functional templates/substrates
  - Sharp PL emission ~1.7 meV
  - Control Ga/N_2 ration by tuning partial pressure of Ar/N_2
- **Selective-area growth of GaN nanorods**
  - Pre-patterning by NSL and FIBL, employing a TiN_x mask
  - Well-defined single and uniform nanorods
  - Initial growth stages and time evolution → 5-step growth model
  - Temperature : surface diffusion, selectivity, coalescence, and morphology
  - Milling conditions: current and time → minimize substrate and mask damage

Presentation 2

iBeam Materials

GANOX

A new paradigm for epitaxial GaN films and devices on large-area substrates

Vladimir Matias
iBeam Materials, Inc.
Santa Fe, NM, USA

LiU LINKÖPING UNIVERSITY

PVD PRODUCTS

iBeam Materials

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Santa Fe, NM, USA

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Julian Osinski

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Albuquerque, NM, USA

Brendan Gunning
Daniel Koleske (in memoriam)

University of New Mexico
Albuquerque, NM, USA

Abdel Elshafiey
Daniel Feezell

Los Alamos National Lab
Los Alamos, NM, USA
Terry Holesinger
Alp Findikoglu

Stanford University
Stanford, CA, USA
Robert Hammond

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Outline

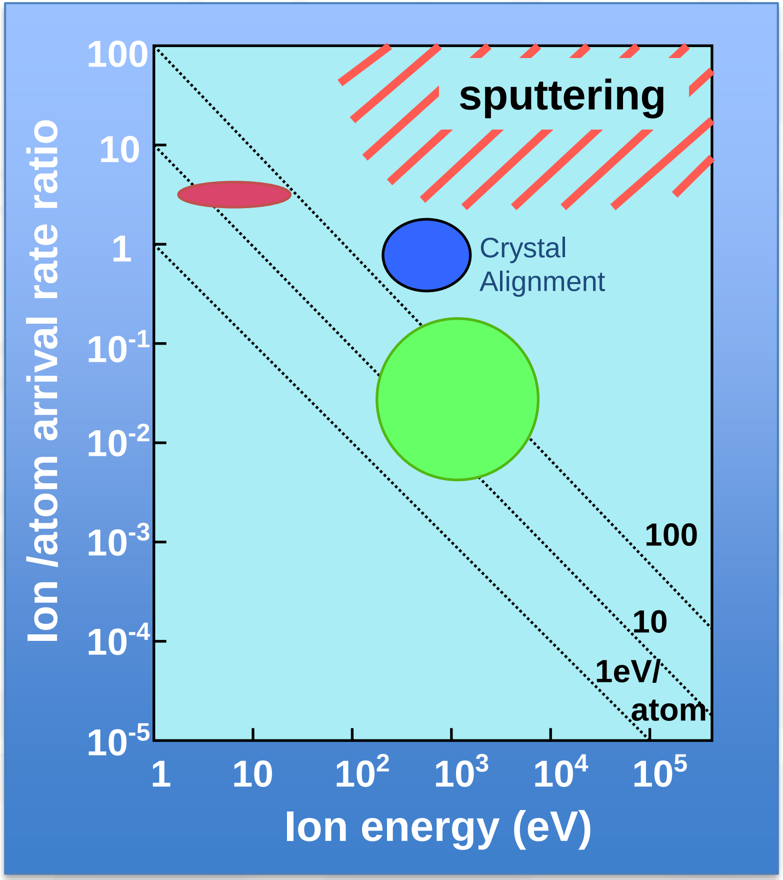
- Introduction to Ion-Beam Assisted Deposition (IBAD) texturing
- GANOX technology

  GANOX = **GaN O**n single-**X**tal films
- Results on GaN to date (work with Sandia Labs)
- Implications and Novel Applications

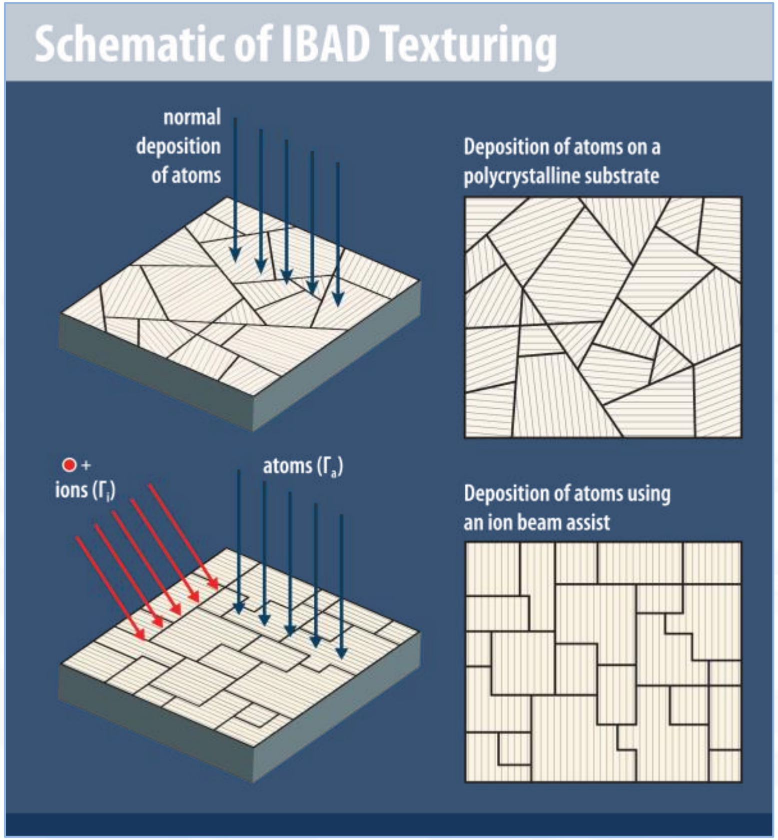
Ion Beam Assisted Deposition

Materials property modification by ion bombardment during deposition (IBAD):

- Compositional effects by preferential sputtering
- Incorporation of (inert) ion species
- Compound formation by reactive ion species
- Improved step coverage
- Change of film stress
- Crystal alignment

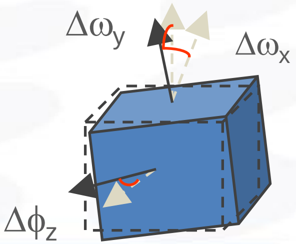


Ion Beam Crystal Alignment



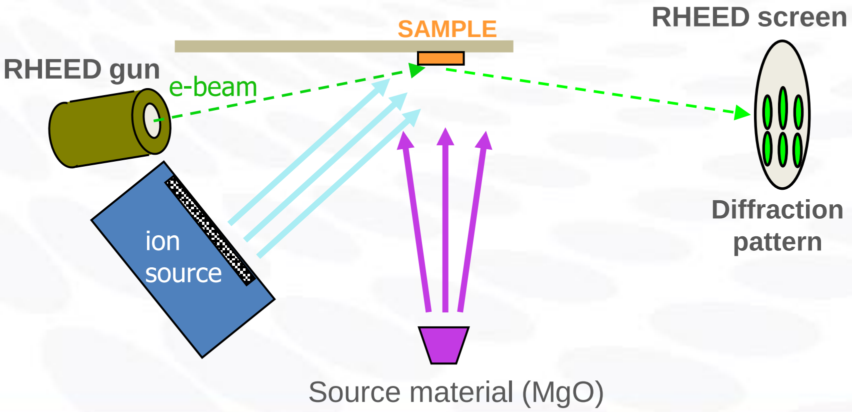
- IBAD induces in-plane and out-of-plane texture:
  IBAD TEXTURING or **Ion Beam Crystal Alignment**
- Particular version of IBAD Texturing we call Ion Texturing at Nucleation; discovered originally at Stanford University
- Process is extremely fast, with only ≤ 5 nm of deposit required; demonstrated in < 1 second
- Process that allows formation of single-crystal like films on arbitrary but smooth substrates (such as glass, metal and plastic foils)
- Key parameters are ion-to-atom ratio, *r*, and ion beam energy

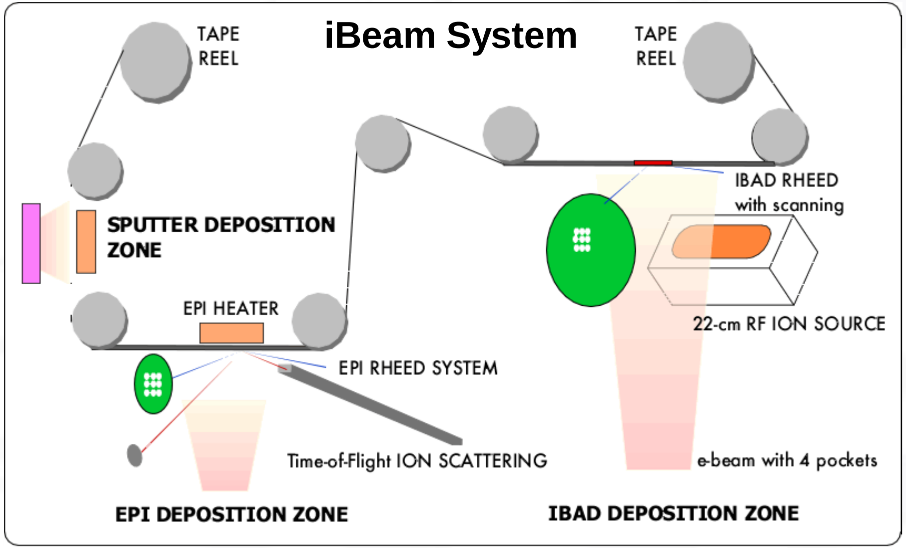
$$r = \frac{\Gamma_i}{\Gamma_a}$$



Ion Beam Assisted Deposition System

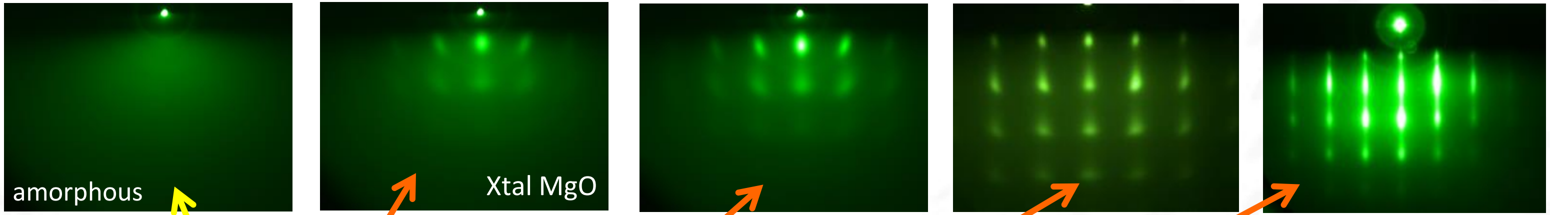
- Ion beam is incident during deposition: medium energy (500 – 1500 V) ions, typically Ar
- Source atoms/molecules can be evaporated/sublimed or deposited by sputtering
- *In situ* monitoring by RHEED (Reflection High Energy Electron Diffraction) is **critical** to determine crystalline orientation during deposition

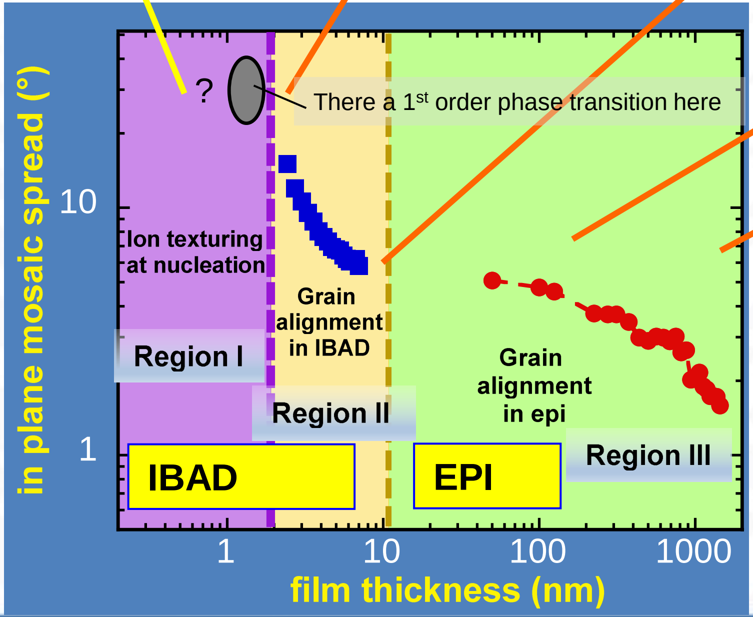




iBeam Materials uses a deposition system specifically designed for IBAD and other depositions on long metal tape with *in situ* monitoring and diagnostics

IBAD texture evolution in three different regions (MgO)





Region I: MgO is first deposited amorphous

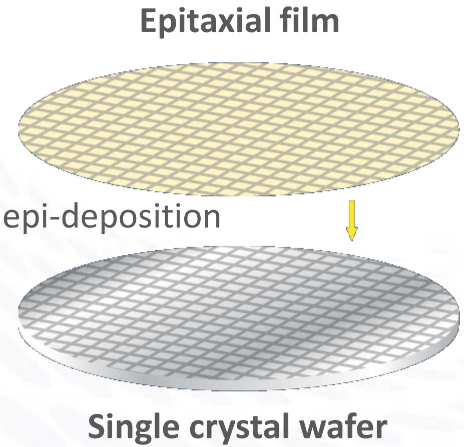
- MgO crystallizes after 1-2 nm of deposit

Region II: Texture improves rapidly with additional IBAD – 2D region

- There is an optimum point after which there is no further improvement in texture

Region III: Texture improves further with homoepi, but much more slowly with thickness

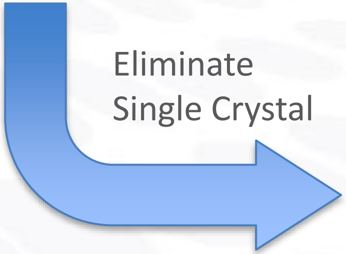
How does IBAD change the game for Epitaxy?

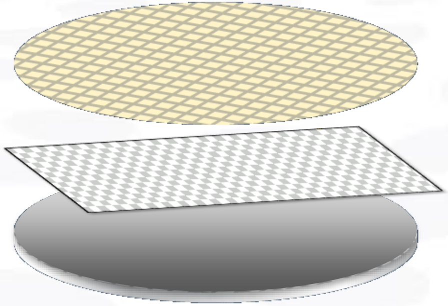


EPITAXY on IBAD Template

Insertion of an ion-beam aligned layer on a non-oriented substrate

- Deposit an ion-beam aligned single-crystal-like layer (few nm) on an amorphous or polycrystal substrate
- Substrates can have desired mechanical, thermal or electrical properties independent of lattice match
- Enables large-area substrates, such as glass, metal, plastic, including Roll-to-roll





By replacing single crystal wafers, IBAD reduces cost and enables Large area deposition and New functionalities

IBAD Texturing allows for Lattice Engineering

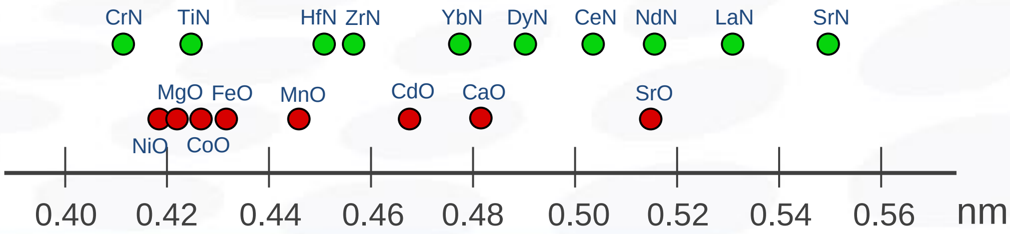
A) Lattice Orientation

IBAD <100>	IBAD <111>
MgO – Prototype	CeO_2 – Prototype
Rock-salt structures	Fluorite and Bixbyite structures
NiO, CaO, SrO	ZrO_2, CaF_2
TiN, CrN, ZrN	Mn_2O_3, Sc_2O_3

B) Lattice Parameter Engineering

- IBAD texturing material can be chosen from a variety
- Lattice parameter can be further engineered with solid solutions of compounds (e.g. CaO-MgO solution)

Rock-salt structures



GaN on IBAD Templates

- DOE ARPA-E funded project
- Lead was iBeam Materials, a technology startup company in Santa Fe, New Mexico
- iBeam worked with Sandia National Labs to develop GaN on IBAD substrates using metal foil

iBeam Materials ↔ **Sandia National Labs**

Template developed in R2R reactor

GaN growth in wafer reactor

Los Alamos National Lab

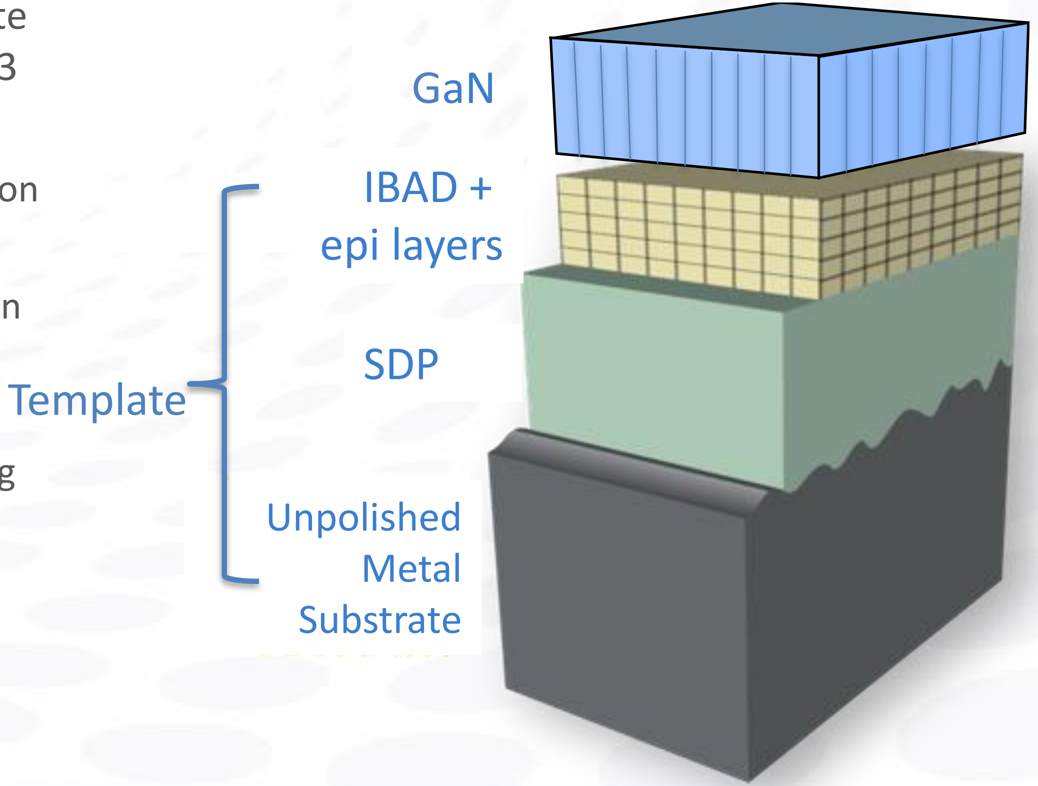
University of New Mexico

Our approach to preparing epi-GaN on metal (GANOX)

iBeam's GANOX, GaN on X, X = any substrate with a single-Xtal layer. Process consists of 3 steps:

1) Planarize the metal substrate using solution deposition planarization (SDP^{TM})
2) Create textured and buffer layers using ion beam assisted deposition (IBAD) and physical vapor deposition
3) Deposit GaN and other device layers using Metal organic chemical vapor deposition (MOCVD)

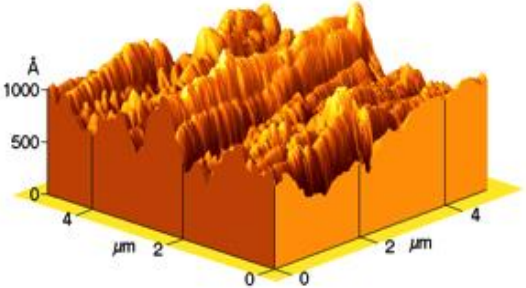
Artificially aligned templates allow one to separate the substrate requirements from epitaxy lattice matching requirement



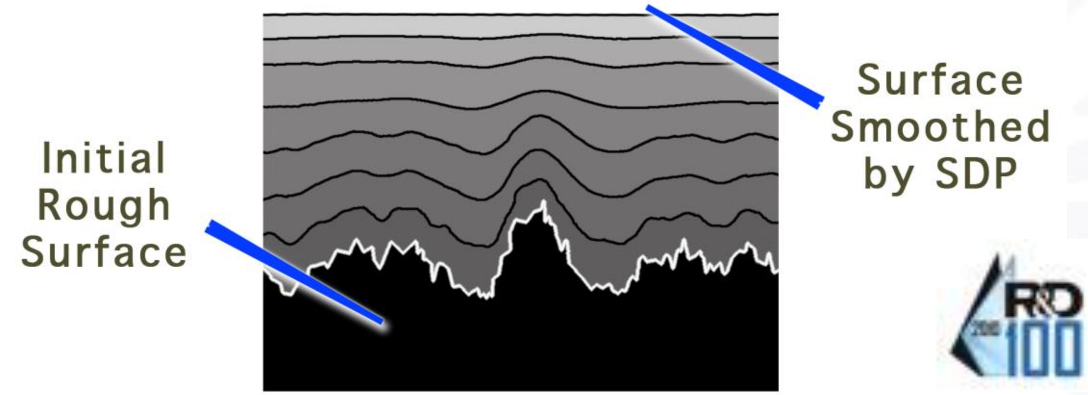
Solution Deposition Planarization (SDP)

- Chemical solution deposition planarizes by liquid layer surface tension
- Multiple coatings reduce roughness as much as required
- Typically roughness reduced to less than 1 nm RMS
- Start with a molybdenum metal foil with good CTE match
- Can use a variety of oxide materials (process done in air)

RMS Roughness 19 nm



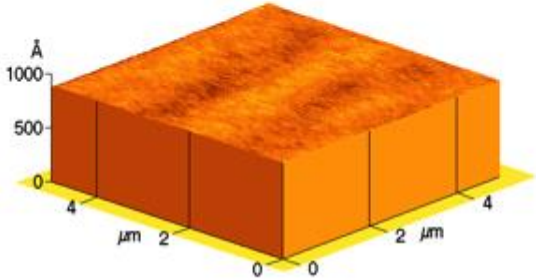
UNPOLISHED



Initial Rough Surface

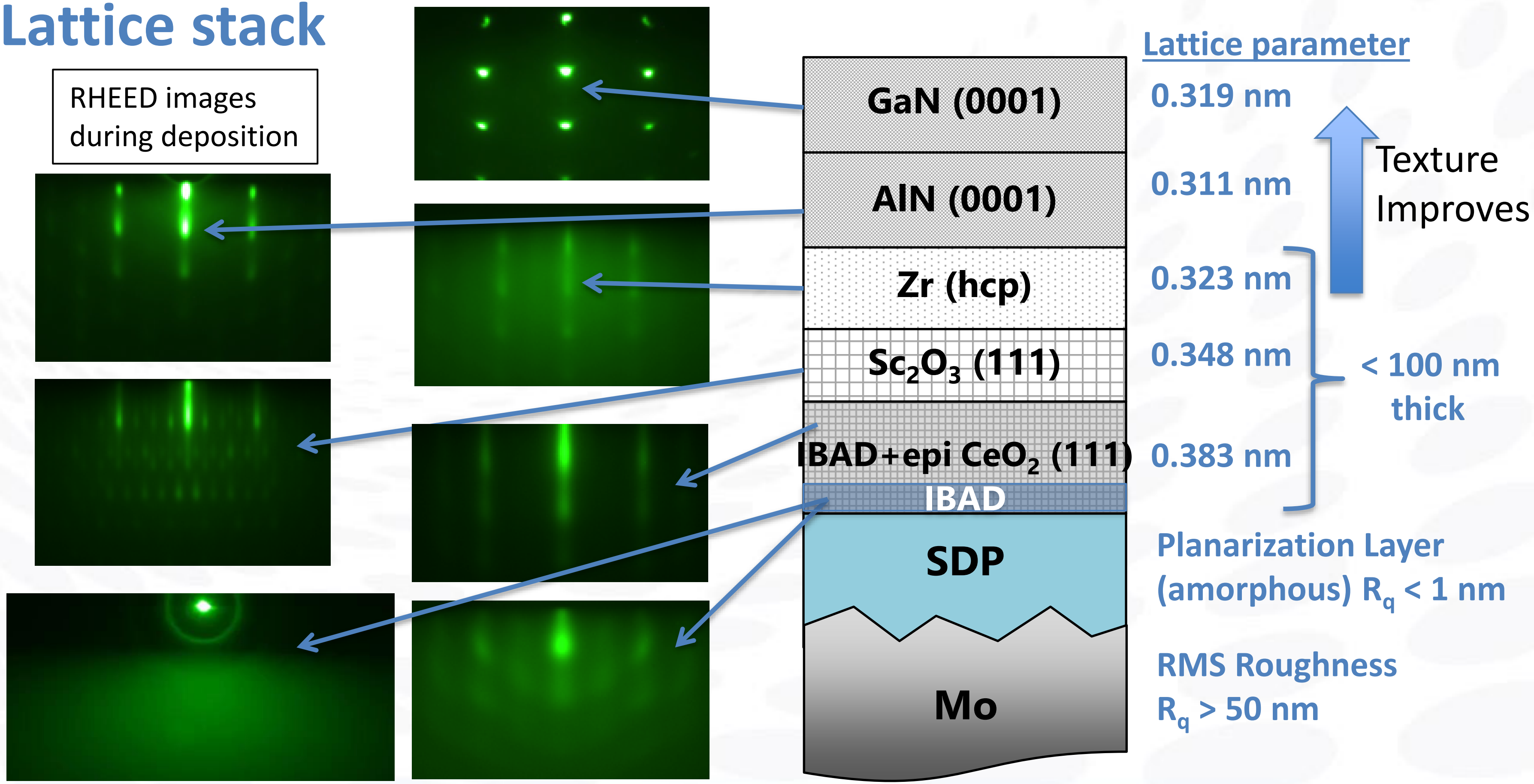
Surface Smoothed by SDP

RMS Roughness 0.5 nm



PLANARIZED

Lattice stack



RHEED images during deposition

Lattice parameter

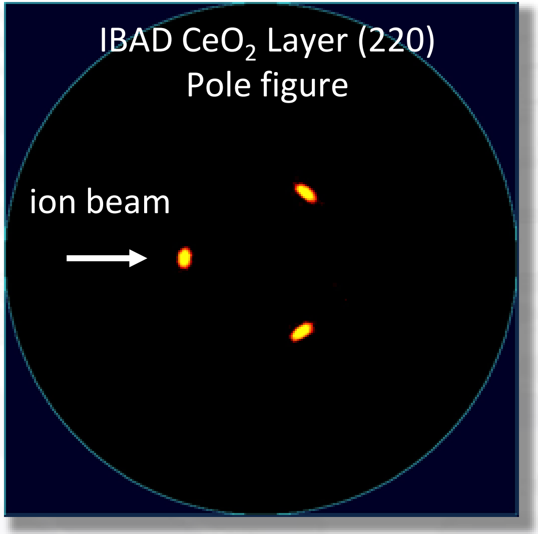
Layer	Lattice parameter
GaN (0001)	0.319 nm
AlN (0001)	0.311 nm
Zr (hcp)	0.323 nm
Sc_2O_3 (111)	0.348 nm
IBAD+epi CeO_2 (111)	0.383 nm
IBAD	
SDP	Planarization Layer (amorphous) R_q < 1 nm
Mo	RMS Roughness R_q > 50 nm

Texture Improves

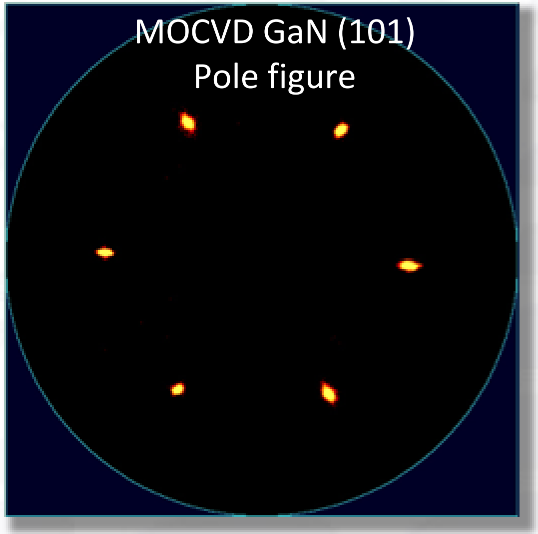
< 100 nm thick

IBAD Texturing of Templates for epi-GaN

- Fast IBAD <111> texturing: CeO_2
- 1000 eV Ar ions, e-beam evaporate CeO_2
- Epitaxial GaN deposited on a buffered template structure

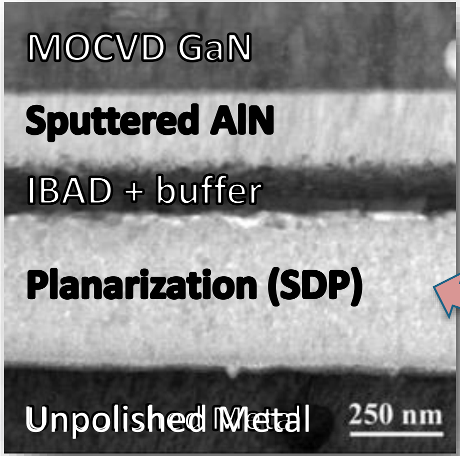


Rocking curve of
< 1.5°
In-plane texture of
< 4°

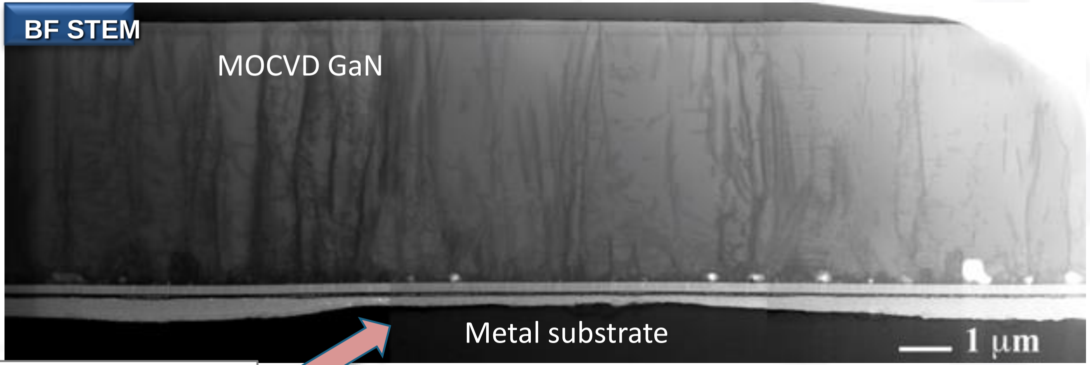


Rocking curve of
< 0.2°
In-plane texture of
< 0.7°

First Epi-GaN on Metal

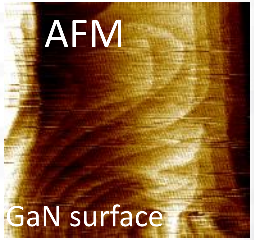


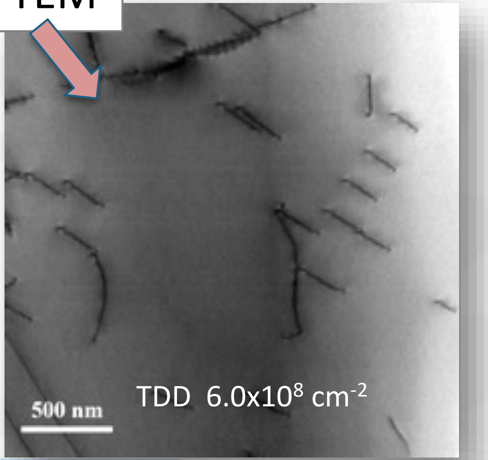
Cross-section TEM



TEM: Terry Holesinger, LANL

Plan-view TEM

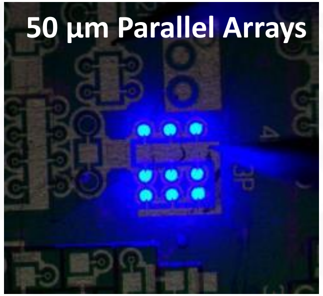




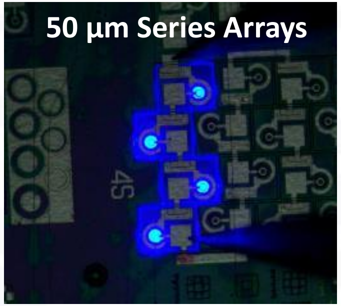
- *First-in-the-world* epi-GaN fabricated completely on a polycrystalline metal foil
- Surface roughness < 1 nm
- GaN TDD of mid to high $10^8/\text{cm}^2$

GANOX LEDs on Metal Foil

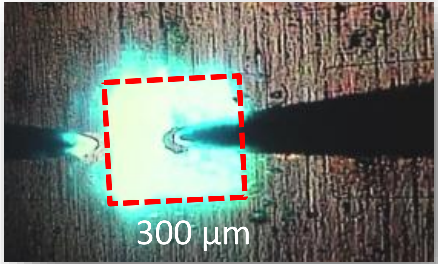
- First LEDs demonstrated: 70% of IQE from PL compared to sapphire LEDs
  - ➢ There is plenty of room for improvements: Better lattice match, optimize GaN growth, optimize reflectance, optimize planarization, can control miscut angle
- Mechanical lexibility demonstrated down to radius of 7 mm

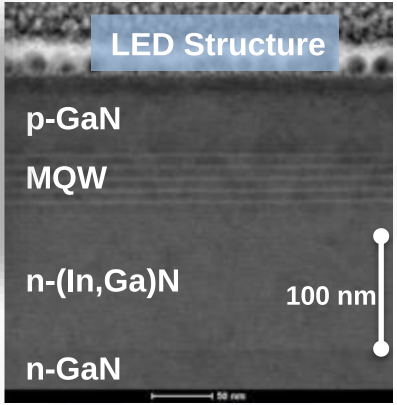


50 µm Parallel Arrays

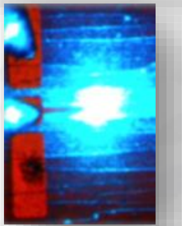


50 µm Series Arrays

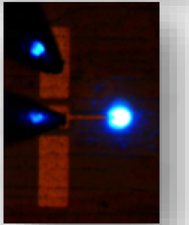




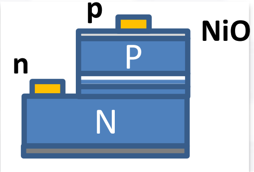
LED Structure

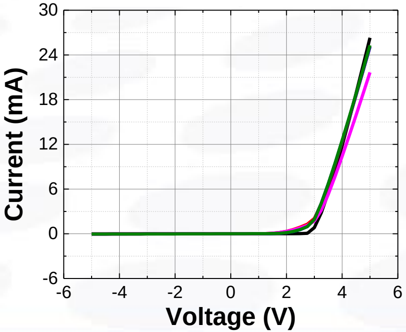


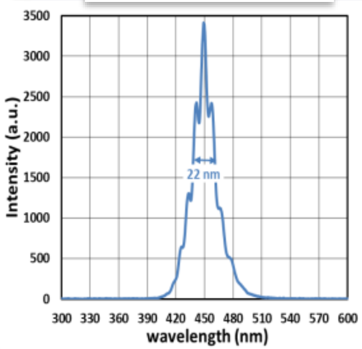
10 µm LED



30 µm LED

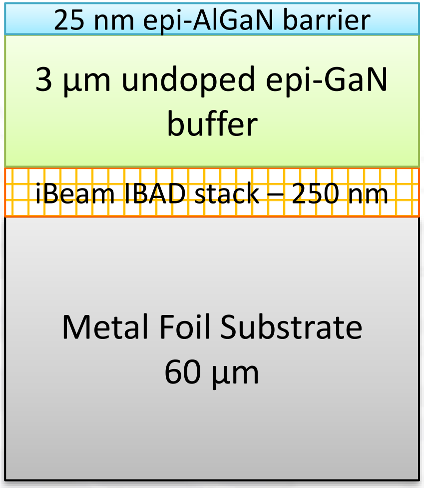




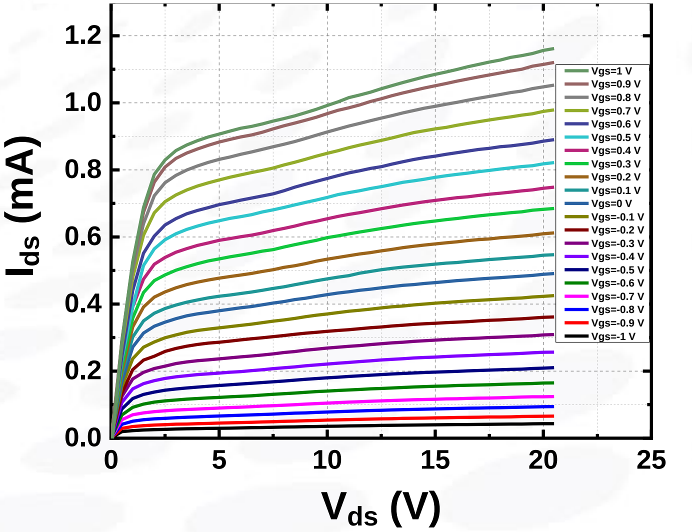


First Transistor Device Fabricated using GANOX

First-in-the-world demonstration of a GaN/AlGaN HEMT on a metal foil (2019)



20 µm gate HEMT Device on Metal Foil Substrate



Smaller device sizes than TFTs are possible, giving higher aperture ratios in an active matrix

How does making GaN devices with GANOX change the game?

Fabricating epi-GaN devices directly on IBAD substrates *fundamentally* changes:

1) How devices can be manufactured

- In large areas, no longer limited to small, rigid wafers
- ROLL-TO-ROLL (R2R) for certain substrates
- Simplifies backend fabrication (pre-packaged on substrate)

2) How devices (LEDs) can be utilized

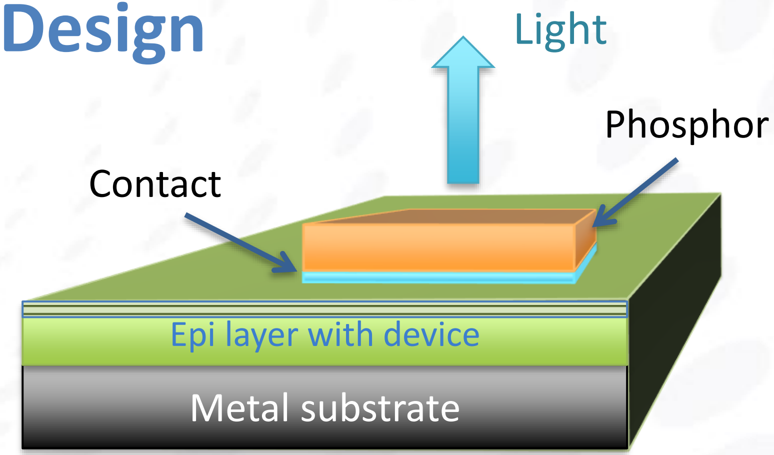
- In large areas, sheets of integrated devices

3) Volume of production and concomitant cost reduction

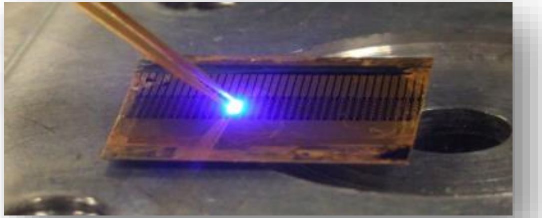
- Single factory can replace today's whole world-wide production volume (needed for microLEDs)
- Cost reduction in epi-GaN can be >20x

Key Features of the iBeam LED Design

- Fabricate GaN sheets on metal foil
- Very simple LED structure
- LED package fabricated directly on metal – completely new platform
- Greatly simplifies packaging steps
- Allows LED integration via printing technology on sheets of LEDs
- Flexibility and scale



Substrate is reflector and heat sink



Large-area LED Epi Deposition using GANOX

GANOX enables large-area substrates:

1) **Large area deposition on rigid substrates such as glass or ceramics**

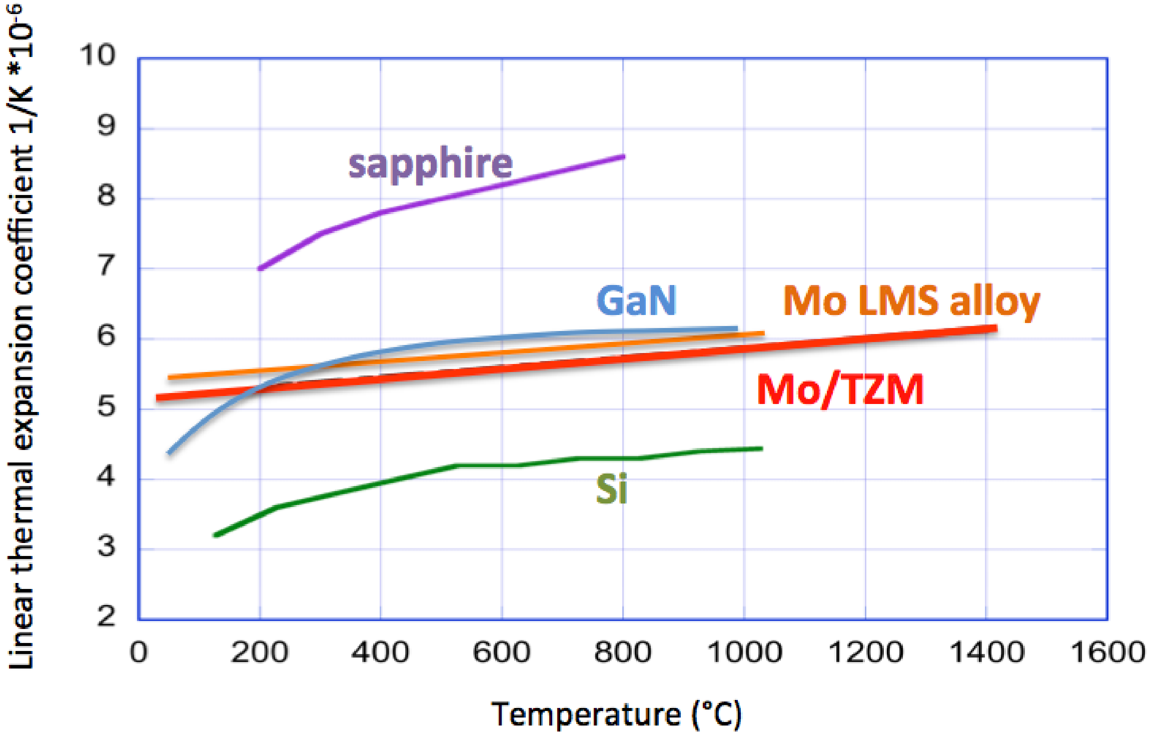
1) **R2R deposition on metal substrates**
   - Appropriate substrate can be used R2R (5 orders of magnitude scale up)
   - Thermal advantages of metal substrates

Mo alloy foil substrate is a good CTE match to GaN

- Coefficient of thermal expansion (CTE) of the molybdenum alloy can be engineered to match GaN as closely as possible

- Standard single crystal substrates are not nearly as good a match

- This yields GaN films that are not stressed as they are on single crystal wafers

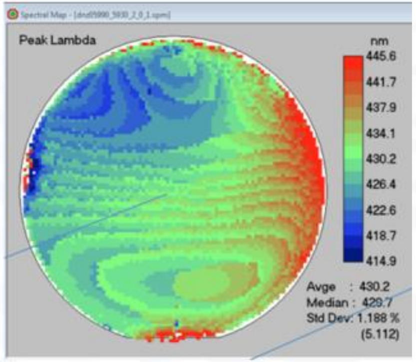


Metal substrate is an excellent thermal conductor

- **Mo metal is a 25x times better** thermal conductor at GaN growth temperature (~1000°C) compared to sapphire

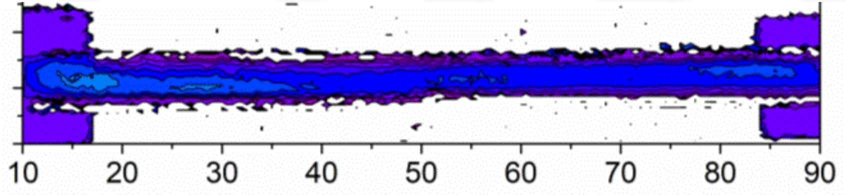
InGaN LED wavelength uniformity comparison

PL mapping of LED 2” Sapphire Wafer



- 5 cm sapphire wavelength variation (Sandia reactor): ± 10 nm

PL map of iBeam LED across 9 cm Metal Tape in same reactor



- 9 cm metal foil: ±6 nm
- **Improved uniformity using a metallic substrate!**

Future of GaN devices: Roll-to-Roll Manufacturing

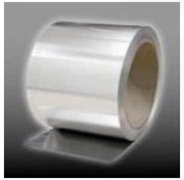
Source: Cree Inc.

PAST

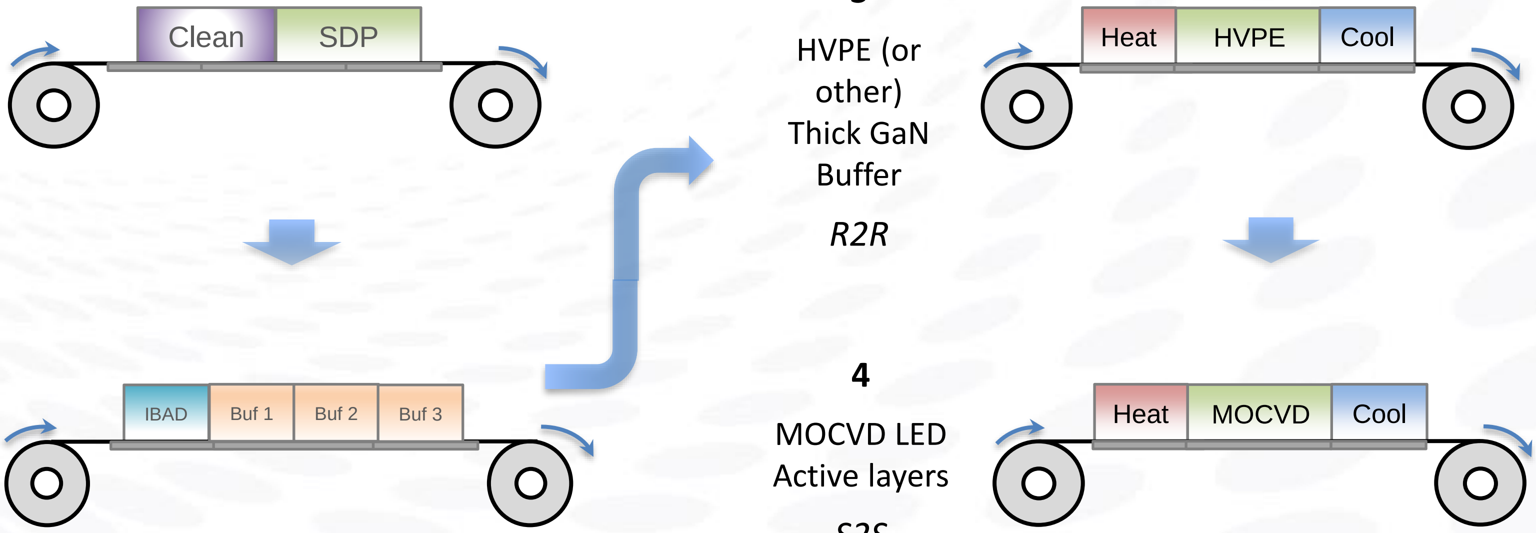
- GANOX process scales GaN production to **kilometer lengths**
- Enables low-cost doubling of global LED capacity needed for microLED displays
- Ultimate Scale-up: reduce Epi cost by >20x
- Metal substrate improves LED wavelength uniformity in production

Example: R2R Deposition system from PVD Products

FUTURE



R2R Process Steps for GANOX Technology



1

Clean + SDP
(planarize)

R2R

2

IBAD + PVD
Buffers

R2R

3

HVPE (or
other)
Thick GaN
Buffer

R2R

4

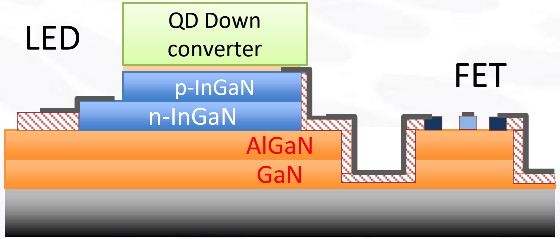
MOCVD LED
Active layers

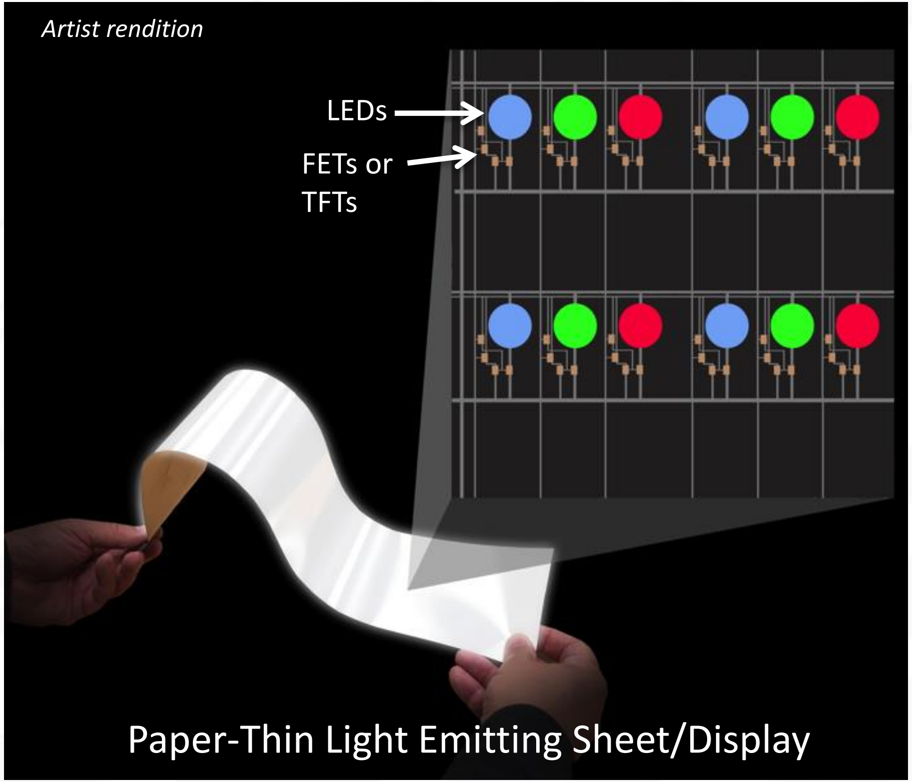
S2S

Step and Repeat

iBeam's GANOX Technology for microLED Display

- **Monolithic integration** of LEDs for µLED displays with NO TRANSFER
- Yield and Reliability improve greatly compared to mass transfer approaches
- Overlayed TFTs or epi-integrated GaN transistors to control LEDs
- QD downconversion for red and green colors, easily exceeding DCI-P3 gamut
- **Paper thin and flexible substrate**

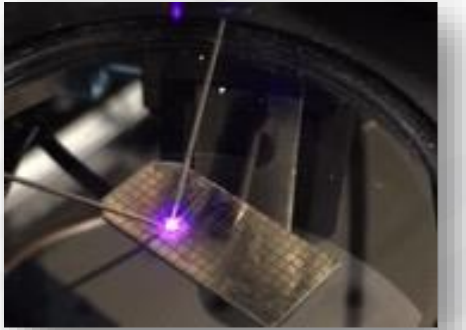


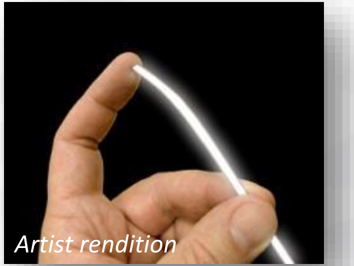


Paper-Thin Light Emitting Sheet/Display

IBAD Substrate: A completely new platform for LEDs

- We demonstrated the **first InGaN LEDs and GaN/AlGaN HEMTs** fabricated directly on metal foil using Ion Beam Crystal Alignment (IBAD)
- IBAD templates are a path to Large-area deposition of GaN and R2R Processing
- Epi-GaN cost can be significantly reduced and new functionalities and products can be enabled
- Materials improvement key challenge ahead
- We welcome collaborations from the community





Artist rendition

arpa·e CHANGING WHAT'S POSSIBLE Thanks to our sponsors at US DOE ARPA-E

Thank you!

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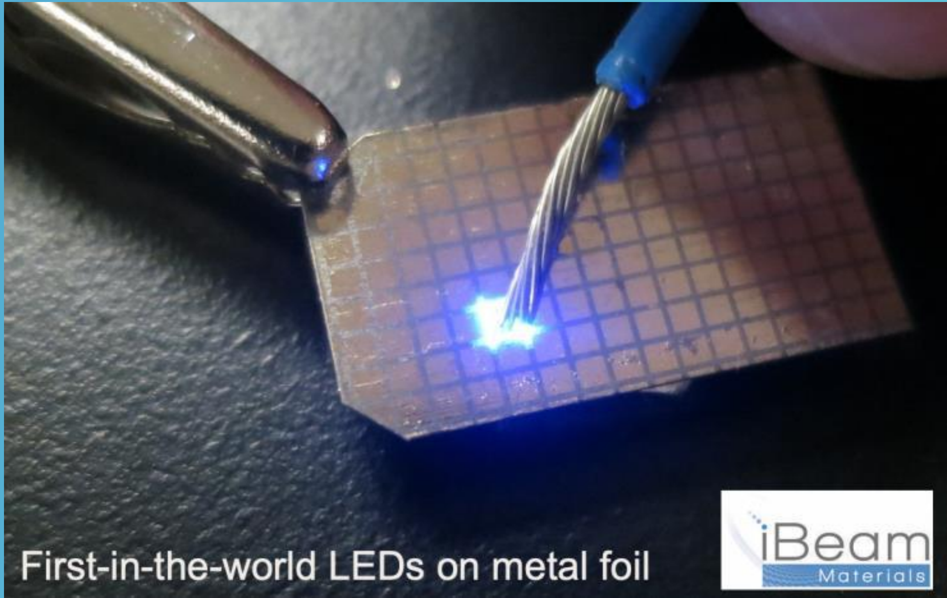
First-in-the-world LEDs on metal foil

Q&A

For questions or advice:

James Greer, Ph.D.
jgreer@pvdproducts.com
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Innovative Techniques and Applications for Gallium Nitride Devices

Thank you!

For questions or advice:

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pvdproducts.com

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iBeam Materials