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Hexagonal BN: Recent Advances and Potential for UV Optoelectronics

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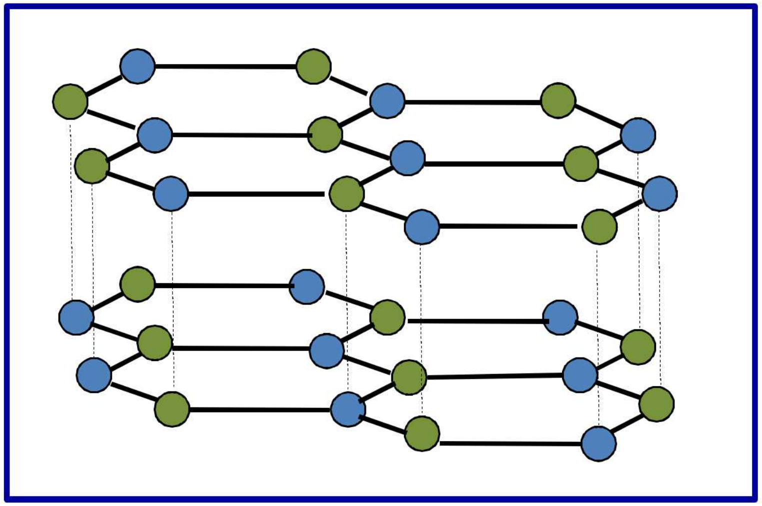
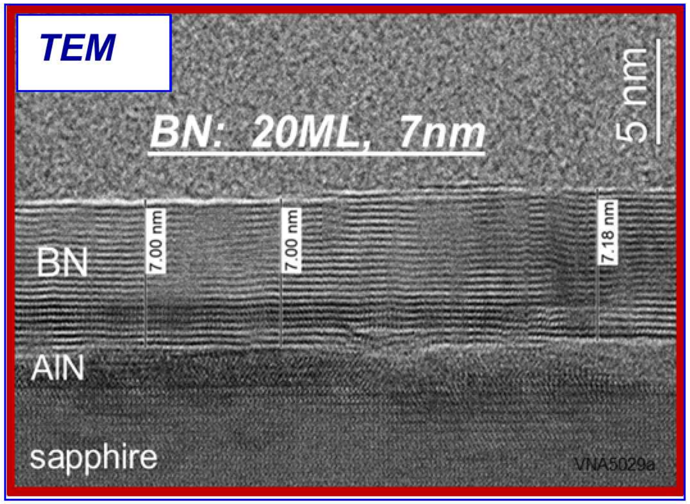
Sandia National Laboratories, Albuquerque, NM 87185





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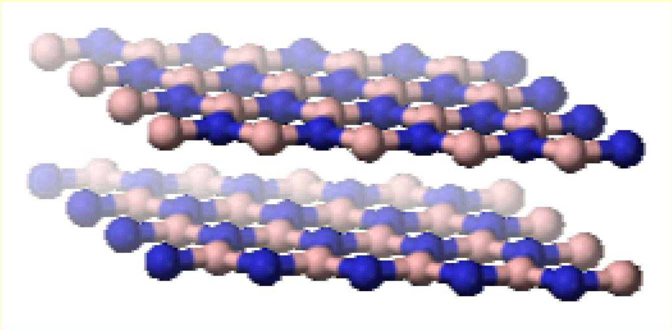
Research and Applications of Photonics in Defense (RAPID), Aug 19-21 2019

Outline

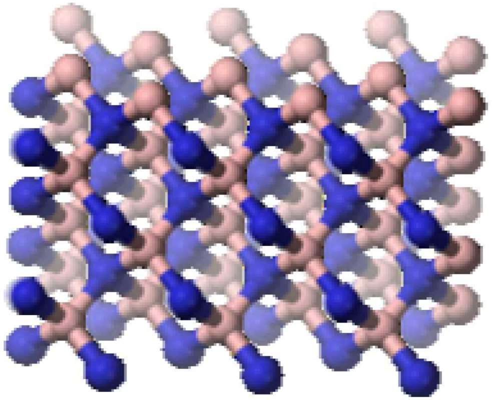
- Photonics applications for hBN
- Distinctive properties of hBN as a deep UV emitter
- Advances toward manufacturable, large-area hBN
- Comparison to other UV emitter candidates
    - emission wavelength tunability
    - p-type doping
- Potential for hBN/AlGaN heterostructure optoelectronics
- Summary

Crystal Forms of Boron Nitride

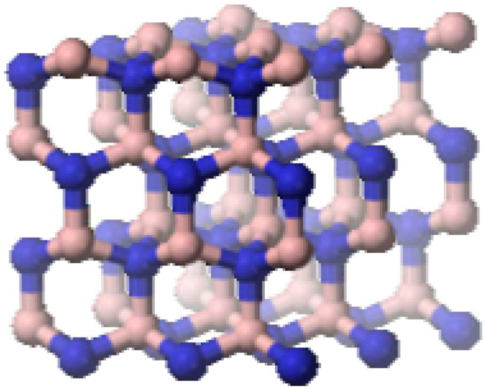
Hexagonal: Analogous to Graphite



Cubic



Wurzite



Figures from Wikipedia

Hexagonal form most chemically stable

Atomically-thin hBN has highly desirable properties

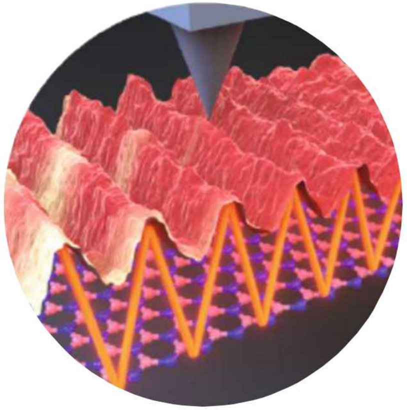
- Large dielectric breakdown strength (~8 MV/cm)
- High chemical stability, oxidation resistant
- Atomically flat surface

Important role in integration with other 2D materials (van der Waals heterostructures)

- Tunnel barrier (graphene/hBN/MoS_2)
- Encapsulant
- Substrate/buffer layer (highest mobility graphene)

Photonics Applications for hBN

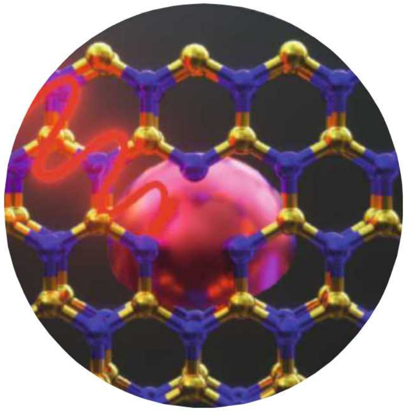
Infrared Nanophotonics



Natural hyperbolic material with strong, non-linear optical properties

→ Hyperlensing for bio-imaging, failure analysis, nano-scale IR photonics

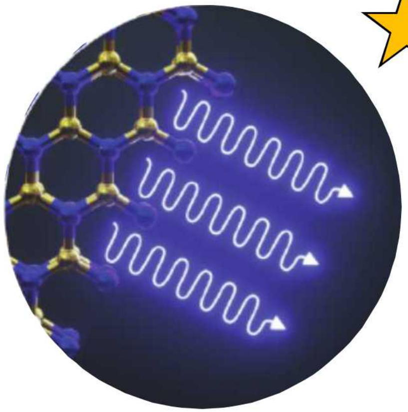
Single Photon Emitters



Defect mediated SPE; ultra-wide bandgap enables deep UV (~4 eV) SPE[2]

→ Quantum information applications including quantum cryptography

Deep UV Optoelectronics



Ultra-wide bandgap enables emitters and detectors in deep UV

→ covert communications, bio-agent sensing, water purification, sterilization

2. Bourrellier et al., Nanolett. 2016

Schematics from Caldwell et al, Nature Rev. Mat. 2019

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Potential for hBN as a DUV Emitter

ARTICLES

Direct-bandgap properties and evidence for ultraviolet lasing of hexagonal boron nitride single crystal

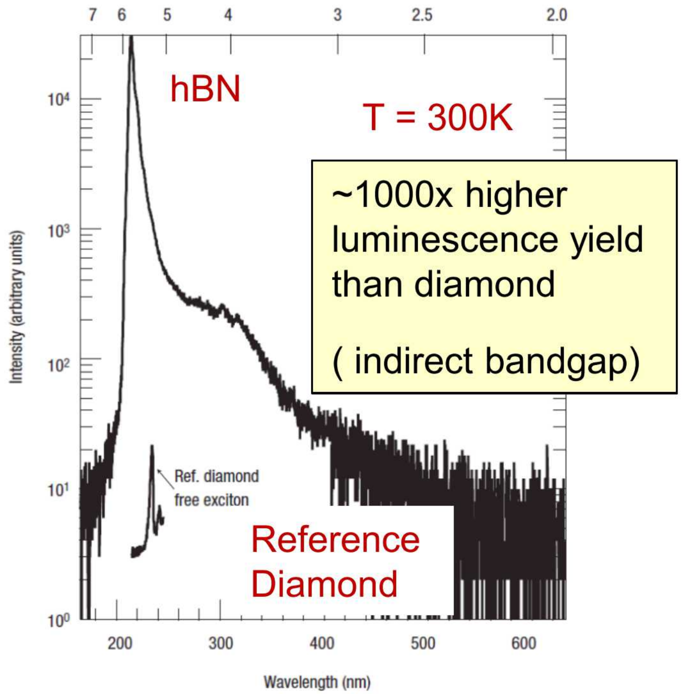
nature materials | VOL 3 | JUNE 2004

KENJI WATANABE*, TAKASHI TANIGUCHI AND HISAO KANDA

Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, 305-0044, Japan
*e-mail: WATANABE.Kenji.aml@nims.go.jp

- Small single crystals of hBN fabricated with Ba-B-N solvent under <u>high pressure and temperature (HPHT)</u>
- Made at National Institute of Materials Science (NIMS, Tsukuba, Japan)
  ➔ High-purity standard, even today

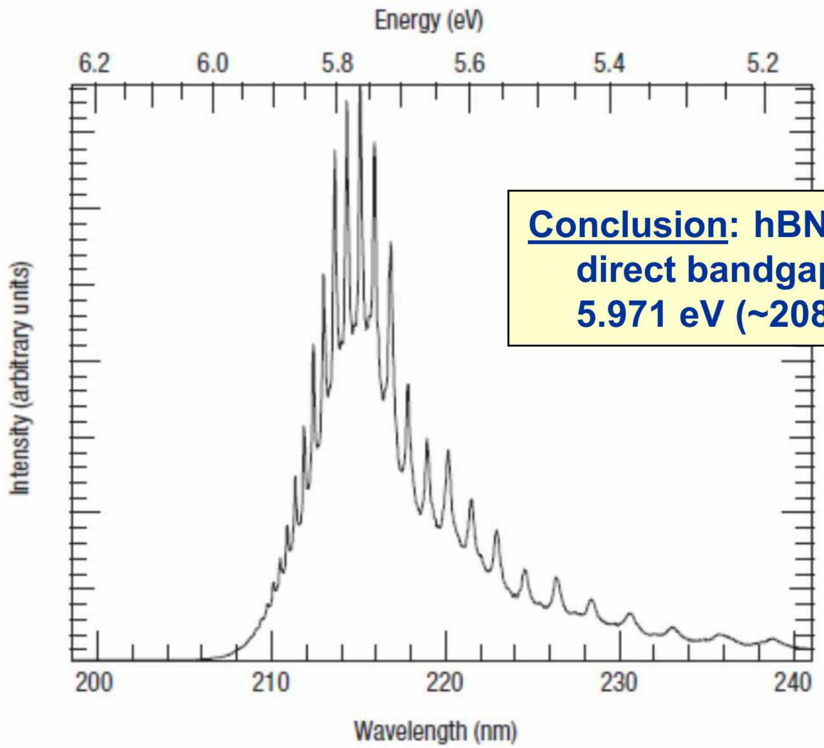
Room Temp Cathodoluminescence



~1000x higher luminescence yield than diamond

(indirect bandgap)

Electron-beam-pumped lasing



<u>Conclusion</u>: hBN has a direct bandgap of 5.971 eV (~208 nm)

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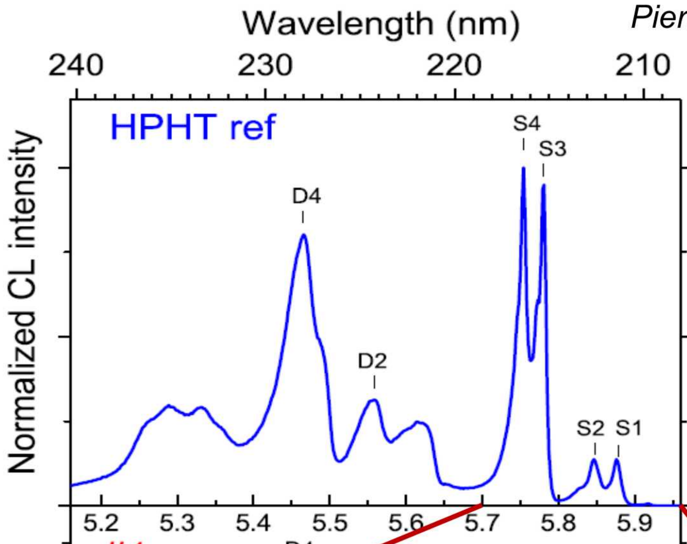
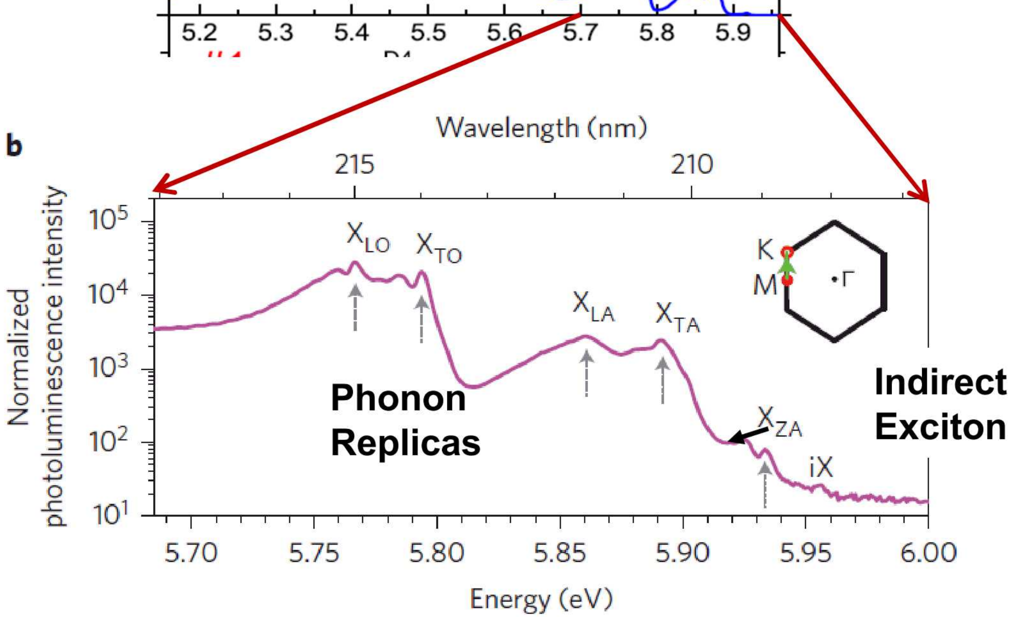
Recent evidence: hBN has an ***indirect*** bandgap

Low temp CL of HPHT hBN

Pierret, 2014

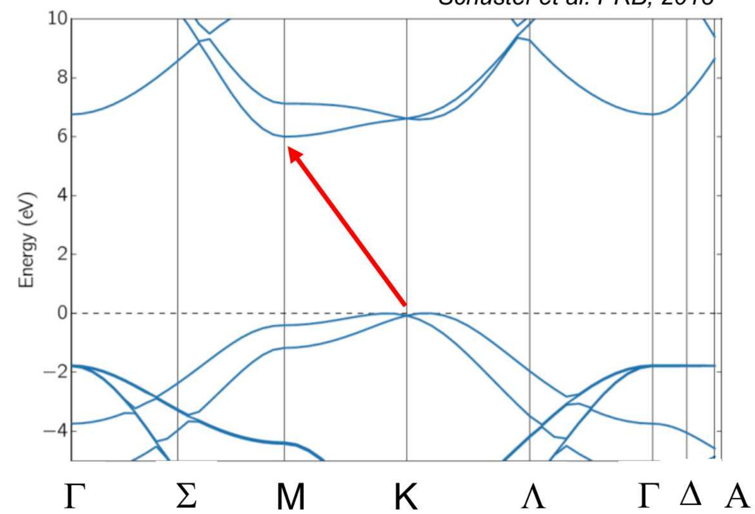




Cassabois et al., Nat. Photon 2016

Bandstructure of hBN

Schuster et al. PRB, 2018



Further evidence of indirect bandgap by:

- Angle-resolved photoemission spectroscopy (Henck et al., PRB 2017)
- Electron Energy-Loss Spectroscopy + Density Functional Theory (Schuster et al., PRB 2018)

Transition to direct bandgap at 1 monolayer reported, analogue to TMDs like MoS_2
(Elias et al., Nature Comm., 2019)

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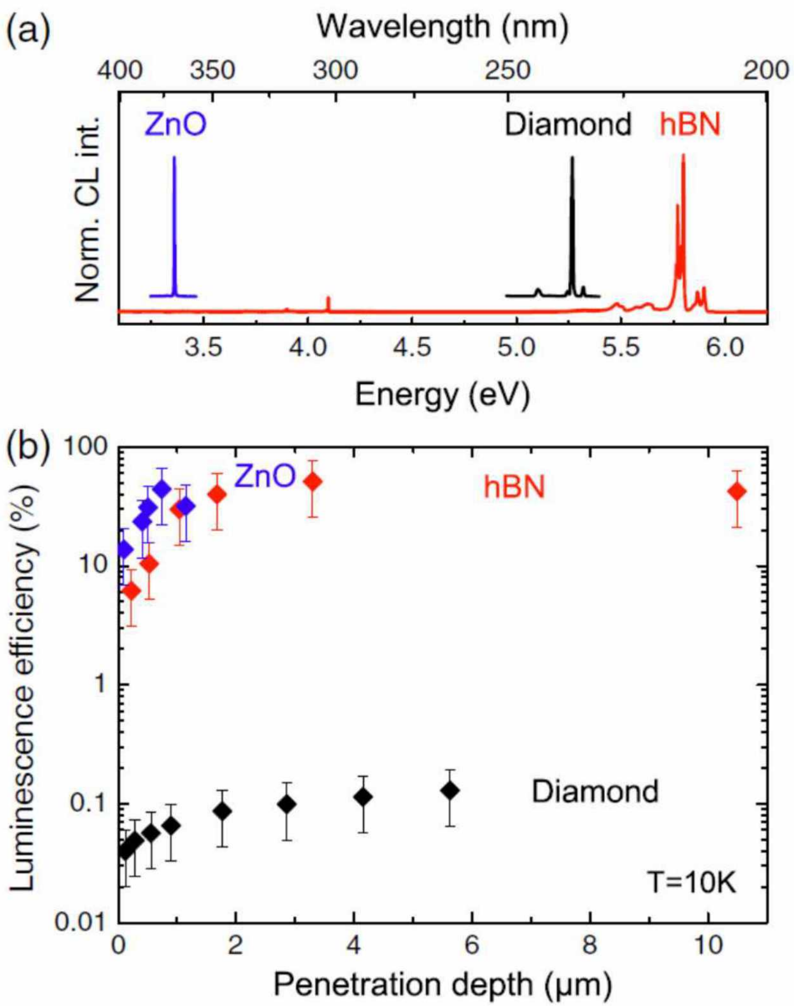
Measurement of hBN Luminescence Efficiency

Low Temperature CL

Schue et al., PRL 2019



- hBN has luminescence yield similar to direct bandgap ZnO (~ 50%)
- Highly unusual combination of indirect bandgap material with high luminescence efficiency!

UV emission dominated by excitons well above room temperature

Material	Exciton Binding energy (meV)
hBN	~ 300*
Diamond	80
ZnO	60
GaN	25
GaAs	4

*Schue et al., PRL 2019, other reported values ~130-700 meV

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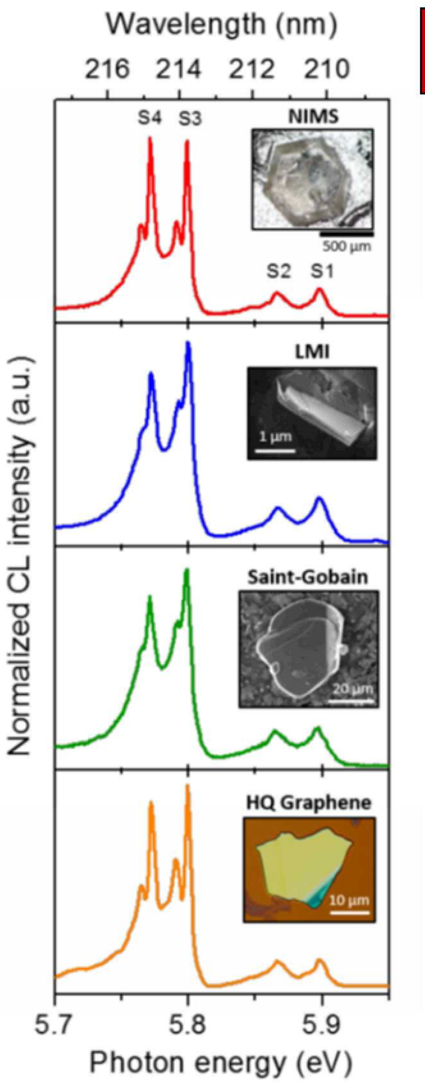
Towards large-area, manufacturable hBN

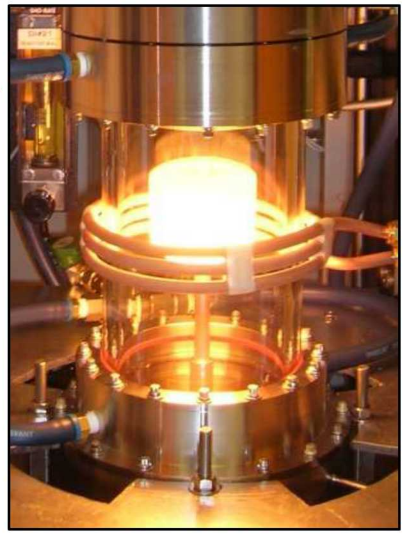
NIMS & Commercial Sources of hBN



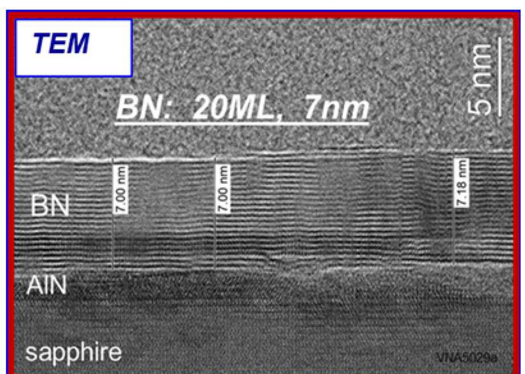
Schue, Cond Mat Matl Sci, 2016

Epitaxial growth

High-Temperature MOCVD System (up to ~ 1900°C)



- **Sapphire or SiC substrates (2" diam)**
- **Triethylboron (TEB) and NH_3 precursors**
- **N_2 diluent and carrier gas**
- **SiH_4 for Si doping**



Outstanding Questions for Epitaxy:

- Free-exciton-related emission at room-temperature?
- ML to few-ML thickness control?
- Large-area hBN with high quality surfaces for 2D heterostructures?

Reactor design:
Prof. Zlatko Sitar, NCSU

Earlier MOCVD work,
H. Jiang, TTU

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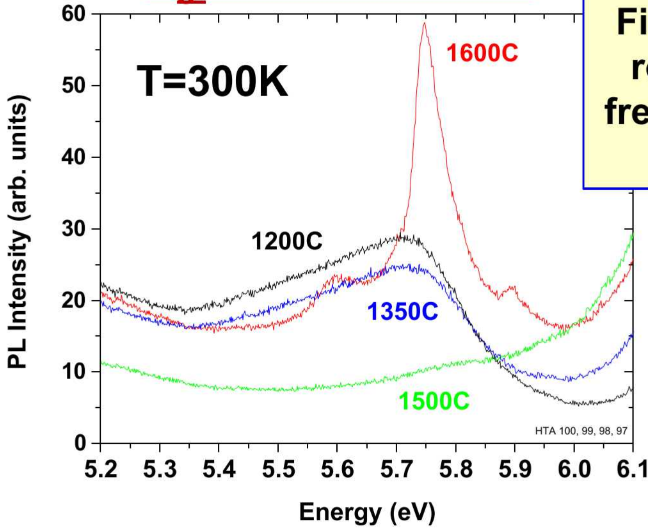
Impact of Growth Temperature on hBN Photoluminescence

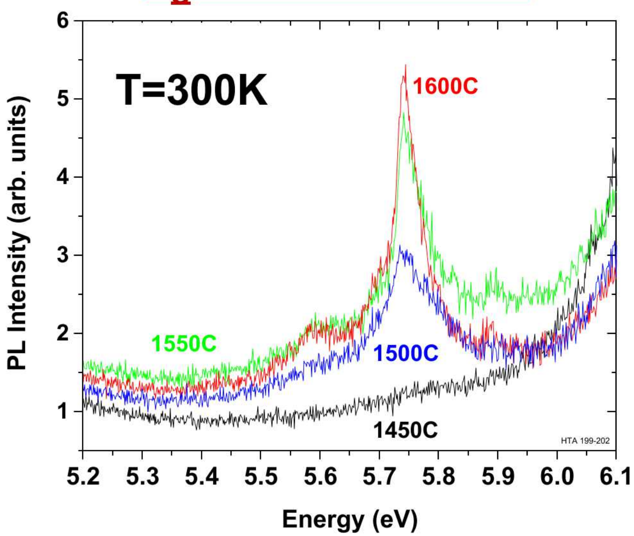
Laser excitation: ~198 nm Ti: sapphire

T_g = 1200-1600°C

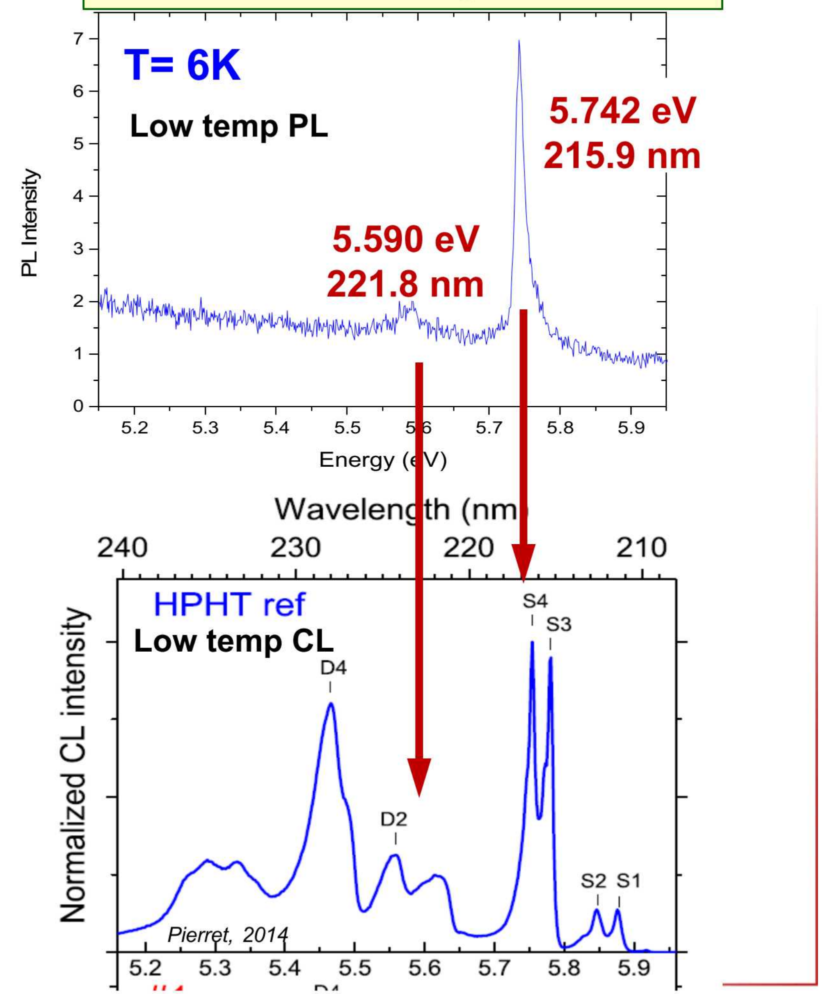


First observation of room temperature free (5.75 eV) exciton in MOCVD hBN

T_g = 1450-1600°C

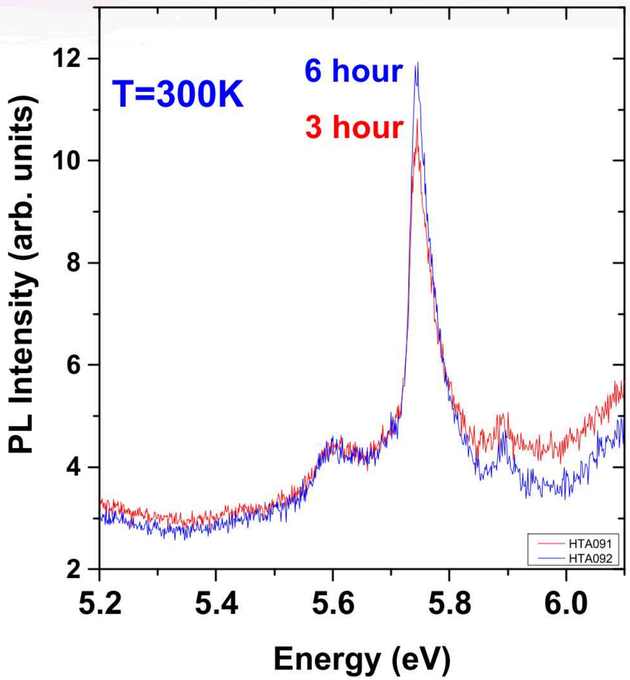


MOCVD hBN: Tg = 1600°C



MOCVD: Potential for Self-limiting Growth at high T_g

PL Measurements



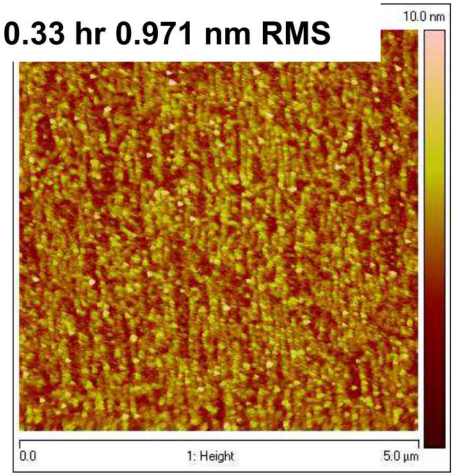
- Relatively little change in PL intensity over a large range of growth times
- Raman ratio (hBN/Sapphire) suggests only a few MLs even for 24 hours of growth
- Films roughen, largely due to increased number of larger particulates with longer growth times

Results from Raman Measurements

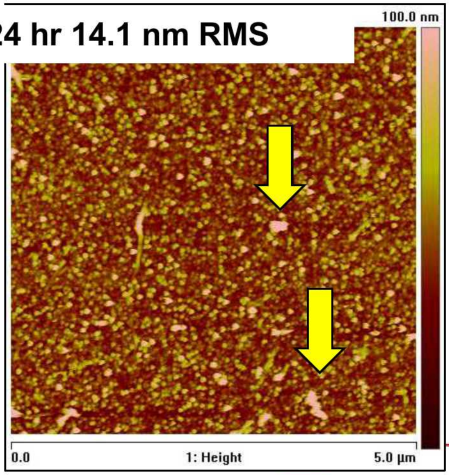
Growth Temp (°C)	Growth Time (hrs)	Raman peak ratio	STEM calibration (MLs)
1600	0.25	0.1	~1
1600	3	0.09	~1
1600	3	0.18	~2
1600	6	0.16	~2
1600	24	0.26	~3

AFM Measurements

0.33 hr 0.971 nm RMS



24 hr 14.1 nm RMS



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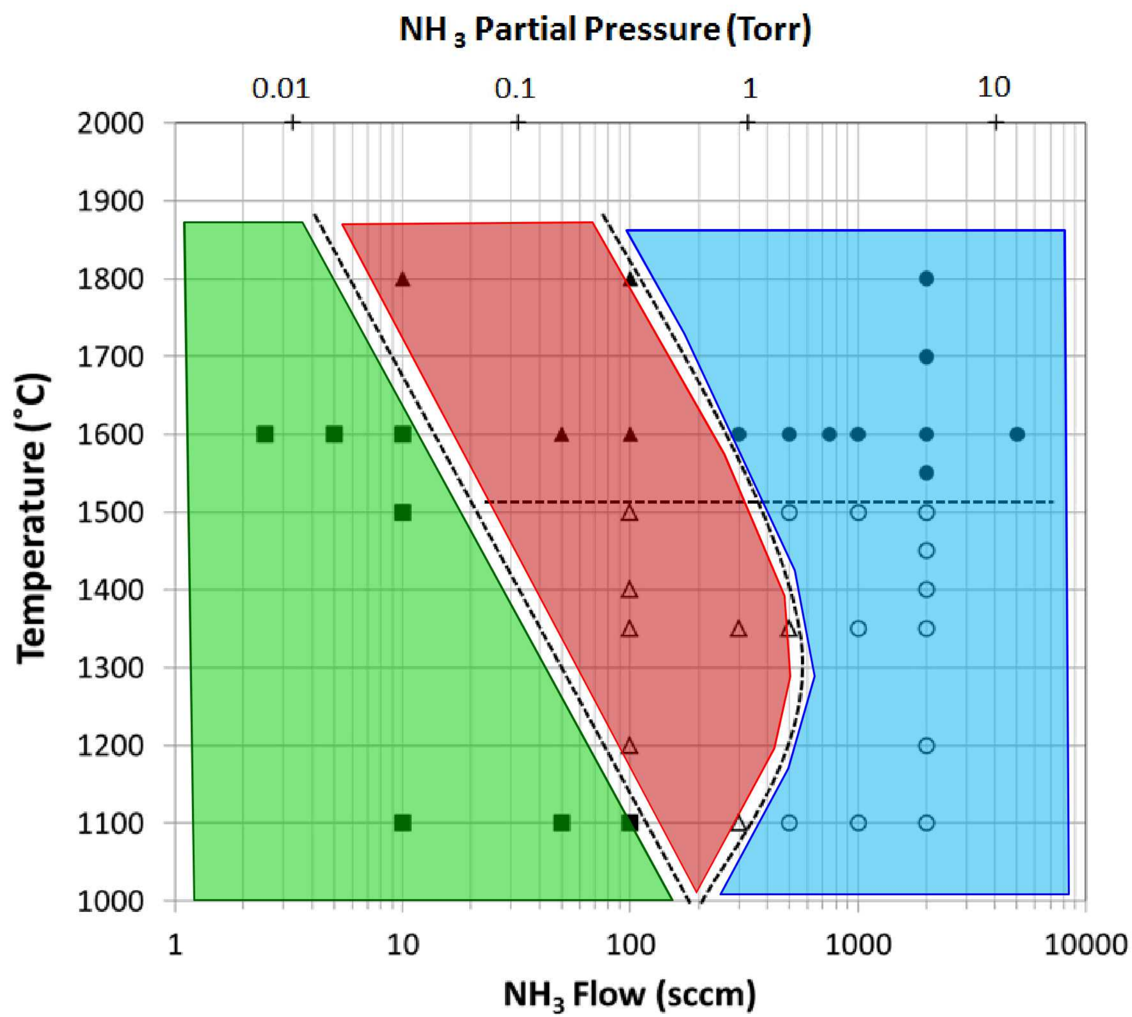
Growth parameter space for achieving few-ML-thick films

Growth Regimes

- Low NH_3
  - Thick films
  - Discolored films
- Intermediate NH_3
  - Thick films
  - Clear films
- High NH_3
  - Self-limiting films



→ NH_3 flow is the critical parameter, high Tg is not essential

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Possible Model: Langmuir-Hinshelwood

- **Competitive absorption of species that react on a surface**
- **Controlling reactions:**

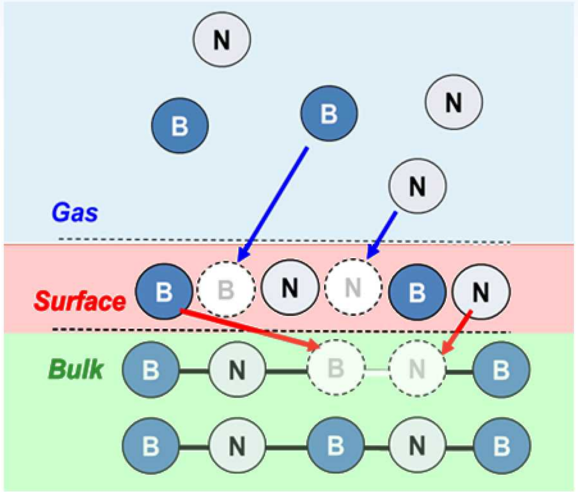
$$B_{gas} + Open_{surface} \overset{k_B}{\leftrightarrow} B_{surface}$$

$$N_{gas} + Open_{surface} \overset{k_N}{\leftrightarrow} N_{surface}$$

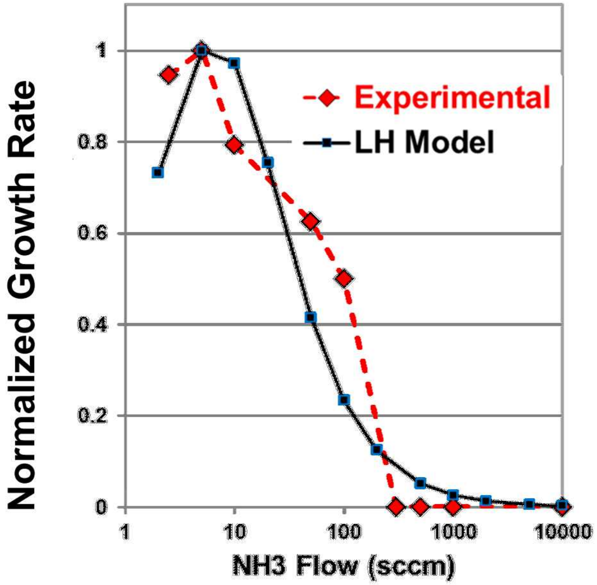
$$B_{surface} + N_{surface} \overset{k_{rxn}}{\longleftrightarrow} BN_{bulk} + 2Open_{surface}$$

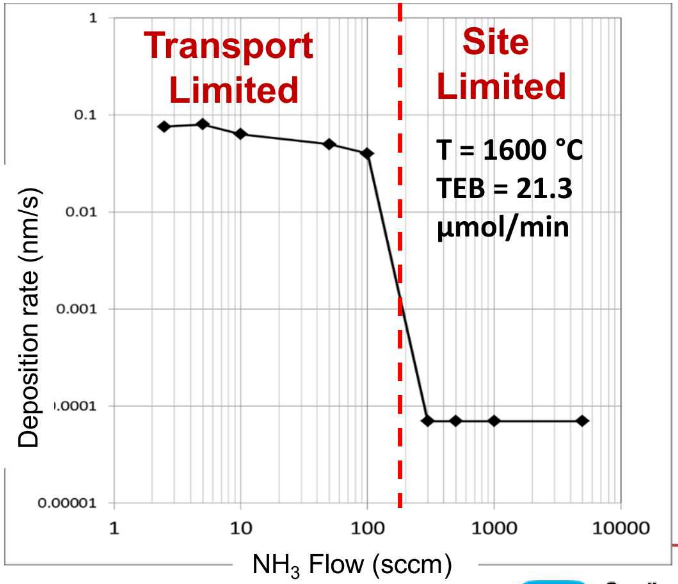
- **Growth rate:**

$$G = \frac{k_{rxn} k_B k_N p_B p_N \Gamma^2}{(1 + k_B p_B + k_N p_N)^2}$$



Model captures large decrease in growth rate from microns to monolayers per hour



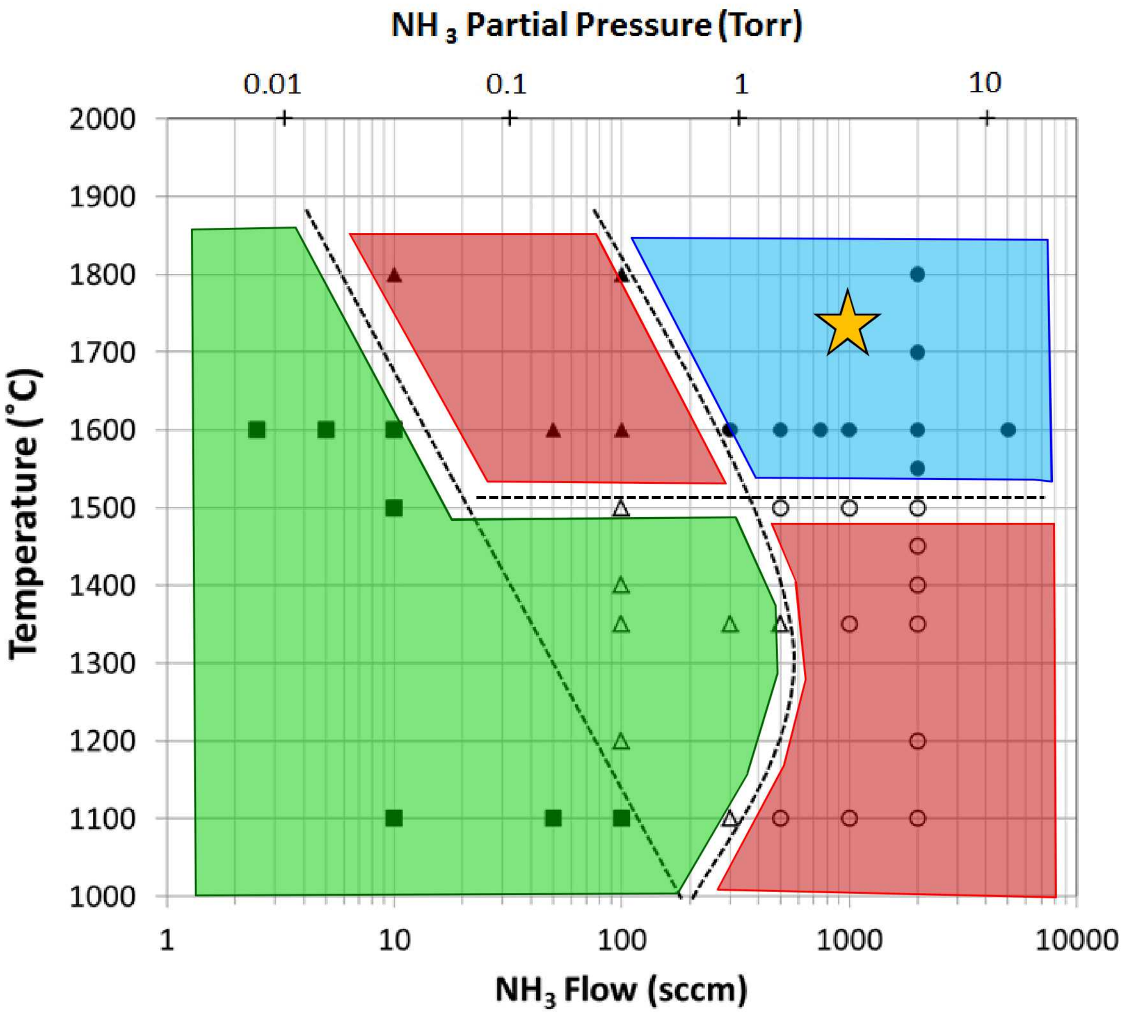


Correlation of Growth Conditions and Excitonic Properties

3 regimes in room temp PL

- No exciton emission
- Defect bound exciton
- Free exciton

RT PL



High NH_3 and high temperature needed for RT excitons

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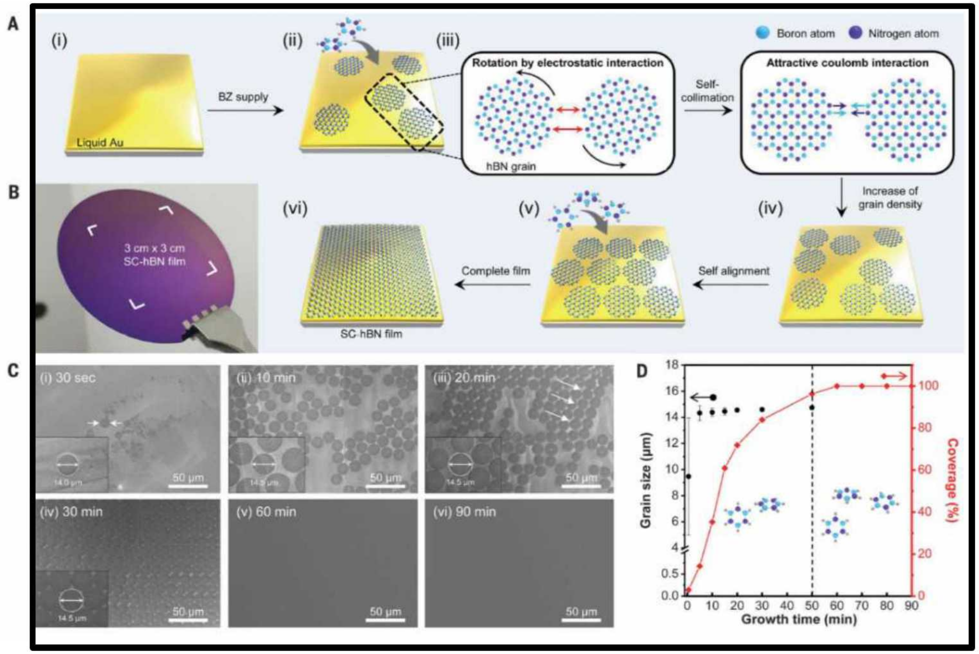
Other recent advances in growth of large-area hBN

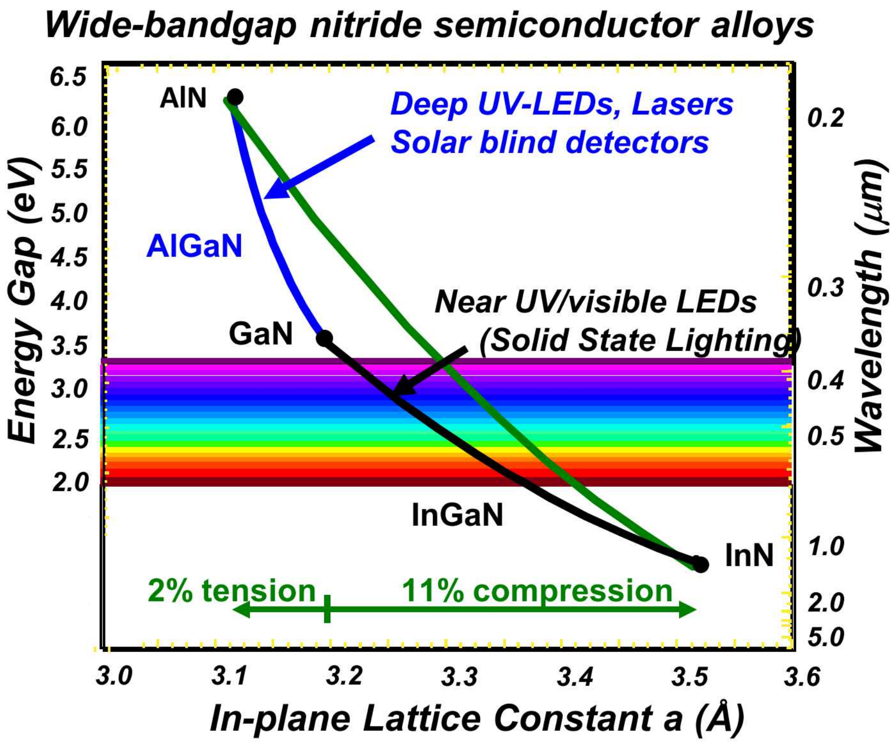
- High-temperature Molecular Beam Epitaxy (Vuong et al., 2D Mat. 2017; Laleyan et al., Opt. Express, 2018)
  ➔ high-optical-quality monolayer and bulk hBN growth, single-crystal regions
- CVD on Single Crystal Cu substrates (Wang et al., Nature, June, 2019)
  ➔ 10 x 10 cm^2 monolayer, single-crystal hBN
- Self-collimated Grain Formation on Liquid Gold by CVD (Lee et al., Science, 2018)
  ➔ 3 x 3 cm^2 monolayer, single-crystal hBN



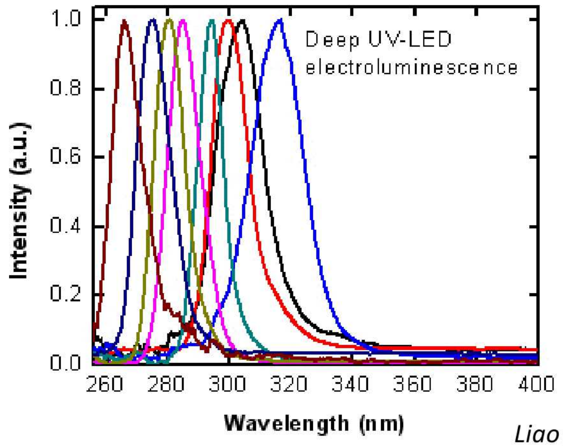
- Au film on Tungsten foil substrates
- Growth temperature of ~ 1100°C
- Grains form, self-align and coalesce on liquid Au template

Distinctive Properties of AlGaN Alloys for UV Optoelectronics

- **Amazing bandgap range!**
  → 3.4-6.2 eV, customizable with alloy composition control, QW design



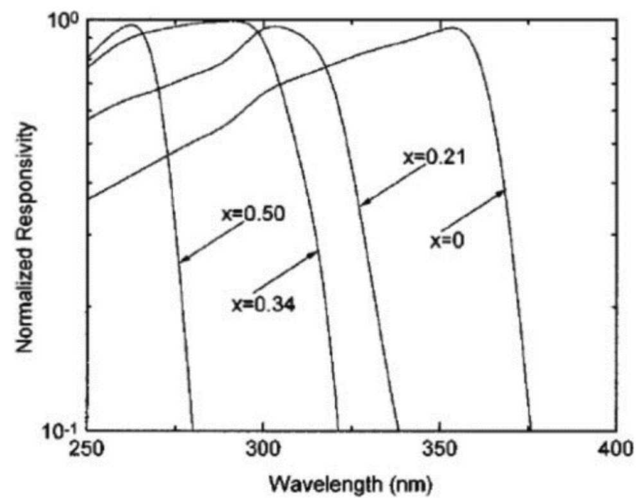
Unique Optical Sources



Liao (BU), APL 2011

Custom, Reconfigurable Multi-λ

Tailorable UV detectors



Khan Nat Photonics, 2005

All "Blind" to visible light

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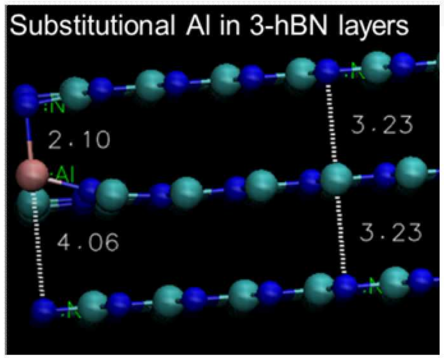
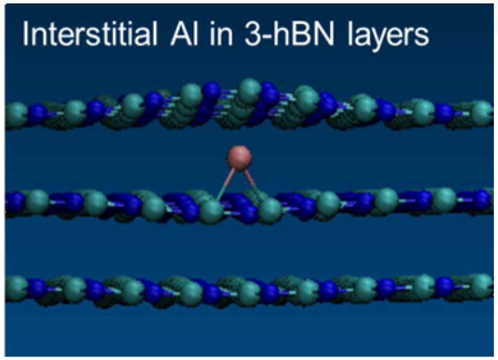
Potential for hBN-Alloys and tunable UV properties

Density Functional Theory (C. Spataru, SNL)

Modeling shows <u>high activation energy</u> for formation of B-rich BAlN & BGaN alloys



$\Delta E = 3.06$ eV

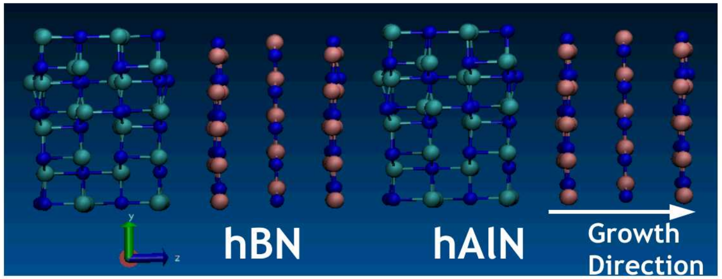


$\Delta E \approx 5$ eV

Spataru et al., Appl. Phys. Lett., **114** 011903 (2019)

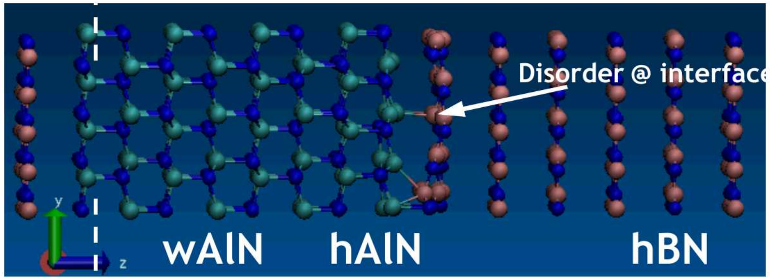
<u>Modeling of short-period hBN-AlN superlattices for digital alloys</u>

$5x5(hBN)_3$ - $4x4(AlN)_4$: 1nm/1nm



- Hexagonal AlN for ≤ 1 nm thick layers
- Predict insulating behavior & Type II energy band alignment
- Optical gaps down to 5.2 eV (~238 nm)

$5x5(hBN)_6$ - $4x4(AlN)_8$: 2nm/2nm



- Mixed w- and h-AlN, disorder at interface with hBN for ≥ 2 nm-thick AlN
- Predict metallic behavior (w/o dopants) due to interface charge

Modeling shows potential for tuning with ultra-thin-layer SLs

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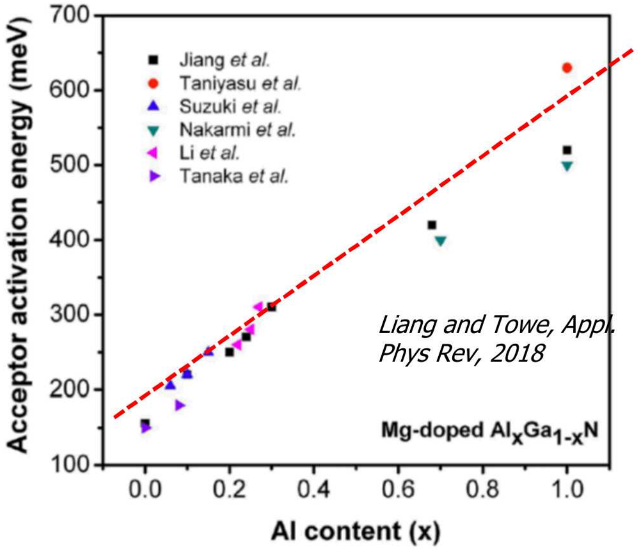
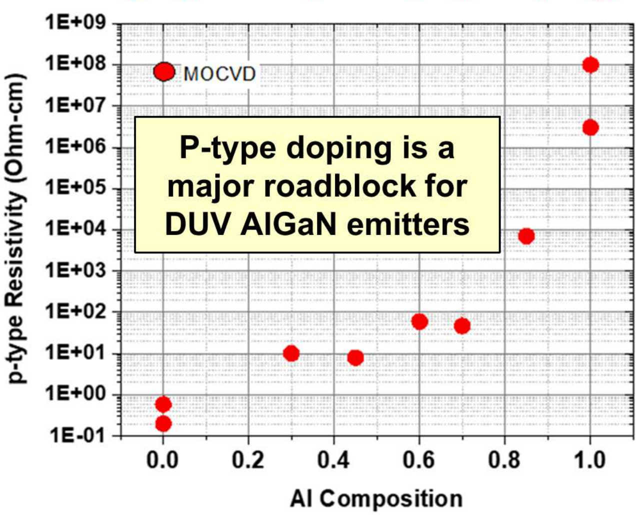
Potential for p-type doping

$Al_xGa_{1-x}N$

Mg Activation Energy vs. Al %



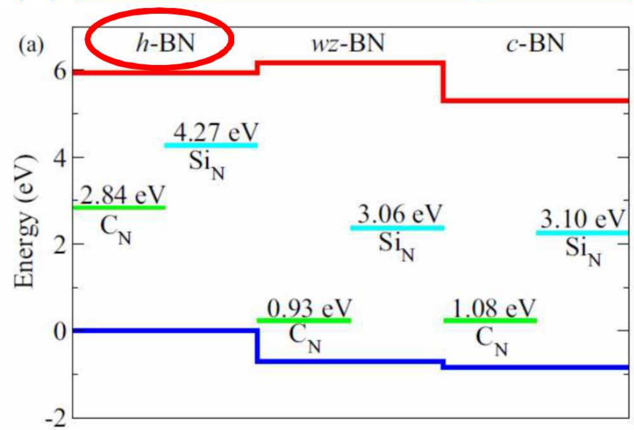
Highlights of reported p-type $Al_xGa_{1-x}N$



hBN

Theoretical Predictions (DFT)

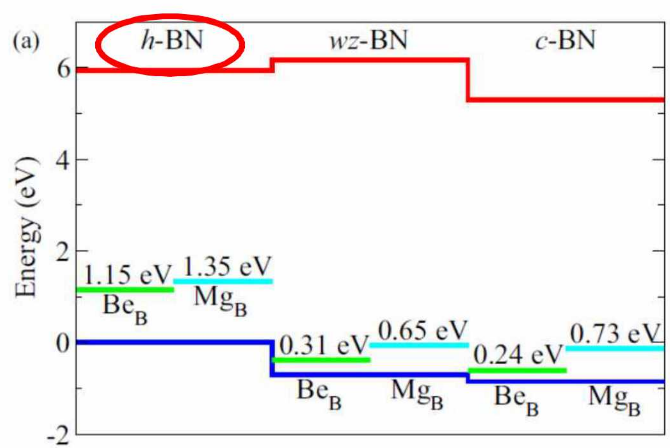
(a) C or Si on the Nitrogen Site



Deep Acceptors for all crystal polytypes

➔ Expect p-type hBN not possible

(b) Be or Mg on the Boron Site



Deep Acceptors for hBN, Be relatively shallow for c-BN and wz-BN

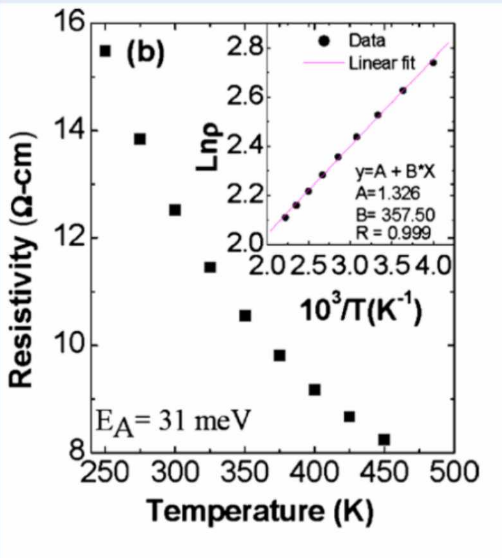
Weston et al., PRB 2017

Experimental Reports of p-type hBN

Mg-doping (MOCVD)

AlN: $E_A \sim 500$ meV

hBN: $E_A \sim 31$ meV



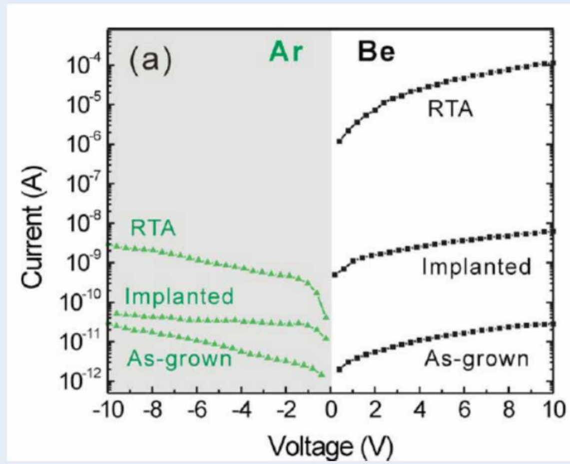
Cp_2Mg: Mg ~ 1e19 cm^{-3}

$\rho \sim 12\ \Omega$cm (300 K)
p ~ 1e18 cm^{-3}
$\mu \sim 0.5\ cm^2/Vs$

Dahal et al., APL, 2011

Be-implantation & annealing

hBN: $E_A \sim 210$ meV



- hBN by magn. sputtering
- 50 keV Be implant
- ~1e15 cm^{-2} fluence
- 1000°C, 1 min RTA (N_2)

p ~ 3e19 cm^{-3}
$\mu \sim 27\ cm^2/Vs$

He et al., APL, 2009

B-vacancies (MBE)

hBN: E_A not reported

- Growth conditions to promote B-vacancies → low T, high N flux

p ~ 7.5e19 cm^{-3}
$\mu \sim 16\ cm^2/Vs$

Laleyan et al., Nanolett 2017

Different approaches: Not yet reproduced by other groups

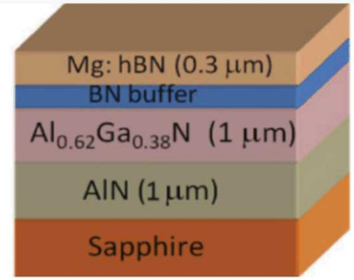
p-hBN /n-AlGaN Heterostructures

MOCVD (Mg: hBN, TTU)

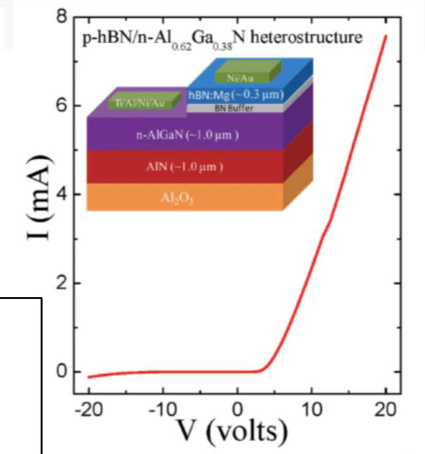
p-hBN advantages over p-GaN/AlGaN:

- Potentially much lower resistivity
- DUV transparent (vs. absorbing p-GaN)
- Improved hole injection, e- blocking
- Improved light extraction (low n)

Modeling: Dong et al., Physica E, 2015

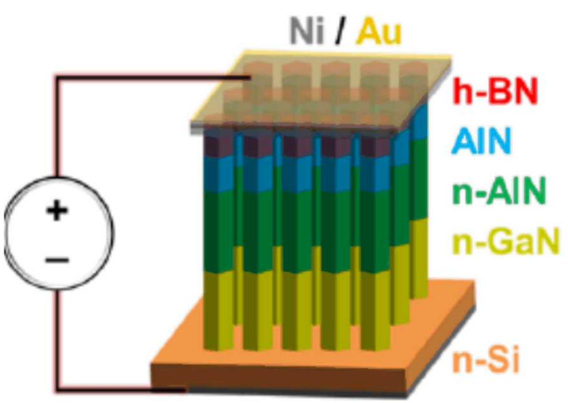


- **7.5 mA @ 20 V**
- **Rectifying but no EL reported**

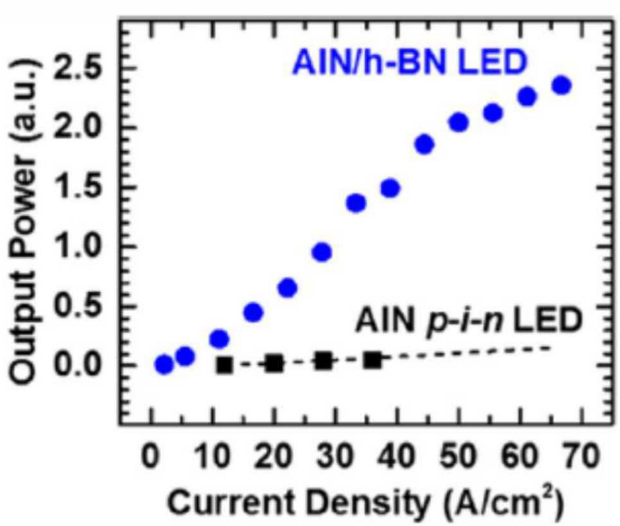


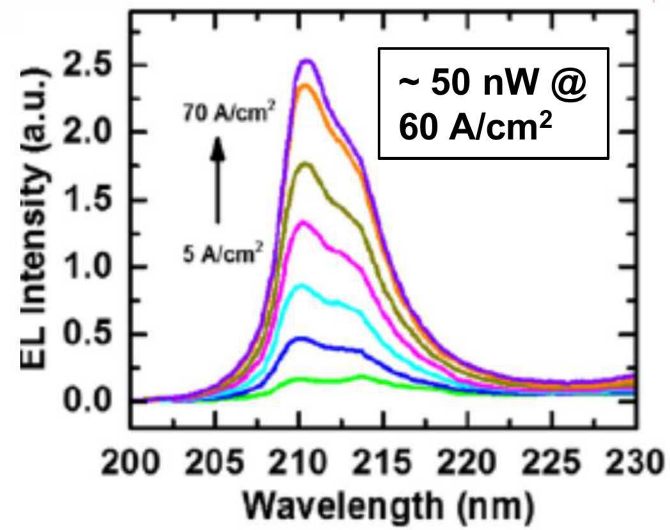
Majety et al., APL, 2012

First DUV EL from hBN/AlGaN heterostructure LED (MBE, V_B: hBN, U Mich)



Laleyan et al., Nanolett 2017





Significant performance improvement over AlN Nanowire p-i-n

Summary

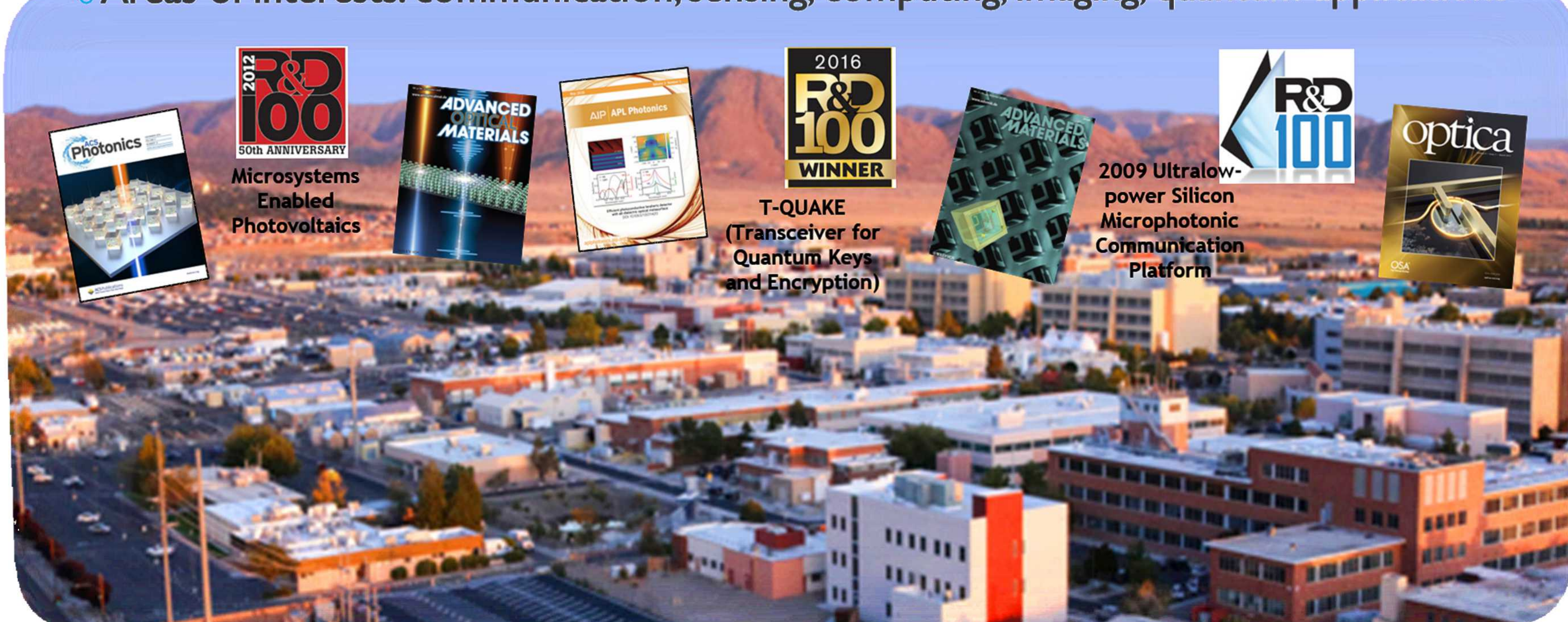
- Well beyond utility in 2D heterostructures, hBN is maturing as a promising material for photonics applications spanning near IR to deep UV
- Rapid, recent advances have been made in understanding the unique nature of this highly-luminescent but indirect-bandgap material
- Decisive progress has been made toward more manufacturable, large-area hBN through multiple approaches (MOVCD/CVD, MBE)
- On-going studies are exploring exciton-phonon interactions, bandgap tunability, p-type doping, nature of defects and origins of single-photon emission, and many other topics of interest.
- Initial demonstrations of p-hBN/ n-AlGaN devices suggest a promising, hybrid approach for next-generation UV emitters

- Back up slides

SANDIA's NATIONAL SECURITY PHOTONICS CENTER

Serve the nation as a center of excellence for national security photonics through scientific excellence and innovations and leading-edge integrated photonics solutions

- >60 photonics staff (plus postdocs and students) with expertise in device design, modeling, simulation, epitaxy, device fabrication, integration, assembly, and test
- Partnership with government agencies, industry, and universities
- Technology transfer to industry
- Areas of interests: communication, sensing, computing, imaging, quantum applications



SANDIA's MESA COMPLEX

MESA= Microsystems Engineering, Science and Applications

Co-jointed Fab Facility

- Silicon Fab
- Compound Semiconductor Fab

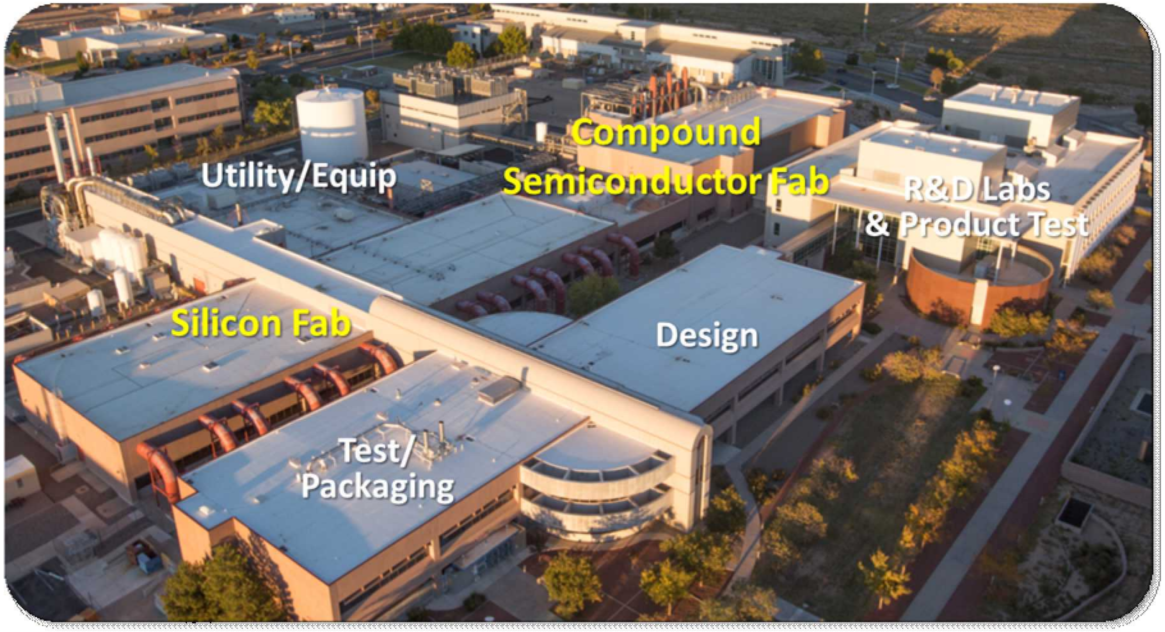
Charter:

- design, develop, fabricate, qualify, and produce at low-volume for DOE applications
- conduct leading edge research

Currently dozens of products:

- ASICs, III-V SSICs, MEMS, FPAs, RFICs, Optoelectronics

MPW services available



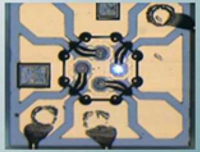
Co-located R&D and Production

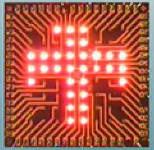
SANDIA's PHOTONIC MICROSYSTEMS

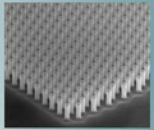
National Capabilities for Advanced Photonics R&D: design, model, fab, package, and test

Materials: Silicon, III-V (Phosphides, Arsenides, Antimonides, Nitrides), Lithium Niobate, Graphene, etc.

Sources

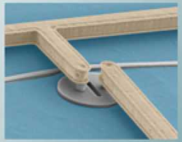

Single-Frequency Tunable VCSELs


High Efficiency VCSELs

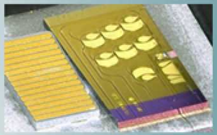

Nanowire Laser

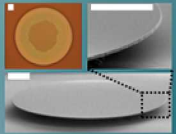

High power GaAs laser

Control / Manipulation

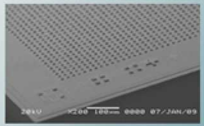

Resonant Optical Modulator/Filter


Array Waveguide Grating Channelizing Filter

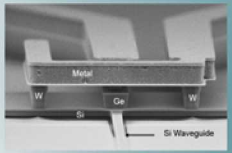

RF Channelizing Filter


LiNbO3 Freq. Converter

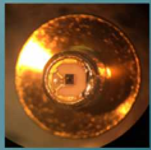
Detection


Infrared Detector


Plasmonic Perfect Absorber



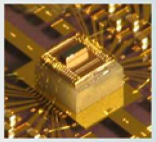
Germanium Detector on Silicon


X-ray Detector

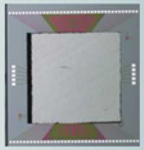
Chip-scaled MicroSystems

Heterogeneous Integration

III-V on CMOS

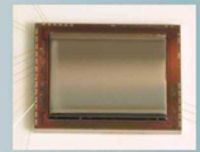


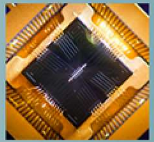
CMOS on Si Photonics

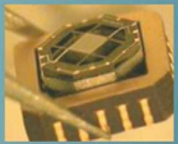


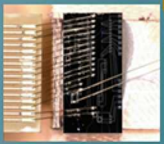
High-speed Optical Transceivers

nBn on CMOS


IR Focal Plane Array w/ ROIC


Quantum Surface Ion Trap


Atomic Clock


Quantum Key Distribution Transceiver

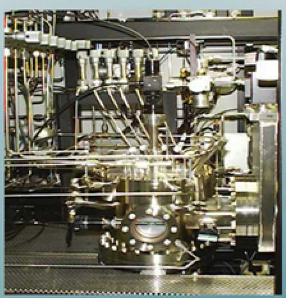

Photovoltaics w/ microlenses


High-speed All-Optical Logic

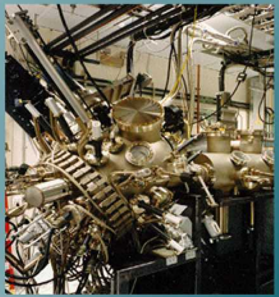
III-V OPTOELECTRONICS CAPABILITIES

Custom, trusted, low-volume, high-reliability products for harsh environments when industry is unwilling or unable to deliver

Custom Epitaxial Growth



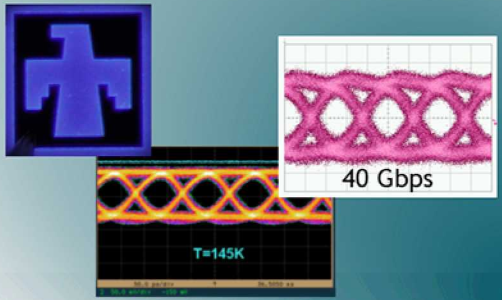
MOCVD:
As, P, Sb, Ga, In, Al, Zn, Si, Te, N, H_2



MBE:
Sb, Ga, As, In, Al, Si,Be,Te, N, H_2

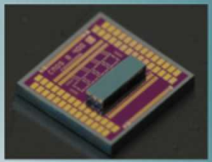
Device Design, Fabrication, and Characterization

- Device design, modeling, simulation
- TRL 1-6+: create, develop, prototype
- Fabrication: 16,600 sq. ft Class 10/100 Cleanroom
- Optical Comm testing to > 40 Gbps
- Cryo-testing
- Reliability and Rad Effects

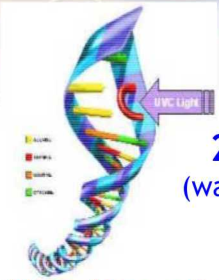


Microsystem Heterogeneous Integration

- Flip chip bonding
- Wafer level oxide bonding
- solder dam and bumps
- Grind, thin and polish
- Substrate removal
- Epoxy underfills
- AR coatings
- Micro-optics: diamond turning and molding
- Active alignment
- Dicing, scribe and break



Motivation for Investment in UV Optoelectronics



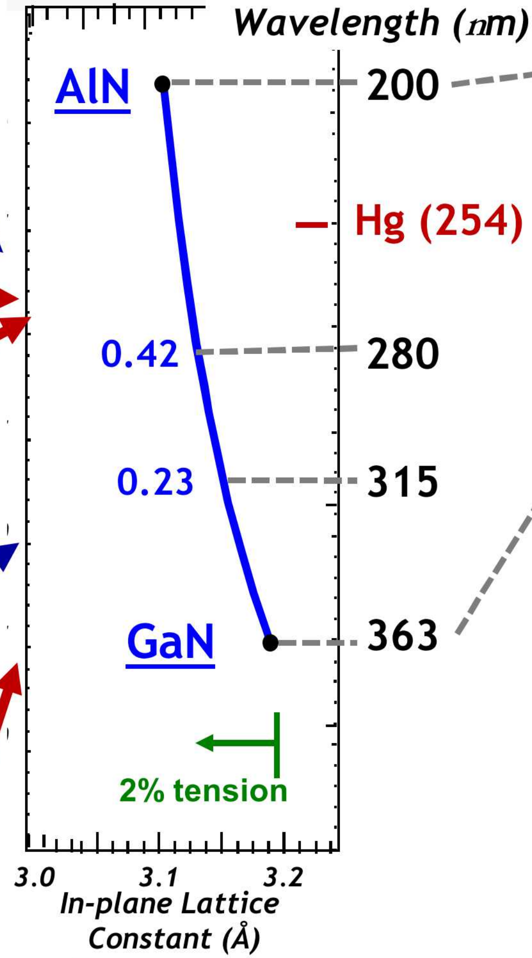
Germicidal
260-275 nm
(water, air, surfaces)

Non-line of sight communication, λ<280 nm

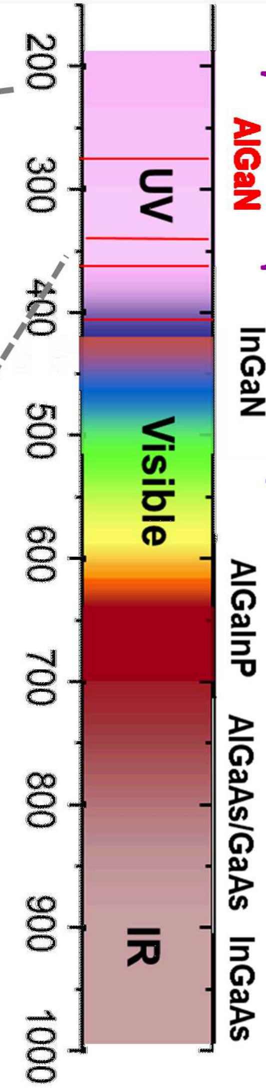
Squad Radio

Solar-blind flame detection, λ<280 nm
(missile launch, flame)

UV-Induced Fluorescence
340, 280 nm
(biological, chemical agents)



UV Processing
300-395 nm
(inks, epoxy)

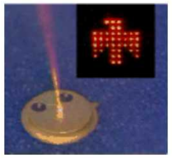


Emerging Technology

New Technology

Solid-state lighting (InGaN)

Mature Technology



SNL Red-VCSEL

Sandia National Laboratories