SAND2017-12464C

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

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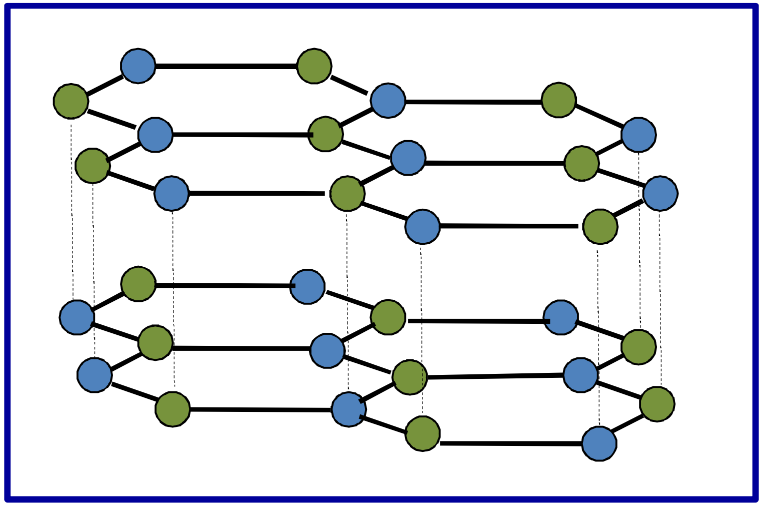

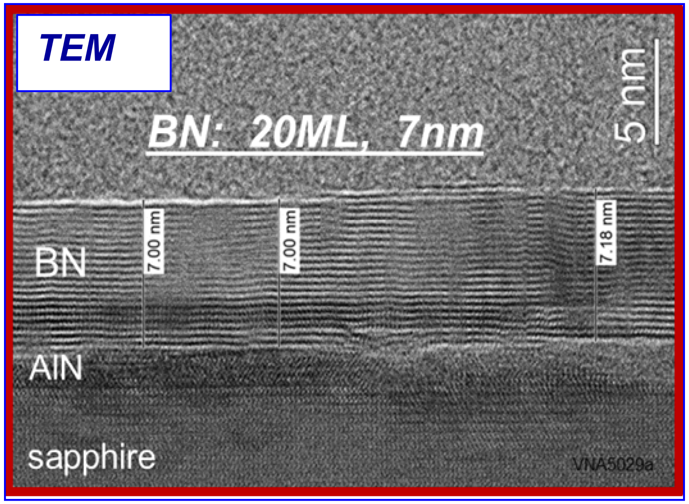

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Outline

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 (expt. and model)
    - Alternative substrates to sapphire
    - Alternative precursors

3. SUMMARY

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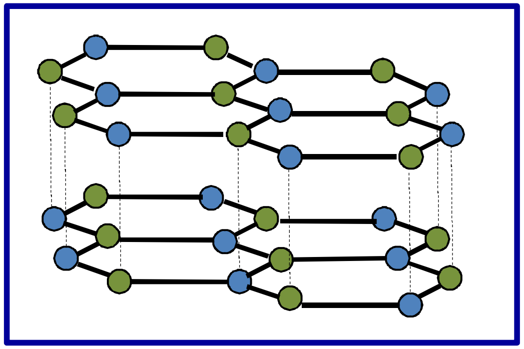
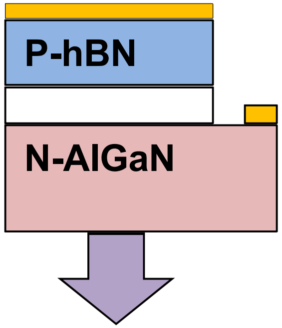
Background

Motivation

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



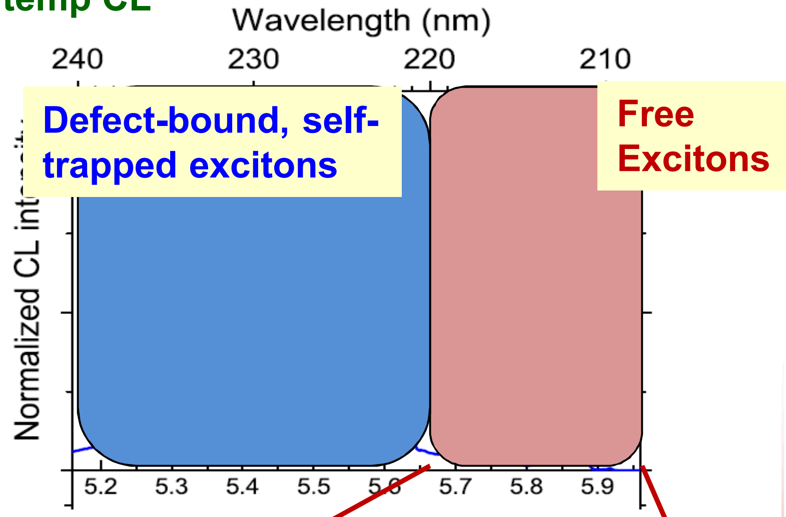


Outstanding Questions for Epitaxy:

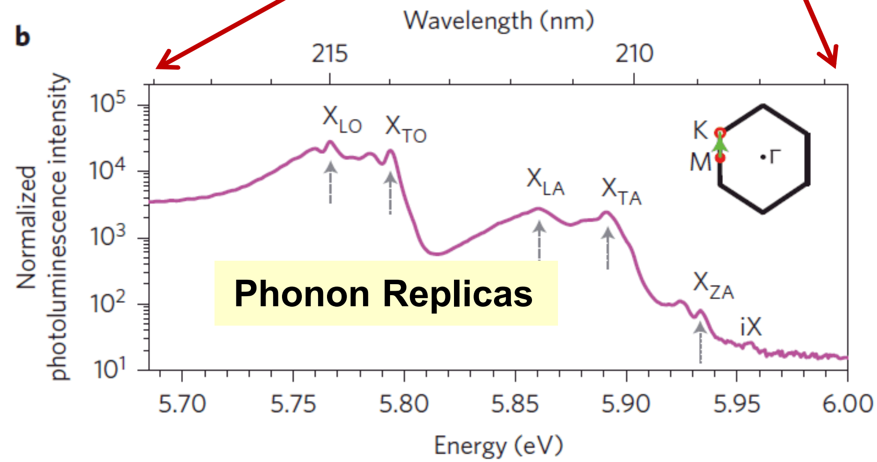
- Can we demonstrate large-area hBN with high quality surfaces for 2D heterostructures?
- Can we demonstrate ML to few-ML thickness control?
- Can we observe free-exciton-related emission at room-temperature?

Excitonic Properties

Low temp CL



Pierret, 2014



Cassabois et al., Nat. Photon 2016

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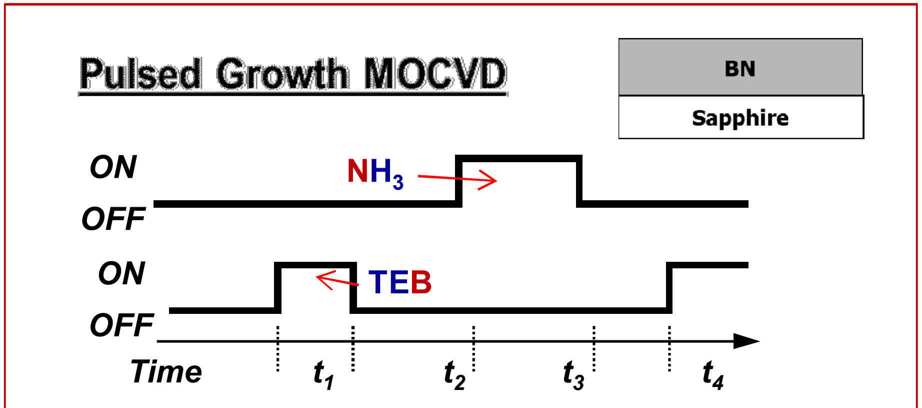
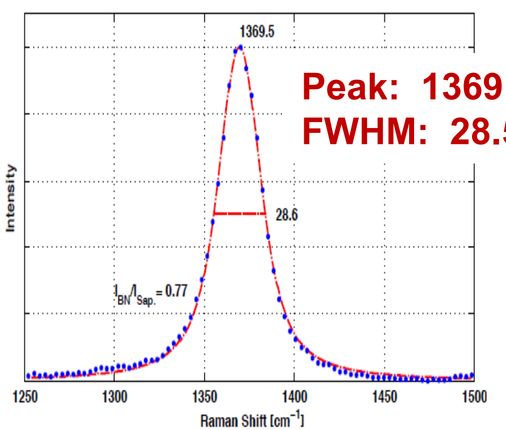
MOVPE Growth (T_g ~ 1175°C)

- **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



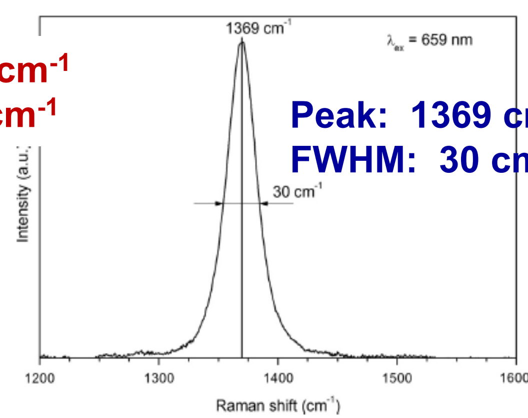
Growth Condition	Parameter Range
Temperature	1175°C
Pressure	50-200 Torr
NH_3 Flow	0.2-10 slm
TEB Flow	3-12 μmoles/min
Pulse Cycles	20-9600
Time per Cycle	1-12 sec

Raman Spectra



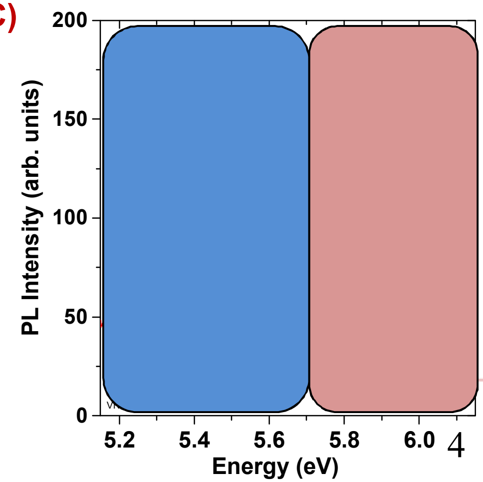
Peak: 1369.5 cm^{-1}
FWHM: 28.5 cm^{-1}

Compare to Chuboruv 2014 (1500°C)



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

Room Temp PL



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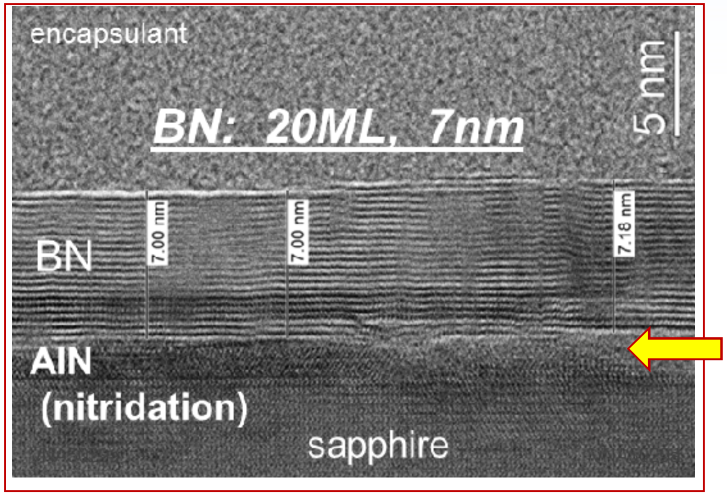
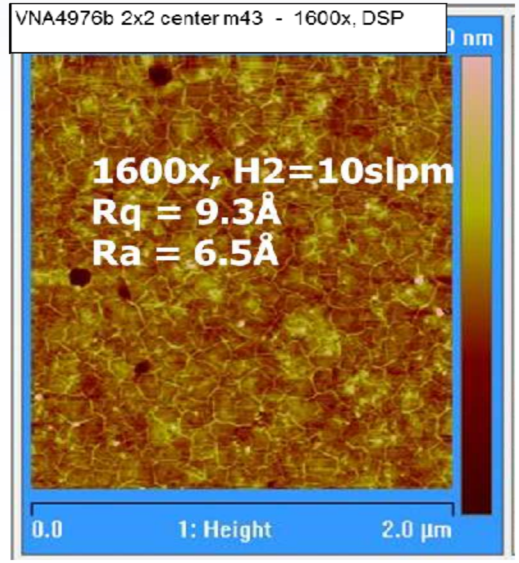
Structure and Morphology of hBN (T_g ~ 1175°C)

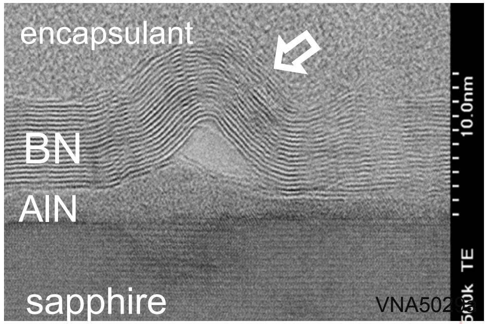
High-resolution cross-section TEM



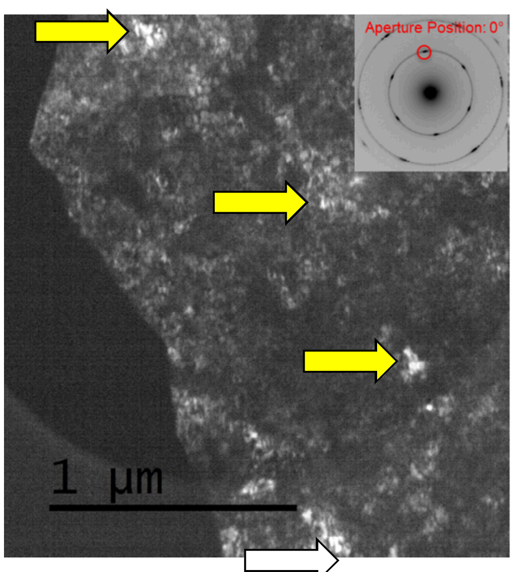
AFM

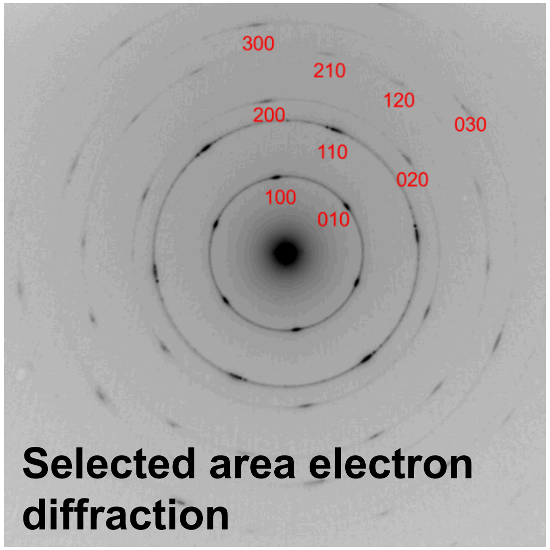


- **Typical "wrinkles"**
- **Also particles forming on surface with increasing thickness**



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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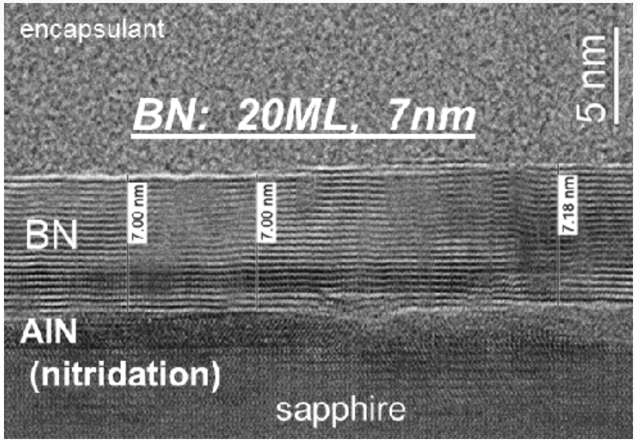
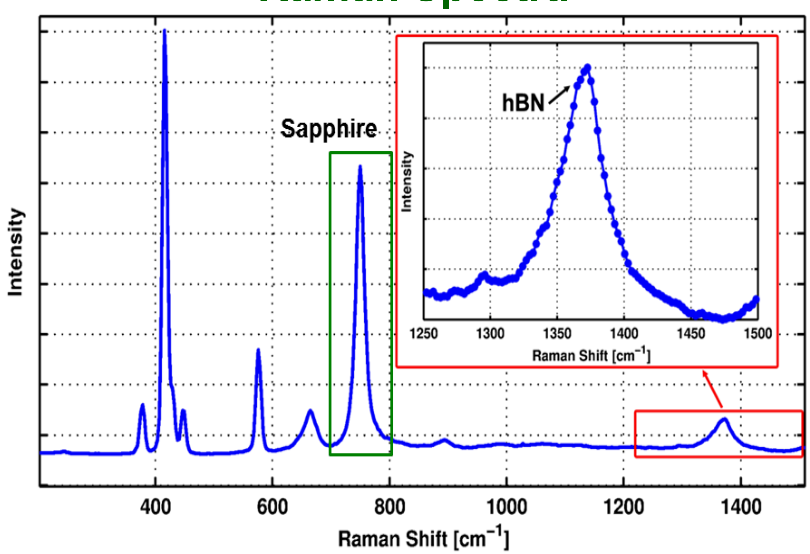
Estimation of Film thicknesses: Raman

Cross-sectional TEM

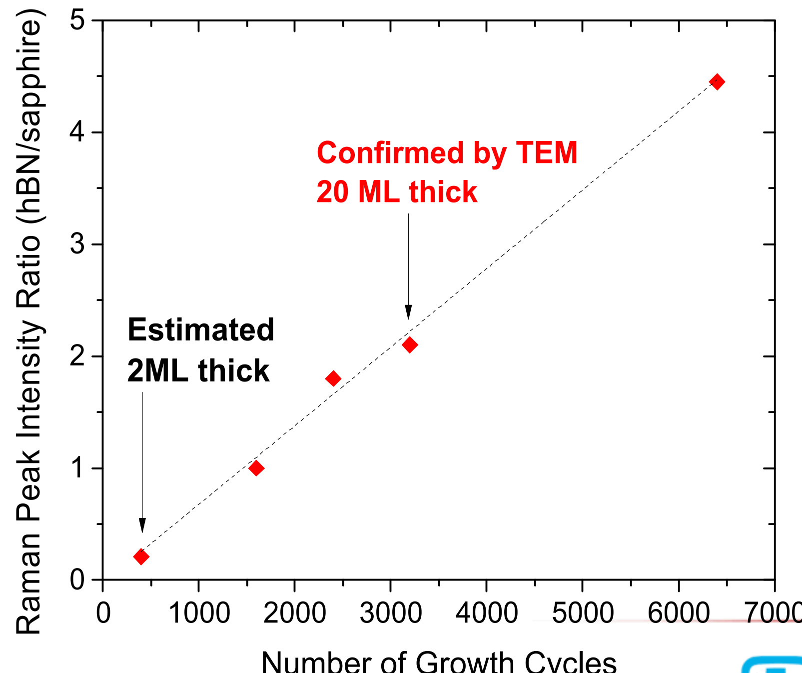


- **Difficulty seeing very thin layers by TEM**
- **Using hBN/sapphire Raman intensity ratio, calibrated to TEM of thicker films, as a rough estimate of thickness**
- **Suggests reproducible 1-3 ML control**

Raman Spectra

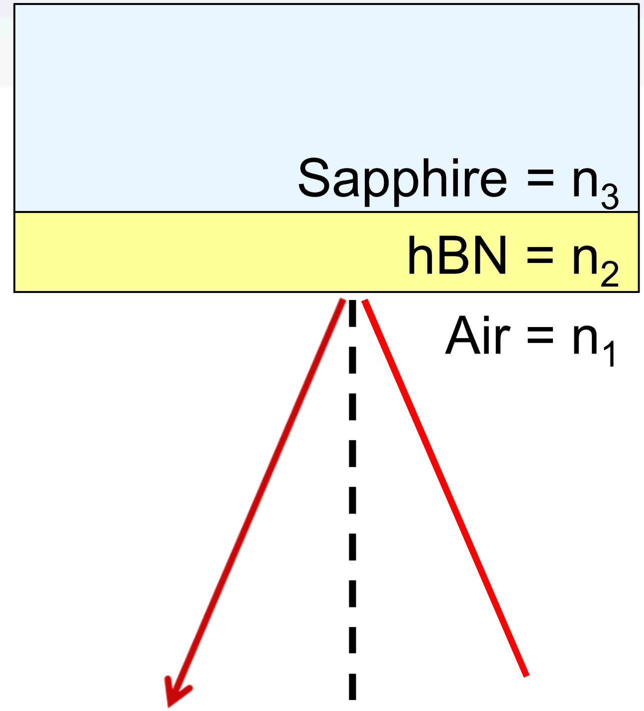


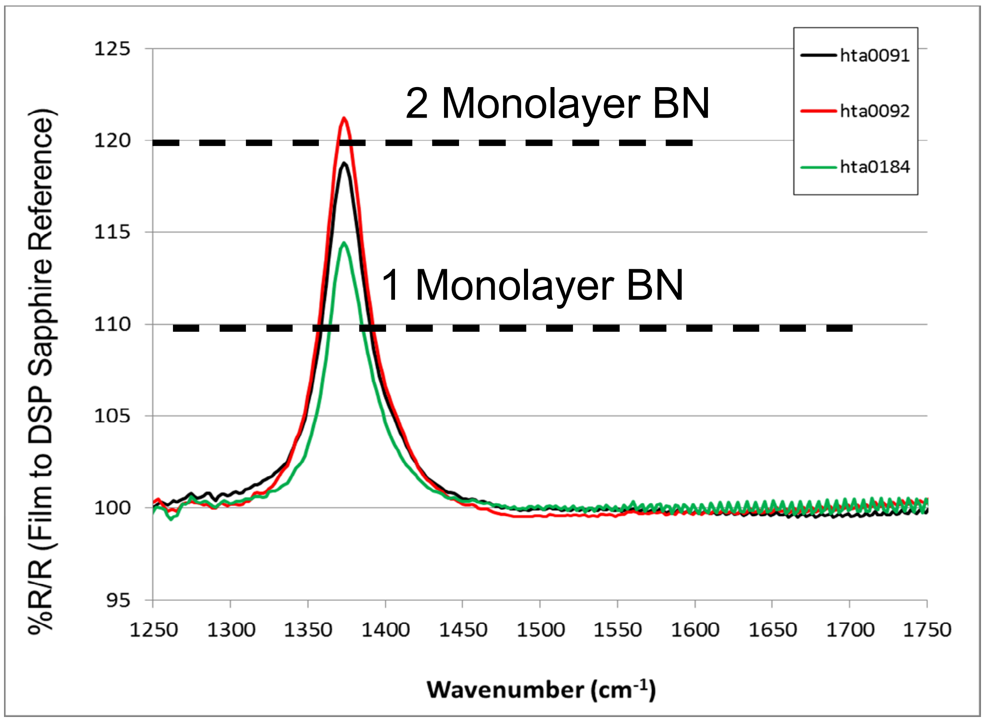
BN Raman peak ratio (I_{BN}/I_{sapp}) vs. Pulse Cycles



Estimation of Film thicknesses: FTIR

- **Take advantage of the large difference between BN and sapphire extinction coefficients**
- **Apply 3-layer differential reflectance model**
- **Yields ΔR/R ~110% for d = 1 ML**
- **Averages for partial coverage**





$$\frac{\Delta R}{R} = \frac{8\pi d n_1}{\lambda} \operatorname{Im}\left(\frac{\hat{\varepsilon}_2 - \hat{\varepsilon}_3}{\varepsilon_1 - \hat{\varepsilon}_3}\right)$$

McIntyre and Aspnes., 1971

R. Creighton, SNL

- hBN films between 1 and 2 monolayers by Raman
- Two techniques give similar results, FTIR more consistent

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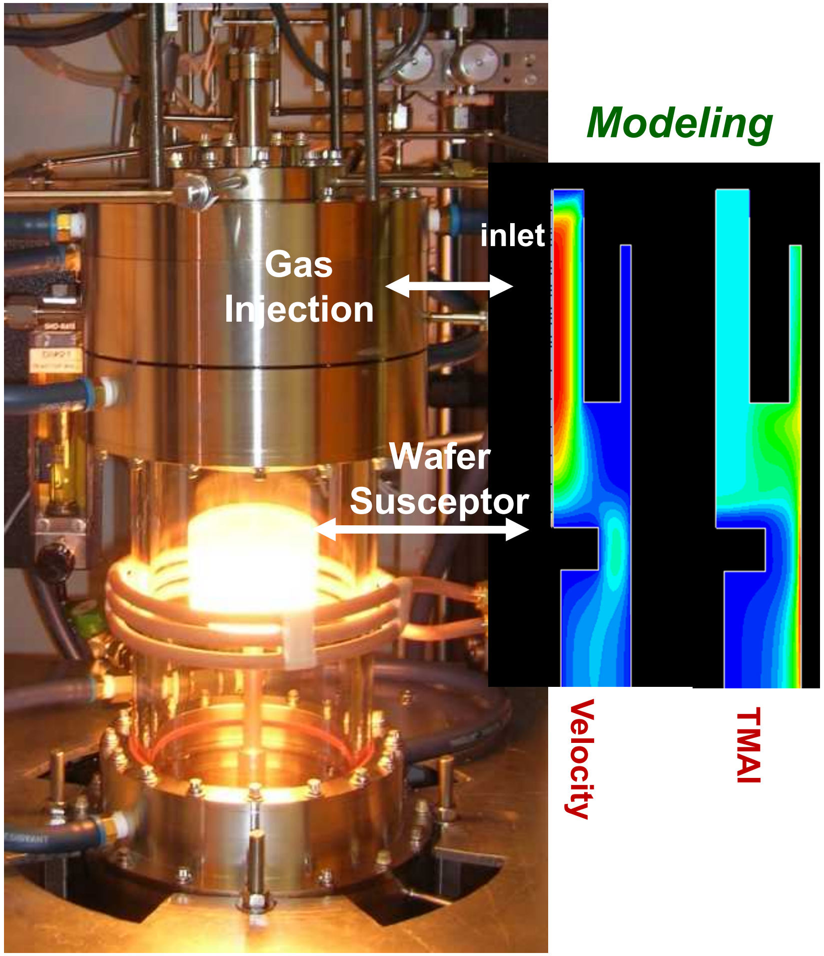
High Temperature MOVPE

>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**

Reactor Design from Prof. Zlatko Sitar (NC State)

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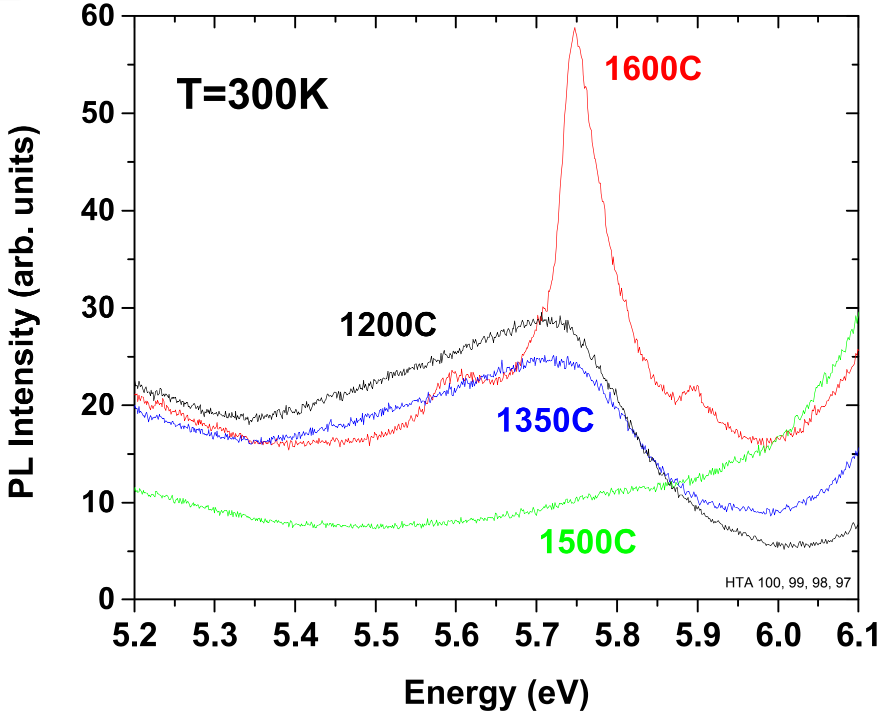
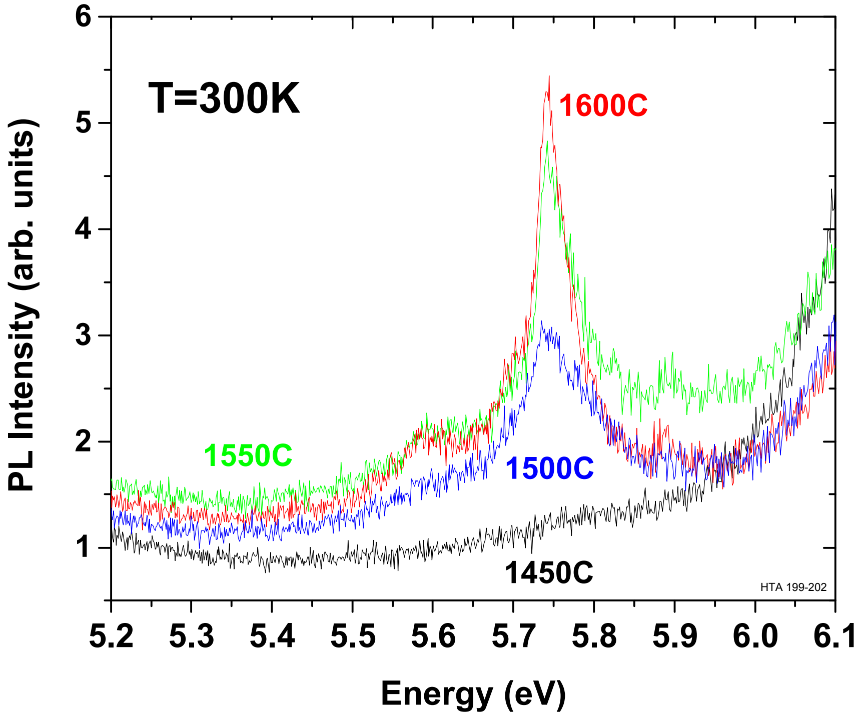
Growth Temperature Study: PL

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**
- **Observation of room temperature free (5.75 eV) exciton in MOVPE hBN**

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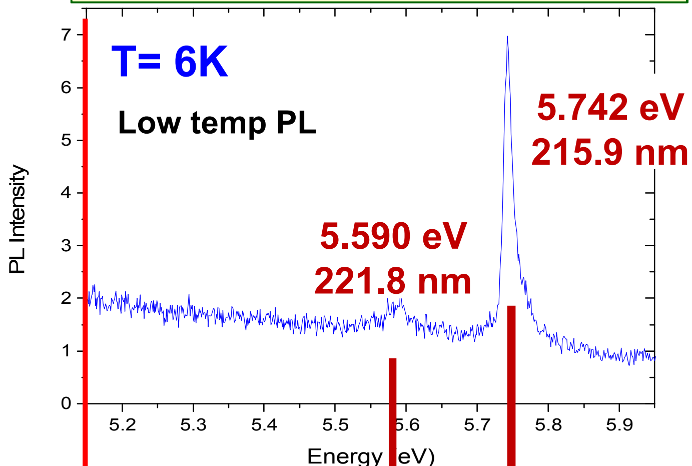
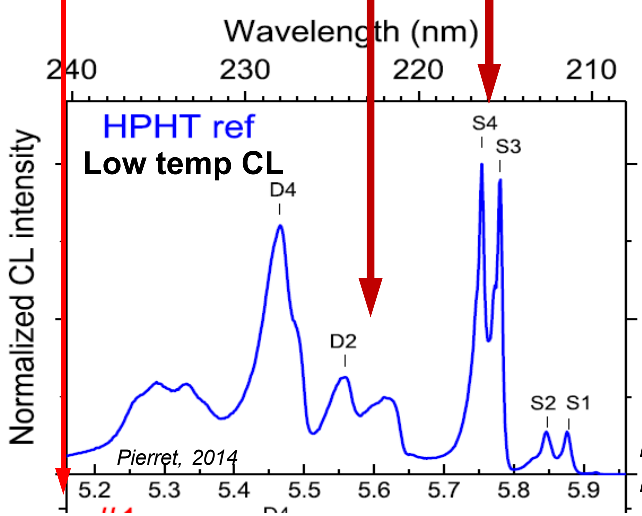
Low-Temperature Luminescence: Comparisons with Bulk and Exfoliated hBN

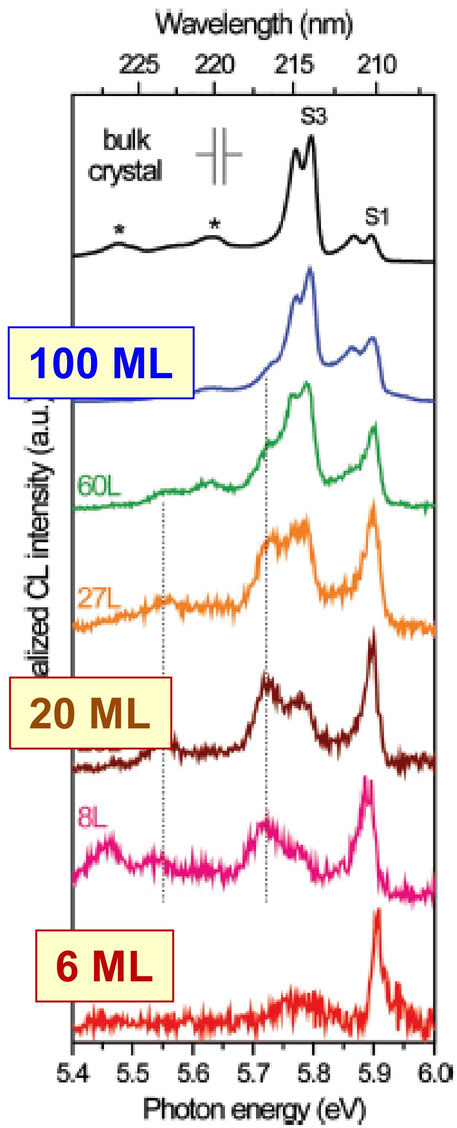
MOVPE hBN: Tg = 1600°C





Pierret, PRB (2014)

High-Pressure/High-Temp hBN Crystal



Exfoliated hBN Flakes

Low temp CL
Schue, Nanoscale (2016)

➔ Excitonic signatures of few ML MOVPE hBN similar to that of best exfoliated samples from high-quality hBN crystals

- **Evolution to 1 dominant peak (S1) near 5.9 eV with thinner exfoliated layers**
- **Few-ML MOVPE sample dominated by 5.75 eV peak (S4)**

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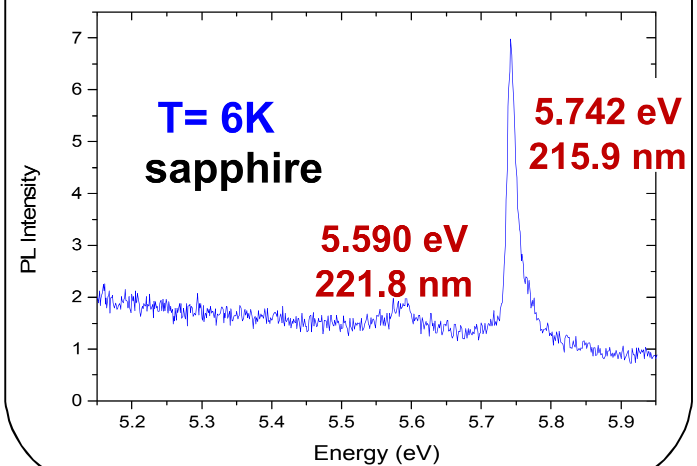
Low-Temperature Luminescence: Comparisons with other Epitaxially-Grown hBN

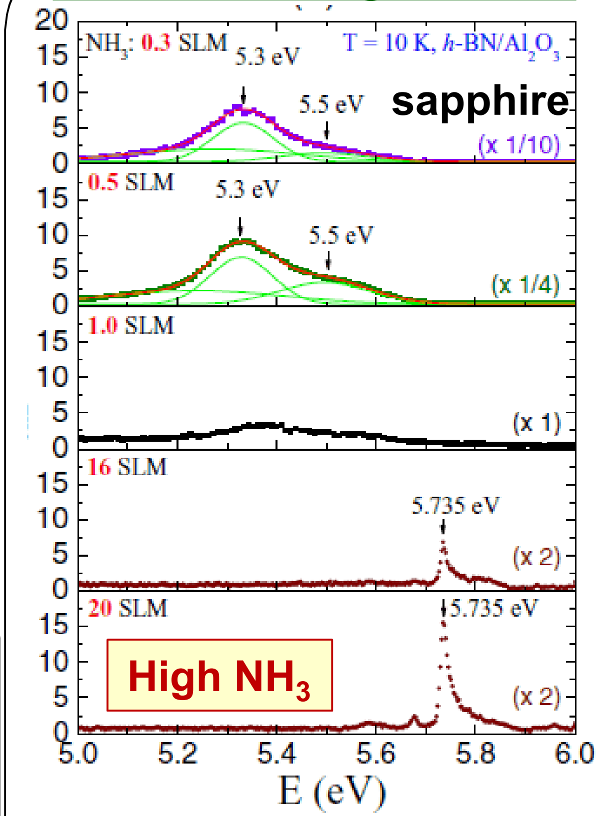
MOVPE: High temp or moderately high temp and high NH_3 yields dominant ~5.74 eV peak

MBE: Moderately high temp yields higher energy ~5.9 eV peaks on HOPG

MOVPE hBN: Tg = 1600°C



MOVPE hBN: Tg = 1350°C

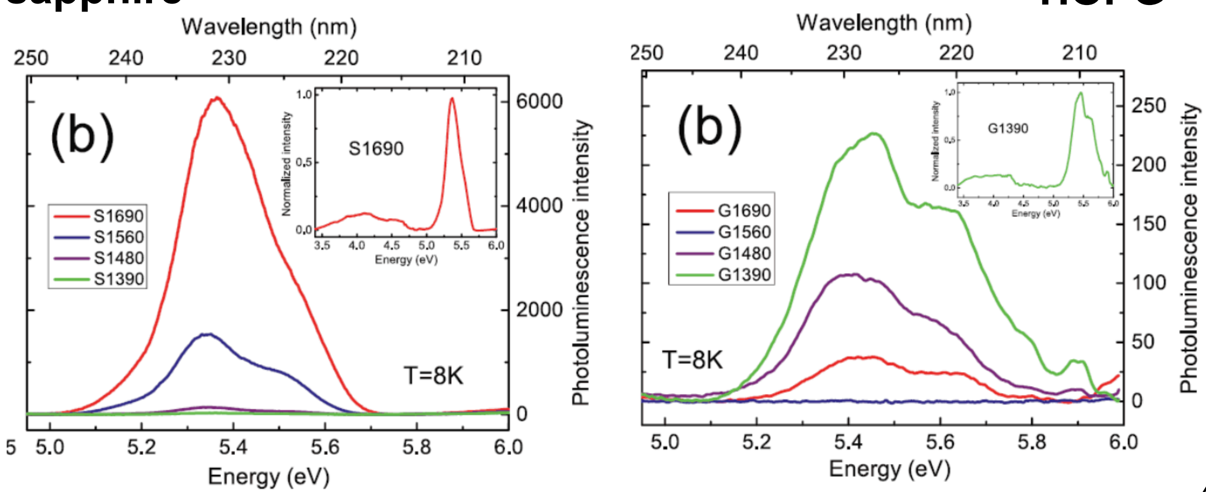


Du et al., APL (2016)

MBE hBN: Tg = 1390-1690 °C

sapphire

HOPG



Vuong et al. 2D Mat 2017

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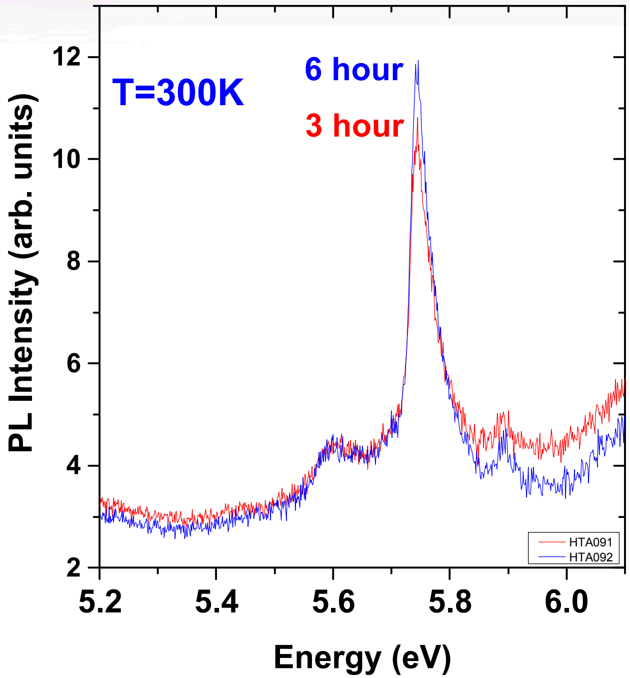
Potential for Self-limiting Growth at high T_g

PL Measurements

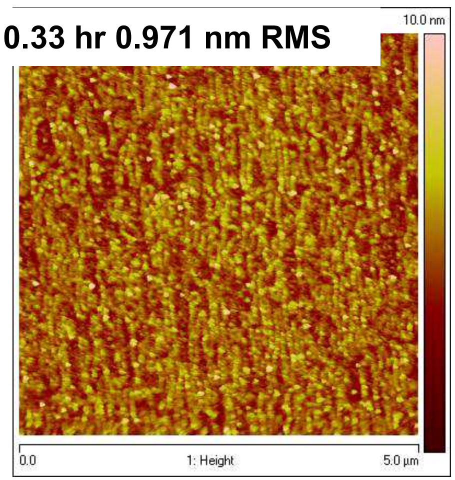


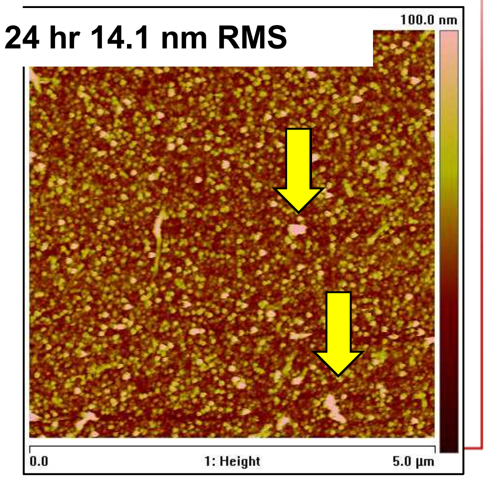
- Relatively little change in PL intensity over a large range of growth times
- Raman ratio (hBN/Sapphire) suggests only a few MLs even for 24 hours of growth
- Films roughen, largely due to increased number of larger particulates with longer growth times

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





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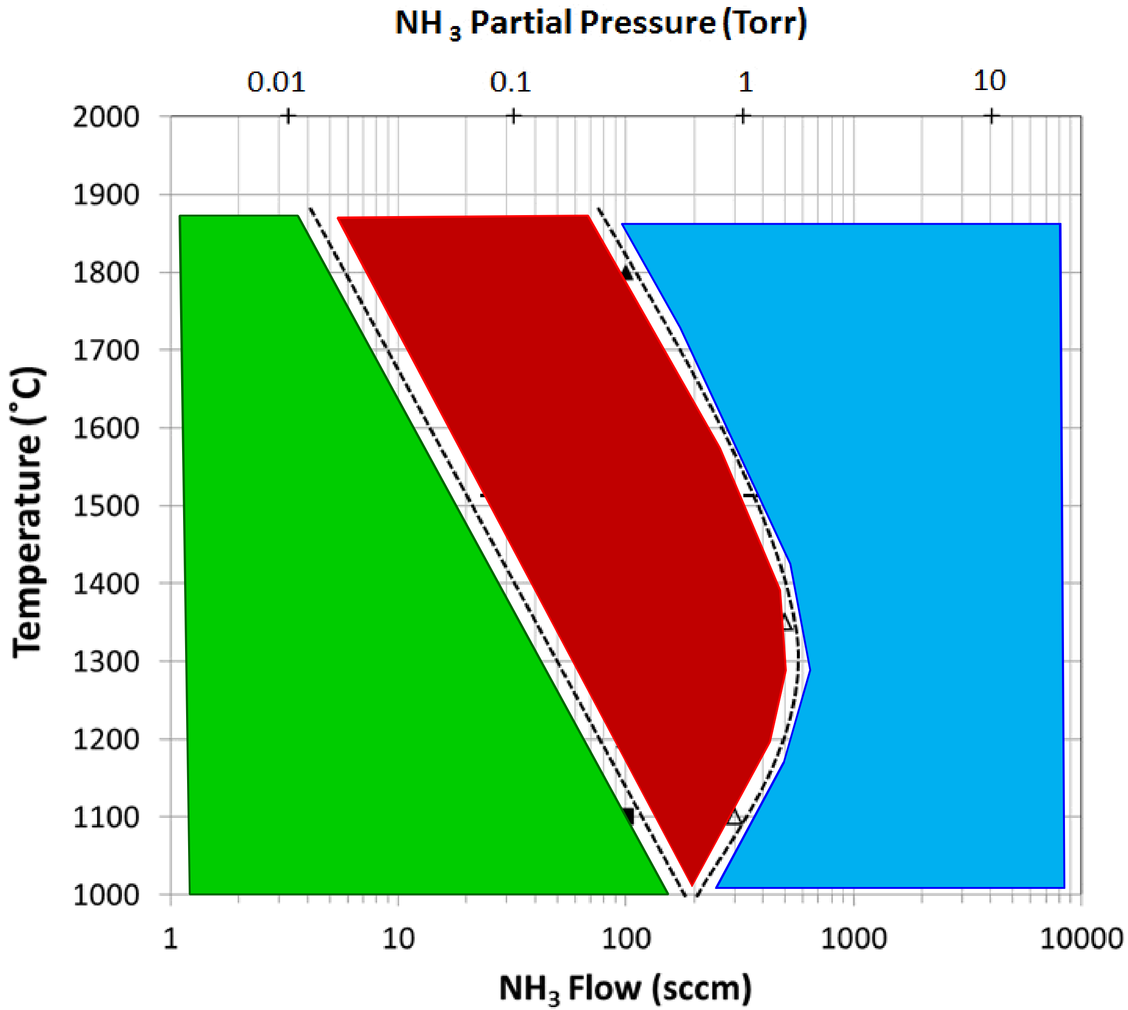
Growth parameter space for achieving few-ML-thick films

→ Focus on Growth Temperature and NH_3 flow

Growth Regimes

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



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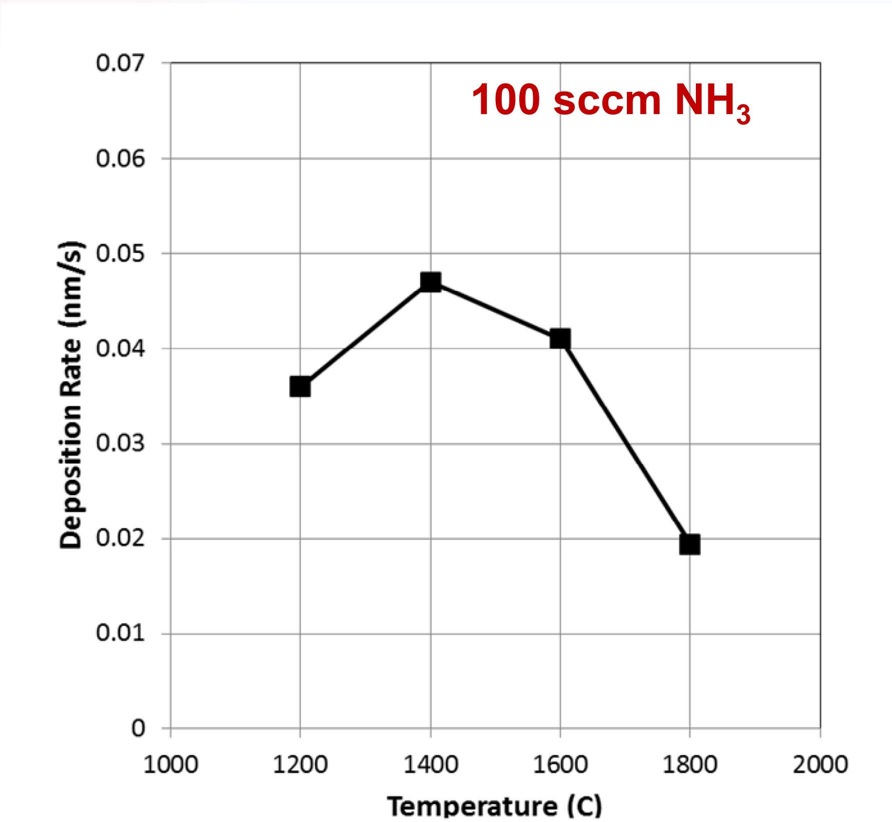
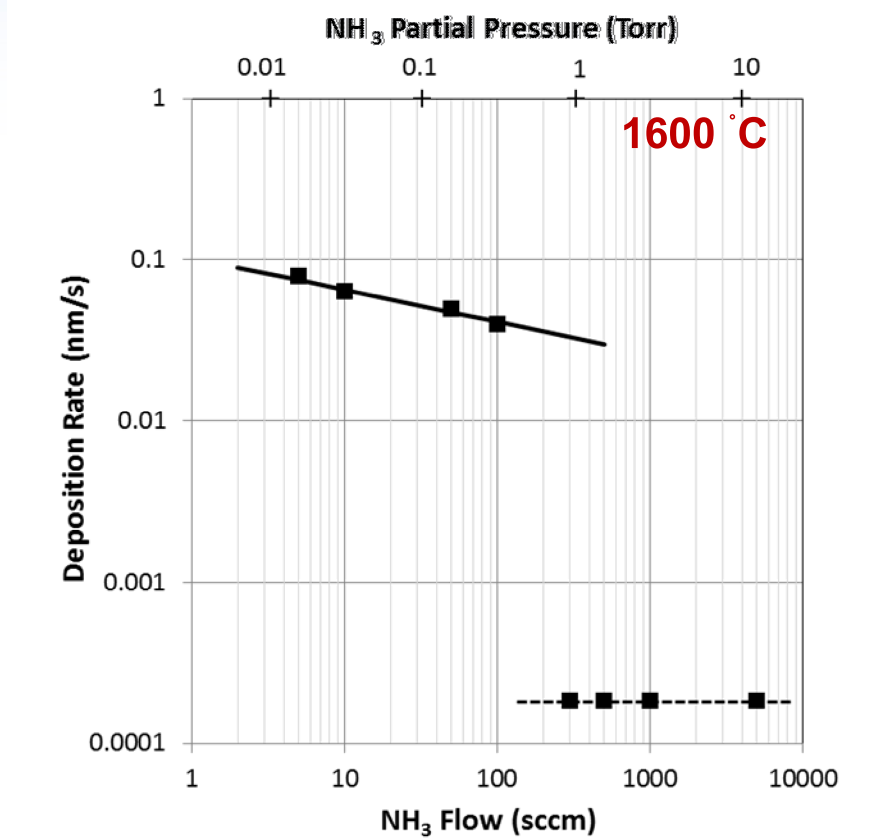
Growth rate studies to evaluate self-limiting mechanism





- Growth rate is weakly temperature dependent
- ~2.5x change over 600 ˚C

- Critical NH_3 threshold exists for all temperatures
- 2-3 orders of magnitude change in growth rate

→ Trends not consistent with parasitic reactions

A. Rice

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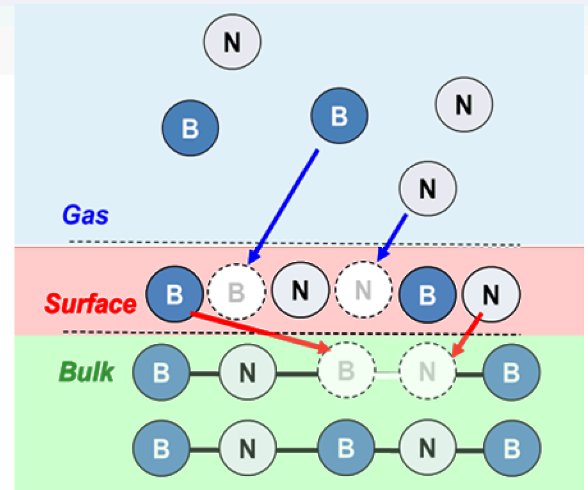
Possible Model: Langmuir-Hinshelwood

- Competitive absorption of species that react on a surface



- Controlling reactions:

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

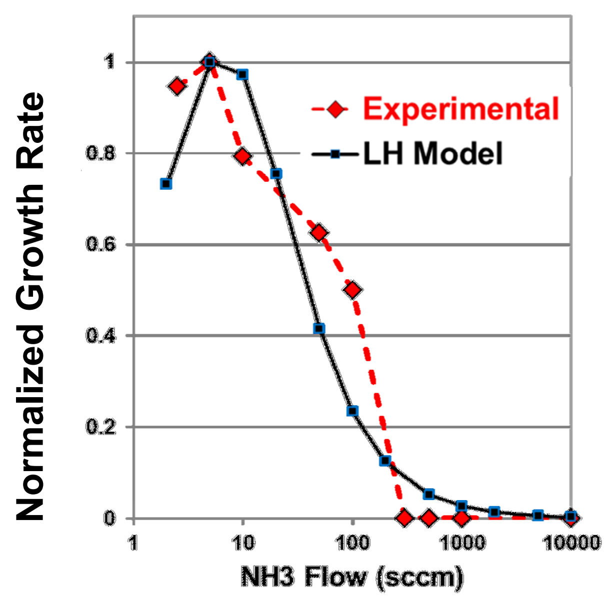
$$N_{gas} + Open_{surface} \overset{k_N}{\leftrightarrow} N_{surface}$$

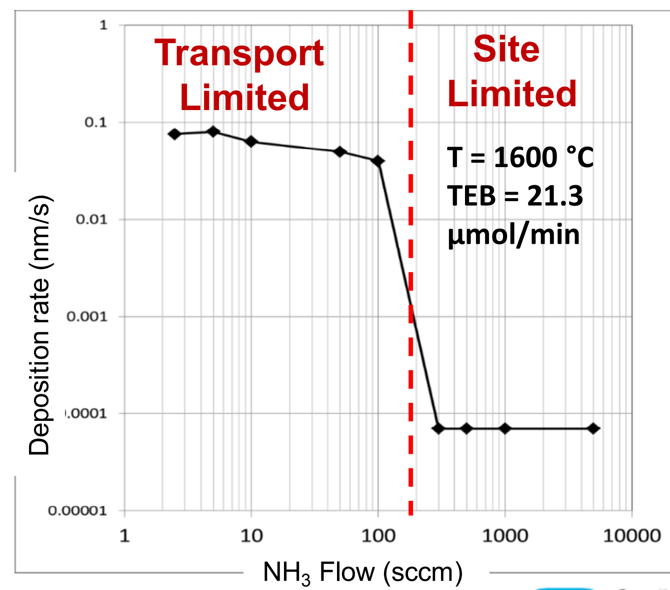
$$B_{surface} + N_{surface} \overset{k_{rxn}}{\longleftrightarrow} BN_{bulk} + 2Open_{surface}$$

- 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





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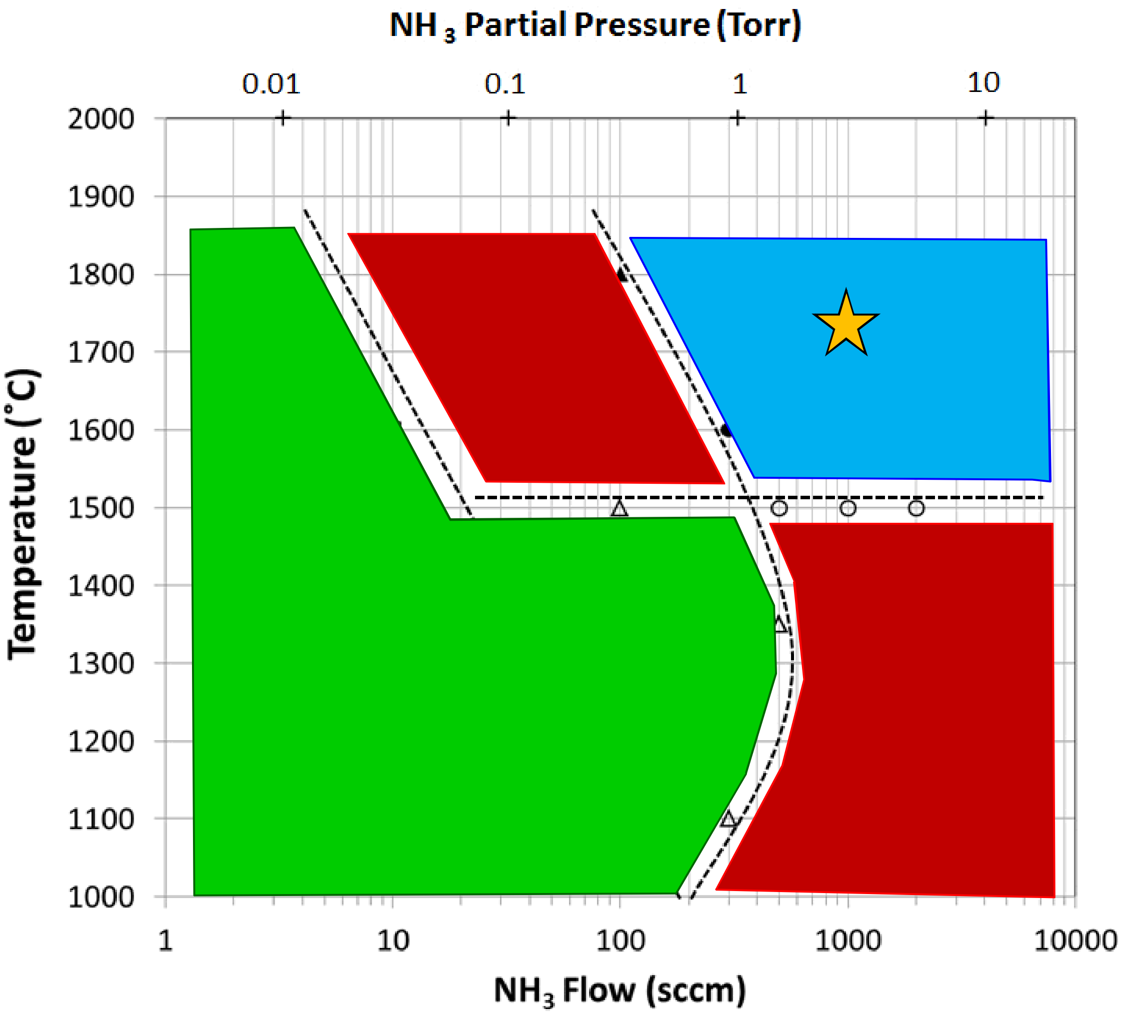
Correlation of Growth Conditions and Excitonic Performance

<u>**3 regimes in room temp PL**</u>

- **No exciton emission**
- **Defect bound exciton**
- **Free exciton**

RT PL



High NH_3 and high temperature for RT excitons

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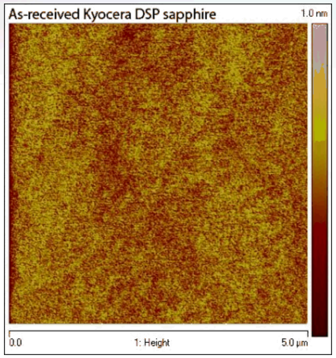
Challenge with High Temp Growth: Nitridization of Sapphire Substrate

Sapphire Substrate

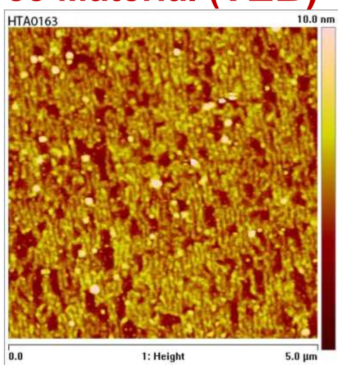
0 min
> 0.1 nm
RMS



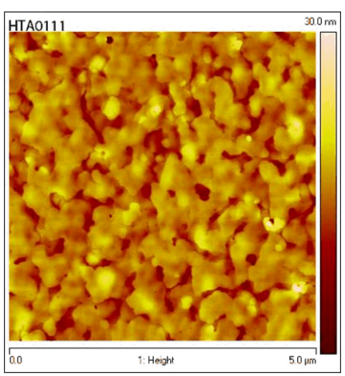
Nitrided Sapphire Substrate

1600°C NH_3 but No Boron Source Material (TEB)

5 min
1.17 nm
RMS

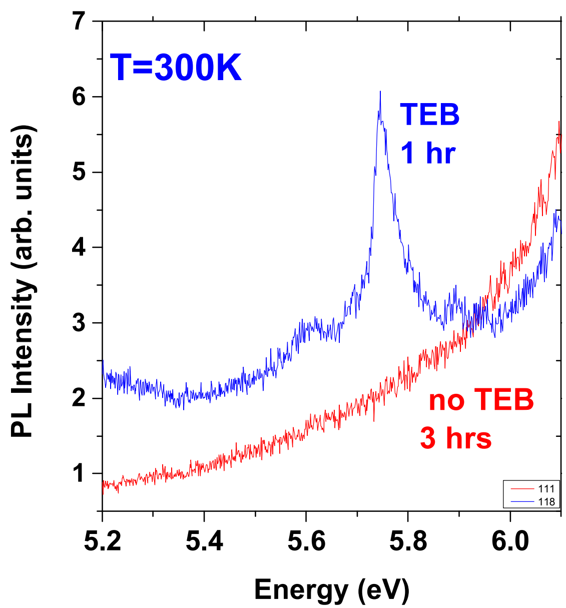


180 min
2.71 nm
RMS

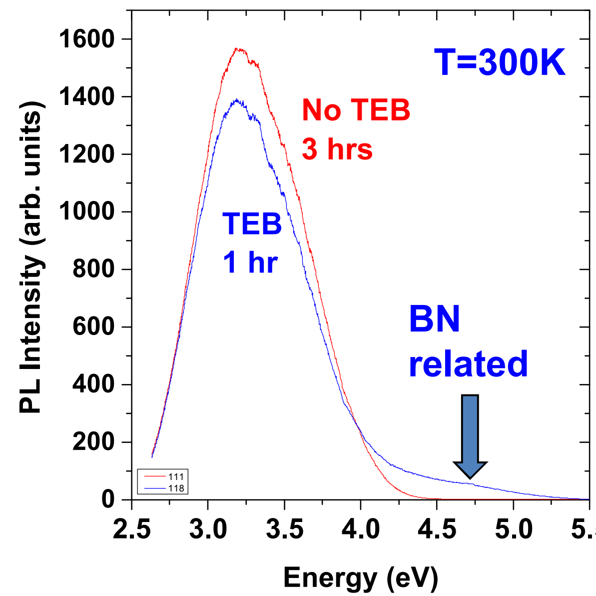


PL comparison: BN on Sapphire vs. Nitrided Sapphire

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 ~ 3.2 eV

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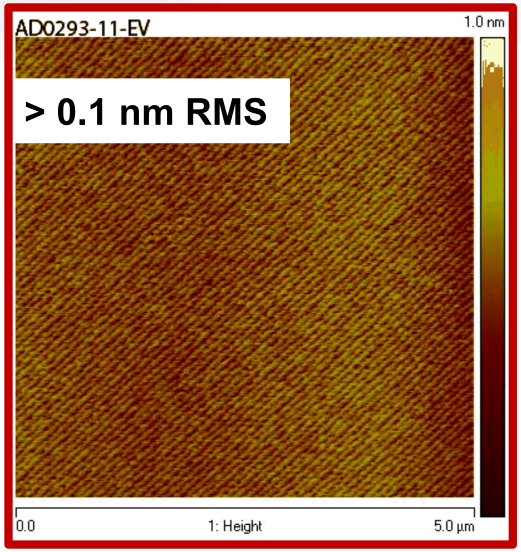
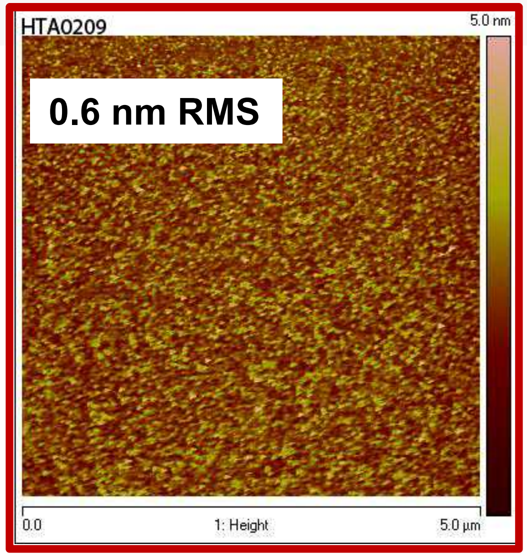
Alternative Substrates: SiC

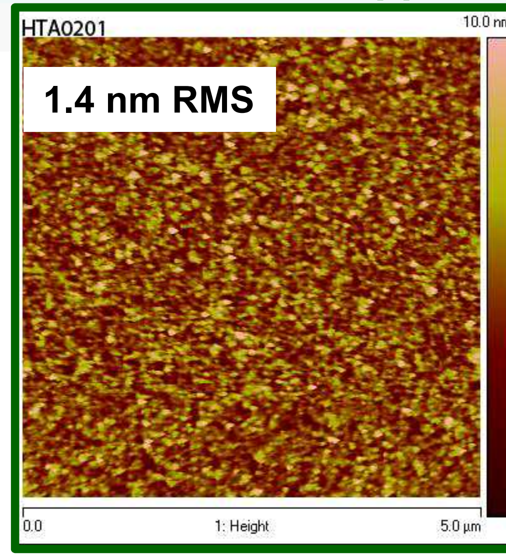
As-received SiC



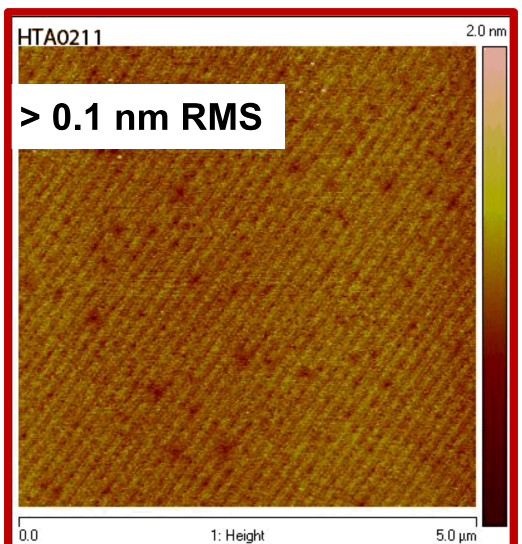
1600°C BN on SiC



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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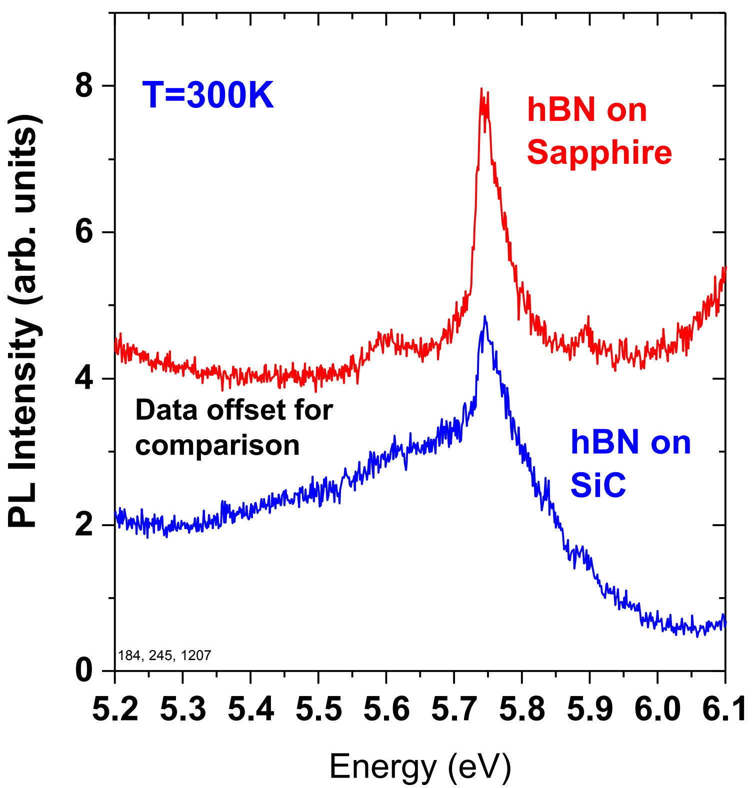
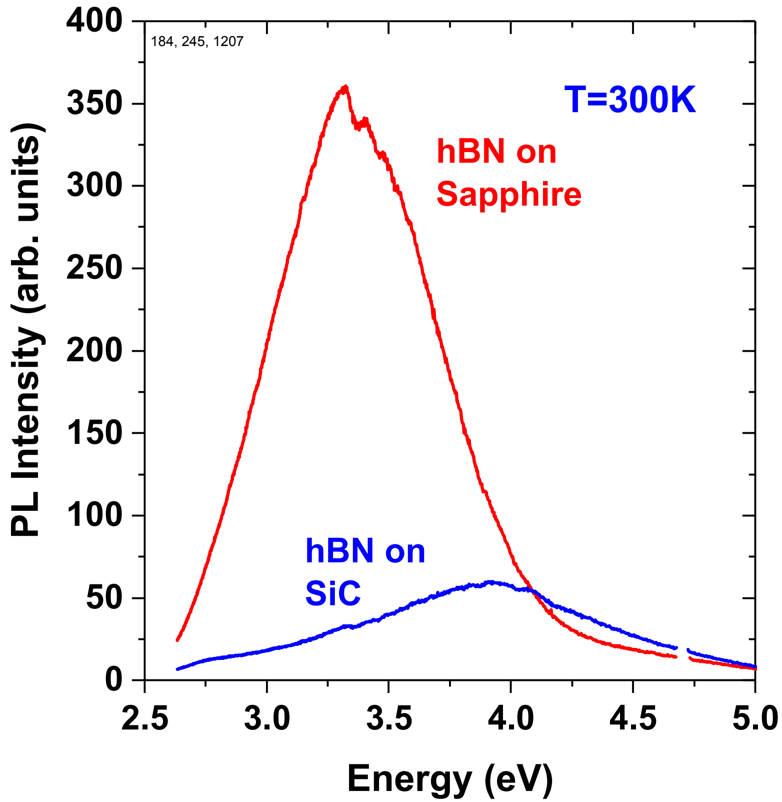
hBN on SiC: Luminescence Properties

Near Band Edge PL



Deep Level Emission



- **Observe 5.75 eV excitonic peak in room-temp PL, not as well defined as on sapphire**
- **Elimination of deep level peak associated with nitrided sapphire**

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Borazine to reduce sapphire substrate degradation at high temperature

Pros

- **Literature reports of BN deposition**
- **High vapor pressure**
- **Liquid source**
- **Single source growth**

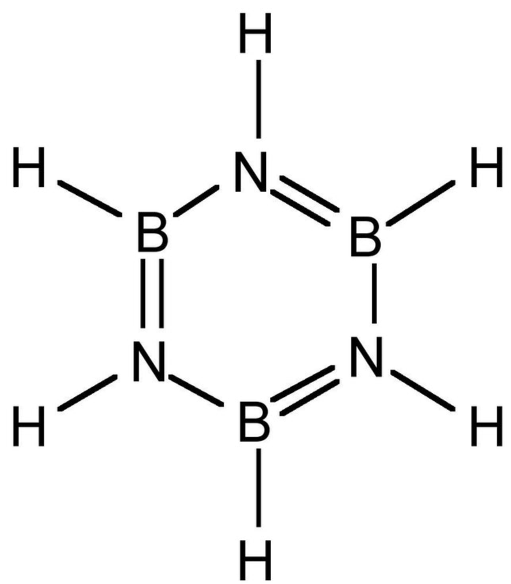
Cons

- **Literature reports are mostly on metal**
- **Stability and purity of source**
- **Single source growth, e.g., no independent control of V/III ratio**

~~TEB + NH_3~~

Borazine

$(NH)_3(BH)_3$



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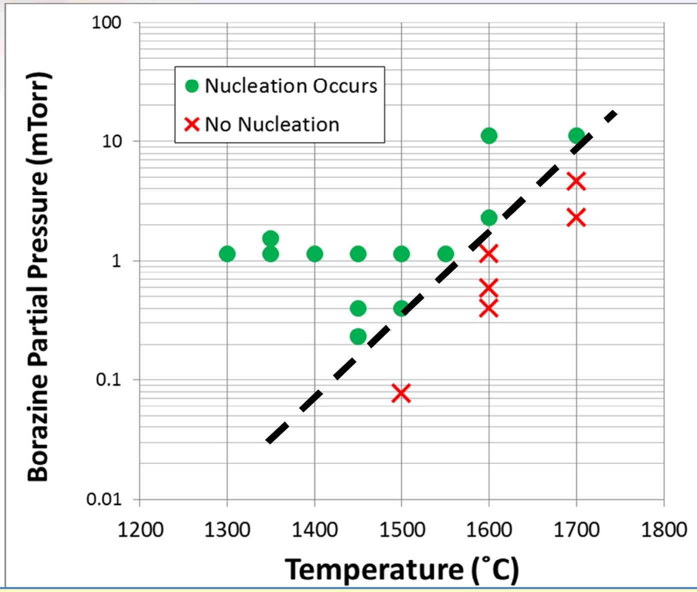
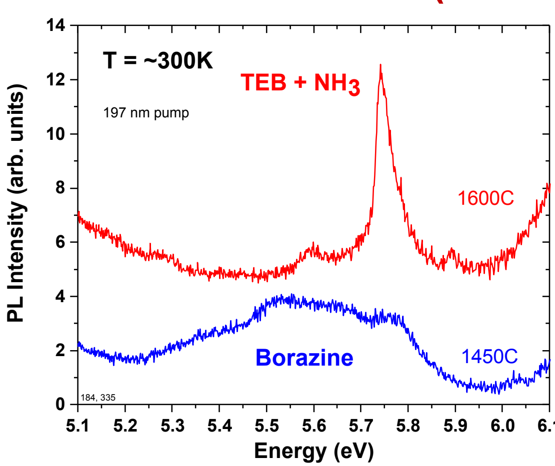
hBN on Sapphire using Borazine

Epitaxial Growth Studies



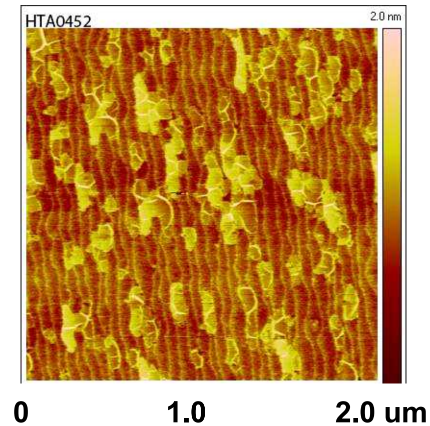
- Critical borazine partial pressure for nucleation
- Strong function of growth temperature

Photoluminescence (~300K)

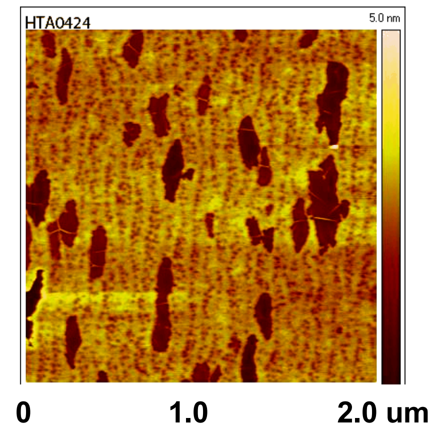


Characteristic Morphologies (AFM)

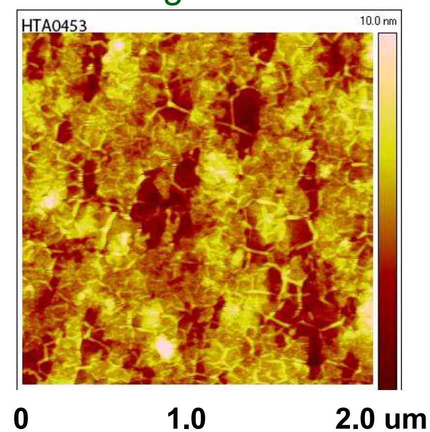
≤ 1 ML
RMS roughness ~0.2 nm



1 - 3 MLs
RMS roughness ~0.5 nm



≥ 3 ML
RMS roughness >1 nm



- Morphology largely determined by thickness
- Not a strong function of borazine partial pressure or temperature

A. Rice

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Summary

- Explored high-T_g MOVPE as an approach to achieving high-quality, few-ML-thick hBN films
- Lower-Tg films (pulsed growth) demonstrated notable in-plane rotational disorder and defect-related excitonic signatures
- Dramatic evolution of excitonic properties with $T_{g;}$ T_g ~ 1600°C yielded strong free exciton features similar to best exfoliated crystals
- Proposed site-blocking model to explain self-limiting growth of few ML thickness at high-Tg
- SiC substrates or Borazine precursor are promising to avoid sapphire substrate degradation at high temperatures
- Growth of few-ML-thick hBN films on sapphire using Borazine; studied nucleation, structural and optical properties

Funding Acknowledgement: This work was funded by Sandia's Laboratory Directed Research and Development Program

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- Extra Slides

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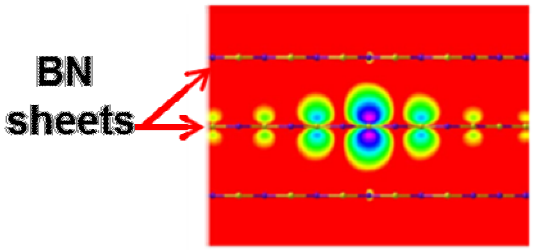
Excitonic Properties at Few-Monolayer Thickness

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

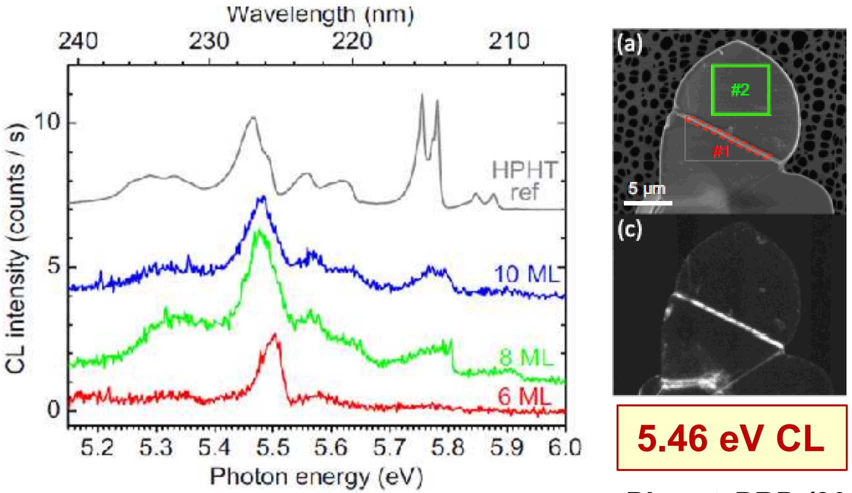
Strong Exciton Confinement



Exciton probability density (5.78 eV)

Arnaud, PRL(2006)

Low Temp. CL: Exfoliated hBN flakes

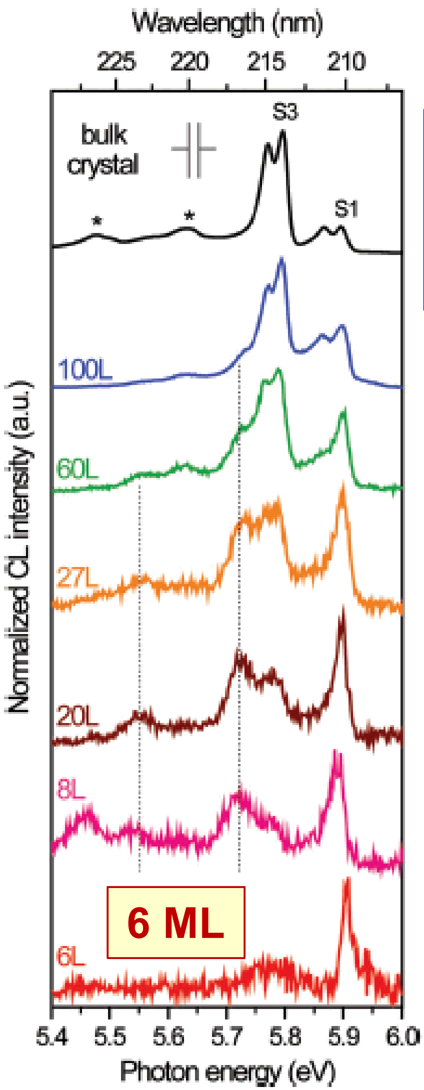


5.46 eV CL

Pierret, PRB (2014)

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

Low Temp CL: Exfoliated hBN Flakes



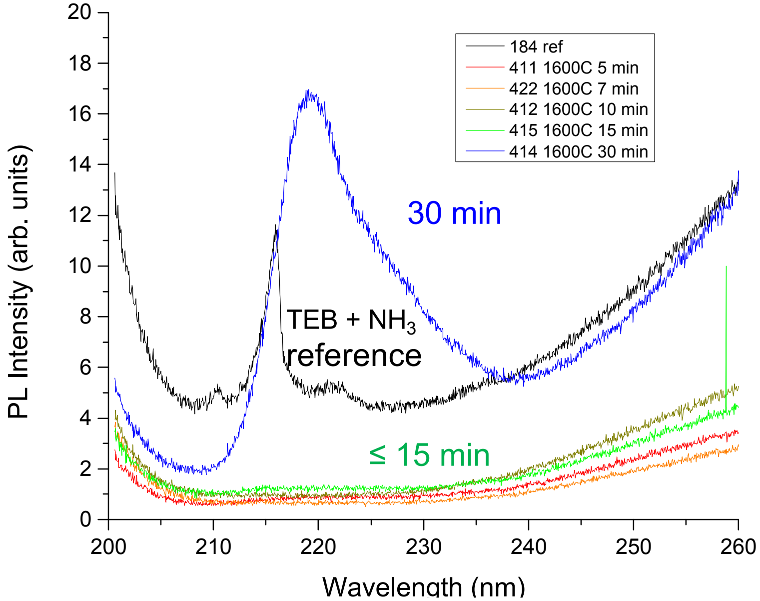
Improved Exfoliation: excitonic evolution down to 6 ML

➔ Explore epitaxial growth approaches

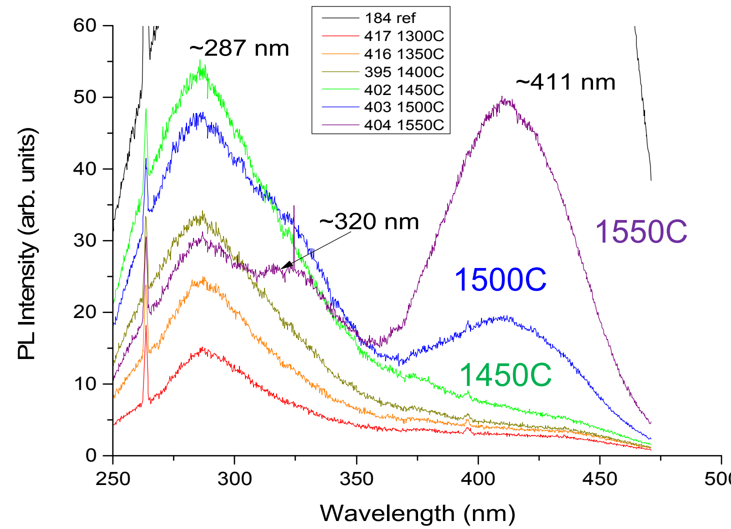
Schue, Nanoscale (2016)

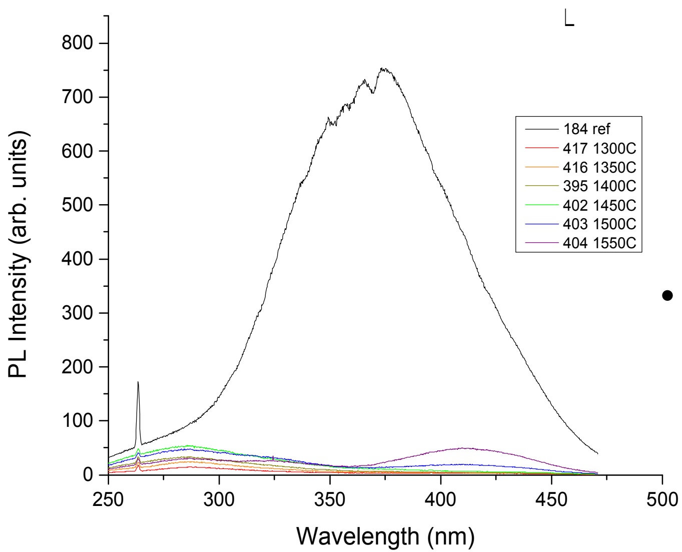
PL variations observed for hBN using Borazine

- Longer growth times/ thicker films needed for near band-edge emission



- Deep level peaks dependent on growth temp
- Origin may be from defects in sapphire





- Nitrided sapphire deep-level peak is avoided with borazine at all growth temperatures

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Nucleation Theory

→ In depth study of nucleation of hBN on sapphire
→ Not possible with commonly-used TEB and NH_3 sources, substrate degradation

Nucleation Theory

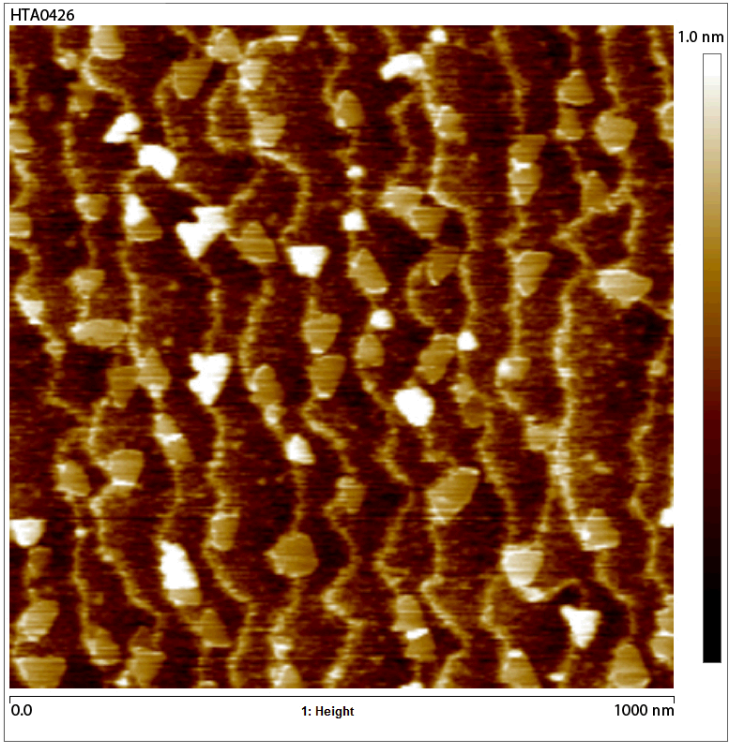
- Control of nucleation is critical for heteroepitaxy
- Classical Nucleation:

$$N = Ce^{-\Delta G/kT}$$

Nuclei Density (N) · Adatom Density (C) · Temperature (T)

- Would expect:
  - Higher temperature = Less nuclei
  - More precursor = More nuclei

AFM



BN nuclei on sapphire
Deposition at 1450 ˚C

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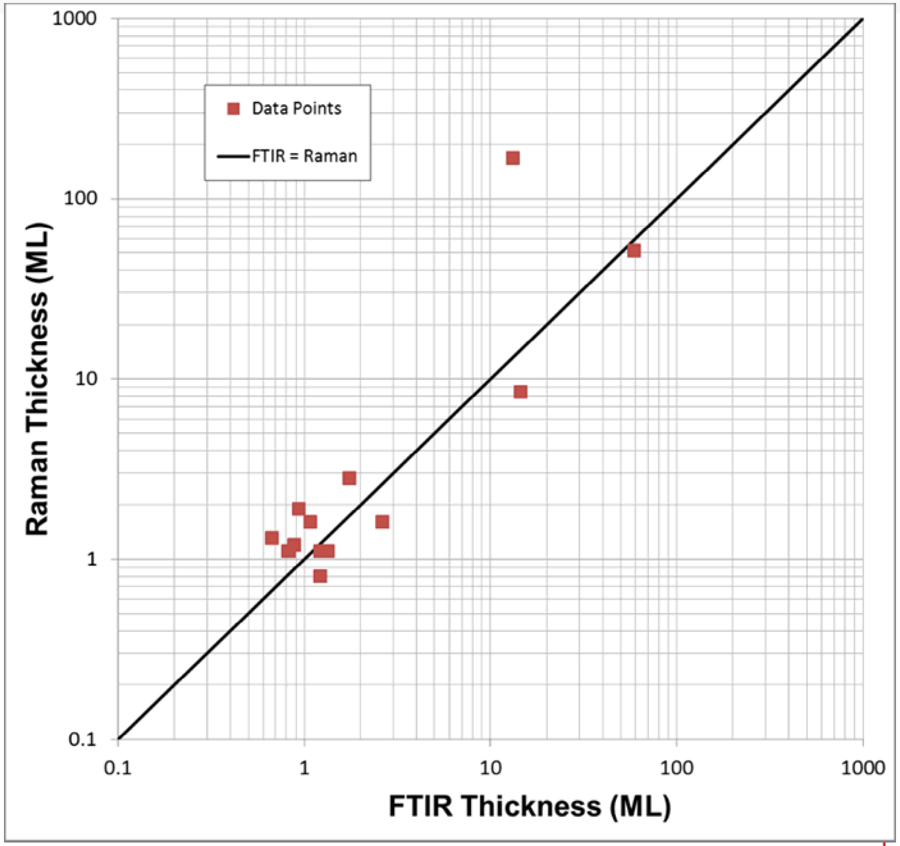
Comparison of Two Techniques

Sample	FTIR Thickness (ML)	Raman Thickness (ML)
427	0.83	1.1
444	0.85	0
445	0.89	1.2
468	59.39	51
473	13.22	168*
474	14.55	8.4
476	1.22	1.1
478	2.64	1.6
479	0.94	1.9
480	0.55	0
481	0.82	1.1
482	0.67	1.3
485	1.34	1.1
488	1.22	0.8
489	1.76	2.8
490	1.08	1.6

* Anomalous data point



- **No systematic over or underestimation between approaches**

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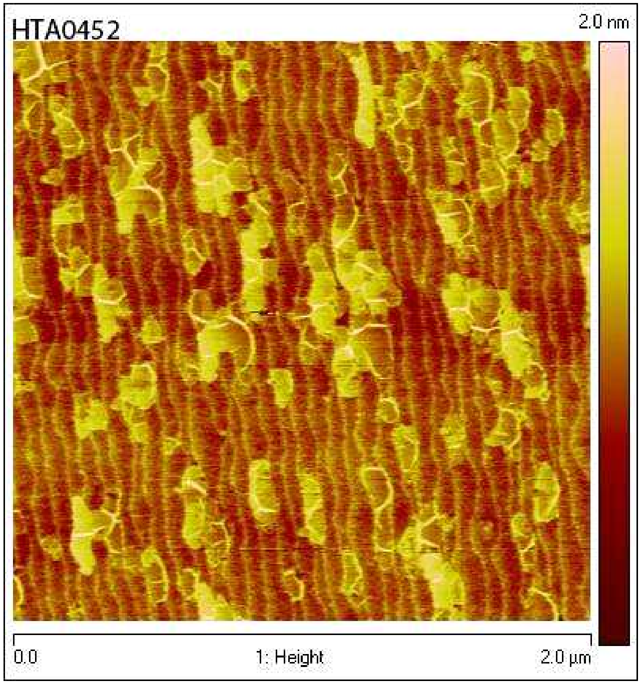
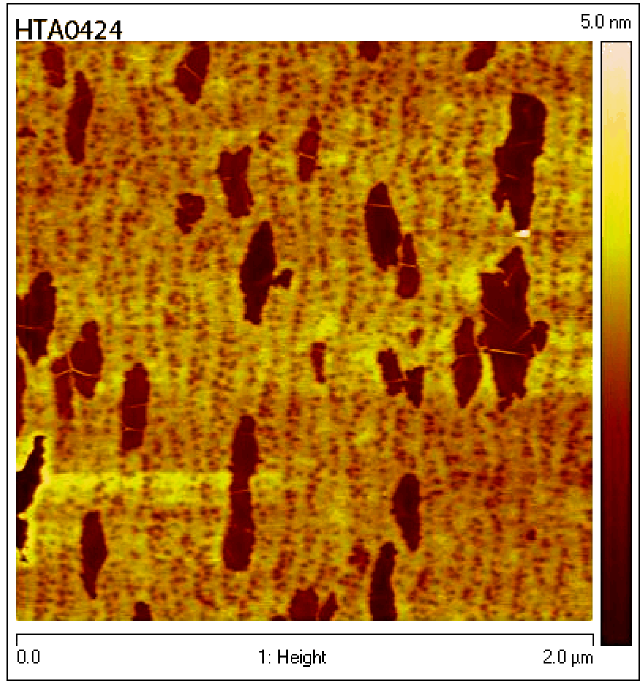
Morphology

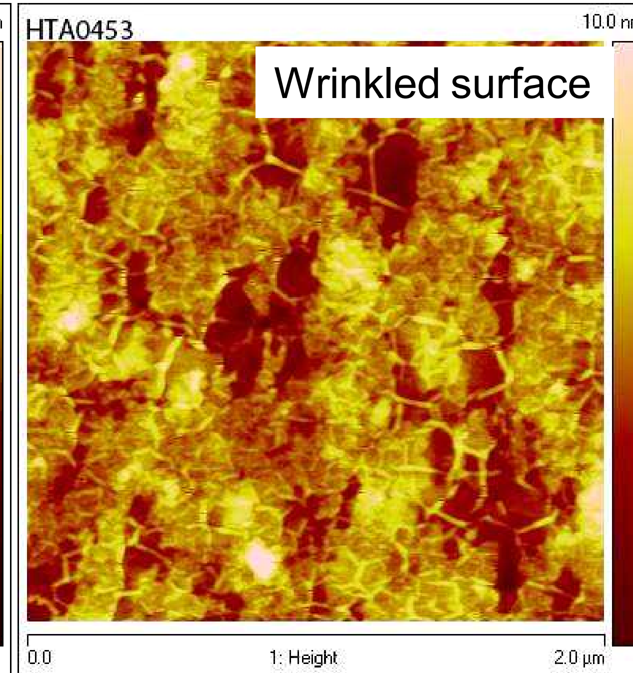
Atomic Force Microscope images: 3 characteristic morphologies



1 monolayer or less
RMS roughness ~0.2 nm



1 to 3 monolayers
RMS roughness ~0.5 nm



3 monolayers or more
RMS roughness >1 nm

- **Morphology dependent only on film thickness**
- **Growth temperature and borazine flux impact only nucleation**

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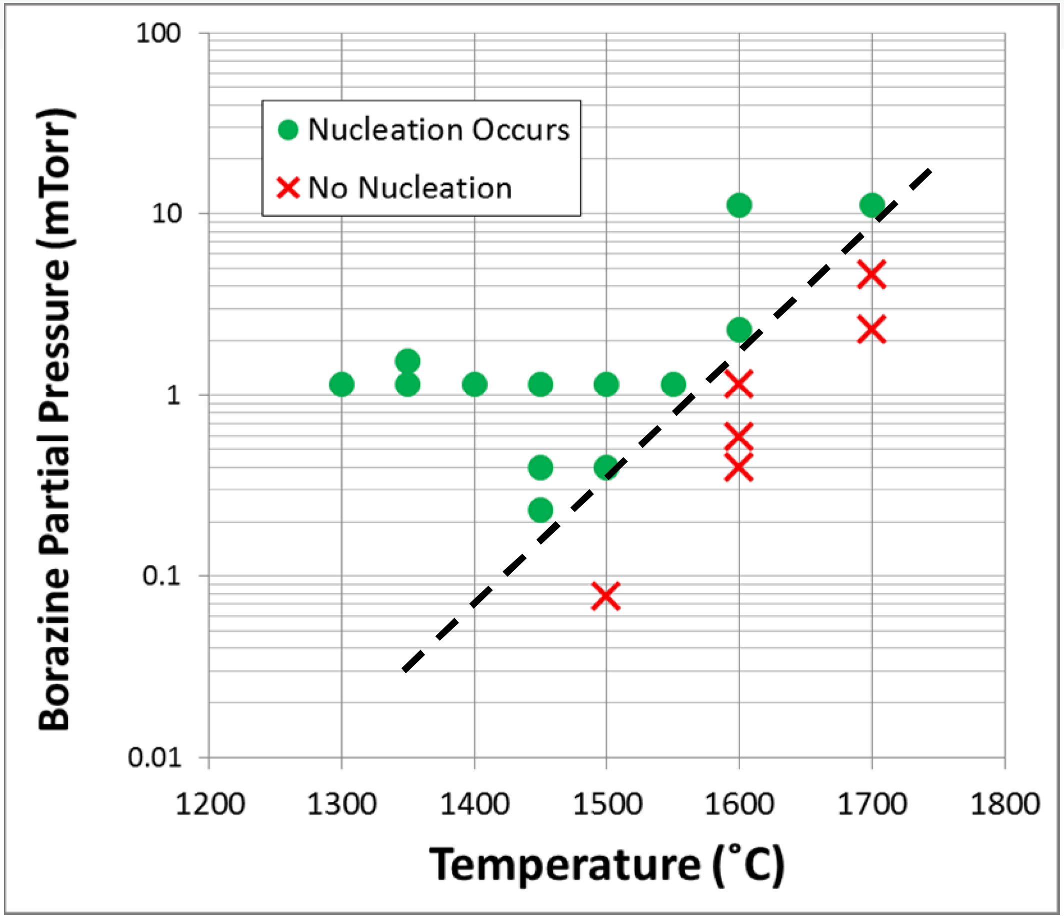
Experimental Nucleation Studies



- Critical borazine partial pressure for nucleation to occur
- Strong function of growth temperature

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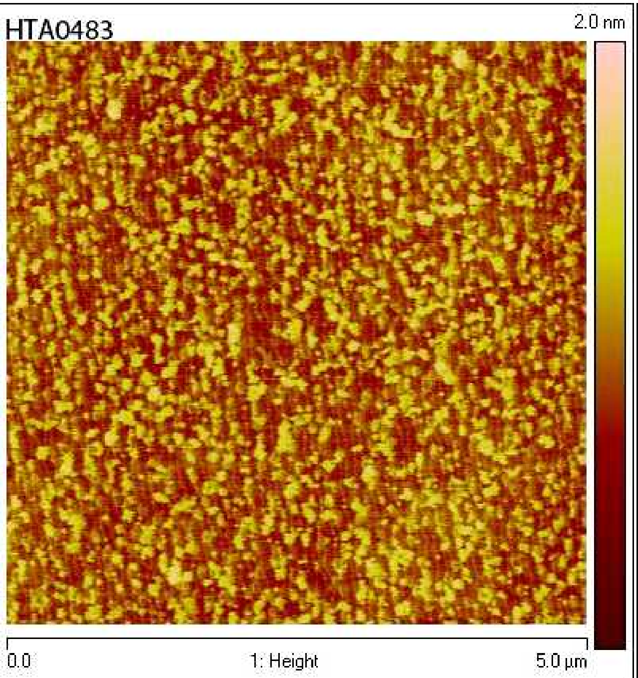
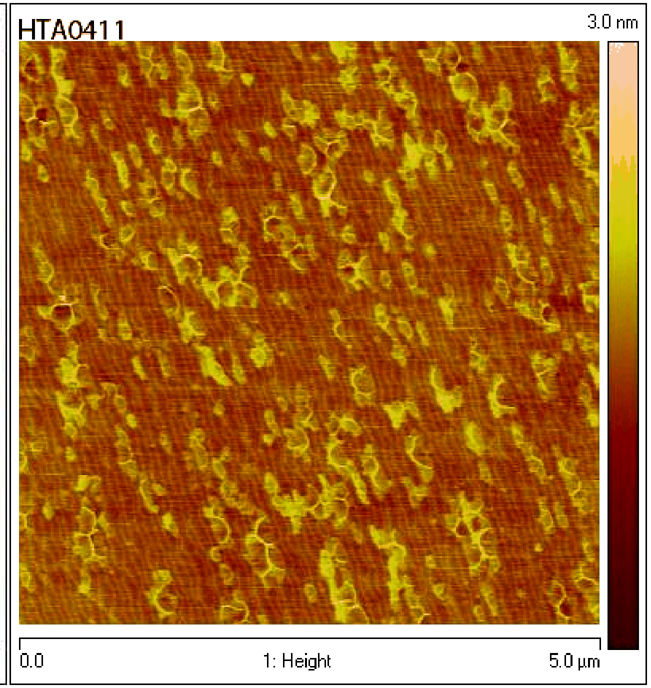
Nucleation with Flux

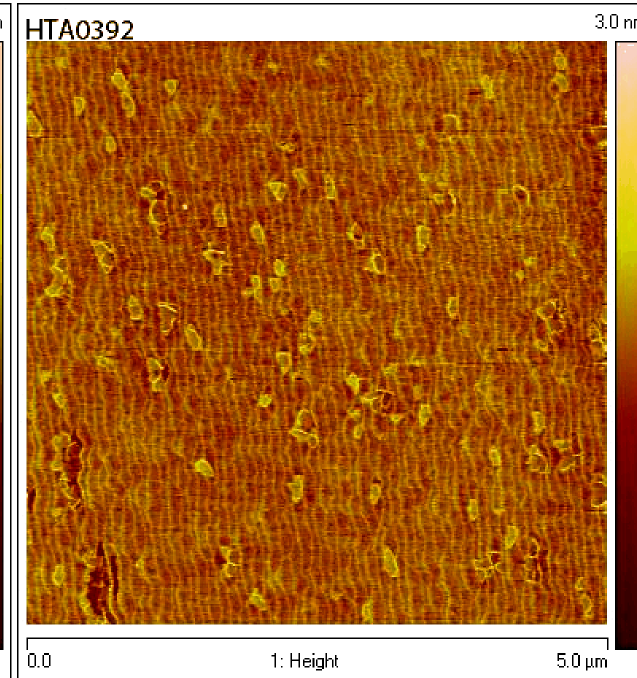
2 min at 1.5 µmol/min



5 min at 0.75 µmol/min



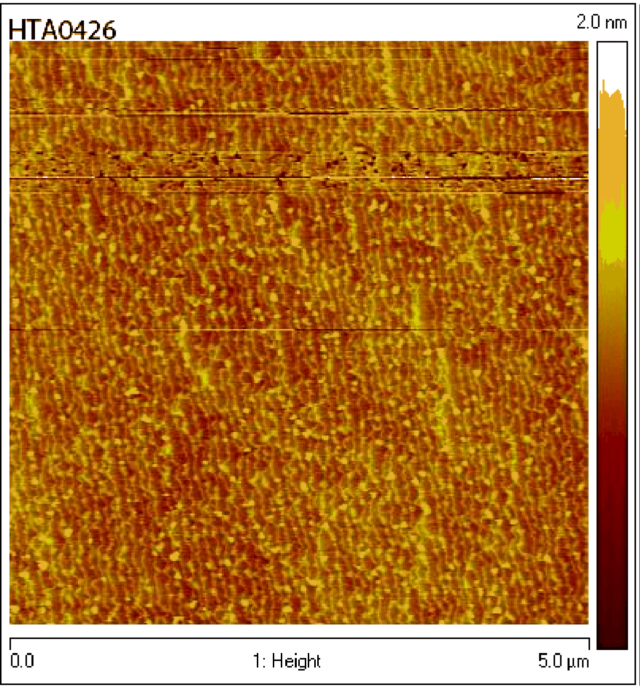
5 min at 0.37 µmol/min +
15 min at 0.13 µmol/min



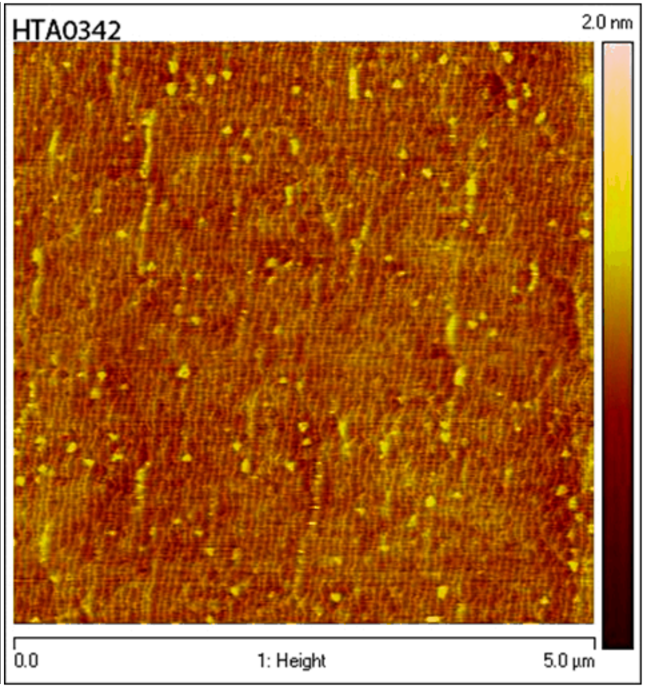
- **Fixed temperature of 1600 ˚C**
- **Nuclei density decreases with decreasing flux**
  - Consistent with classical nucleation theory

Nucleation with Temperature

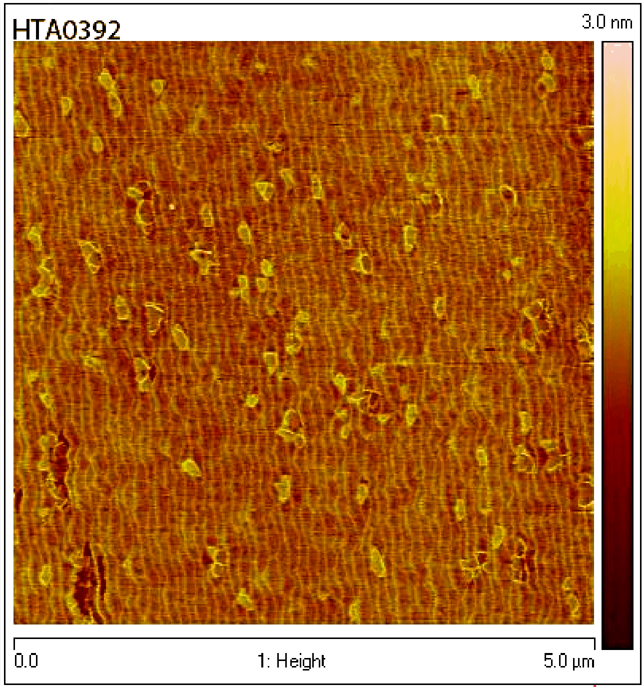
1450 °C



1500 °C



1600 °C



- **Fixed flux and dosage of borazine**
  - 5 min at 0.37 µmol/min + 15 min at 0.13 µmol/min
- **Nuclei density decreases with increasing temperature**
  - Consistent with classical nucleation theory

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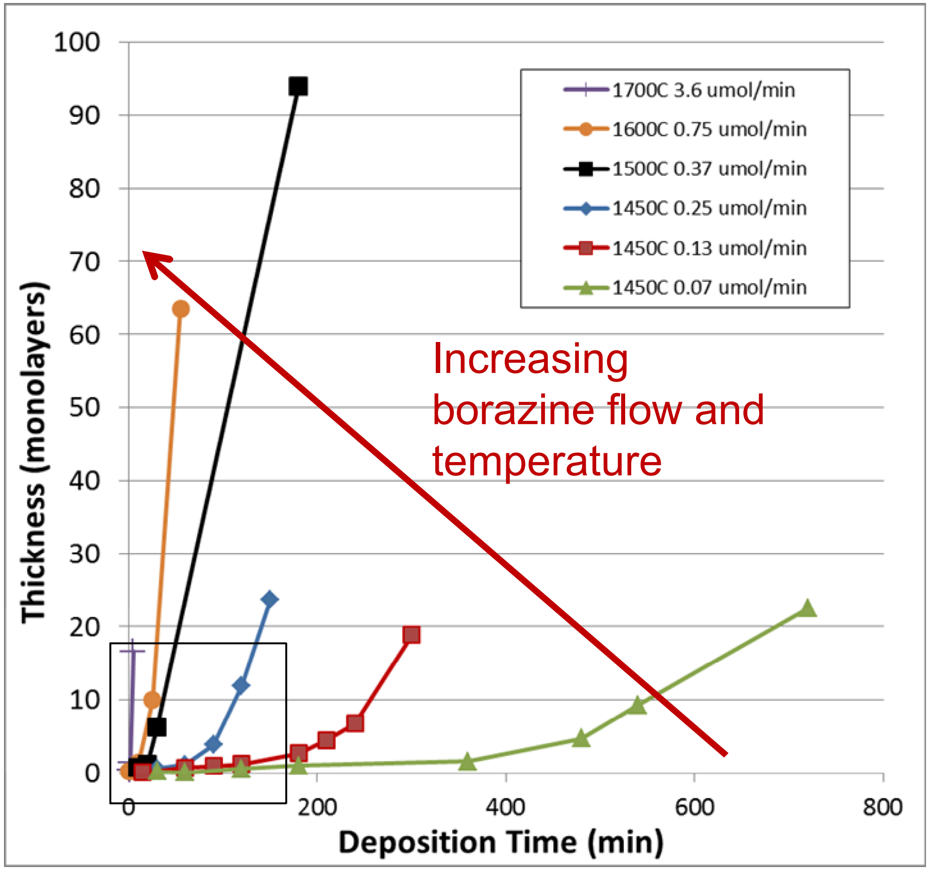
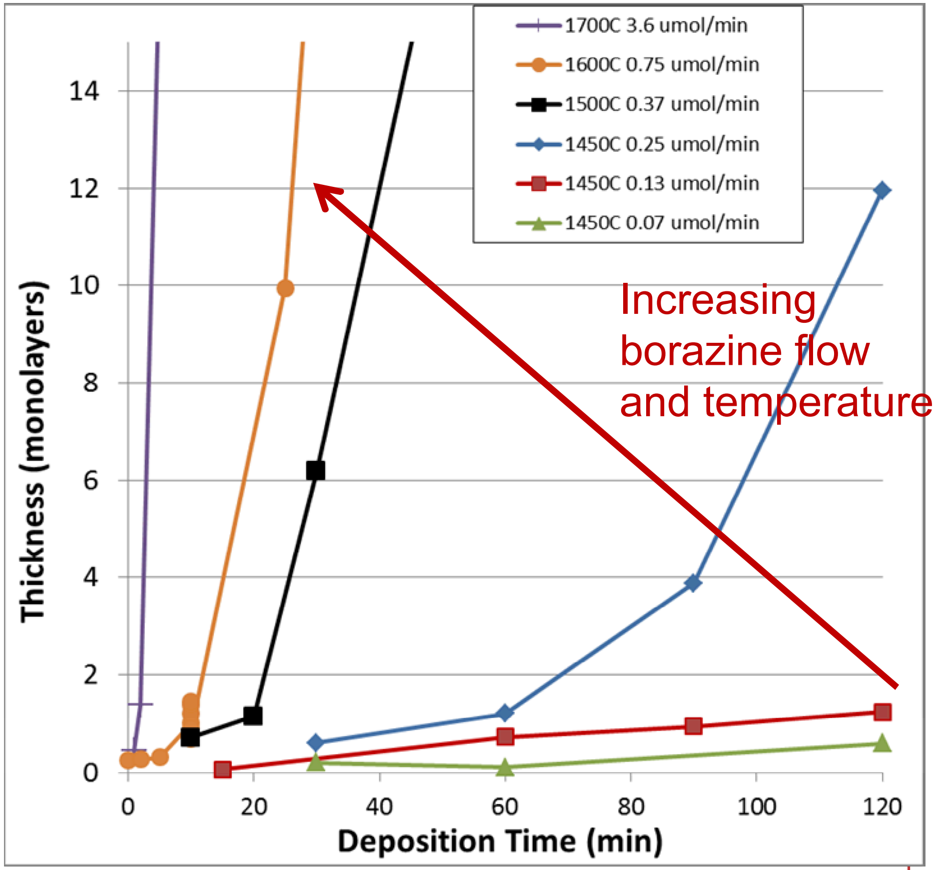
Film Deposition with Borazine



Expanded View



- Deposition rate is not constant with time

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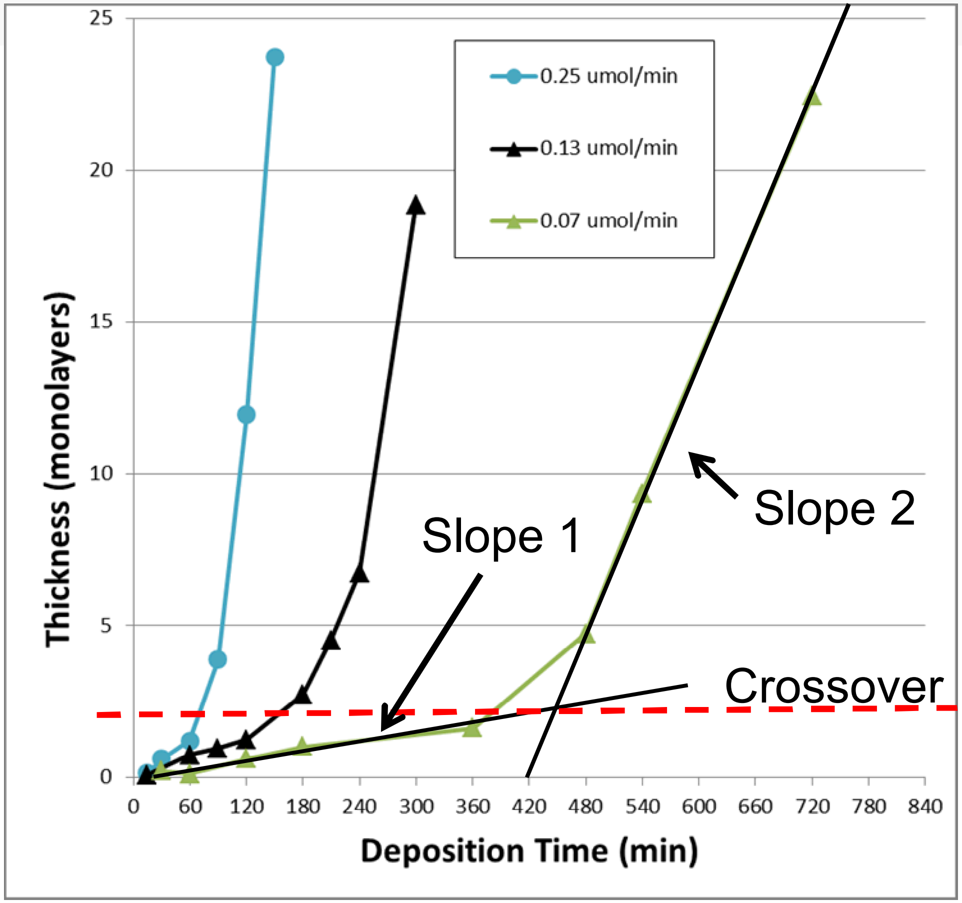
Film Deposition with Borazine



- Change in deposition behavior consistently seen at ~2 monolayers

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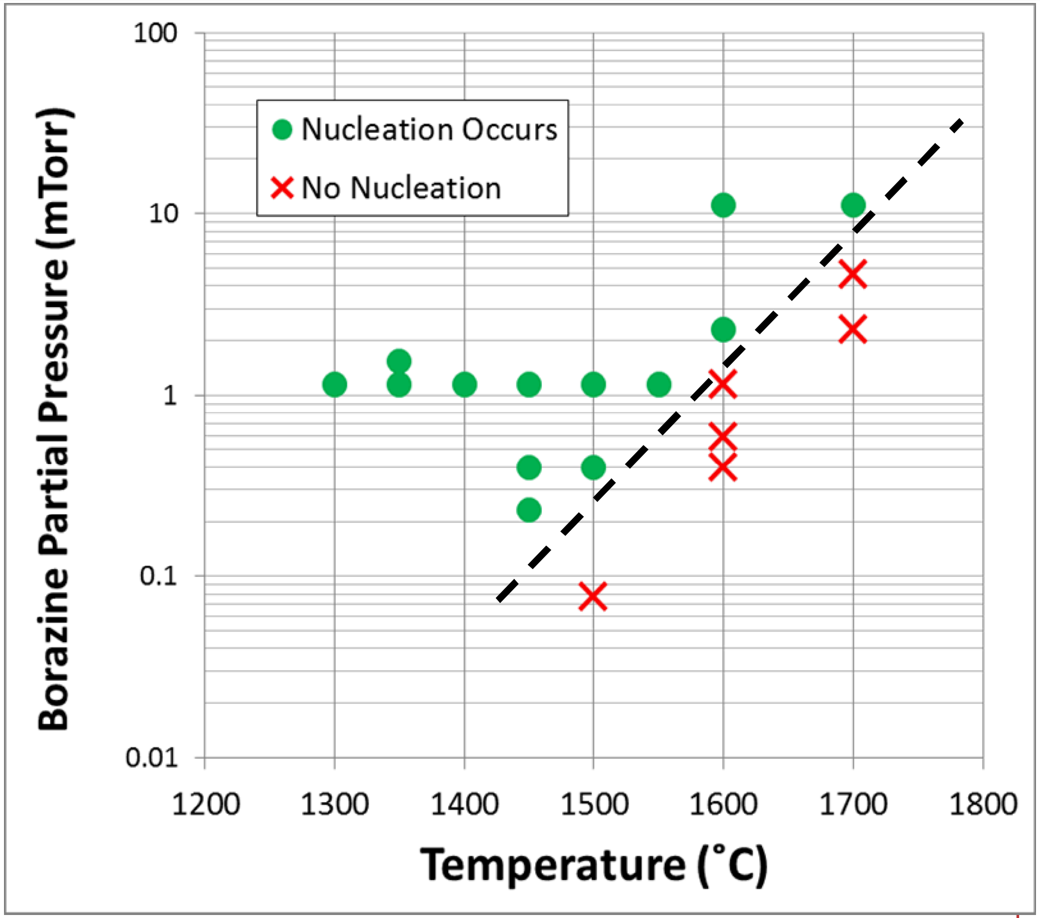
Separating Nucleation and Growth

Nucleation

- Threshold determined by supersaturation
- Must over come an energetic barrier to nucleate

Deposition

- Net mass flux to growth surface must be positive
- Just need a higher input partial pressure than equilibrium partial pressure



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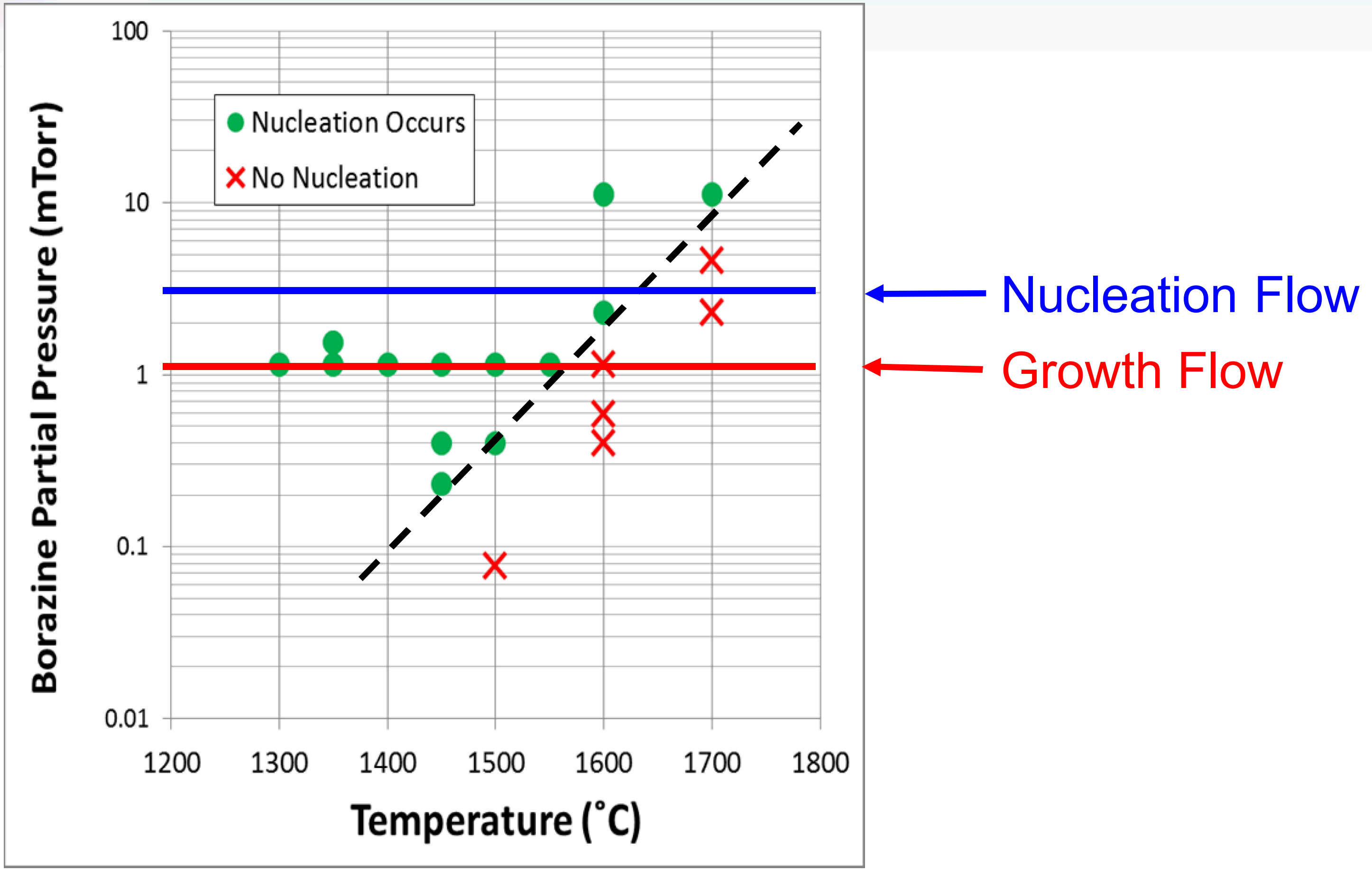
Separating Nucleation and Growth



- “Nucleation step” is 5 minutes at 0.37 μmol/min borazine
- Growth at 0.13 μmol/min borazine

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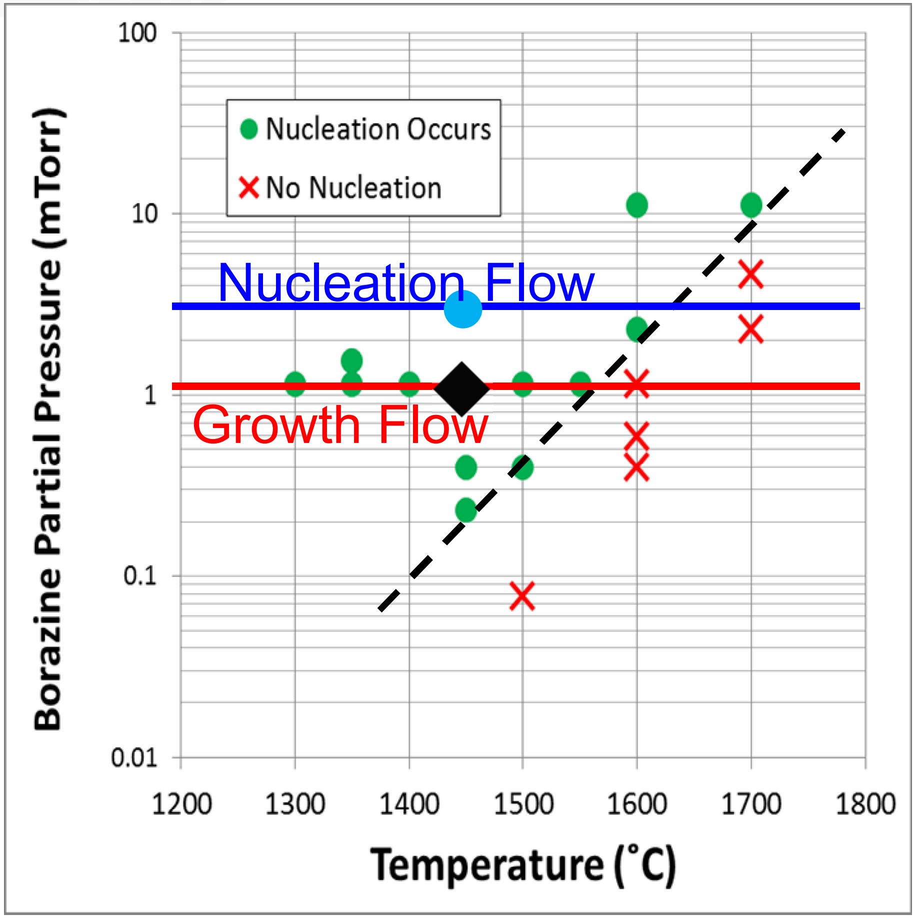
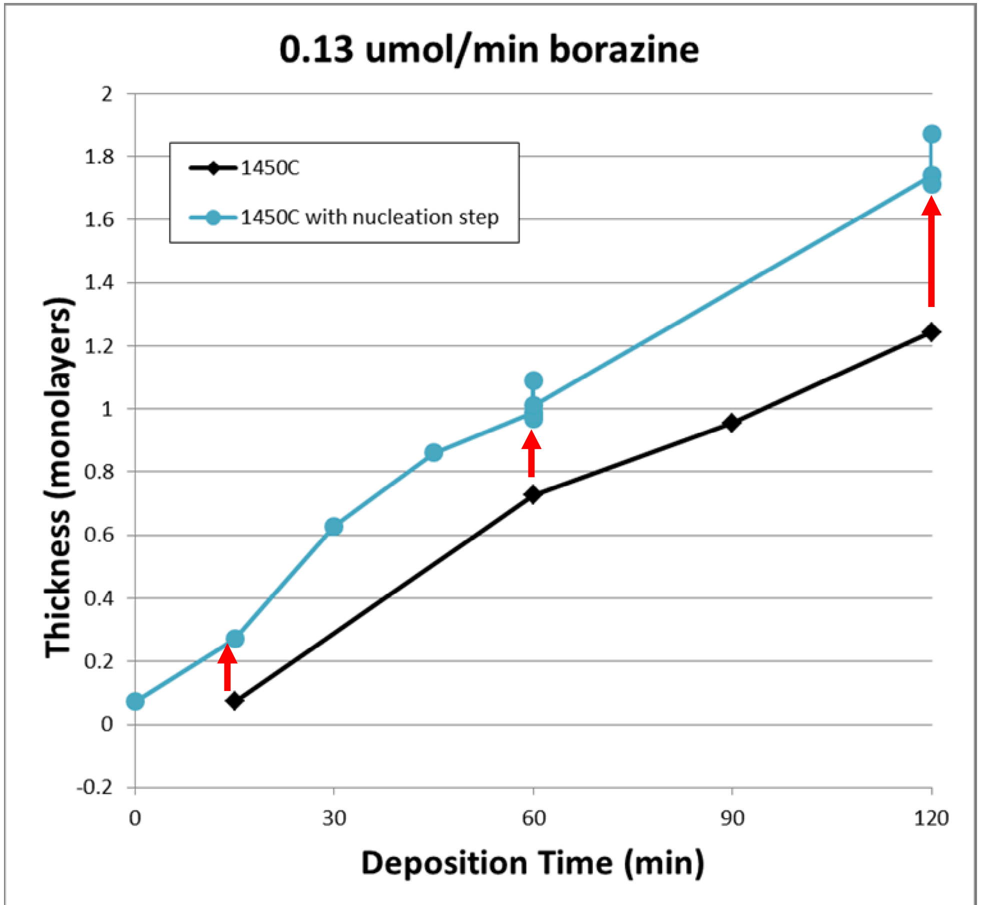
Separating Nucleation and Growth

Case 1: Tg = 1450C





- "Nucleation step" is 5 minutes at 0.37 μmol/min borazine
- Growth at 0.13 μmol/min borazine

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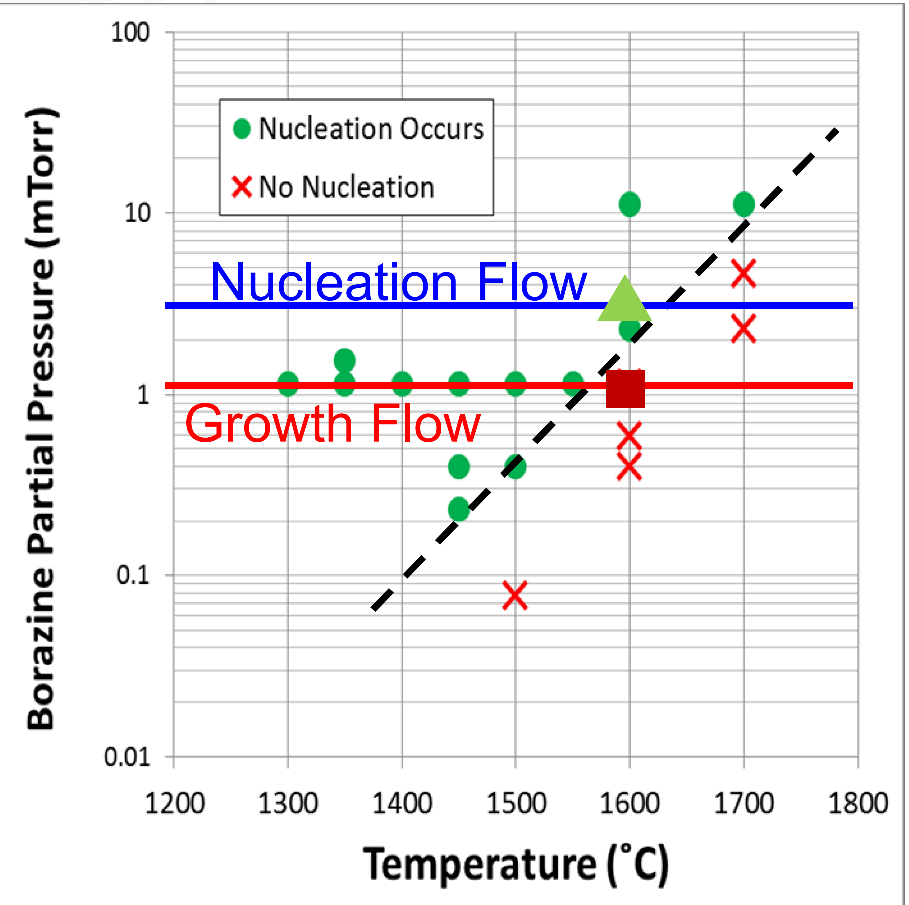
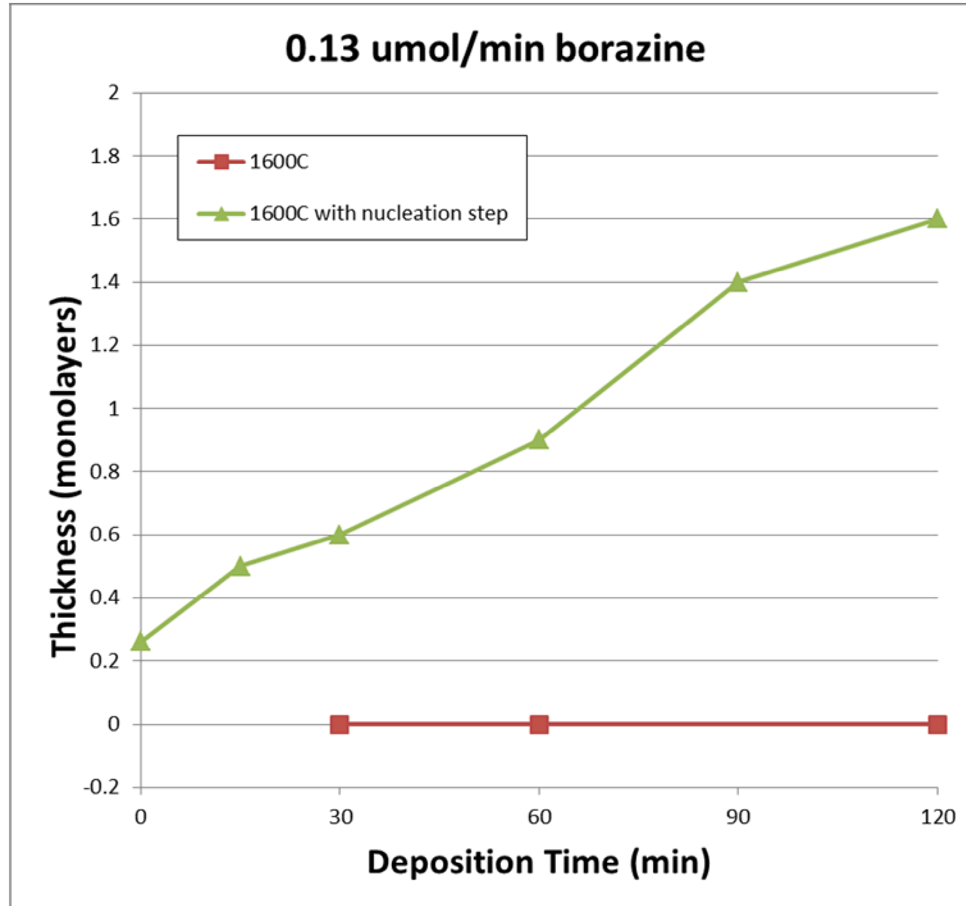
Separating Nucleation and Growth

Case 2: Tg = 1600C





- "Nucleation step" is 5 minutes at 0.37 μmol/min borazine
- Growth at 0.13 μmol/min borazine

→ Nucleation step is critical for higher growth temperatures