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Excitonic Properties of Hexagonal BN Grown by High-Temperature Metal-organic Vapor Phase Epitaxy

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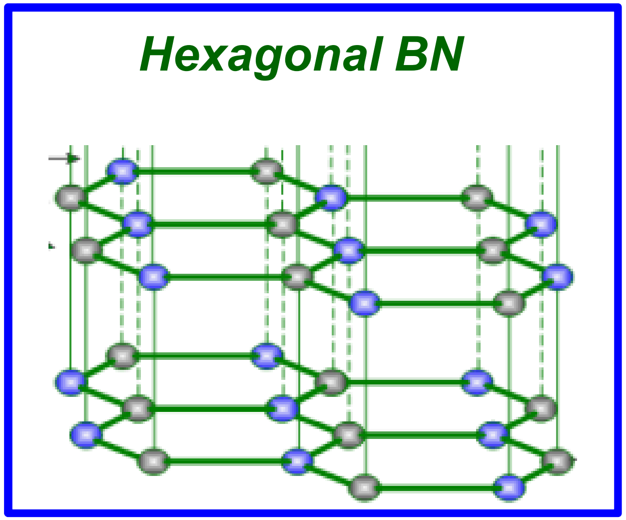

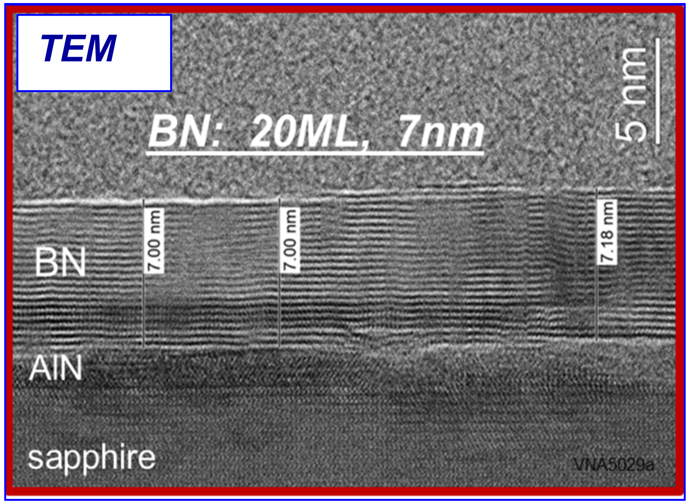

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Outline

- Evolution of excitonic properties vs. MOVPE growth temperature
- Epitaxial growth as an approach to high-quality few-ML-thick hBN films

1. INTRODUCTION

   a) Background and motivation

   b) Excitonic properties

2. EPITAXIAL GROWTH AND CHARACTERIZATION OF hBN

   a) MOVPE Growth at ≤ 1200°C
      - Pulsed growth conditions
      - Structural and optical properties

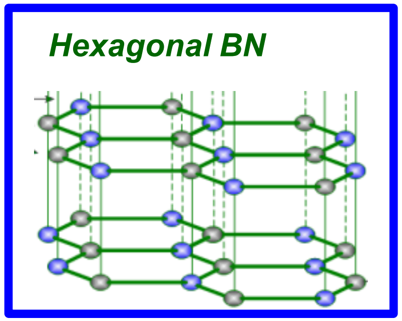
   b) MOVPE Growth at 1200 – 1700°C
      - Excitonic properties vs. growth temperature
      - Growth control to the monolayer limit
      - Alternative substrates to sapphire

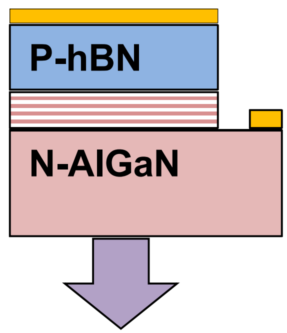
3. SUMMARY

Background

Motivation

- Ideal template for high-mobility graphene
- Very wide bandgap 2D material (deep UV)
- Demonstrated p-type doping
- ~ > 10x exciton binding energy of GaN

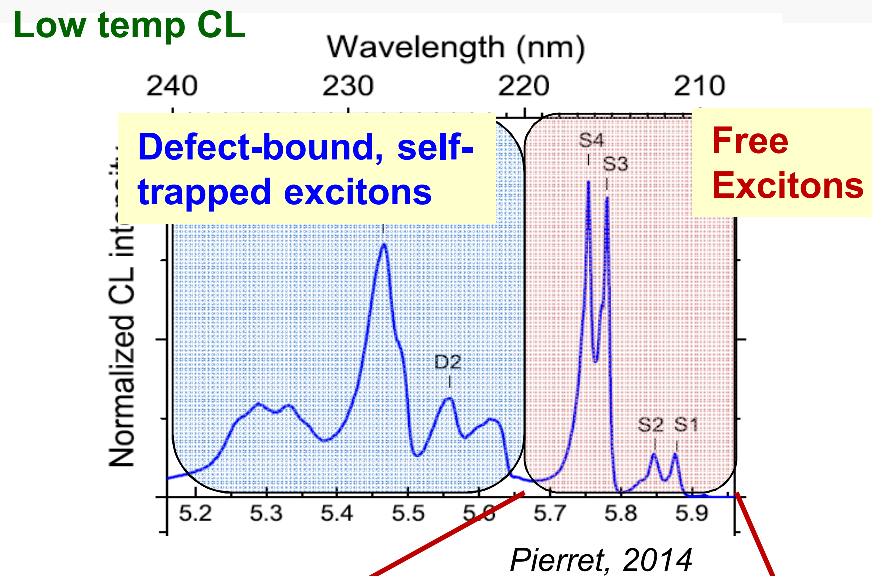




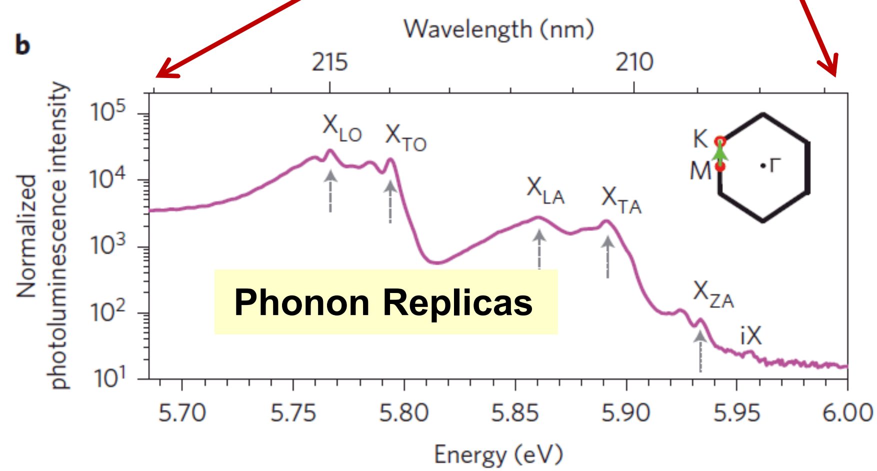
Outstanding Questions:

- **Nature of the bandgap** (indirect or direct)
- **Excitonic properties** (binding energy ~0.13-0.75 eV, Wannier vs. Frenkel)
- **Origins of near-band-edge luminescence** (free/bound excitons vs. phonon replicas)

Excitonic Properties



Pierret, 2014



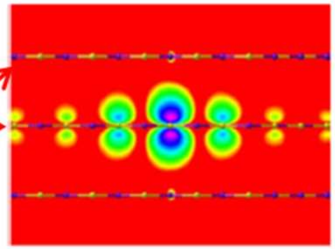
Cassabois et al., Nat. Photon 2016

Excitonic Properties at Few-Monolayer Thickness

Question: How do the excitonic properties of hBN evolve with thickness down to 1 ML?

Strong Exciton Confinement

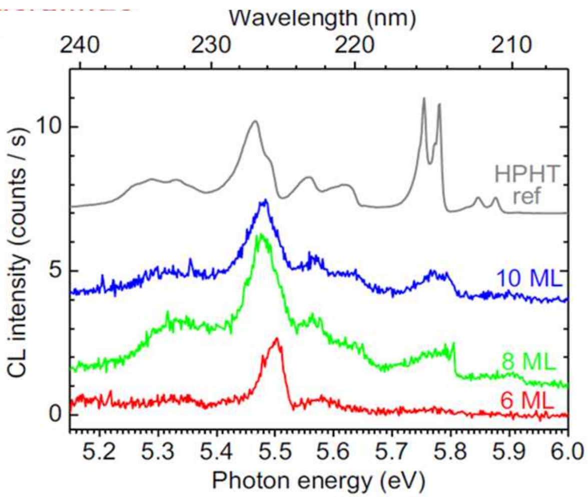
BN sheets

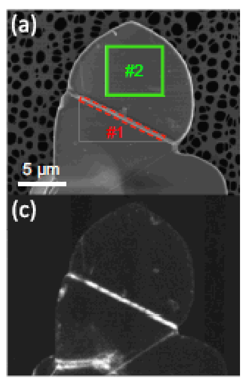


Exciton probability density (5.78 eV)

Arnaud, PRL(2006)

Low Temp. CL: Exfoliated hBN flakes



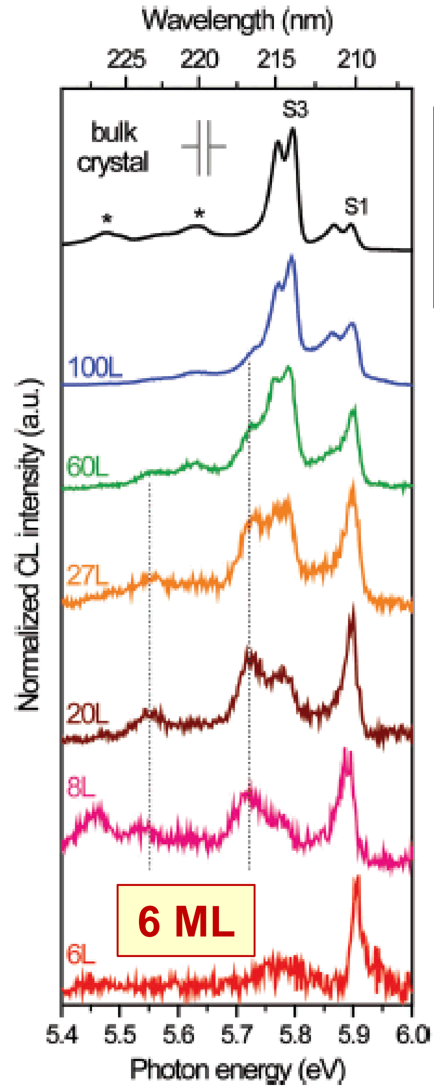


5.46 eV CL

Pierret, PRB (2014)

Loss of higher energy, free-exciton related features with exfoliation

Low Temp CL: Exfoliated hBN Flakes



Improved Exfoliation: excitonic evolution down to 6 ML

➔ Explore epitaxial growth approaches

Schue, Nanoscale (2016)

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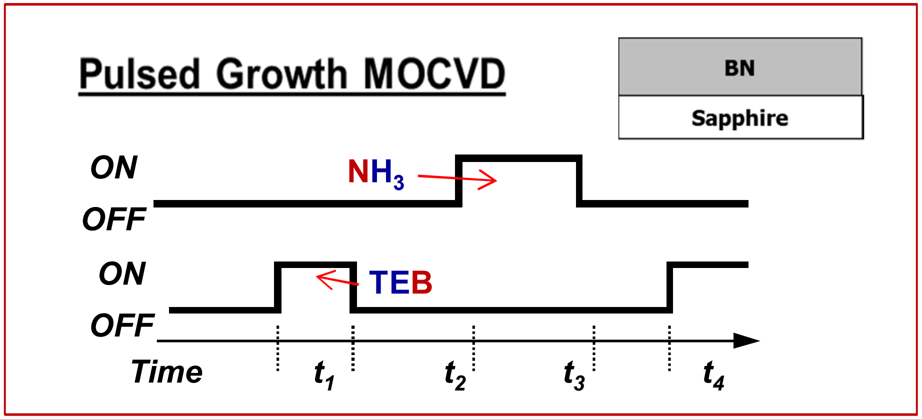
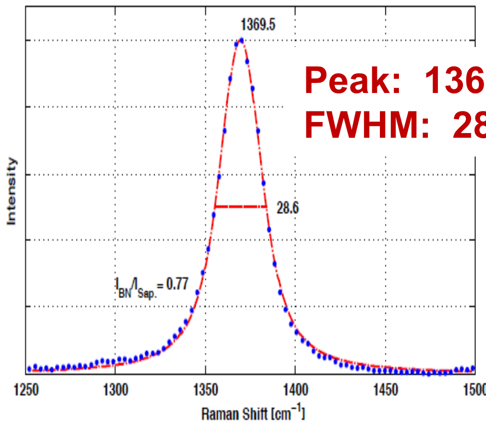
MOVPE Growth (T_g ~ 1175°C)

- **Continuous growth:** **high growth rate at low V/III but poor crystalline quality**
- **Pulsed growth** **chosen to enable higher V/III ratios for improved film quality**



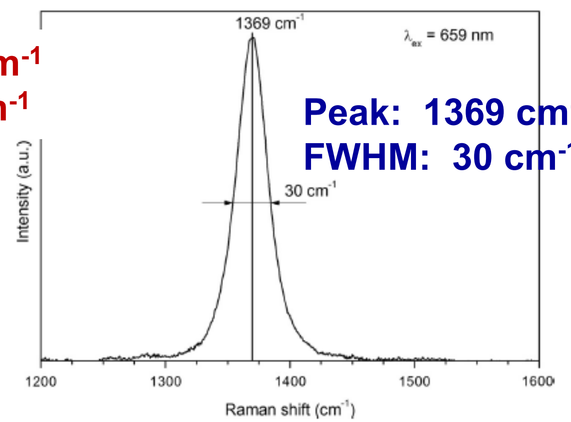
Growth Condition	Parameter Range
Temperature	1175°C
Pressure	50-200 Torr
NH_3 Flow	0.2-10 slm
TEB Flow	3-12 μmoles/min
Pulse Cycles	20-9600
Time per Cycle	1-12 sec

Raman Spectra



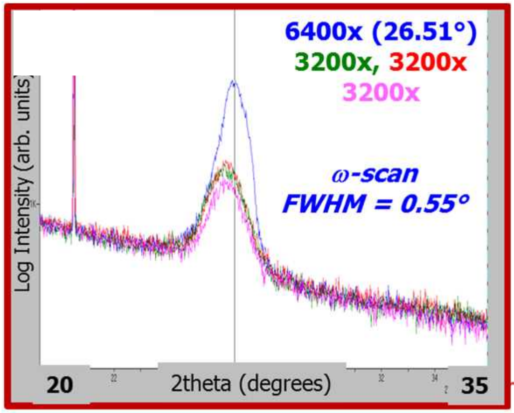
Peak: 1369.5 cm^{-1}
FWHM: 28.5 cm^{-1}

Compare to Chuboruv 2014 (1500°C)



Peak: 1369 cm^{-1}
FWHM: 30 cm^{-1}

(002) XRD reflection



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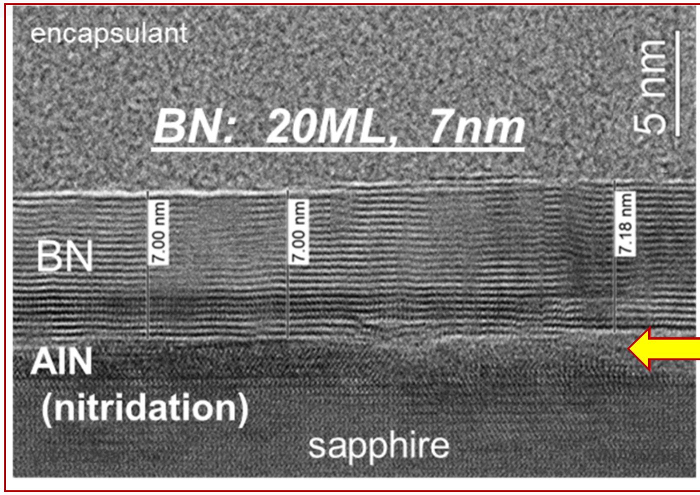
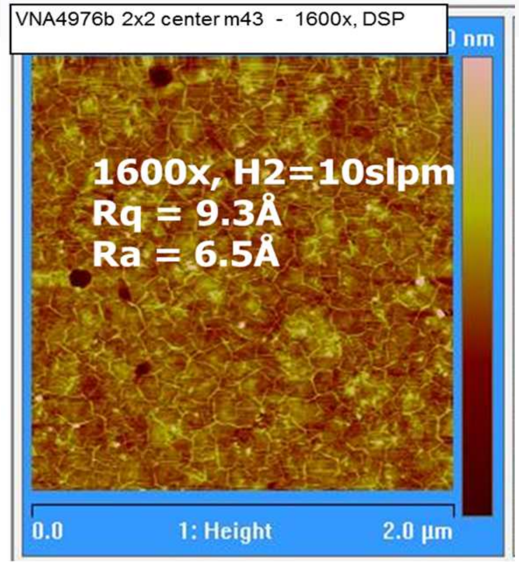
Structure and Morphology of hBN (T_g ~ 1175°C)

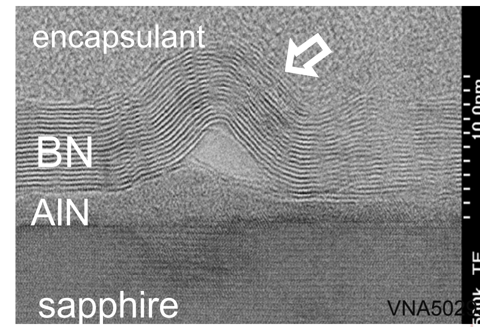
High-resolution cross-section TEM



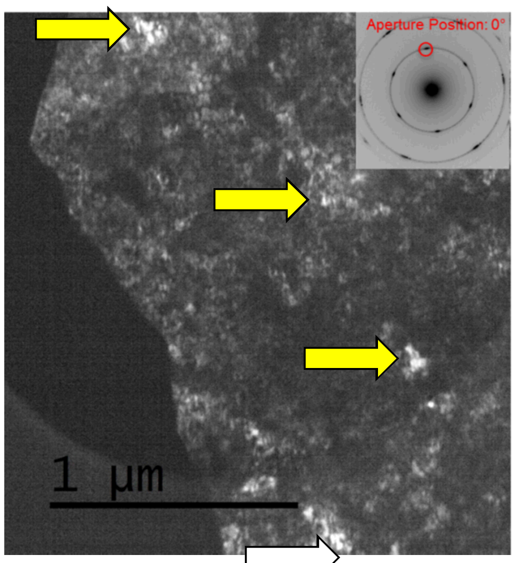
AFM

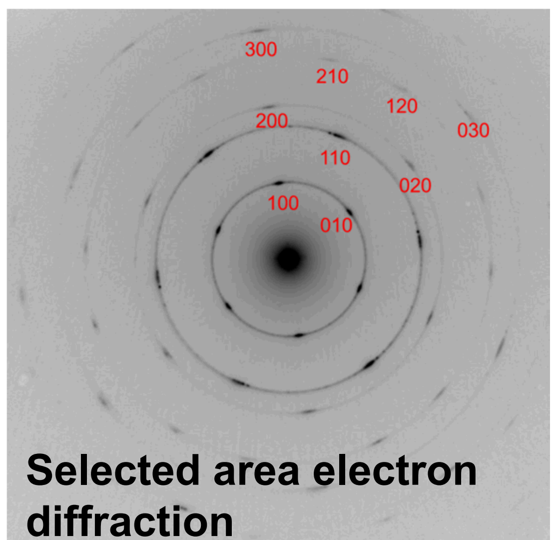


- Typical "wrinkles"
- Also particles forming on surface with increasing thickness



TEM (dark-field) free-standing BN





Selected area electron diffraction

- Bright regions indicate strong in-plane alignment
- hk0 rings indicate in-plane ***rotation disorder***
- hk0 reflection spots indicate ***basal plane alignment***

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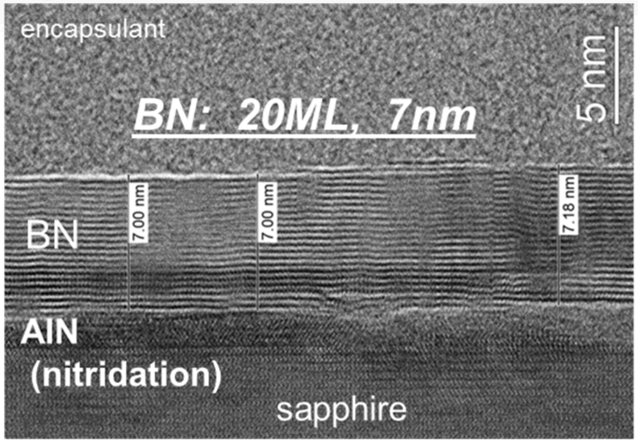
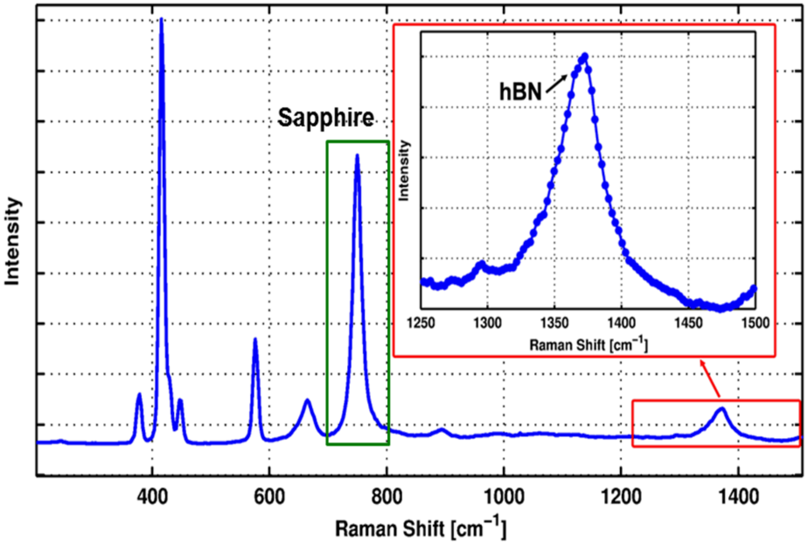
Estimation of Film thicknesses

Cross-sectional TEM

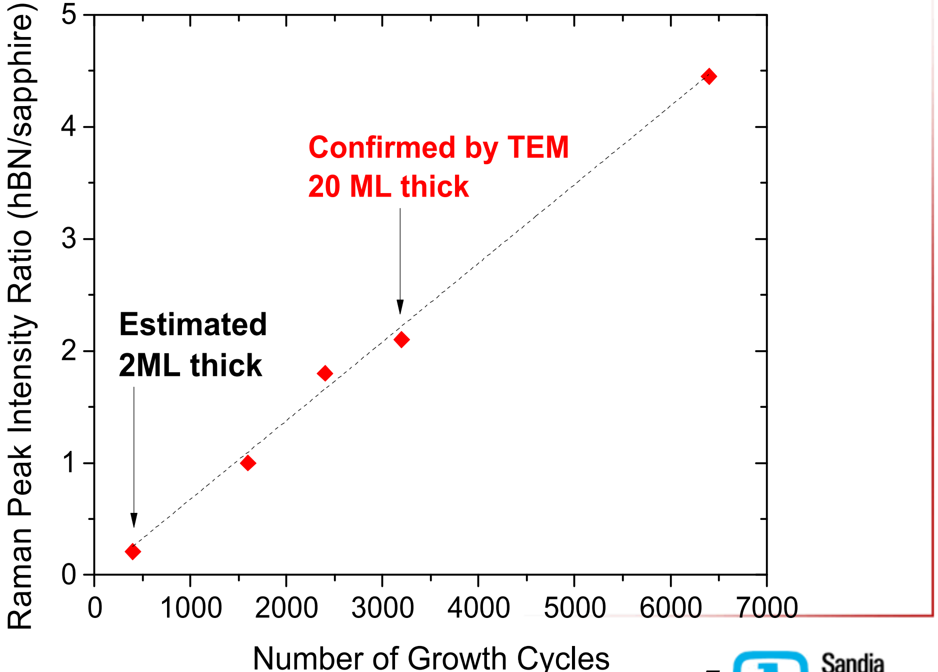


- Difficulty seeing very thin layers by TEM
- Using hBN/sapphire Raman intensity ratio as a rough estimate
- Suggests reproducible 1-3 ML control

Raman Spectra



BN Raman peak ratio (I_{BN}/I_{sapp}) vs. Pulse Cycles



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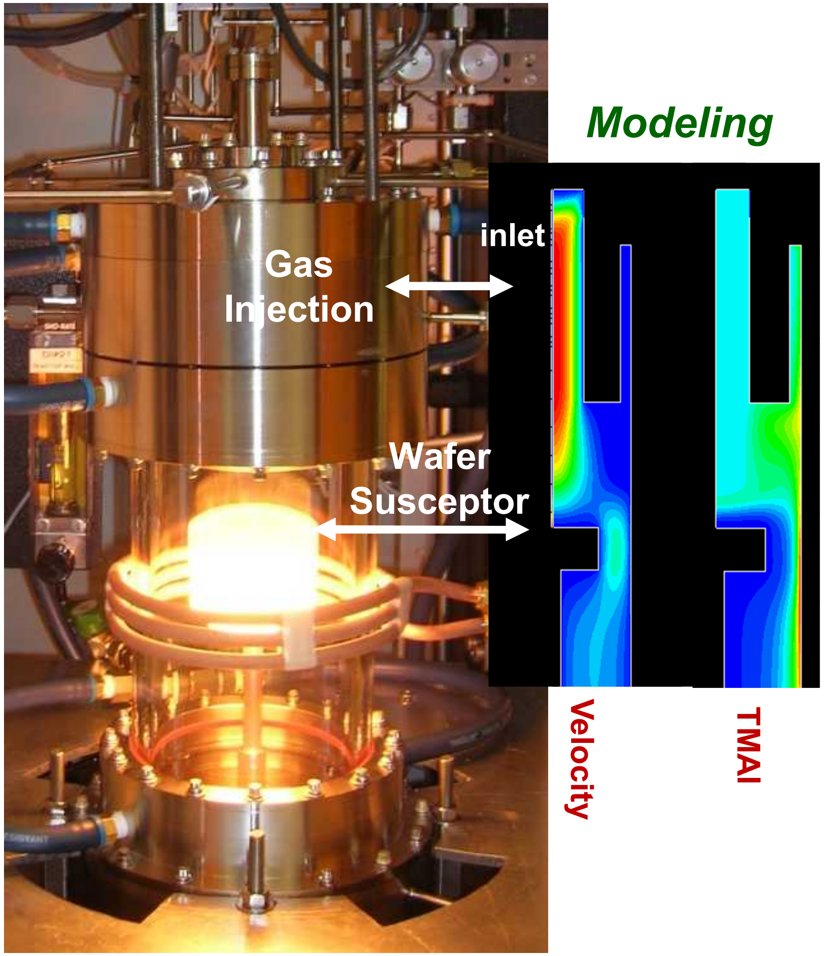
High Temperature MOVPE

>1800°C Operation

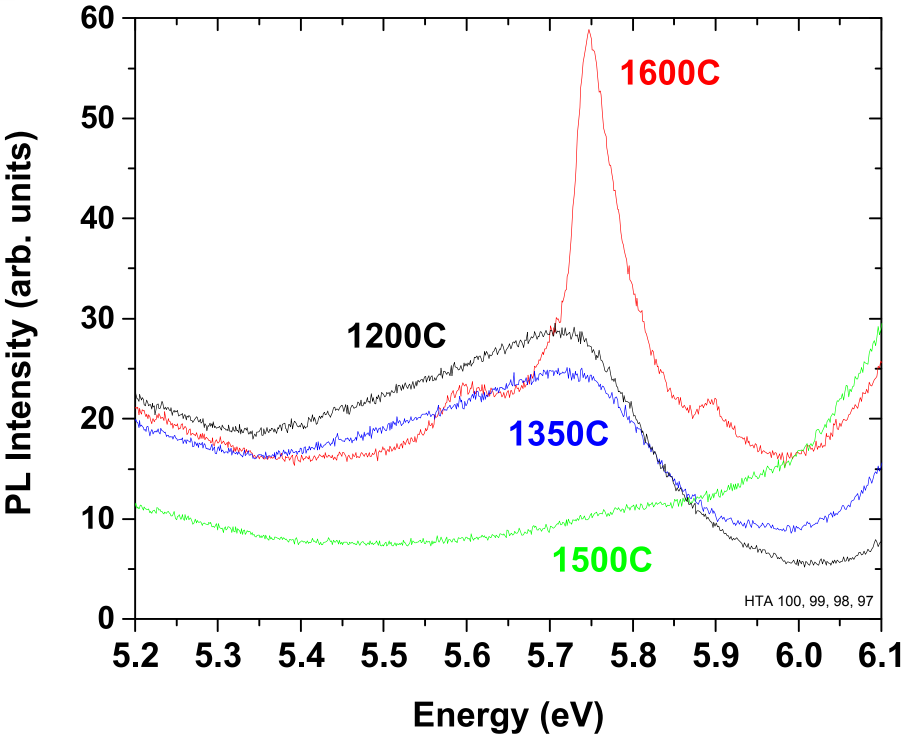


- ***Advantages of HT growth***
  - **Increased surface mobility of Group-III atoms.**
- ***Continuous Growth (TEB + NH3)***
  - **Temperature: 1200 – 1600 - 1800°C**
  - **Pressure: 50 torr**
  - **NH3: 0.1 – 2 - 5 slpm**
  - **TEB: 12 μmoles/min**
  - **Carrier gas: N_2**
  - **H_2: 0 – 5 slpm**
  - **Pulsed growth process is being developed**

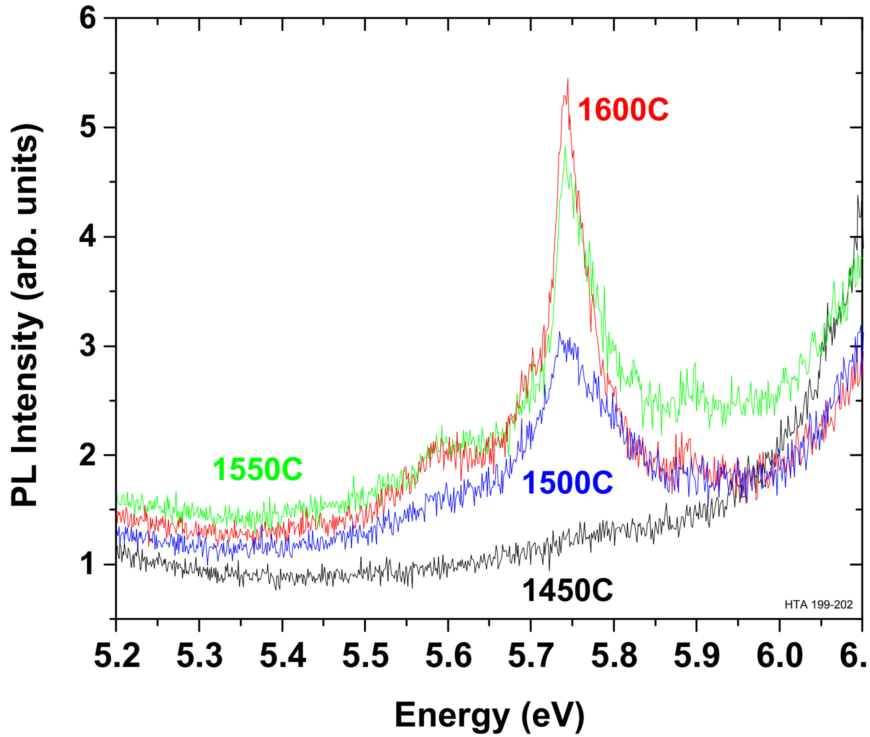
Reactor Design from Prof. Zlatko Sitar (NC State)

Growth Temperature Study: PL

Wide Temp Range: T_g = 1200-1600°C



Transition Region: T_g = 1450-1600°C



- **Unusual evolution of near-band-edge features with increasing growth temperature**
- **Transition to sharp higher-energy free-exciton peak at T_g~1500-1600°C**

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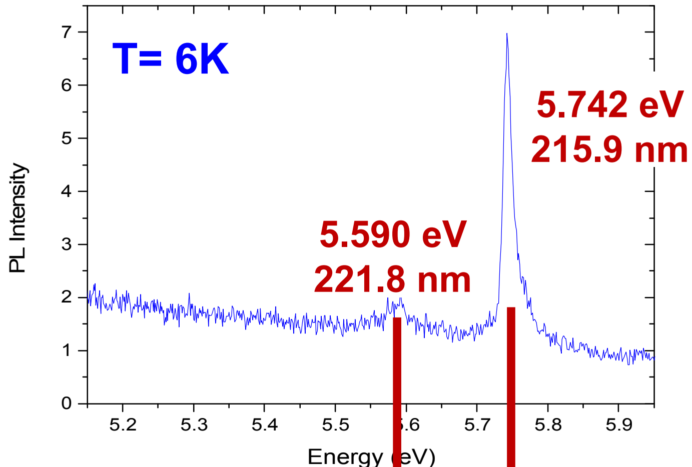
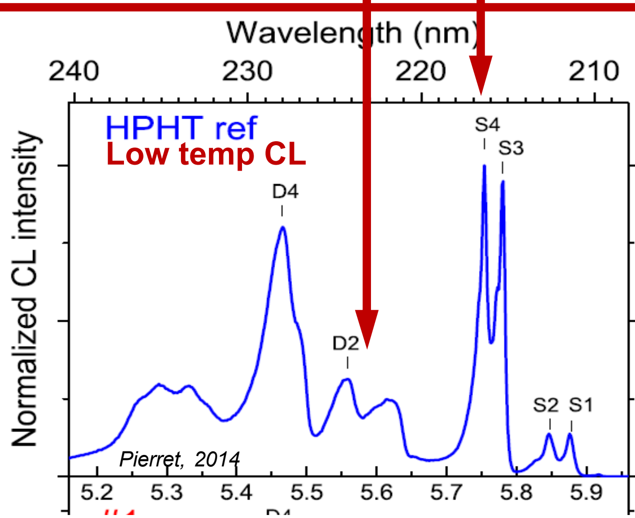
Low-Temperature Luminescence: comparisons

MOVPE hBN: Tg = 1600°C



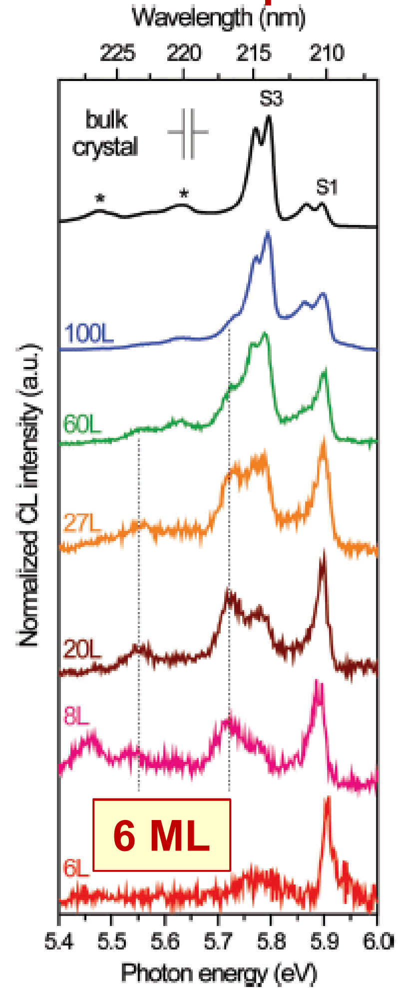


Pierret, PRB (2014)

High-Pressure/High-Temperature hBN Crystal

Best Exfoliated hBN Flakes

Low Temp CL

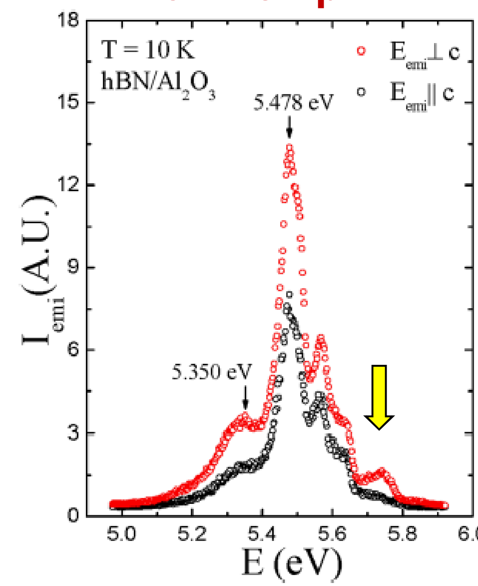


Schue, Nanoscale (2016)

MOVPE hBN

T_g = 1300°C, 1 μm thick

Low Temp PL

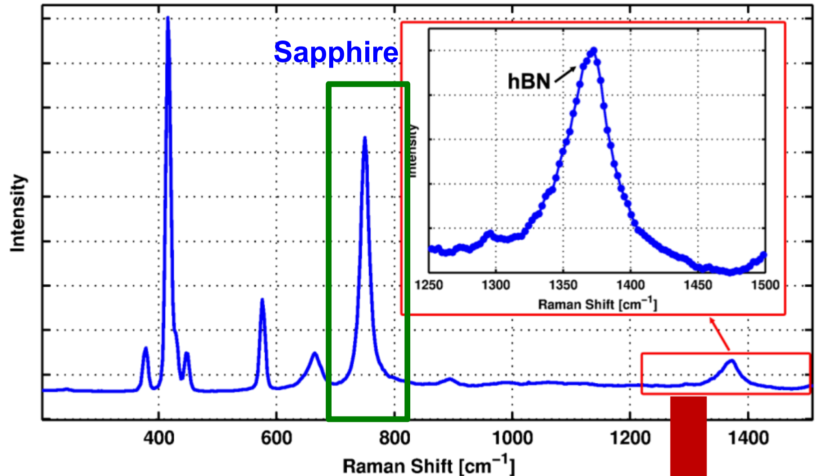


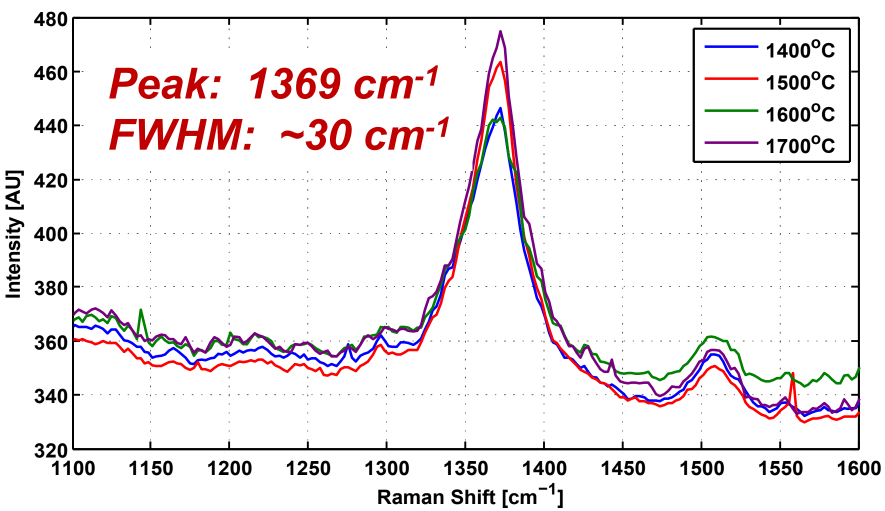
Majety, APL 2012

➔ **Excitonic signatures of high-Tg MOVPE hBN similar to that of best exfoliated crystals**

Estimation of Thickness of high-T_g hBN Films

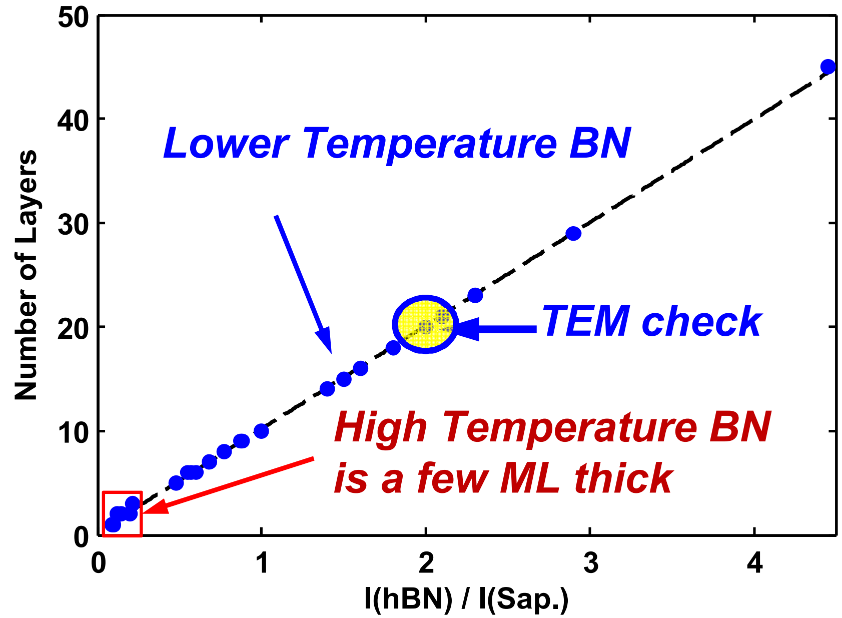
Typical Raman Spectrum





BN Raman peak ratio (I_{BN}/I_{sapp}) vs. Pulse Cycles

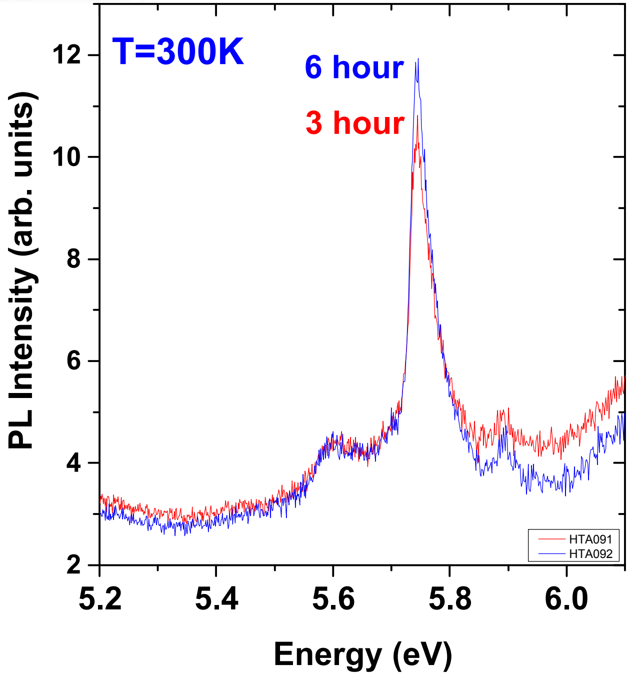
→ Apply calibration from thicker films



- **Raman peak is comparable to published reports, little dependence on growth temperature ≥ 1400°C**
- **BN film appears to be very thin, 1-2 monolayers**

Potential for Self-limiting Growth at high T_g

PL Measurements

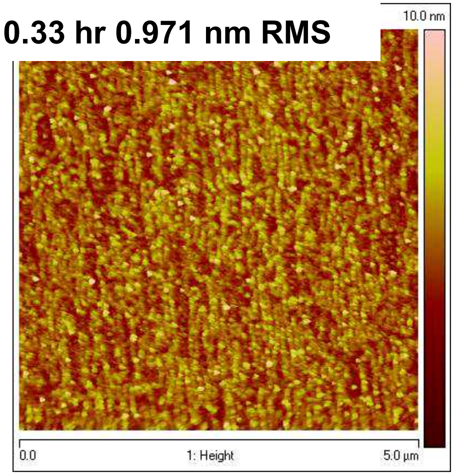


Results from Raman Measurements

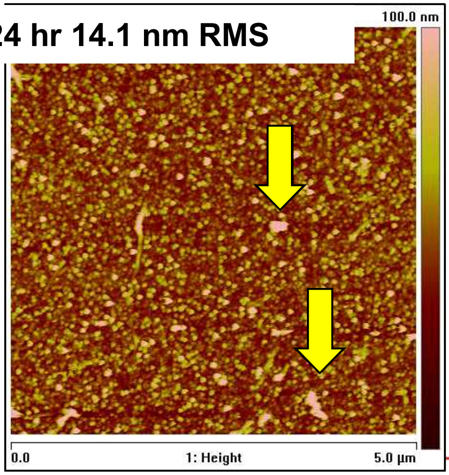
Growth Temp (°C)	Growth Time (hrs)	Raman peak ratio	STEM calibration (MLs)
1600	0.25	0.1	~1
1600	3	0.09	~1
1600	3	0.18	~2
1600	6	0.16	~2
1600	24	0.26	~3

AFM Measurements

0.33 hr 0.971 nm RMS



24 hr 14.1 nm RMS



- 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, with increased number of larger particulates, with longer growth times

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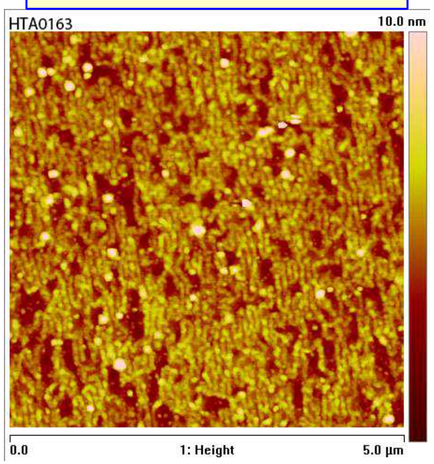
Challenge with High Temp Growth: Nitridization of Sapphire Substrate

Nitrided Sapphire Substrate

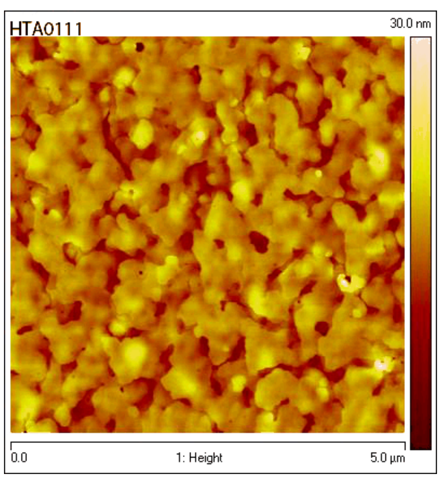
1600°C growth conditions but

No Boron Source Material (TEB)

5 min 1.17 nm RMS

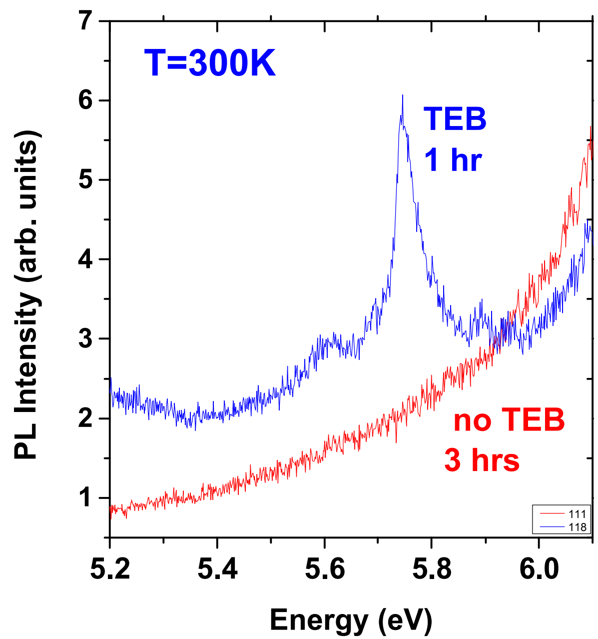


180 min 2.71 nm RMS

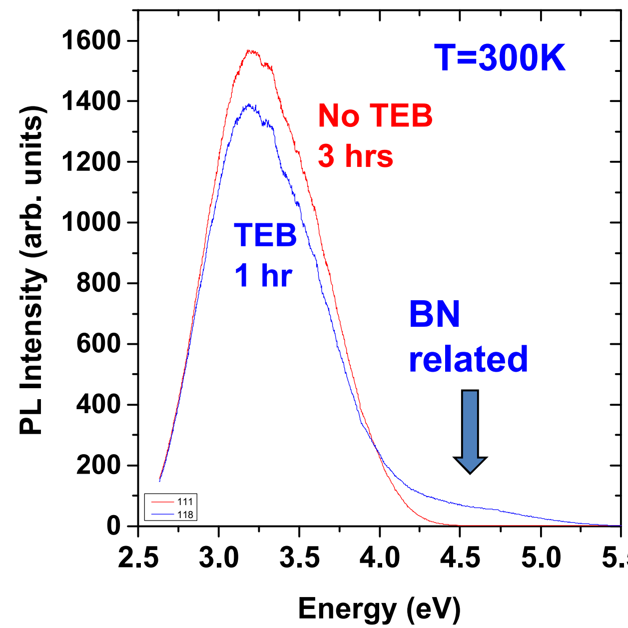


PL comparison: BN on Sapphire vs. Nitrided Sapphire

Near Band Edge



Deep Level



- High temperature NH_3 exposure causes nitridization of sapphire surface (AlN peak seen by Raman)
- Lower crystalline quality than original sapphire, impacts BN morphology
- Contributes strong deep level emission at ~ 3.1 eV

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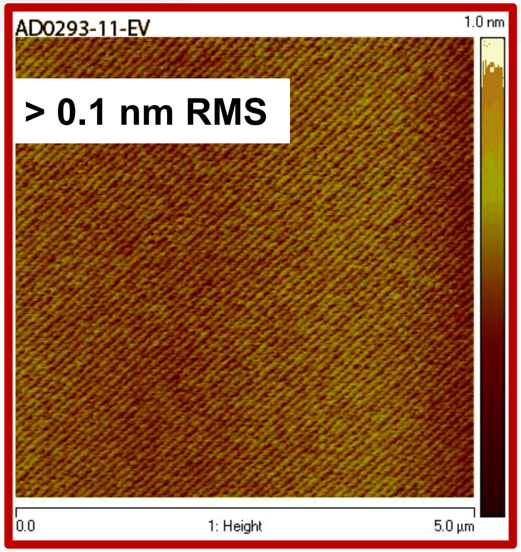
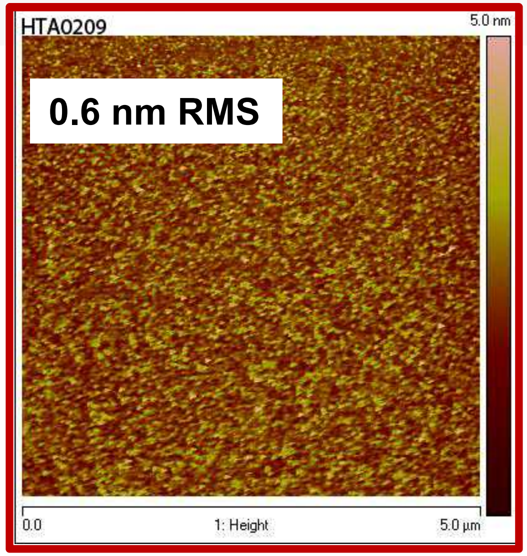
Alternative Substrates: SiC

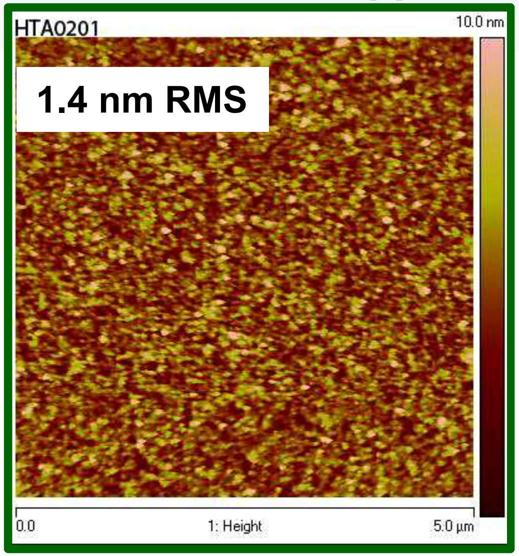
As-received SiC



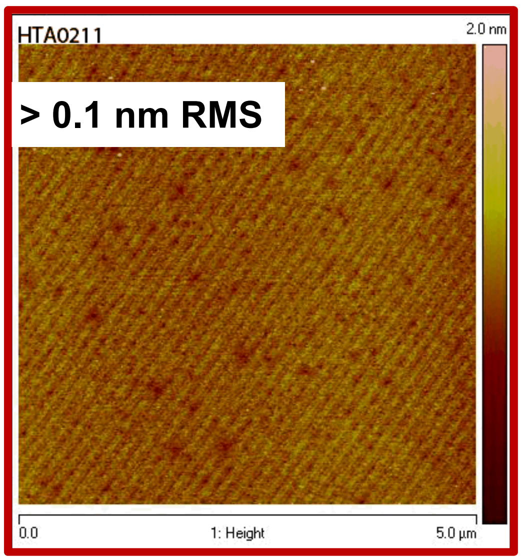
1600°C BN on SiC



1600°C BN on Sapphire



1600°C NH_3 treatment, <u>no TEB</u>



Tg (°C)	RMS roughness (nm)
1400	0.7
1500	0.4
1600	0.6

<u>Growth Conditions</u>: 50 Torr, 25 sccm TEB, 2 SLM NH3, 1 hour

- SiC surface relatively stable with NH_3 exposure
- BN roughness improved over sapphire

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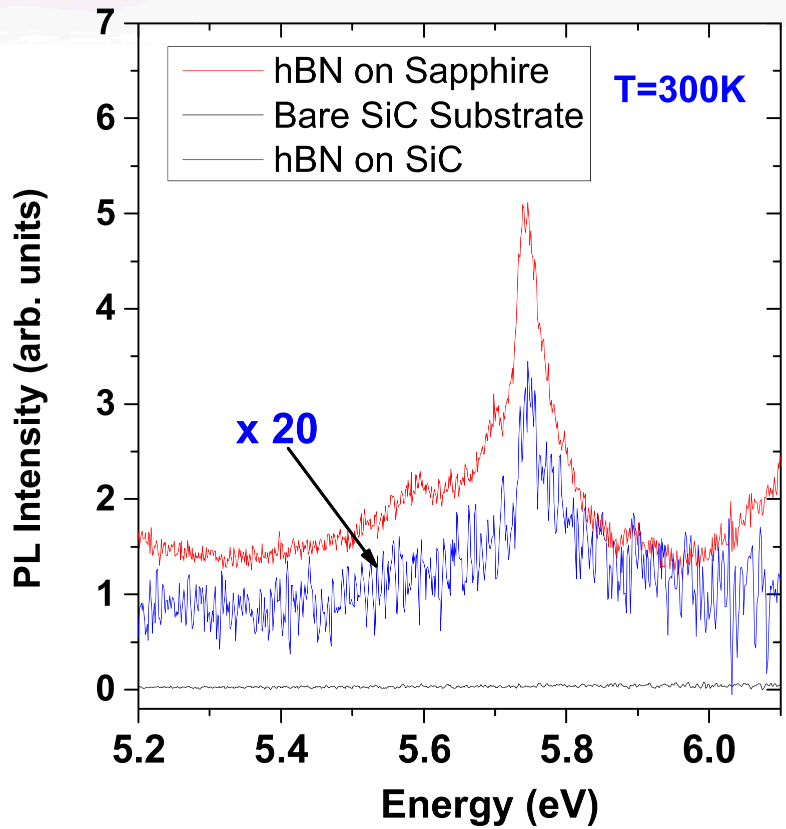
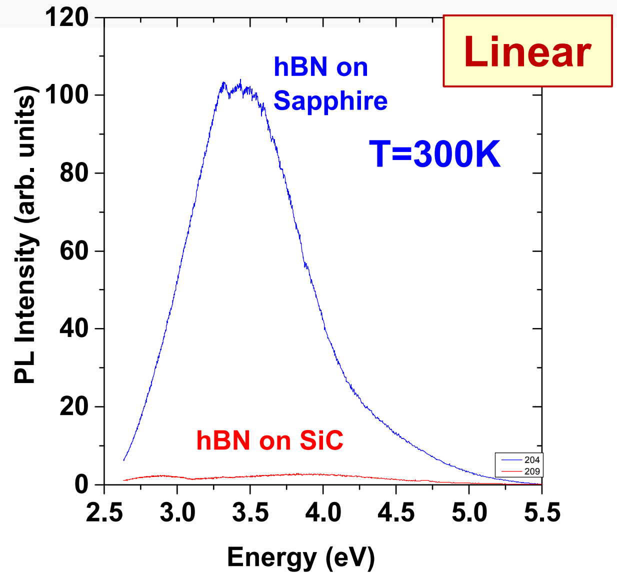
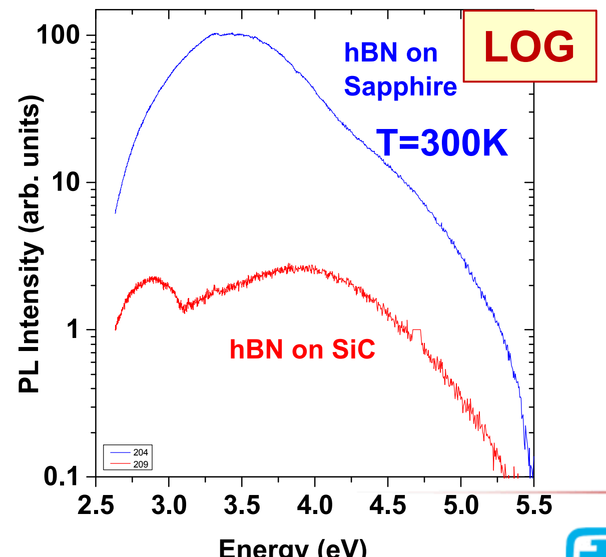
hBN on SiC: Luminescence Properties

Near Band Edge PL | T_g = 1600°C | **Deep Level Emission**







- **Weak ~216 nm peak in 1st - generation samples**
- **Elimination of deep level peak associated with nitrided sapphire**

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Summary

- Explored high-T_g MOVPE as an approach to achieving high-quality, few-ML-thick hBN films
- Determined that lower-Tg films (pulsed growth) demonstrated notable in-plane rotational disorder and defect-related excitonic signatures
- Observed a dramatic evolution of excitonic properties with $T_{g;}$ T_g ~ 1600°C yielded strong free exciton features similar to best exfoliated crystals
- Identified potential for highly-controlled, self-limiting growth of few ML thickness at high-Tg (estimated by Raman spectroscopy)
- Noted challenges with high T_g growth on sapphire, nitridization impacting morphology and deep level PL of hBN
- Presented initial results of hBN on SiC, showing promise for improved structural quality and relatively low defect-related emission

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