SAND2018-1115C

# Chemical Vapor Deposition of Hexagonal Boron Nitride

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This work was supported by Sandia's Laboratory Directed Research and Development program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525.

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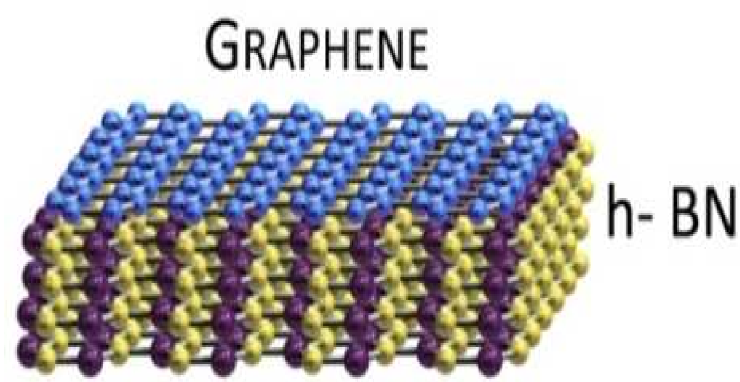
# Outline

- Motivation
- Deposition with TEB + $NH_3$
- Deposition with borazine ($B_3H_6N_3$)

# Why hBN?

## 2D applications

- Substrate for high mobility graphene
- Chemical and thermal stability
- Single photon emitters, gas sensing, hyperbolic optics

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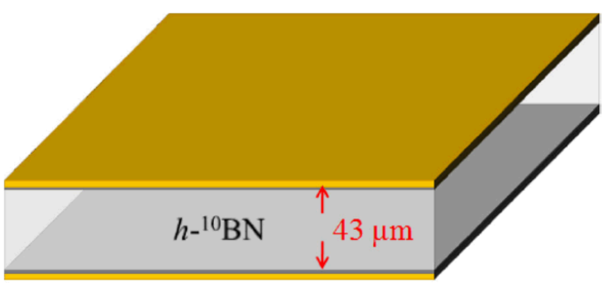
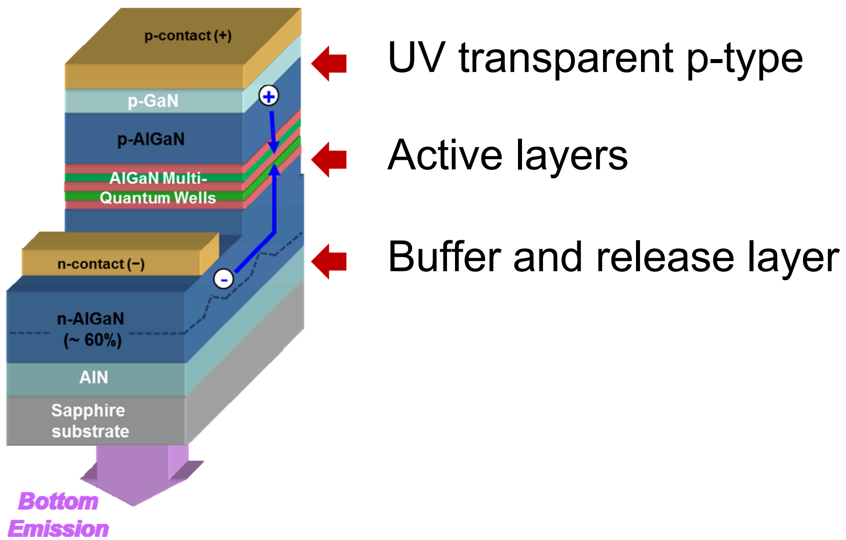
## Bulk applications

- Thermal neutron detection
- UV optoelectronics




*Maity et al., 2016*

### UV AlGaN LED and how hBN could help



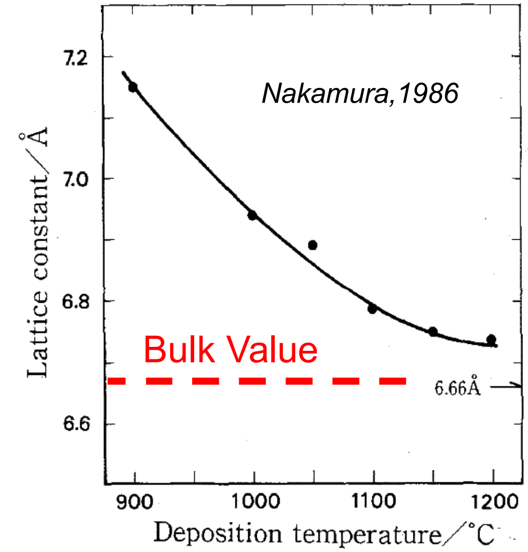
# Why CVD? High temperature?

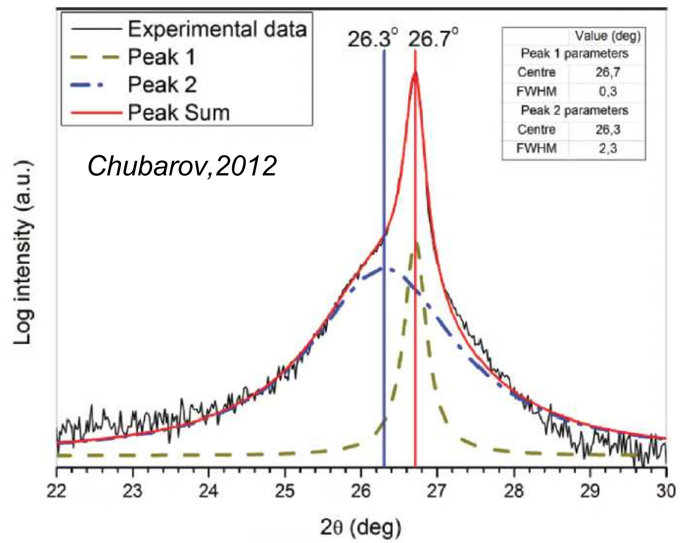
## MOCVD

- Scalable to large area
- Proven industrial technique

## High Temperature

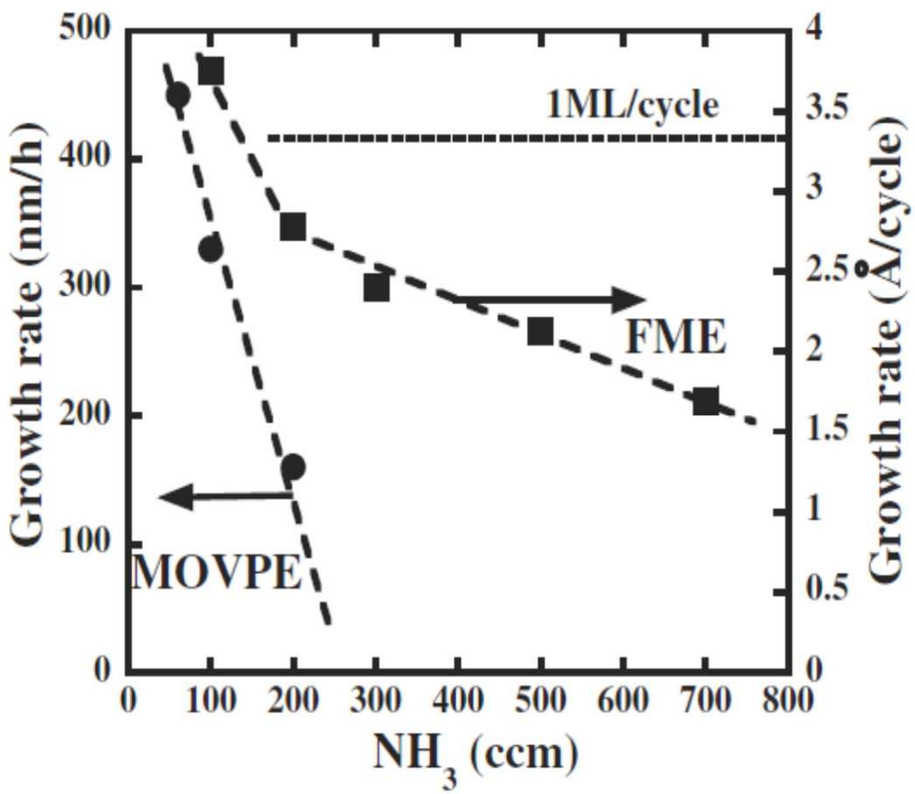
- Semiconductor or oxide substrates
- Prior reports of improving crystallinity with increasing temperatures

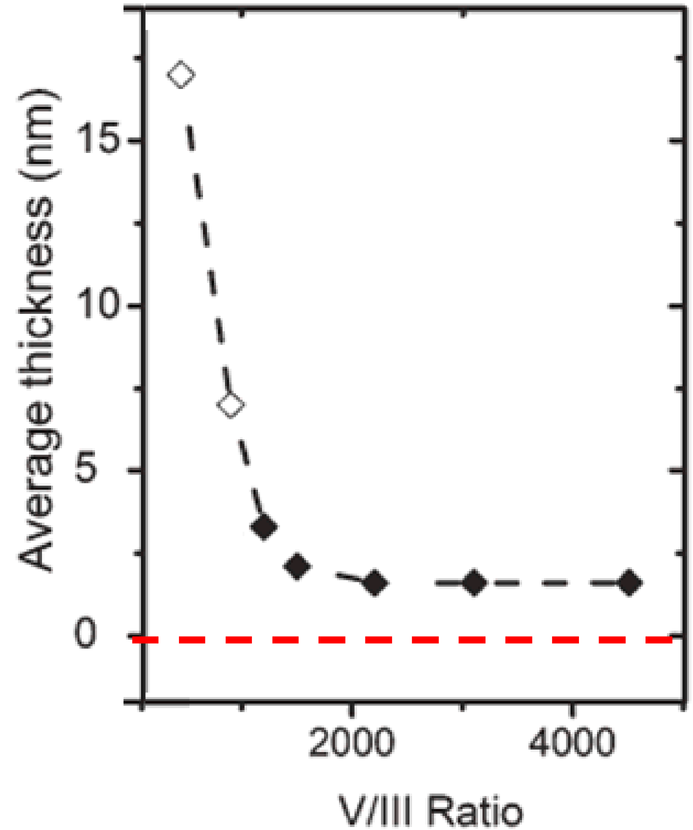


# Effects of Deposition Temperature and Ammonia Flow on MOCVD Hexagonal Boron Nitride

# Prior Literature




Constant TEB + $NH_3$ ↑ = Rate ↓

TEB ↓ + Constant $NH_3$ = Rate ↓

*Kobayashi and Makimoto., 2006*

*Paduano et al., 2014*

# Growth

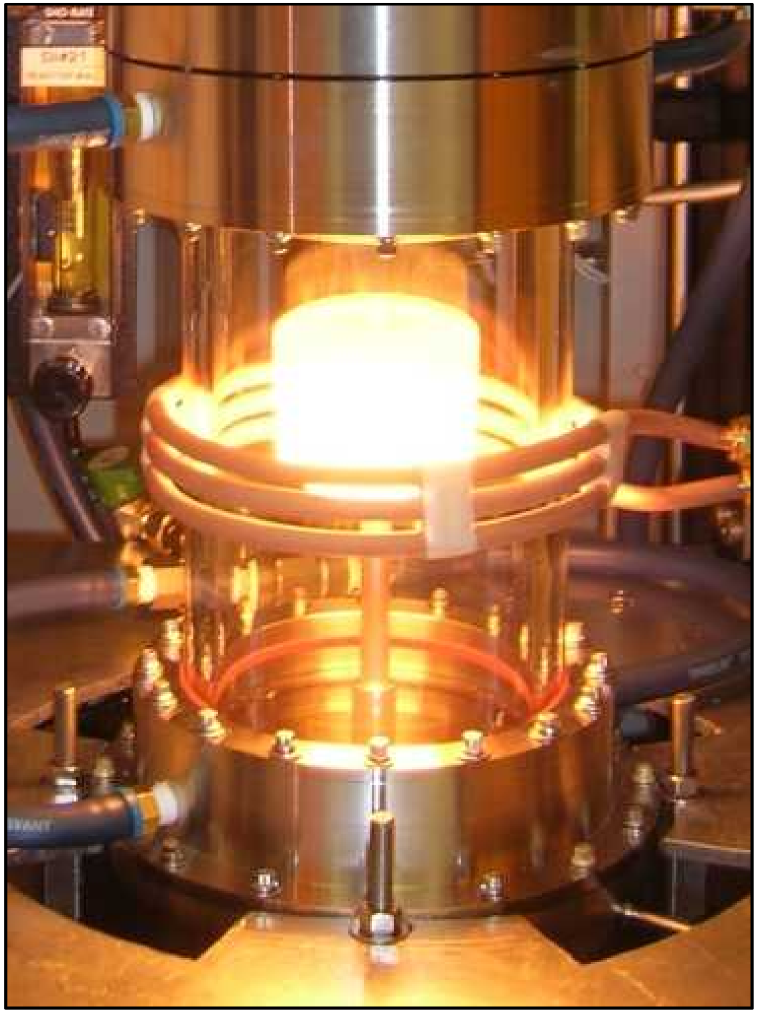
## MOCVD System

- Refitted existing MOCVD with new chamber
  - Cold walled, RF heated
  - Temperatures up ~1900 ˚C
- *In situ* reflectance monitor

## Growth Conditions

- c-sapphire
- 50 Torr
- $N_2$ diluent and carrier gas
- Triethylboron (TEB) at 22 μmol/min
- $NH_3$ varied 2 sccm to 5000 sccm
  - V/III ratio 5 to 10,000
- Temperatures varied 1100 ˚C to 1800 ˚C

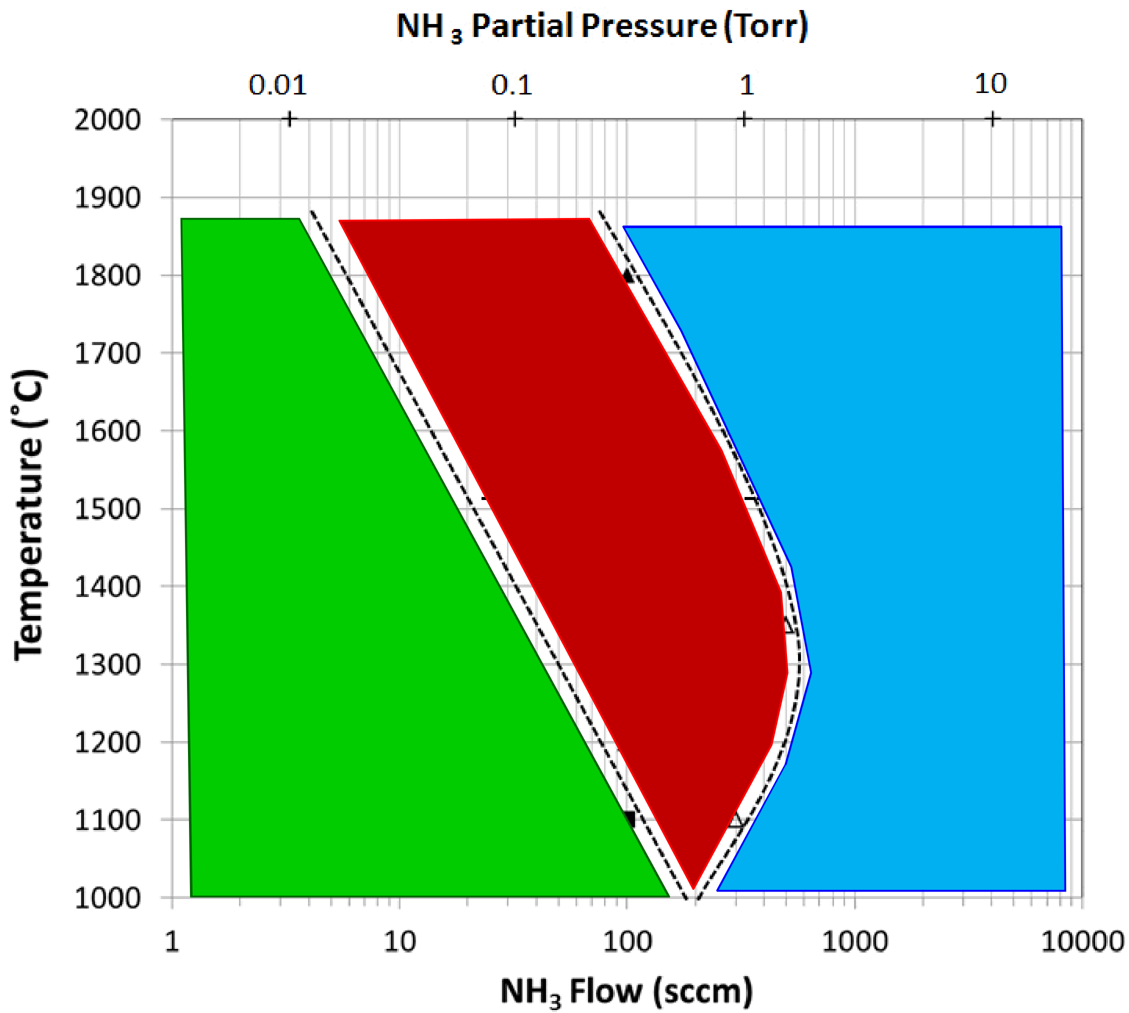
The authors would like to thank Prof. Z. Sitar at NCSU for sharing reactor chamber design



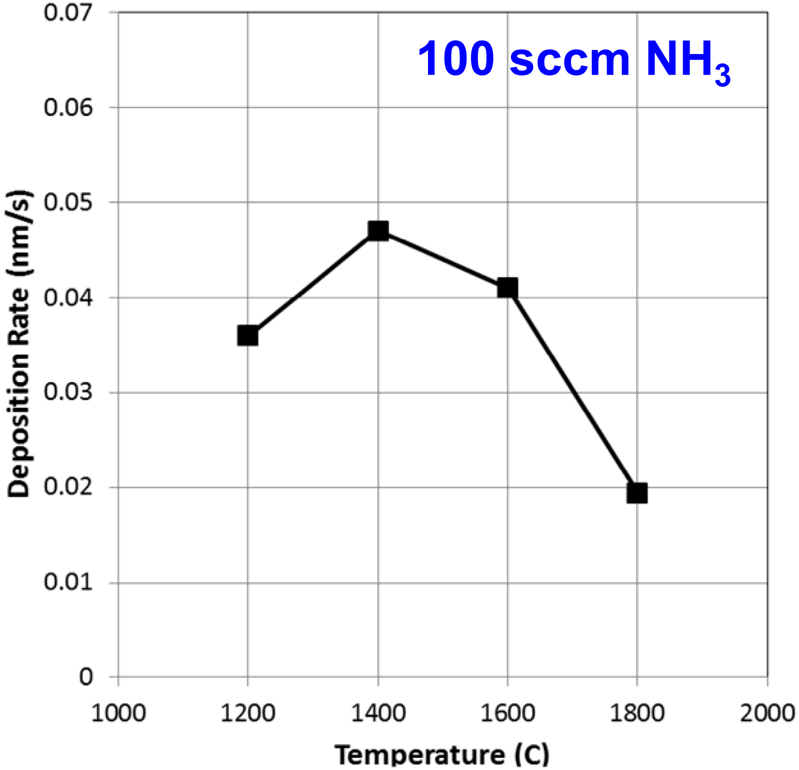
# Temperature and $NH_3$ Space

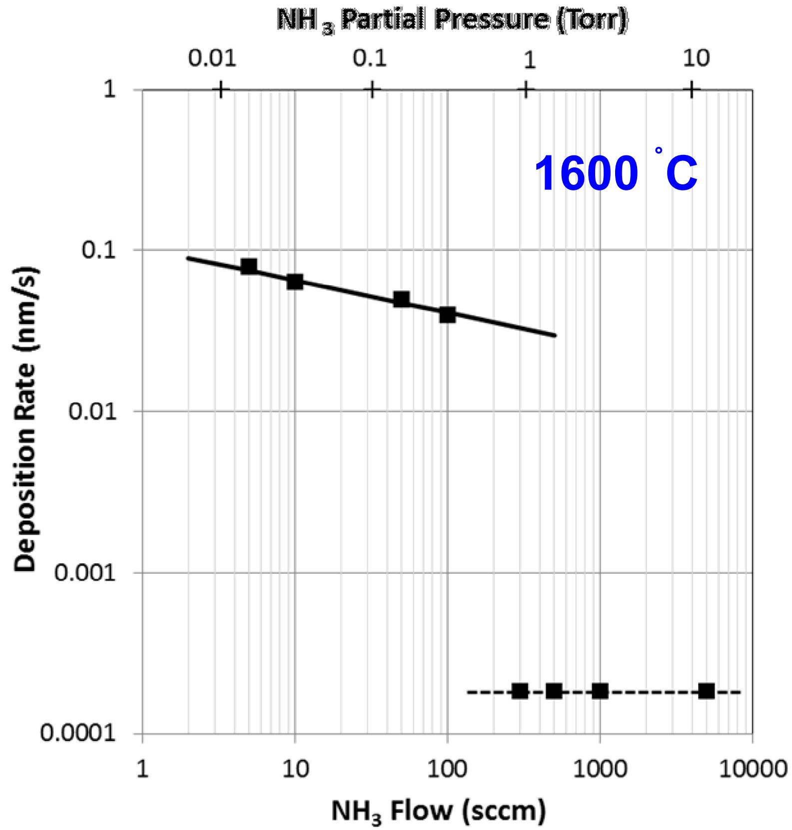
***Growth Regimes***

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




*Rice et al., 2018*




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

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

# Langmuir-Hinshelwood Model

***Langmuir-Hinshelwood***

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

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

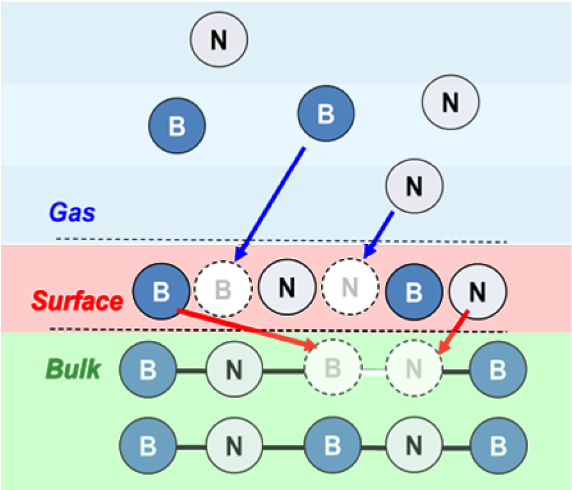
$$N_{gas} + Open_{surface} \overset{k_N}{\leftrightarrow} N_{surface}$$

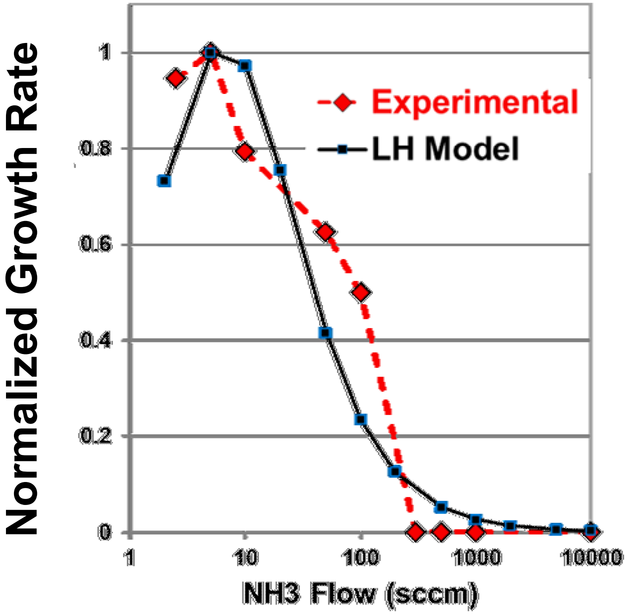
$$B_{surface} + N_{surface} \overset{k_{rxn}}{\longleftrightarrow} BN_{bulk} + 2Open_{surface}$$

- **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**



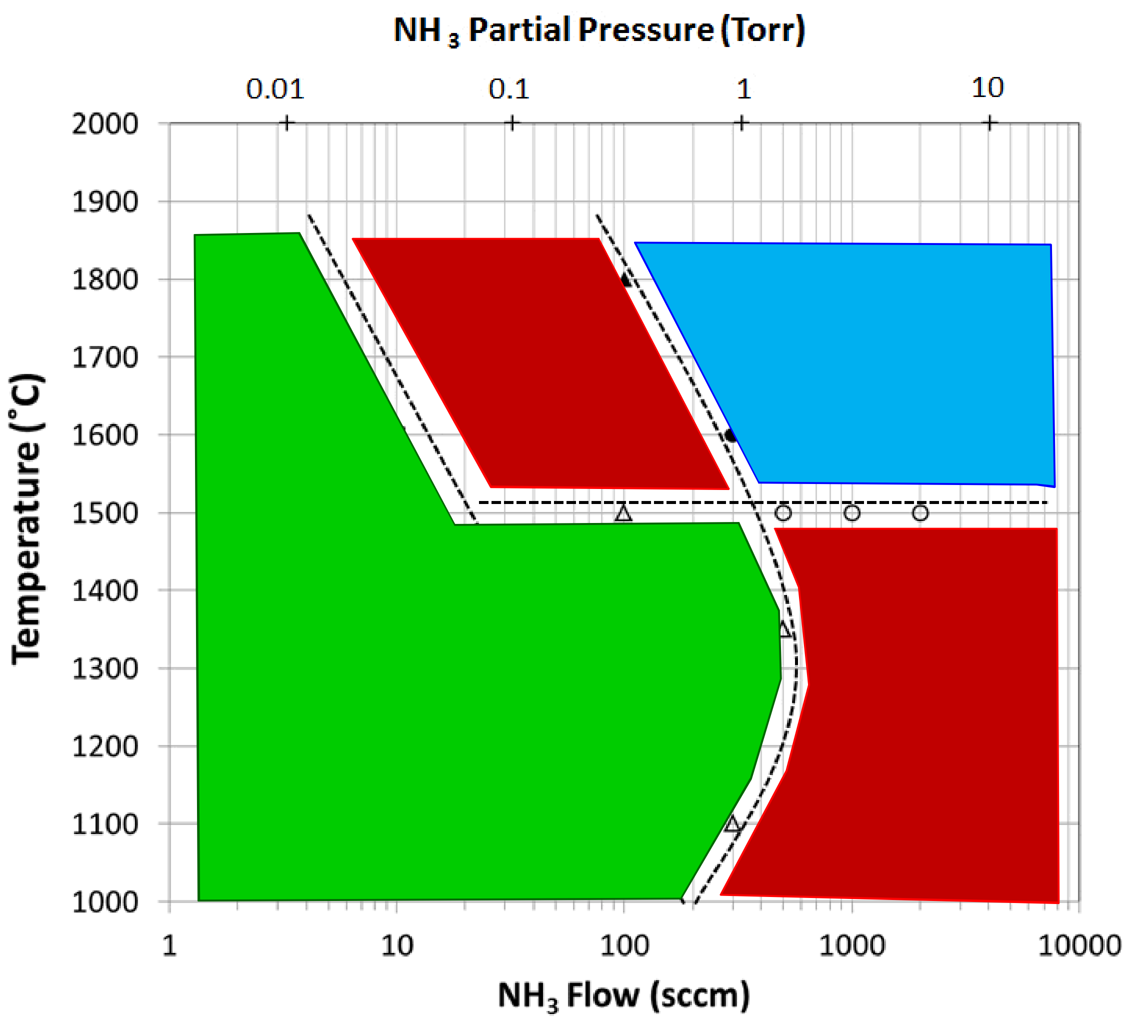



# Photoluminescence Regimes

***PL Regimes***

- No exciton emission
- Defect bound exciton
- Free exciton

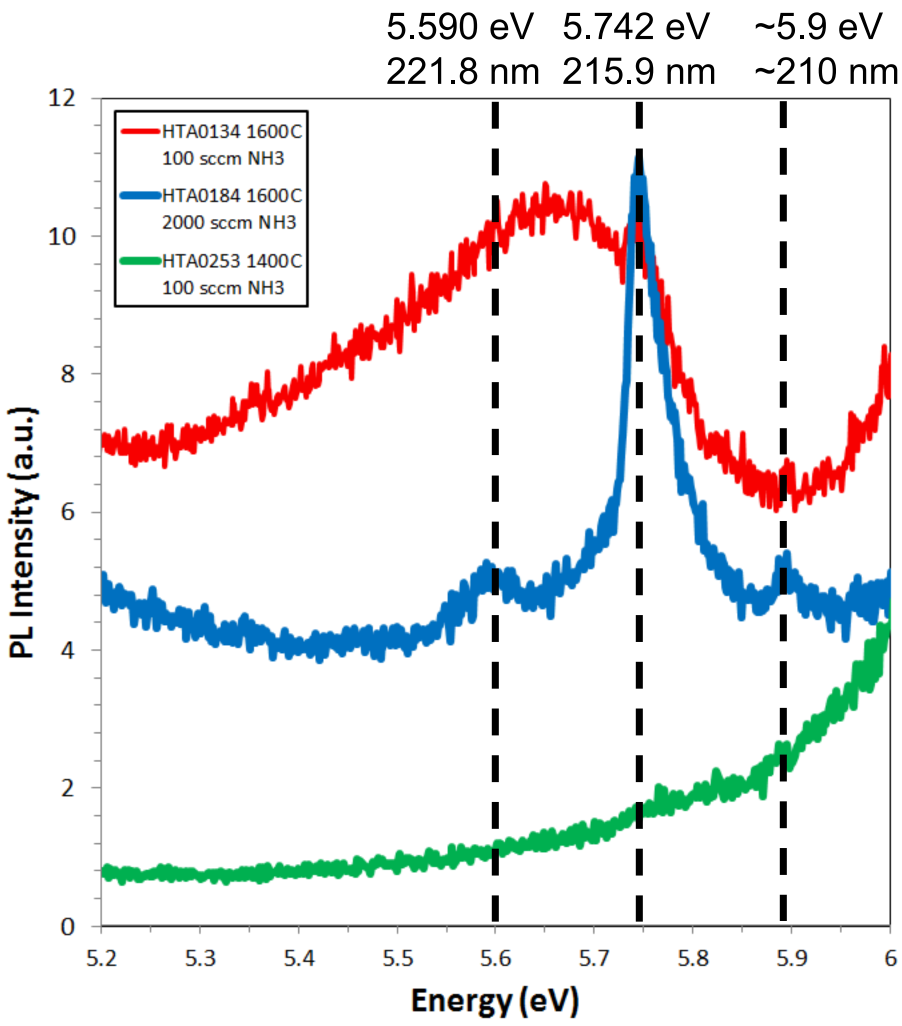
**RT PL**



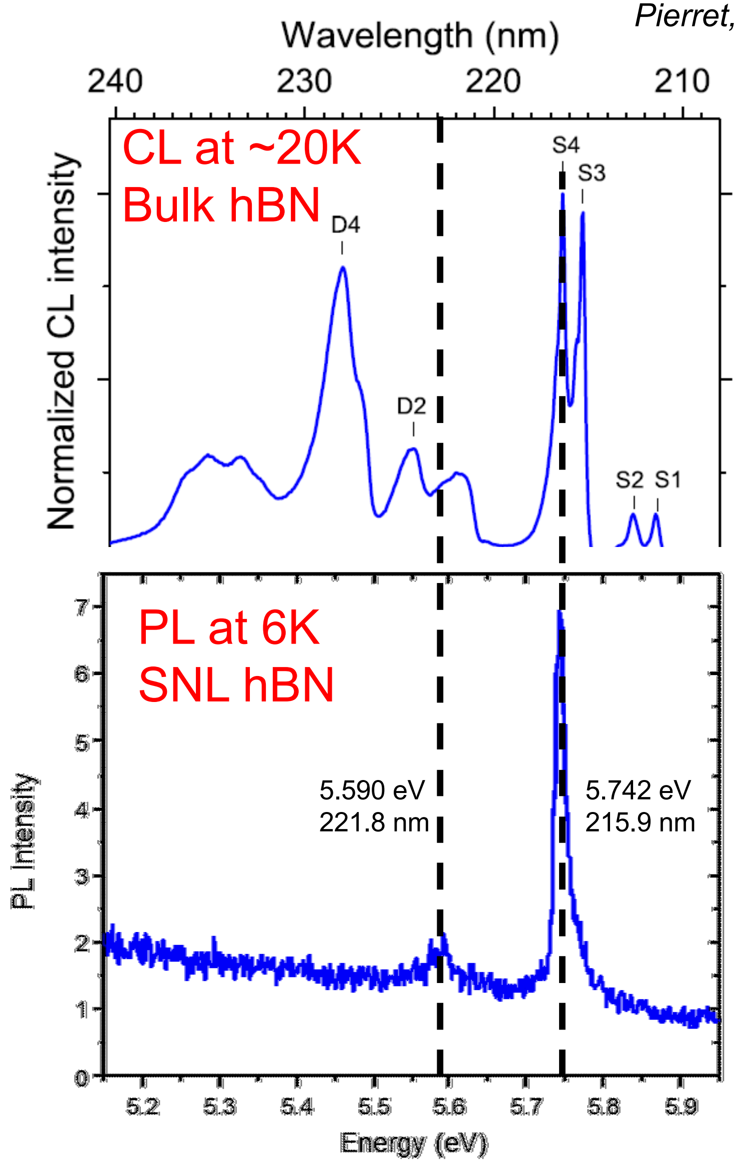

*Rice et al., 2018*

# Photoluminescence Results

## Room Temperature PL



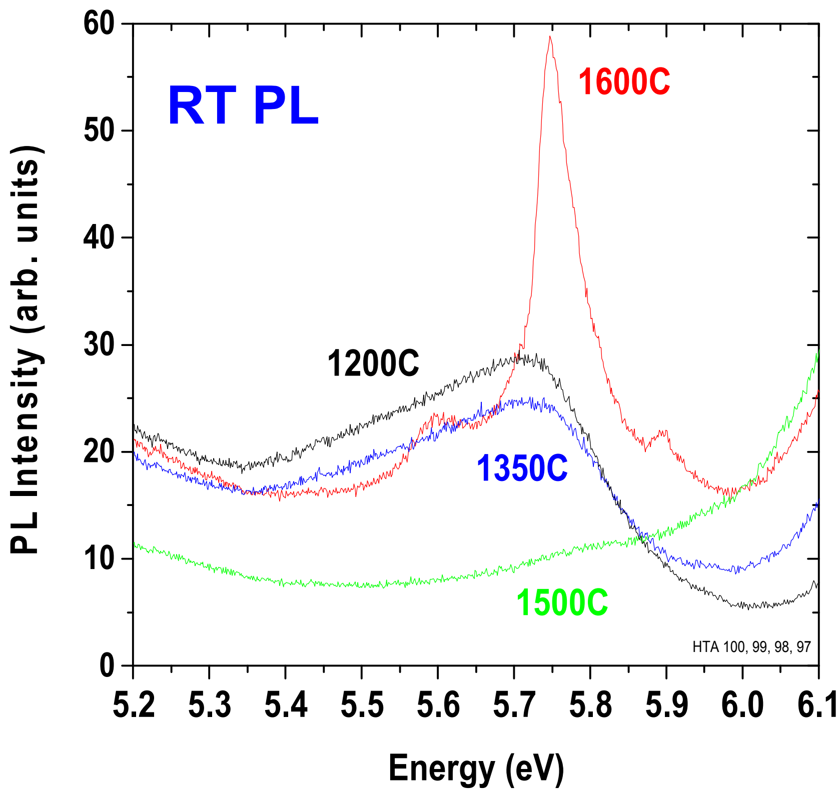

*Pierret, 2014*

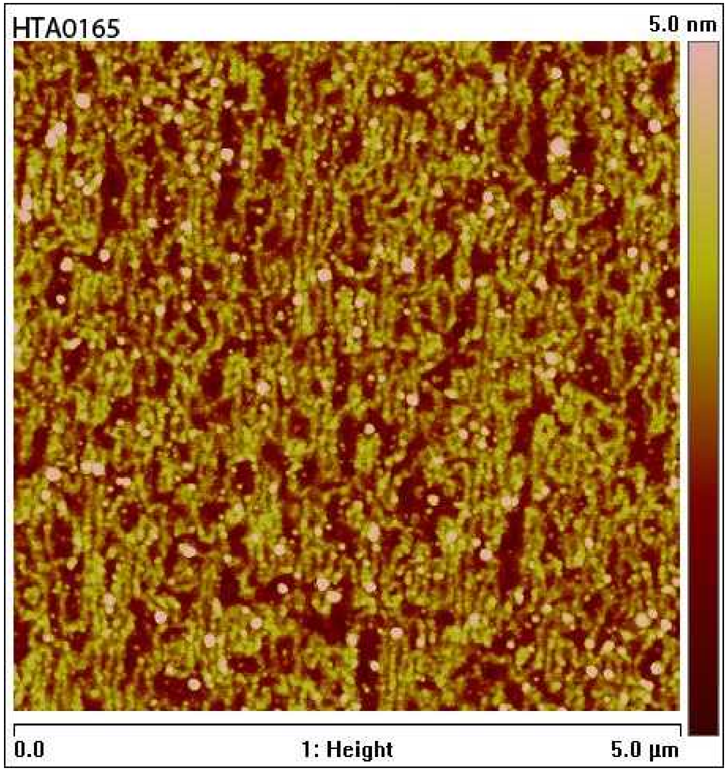


# But…

***TEB + NH$_3$***

- **Monolayer hBN with room temperature free exciton emission**
- **Required temperatures over 1500 ˚C and with $P_{NH3}$ = ~5 Torr**
- **Damaged substrate surfaces**



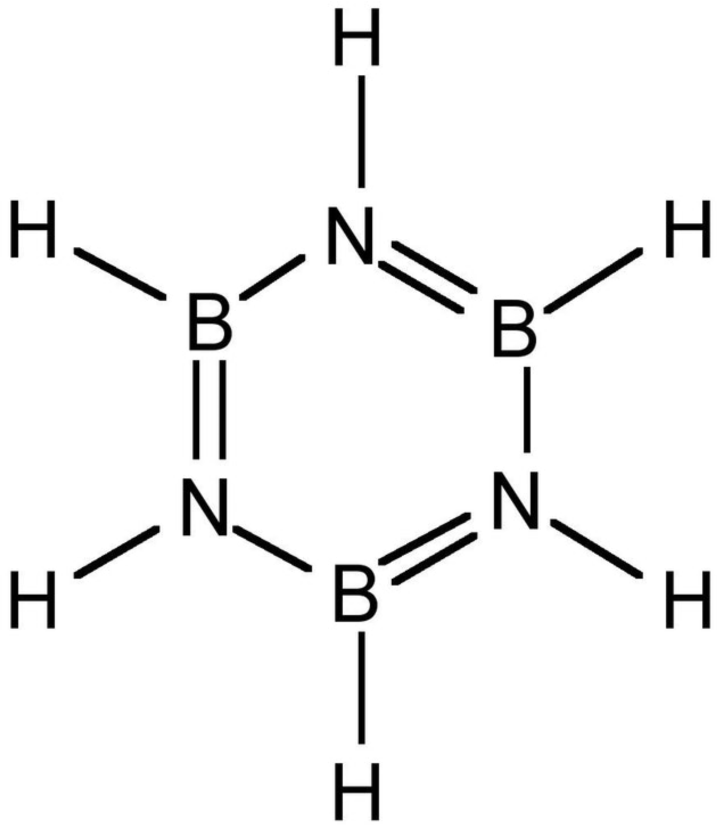

30 sec $NH_3$ exposure at 1600 ˚C
0.8 nm RMS roughness

## Deposition of Hexagonal Boron Nitride by Borazine

# Why Borazine?

## *Pros*

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




$(NH)_3(BH)_3$

## *Cons*

- Literature reports are mostly on metal
- Stability of source
- Purity of source
- Single source growth

# Nucleation Theory

***Nucleation Theory***

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

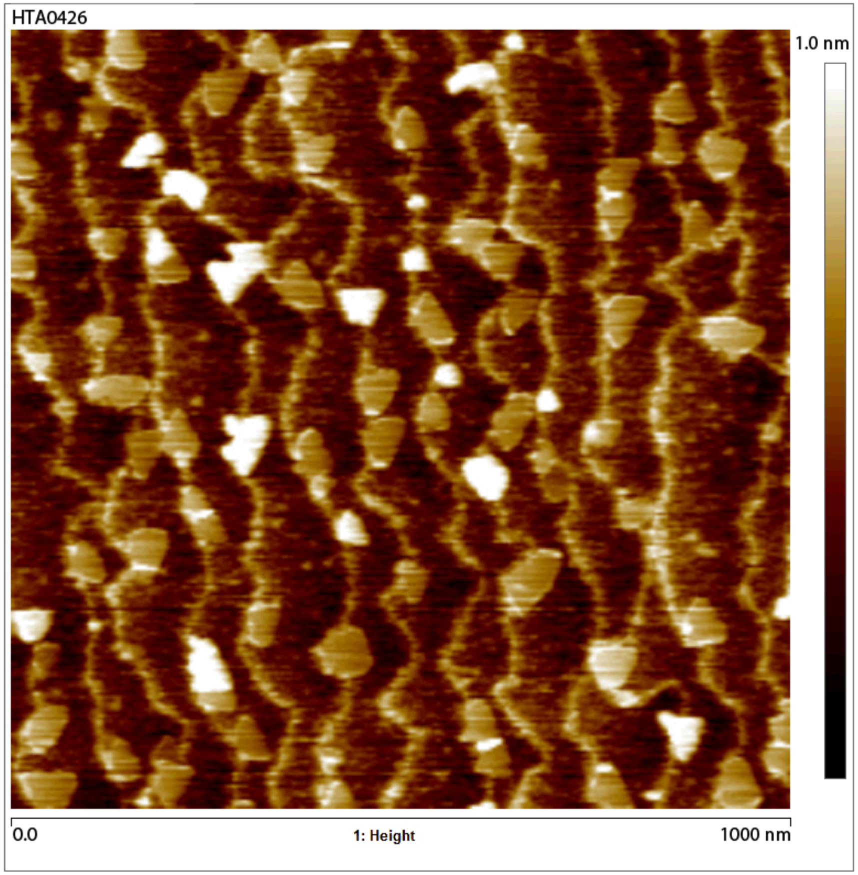
$$N = Ce^{-\Delta G/kT}$$

Nuclei Density (N)

Adatom Density (C)

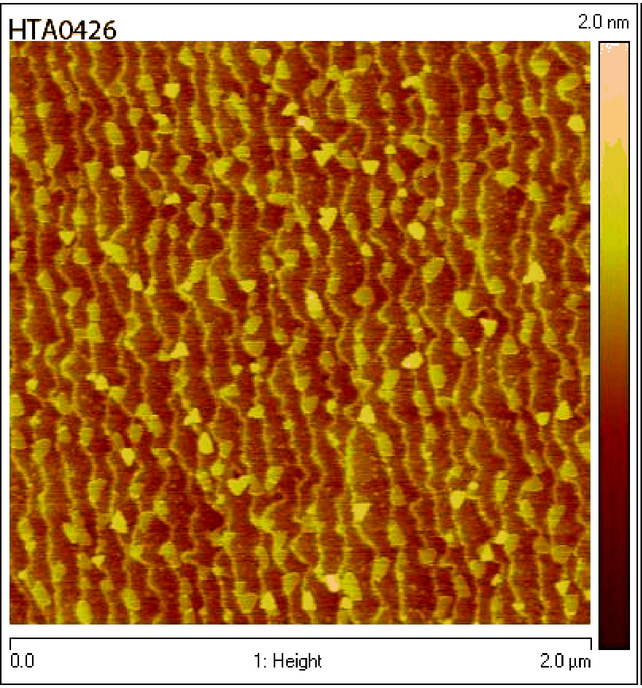
Temperature (T)

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

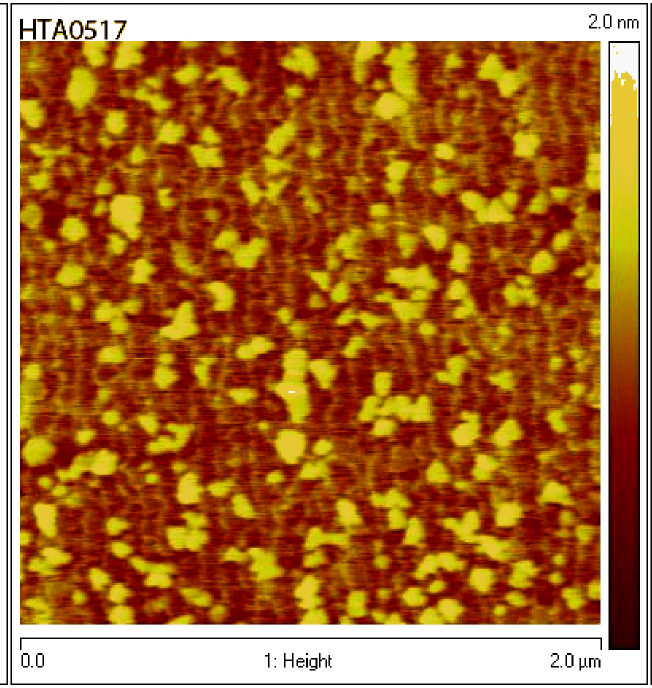



**BN nuclei on sapphire**
**Deposition at 1450 ˚C**

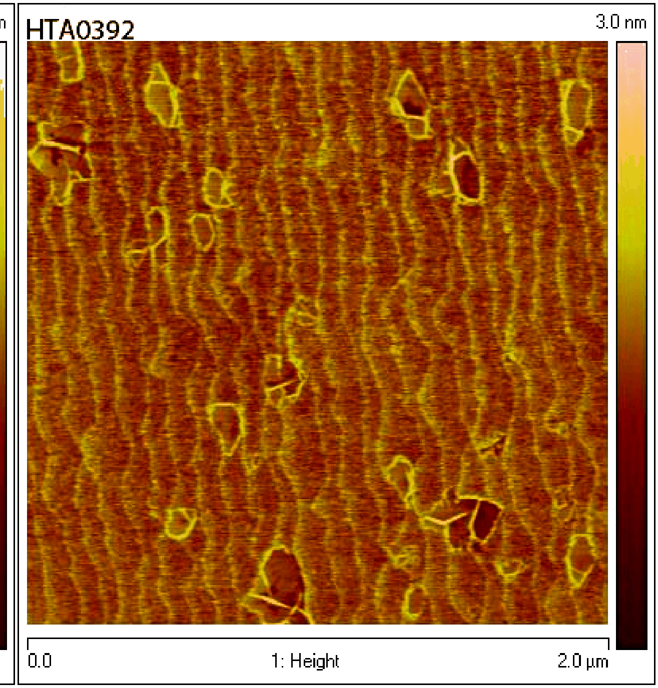
# Nucleation with Temperature




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

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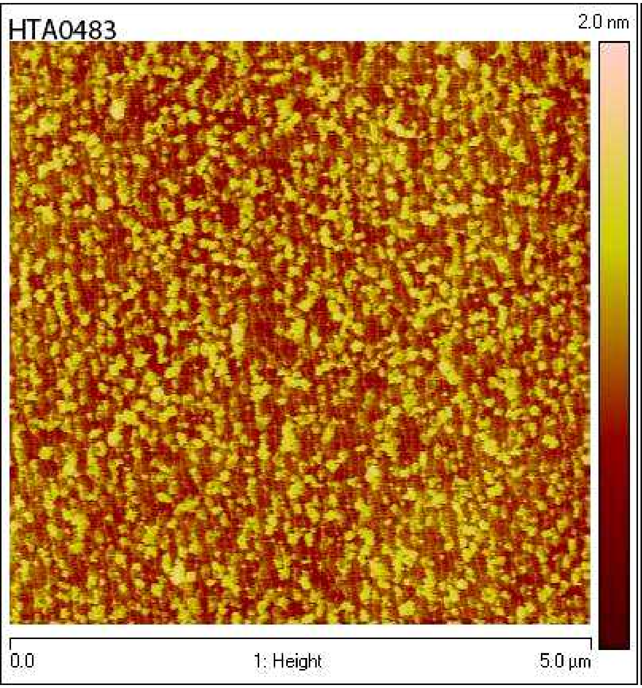
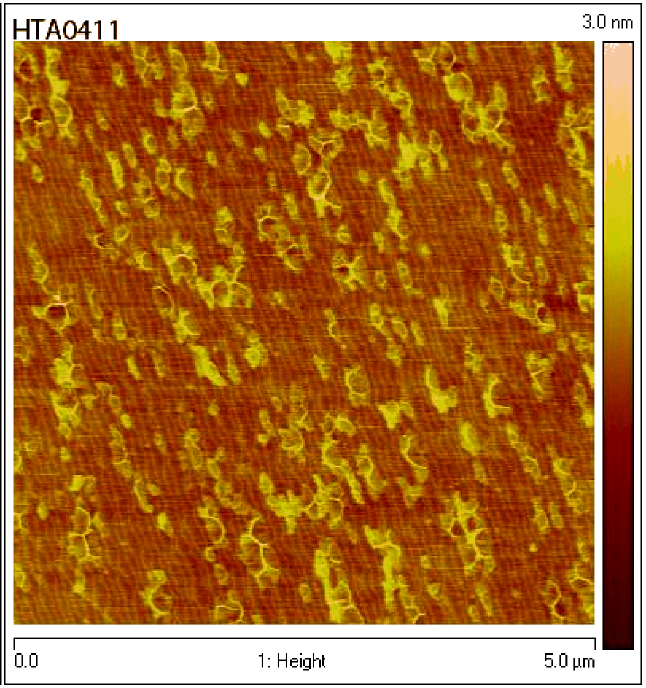
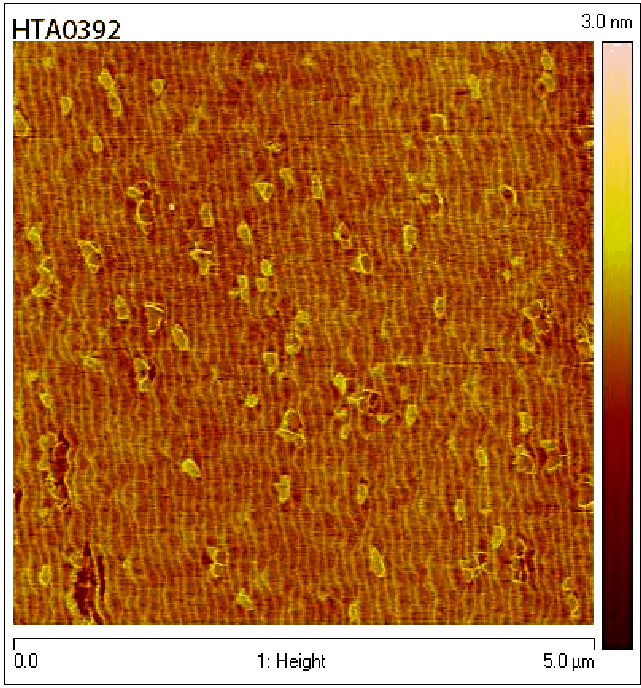
# Nucleation with Flux




2 min at 1.5 µmol/min



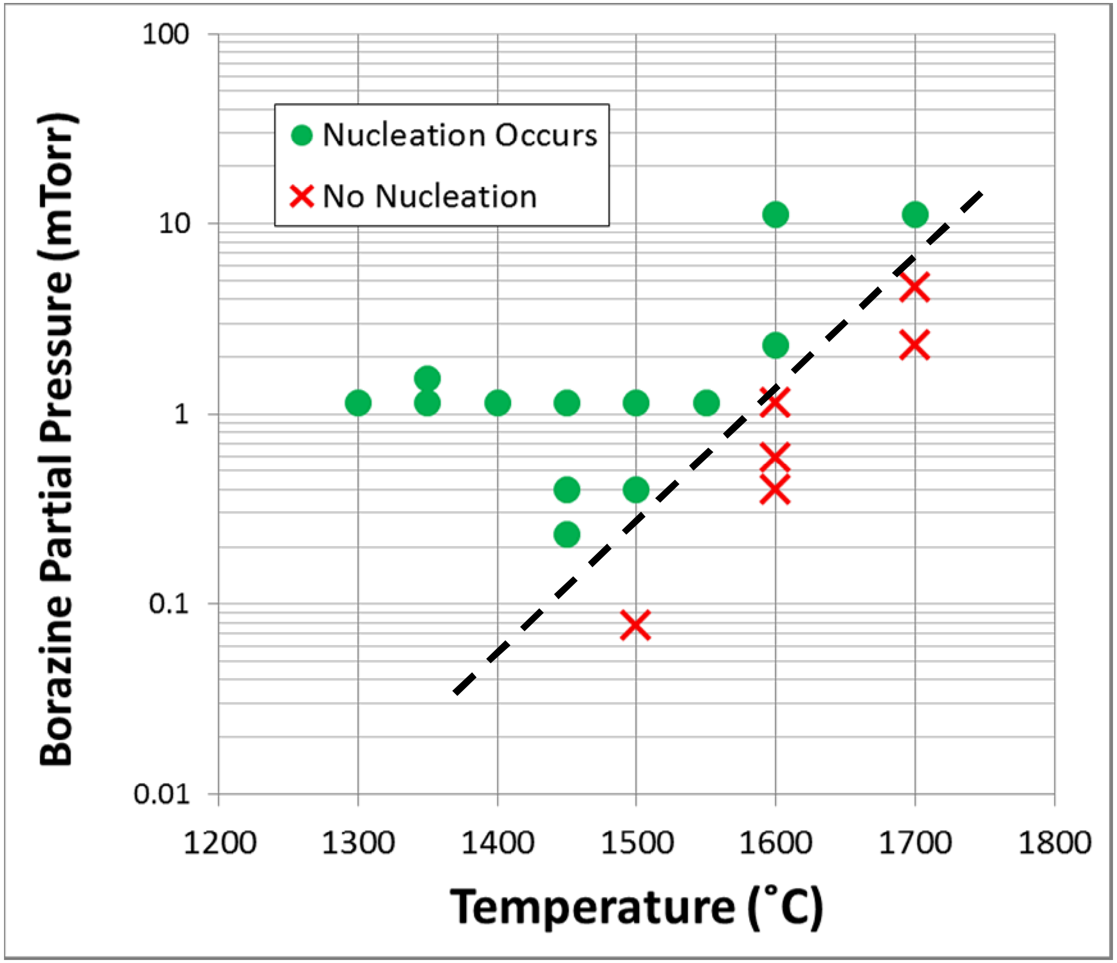

5 min at 0.75 µmol/min




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

# Nucleation Theory

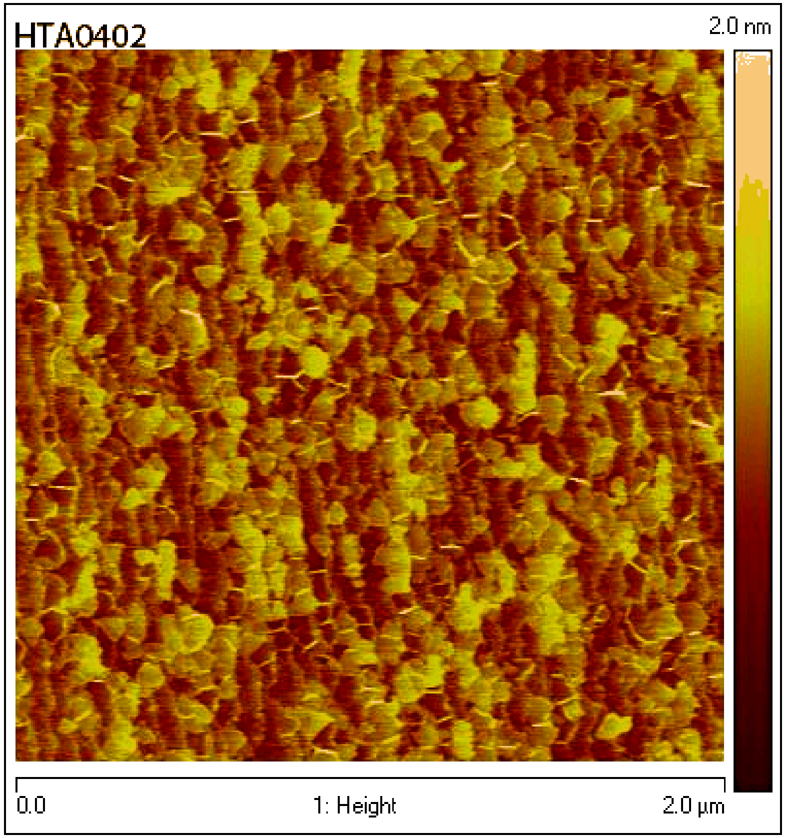



- Critical borazine partial pressure for nucleation

# Characterization…

***Characterization issues***

- **AFM**
  - **Huge numbers of artifacts**
- **XPS**
  - **Still have nitridation of surface**
- **Raman**
  - **BN signal ~10 time less intense than graphene signal**
  - **BN mode overlaps sapphire mode**

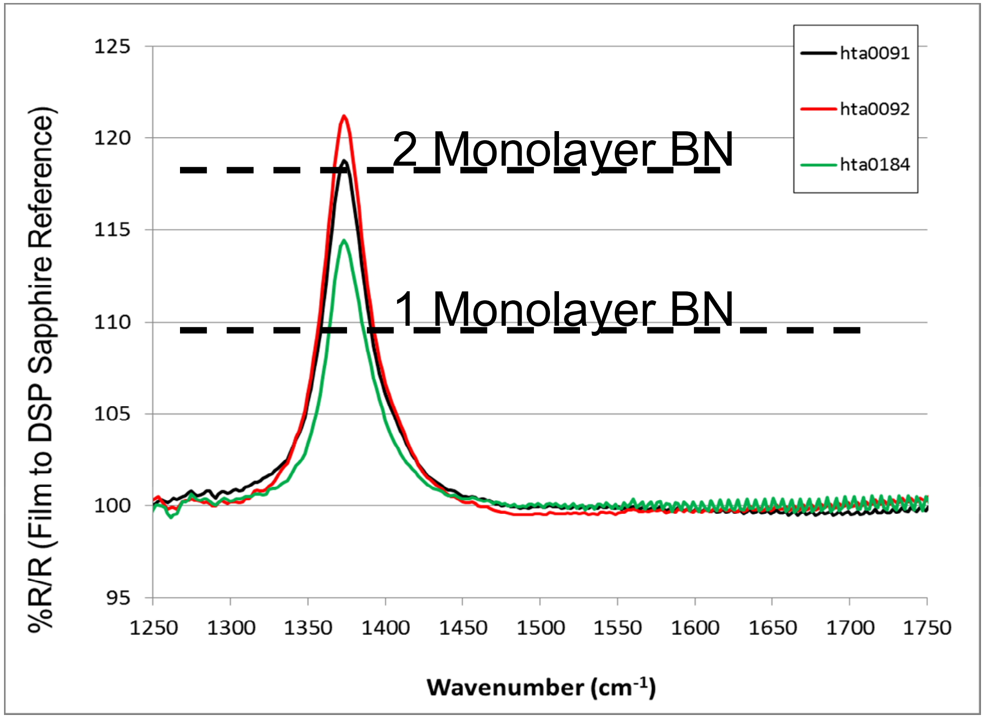



**~1 ML of BN on sapphire**

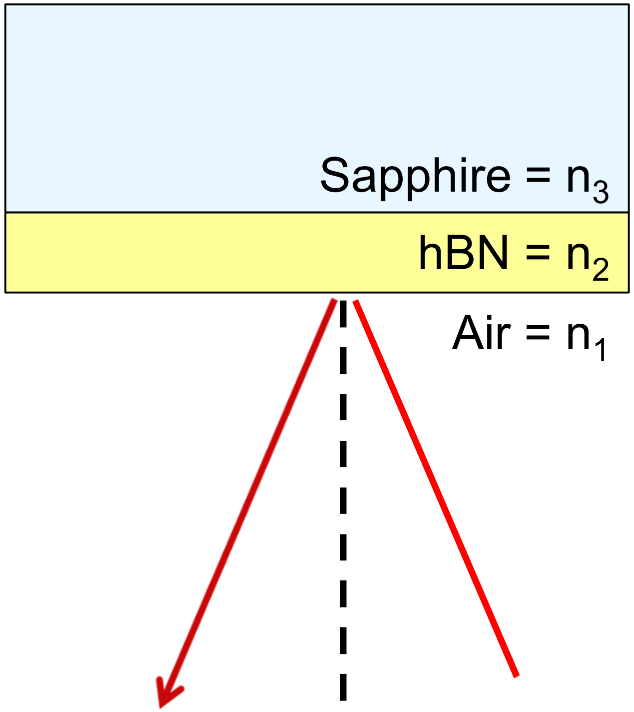
# FTIR Differential Reflectance

## *FTIR*

- **Large difference between BN and sapphire extinction coefficients**
- **3 layer differential reflectance model**



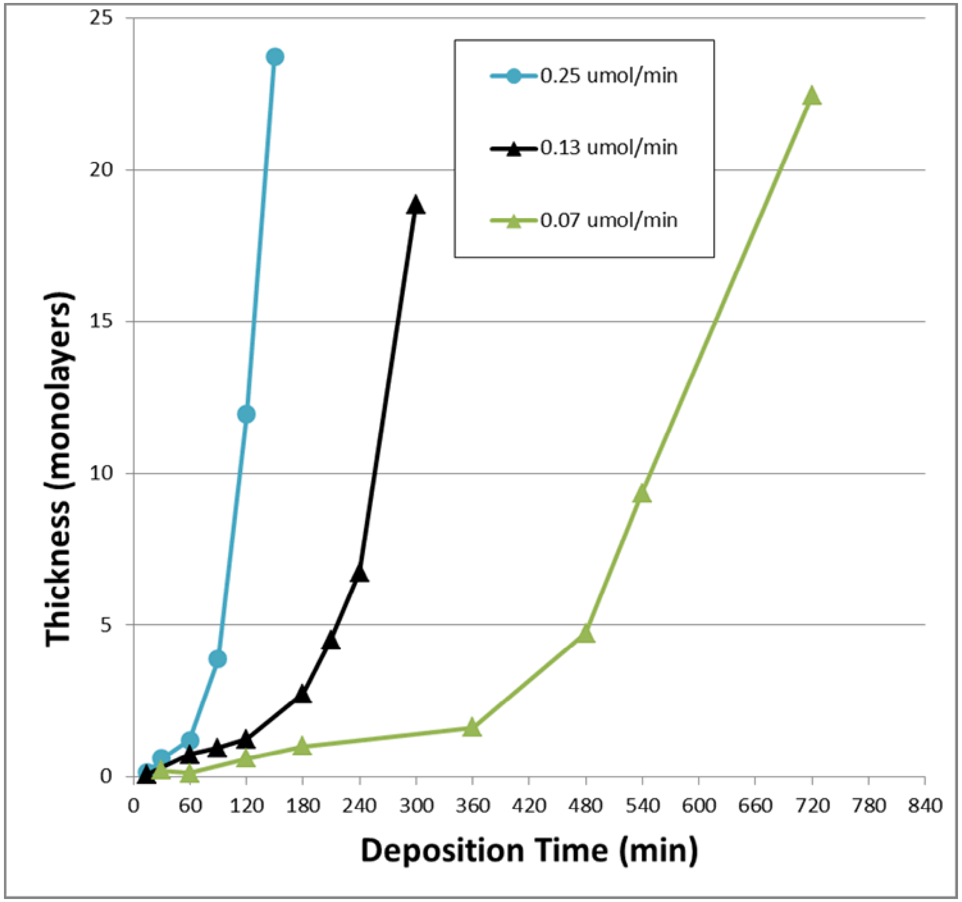

Films between 1 and 2 monolayers by Raman




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

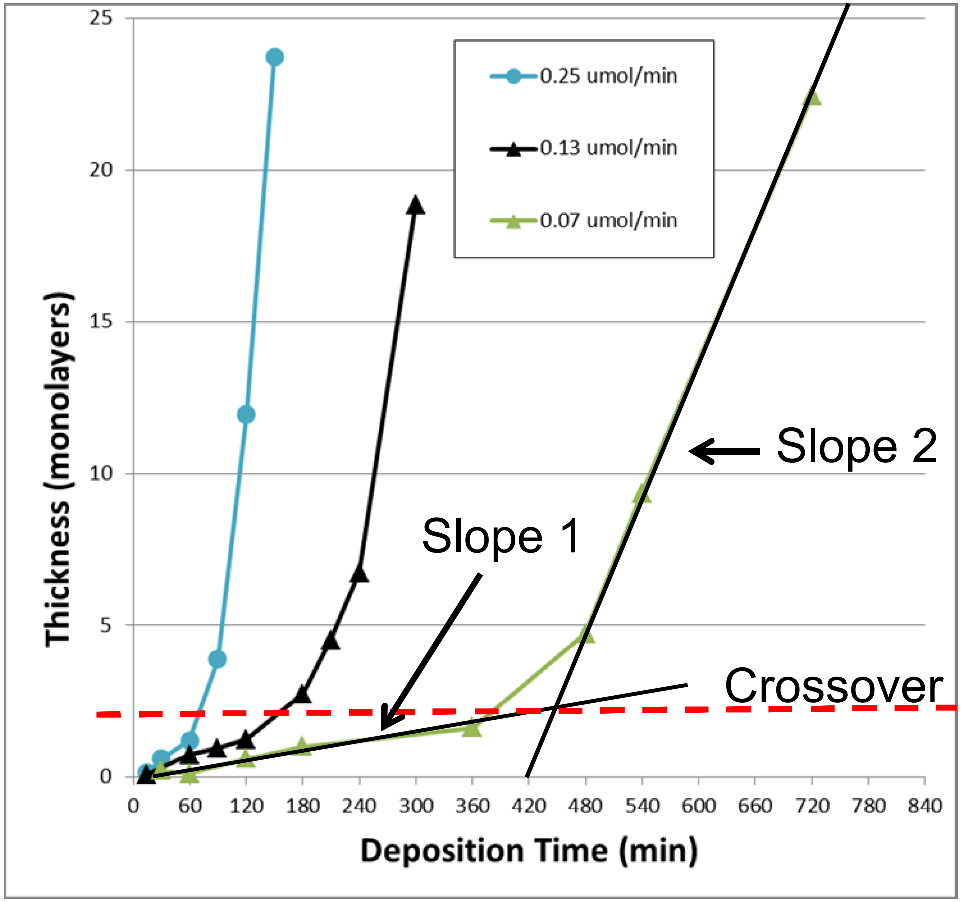
*McIntyre and Aspnes., 1971*

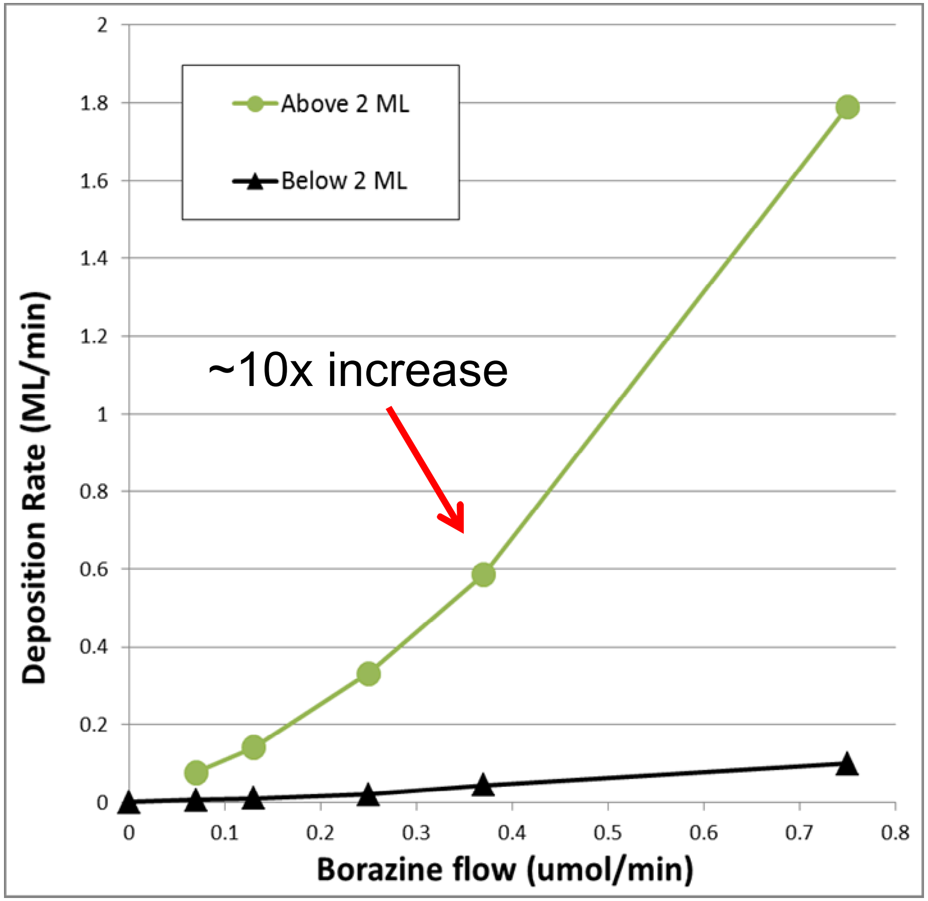
# Film Deposition




- Change in deposition behavior at ~2 monolayers

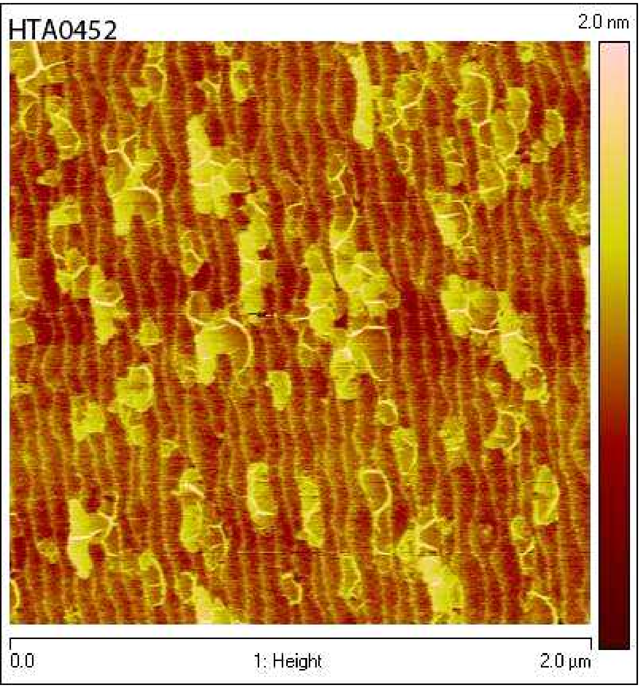
# Film Deposition



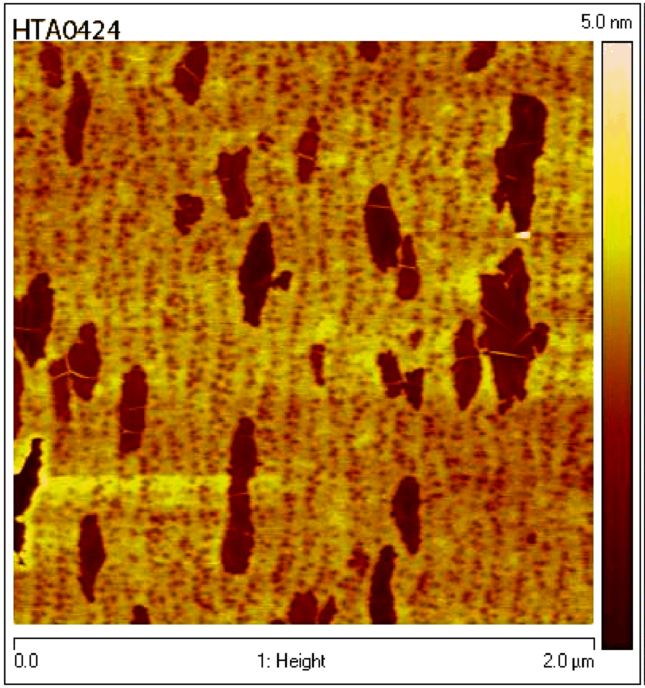




- Change in deposition behavior at ~2 monolayers
- Sapphire surface acting as an inhibitor?

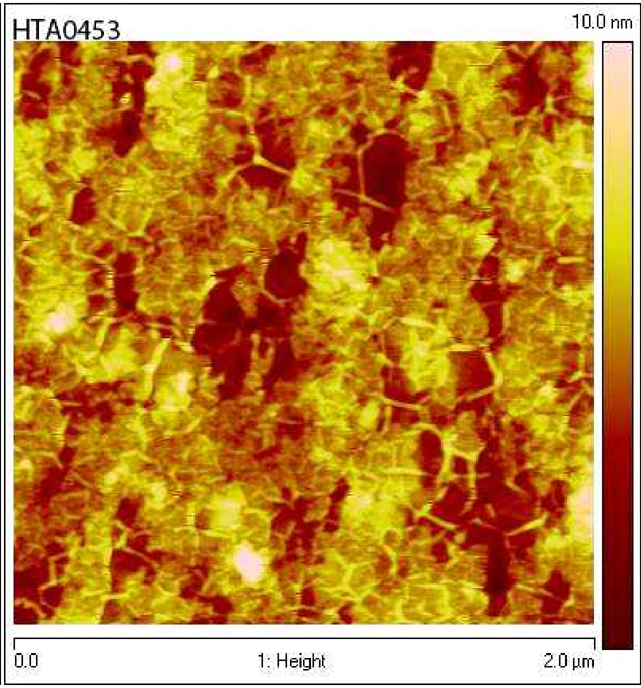
# Morphology




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
- Temperature and borazine flux impact only nucleation

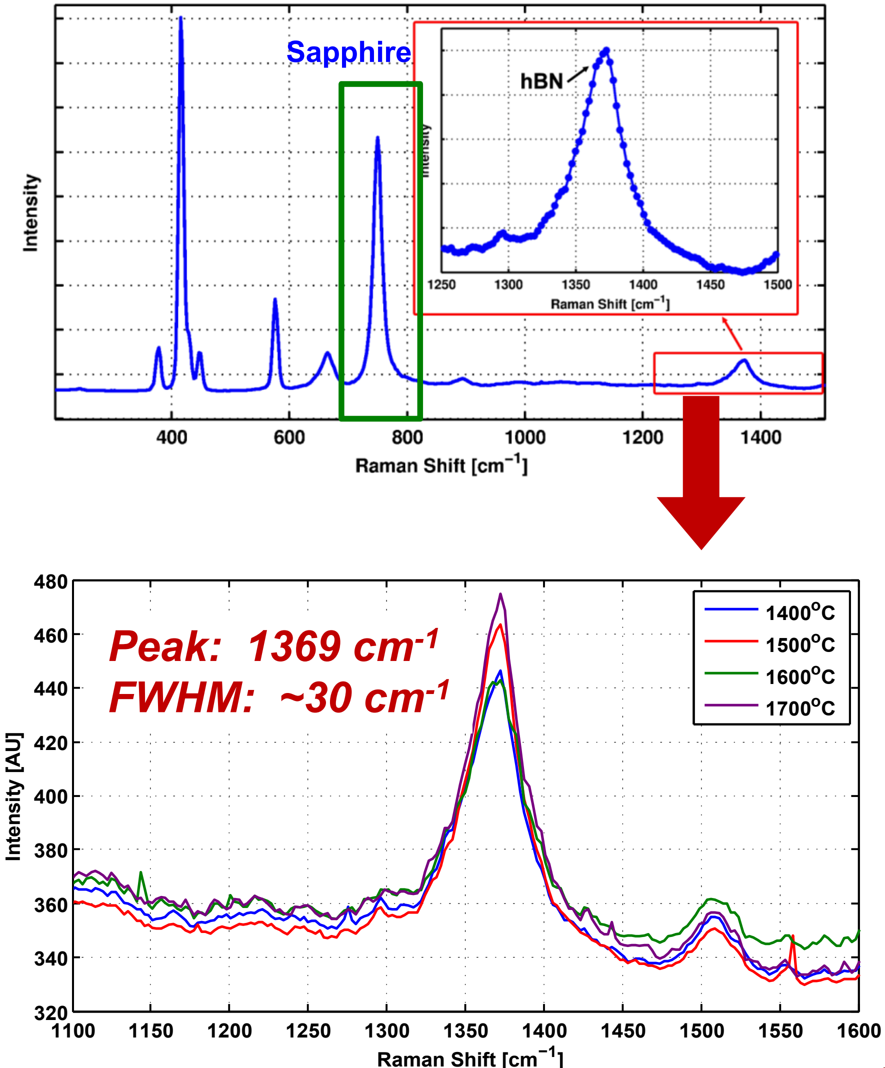
# Summary

- Successful hBN deposition on sapphire
- Room temperature free exciton emission with high temperature and high $NH_3$ flows
- Borazine much less destructive than TEB + $NH_3$
- FTIR differential reflectance very powerful for BN on semiconductor or oxide substrates
- Can still have monolayer thickness control on non-catalytic substrates

# Extra Slides

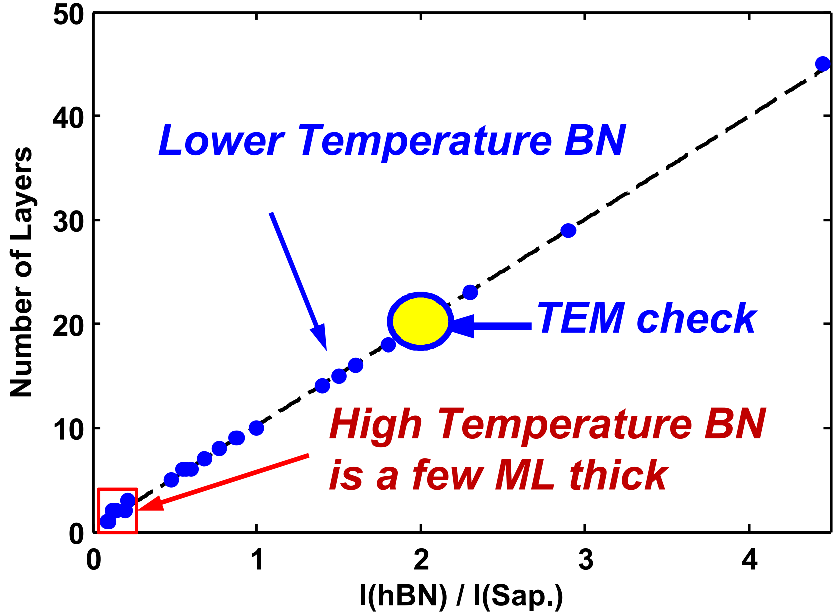
# Estimation of Thickness of hBN Films

## Typical Raman Spectrum

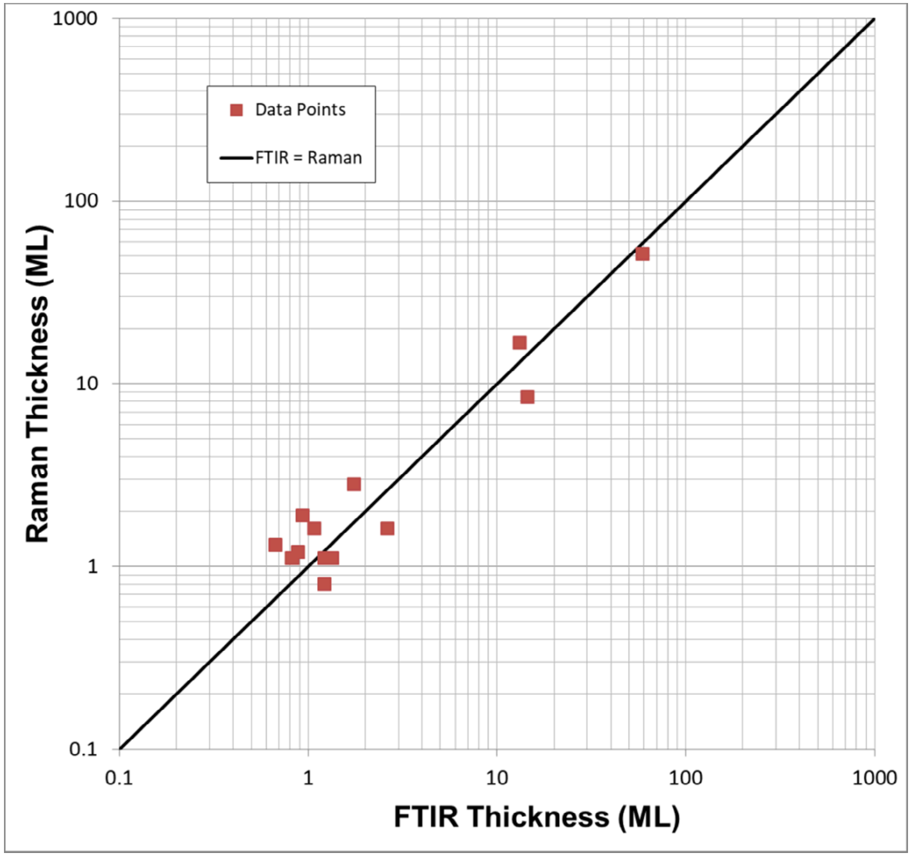



## BN Raman peak ratio ($I_{BN}/I_{sapp}$) vs. Pulse Cycles

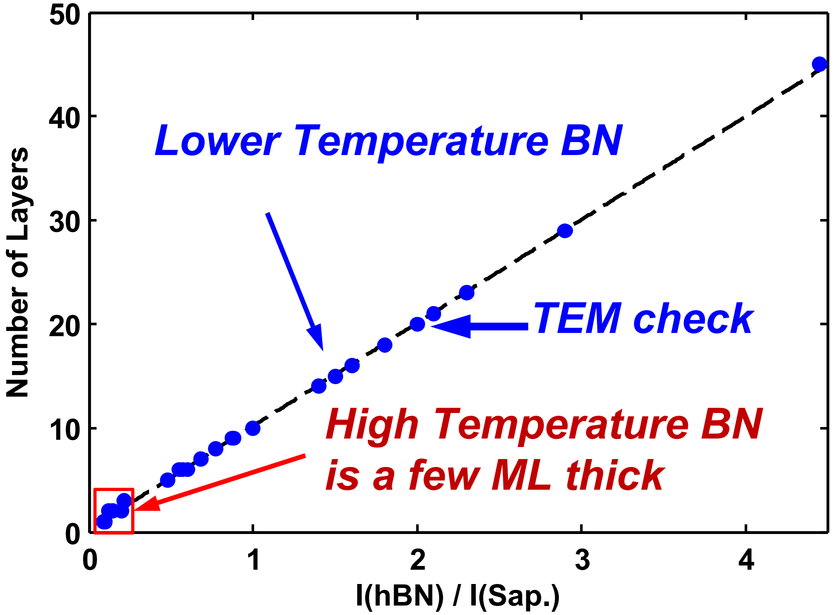
*→ Apply calibration from thicker films*




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



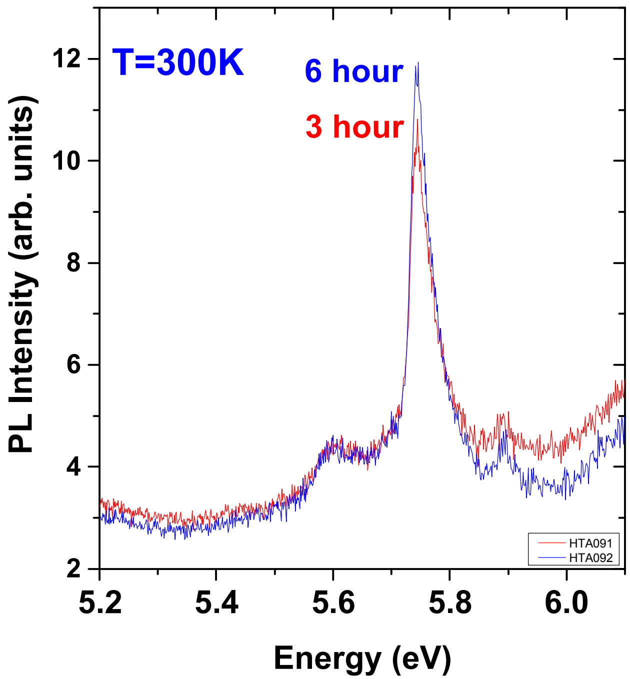

→ *Apply calibration from thicker films*




- **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

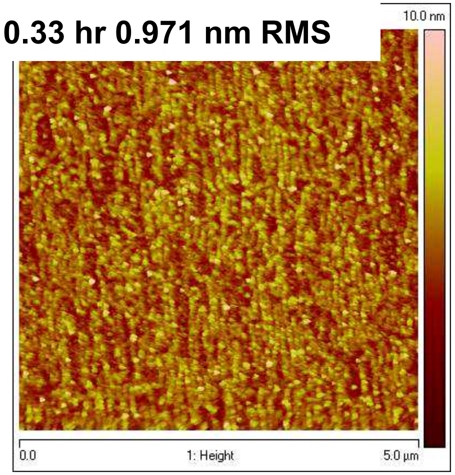


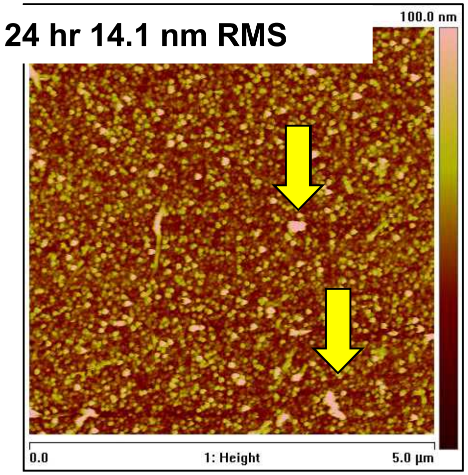

- Relatively little change in PL intensity over a large range of growth times
- Raman ratio (hBN/Sapphire) suggests only a few MLs even for 24 hours of growth
- Films roughen, with increased number of larger particulates, with longer growth times

## 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



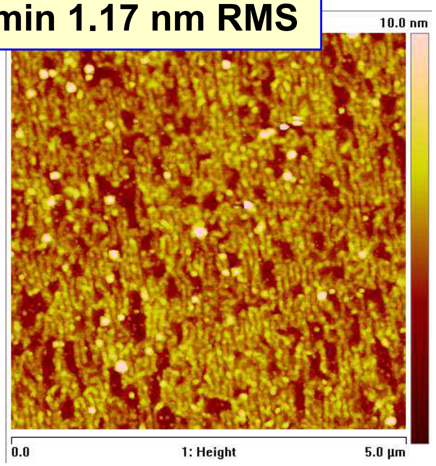
# Challenge with High Temp Growth: Nitridization of Sapphire Substrate

## Nitrided Sapphire Substrate

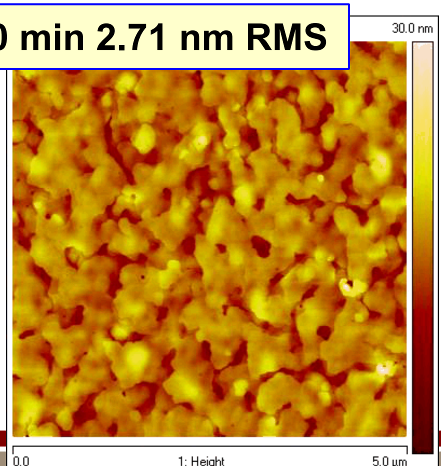
**1600°C growth conditions but**

**No Boron Source Material (TEB)**

**5 min 1.17 nm RMS**

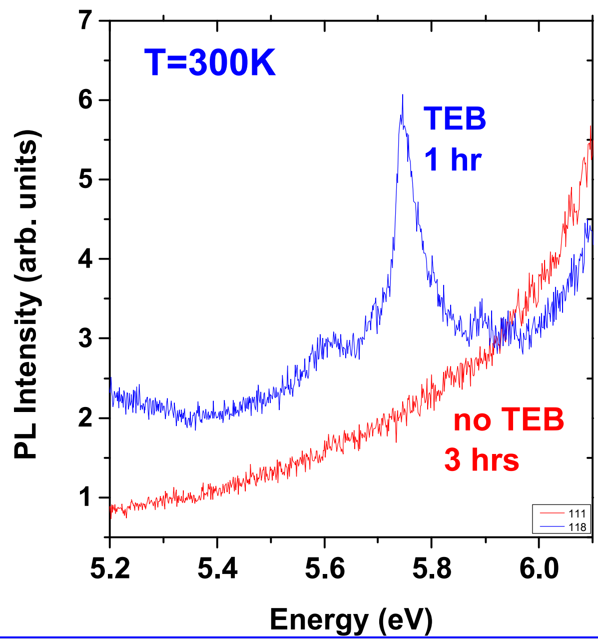



**180 min 2.71 nm RMS**

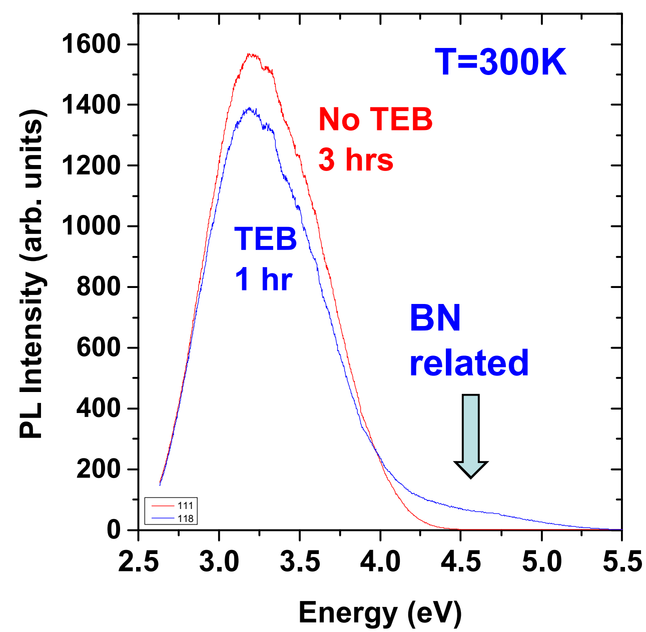



## PL comparison: BN on Sapphire vs. Nitrided Sapphire

**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**

# Surface Passivation by $NH_x$

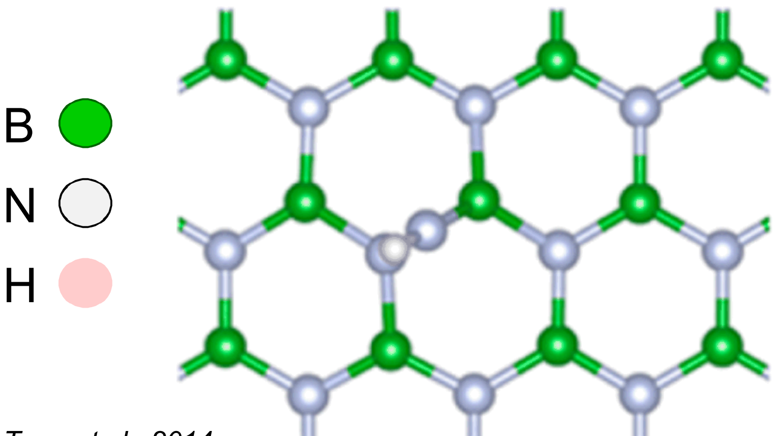
***Surface Passivation***

- **DFT suggest NH is the most stable adsorbate**
  - **Adsorption energy ($E_a$): -2.2 eV or -2.4 eV**
- **Balancing impingement rate with desorption rate**

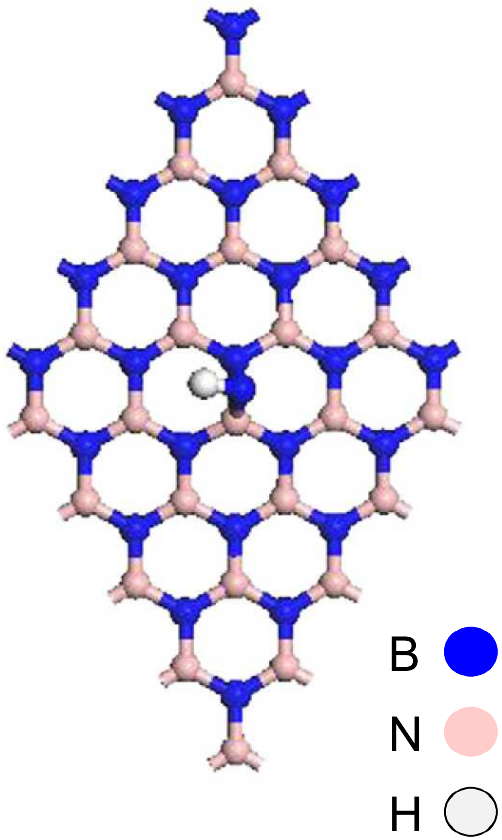
$$\Phi = R$$

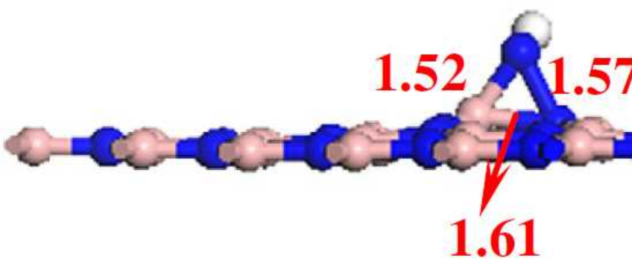
$$\frac{P}{\sqrt{2mkT}} = N^x \nu e^{-E_a/kT}$$

- **Our results consistent with $E_a$ = -2.0 ± 0.5 eV**




Tang et al., 2014



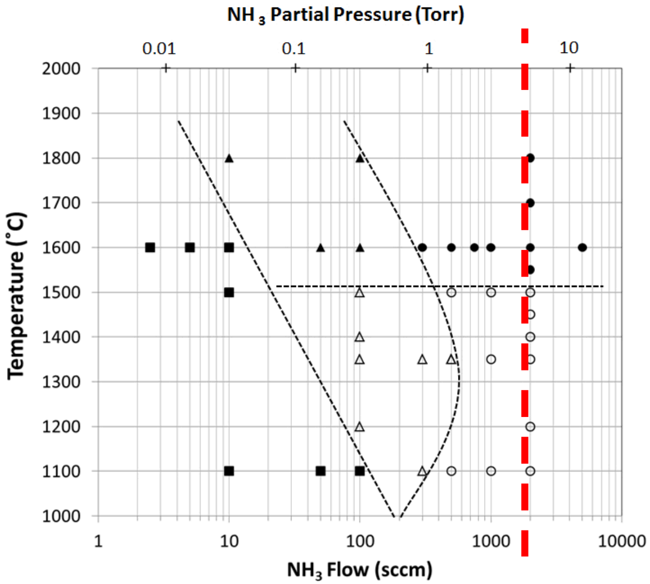




Siegel et al., 2017

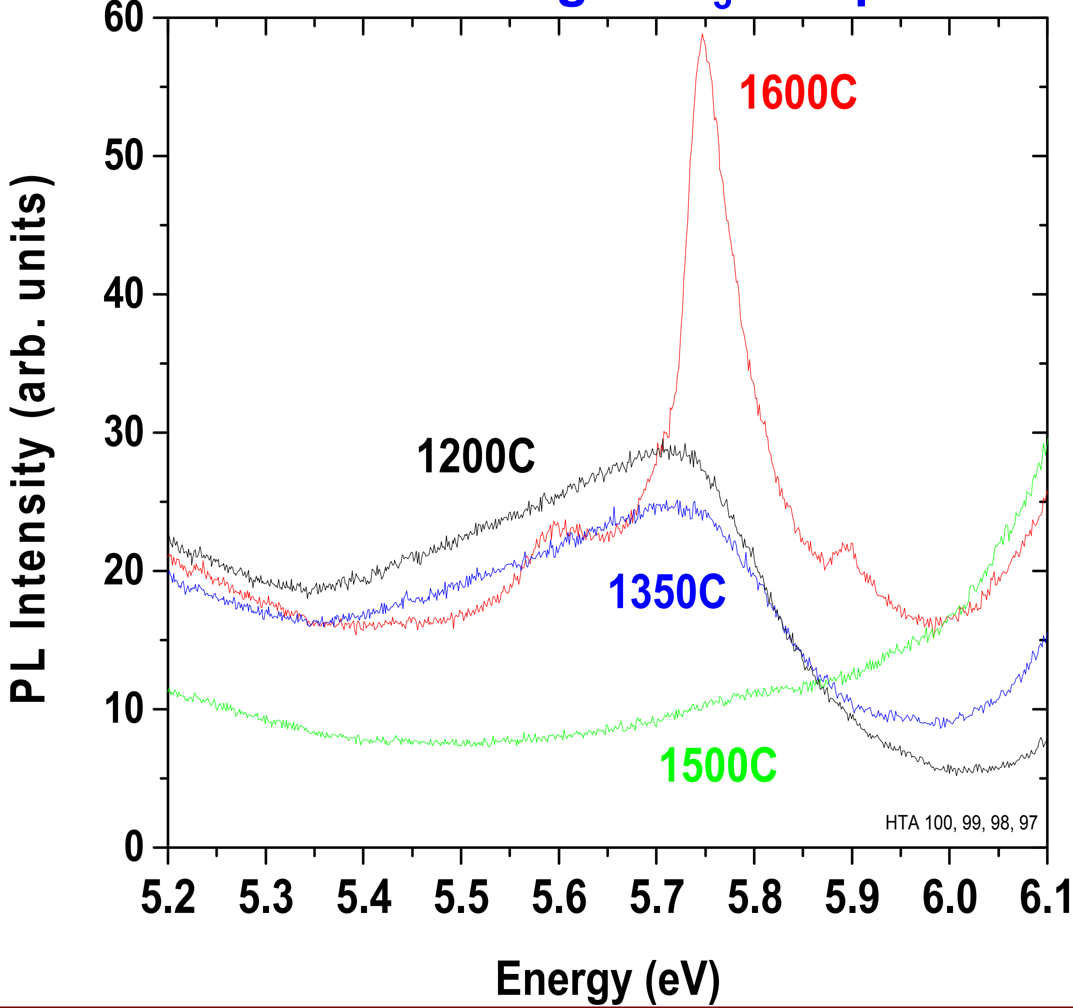
# Growth Temperature Effect

***Growth Temperature***

- Evolution of near band edge emission
- Transition from defect bound to free exciton emission at 1500 ˚C

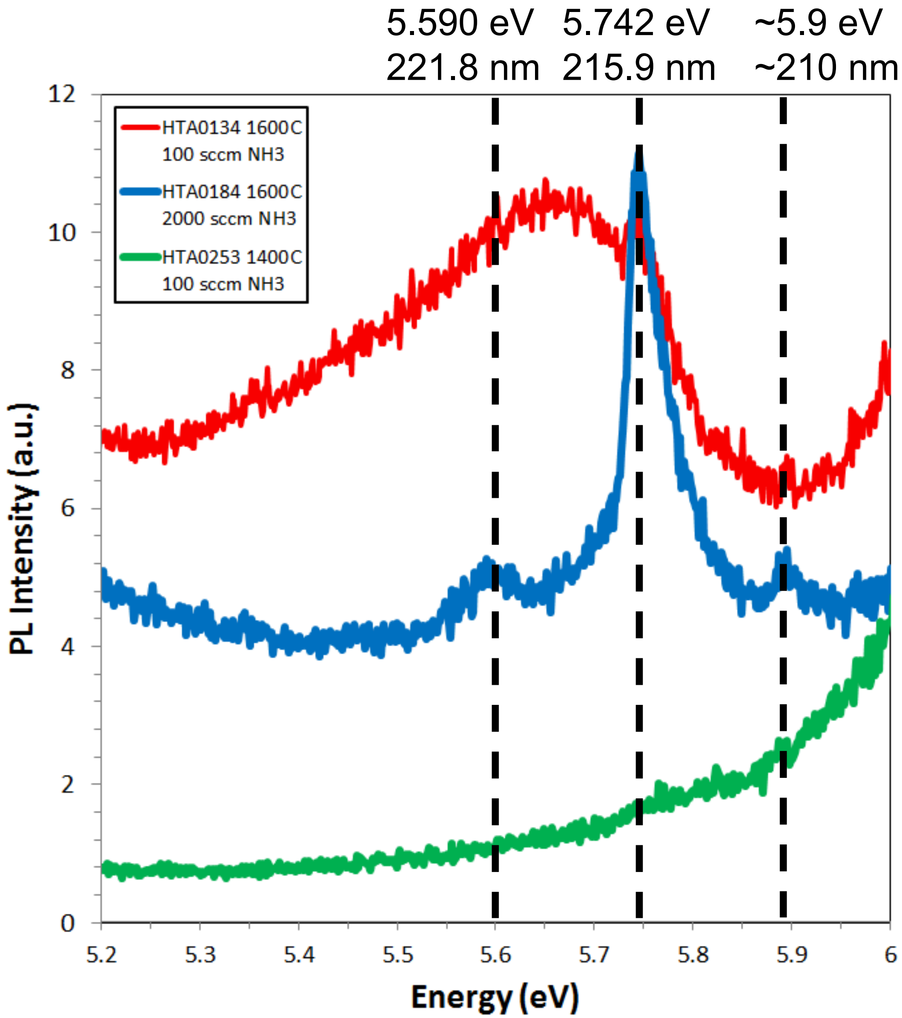



Room Temperature PL
High $NH_3$ samples

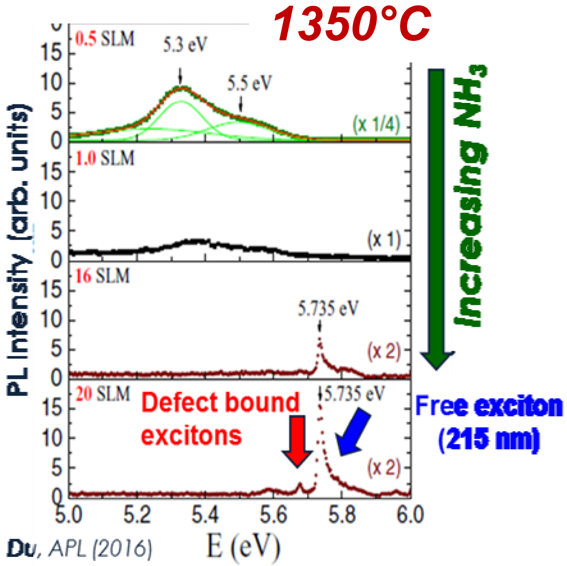


# Photoluminescence Results

## Room Temperature PL

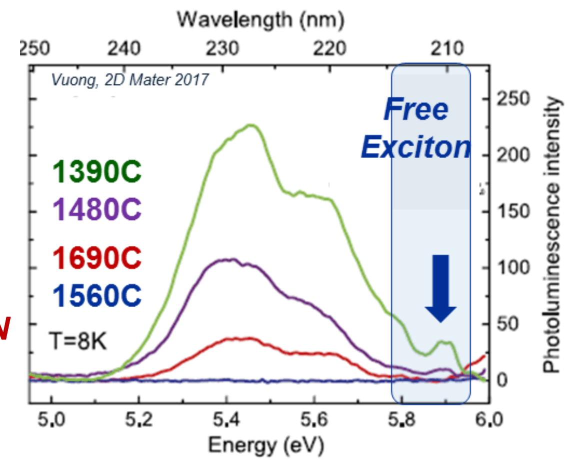



**MOVPE (2016)**
**PL (10K)**
**TEB / $NH_3$**
**Sapphire**




**MBE (2017)**
**PL (8K)**
**B / RF-$N_2$**
**on HOPG**

*(no FE from BN on sapphire)*



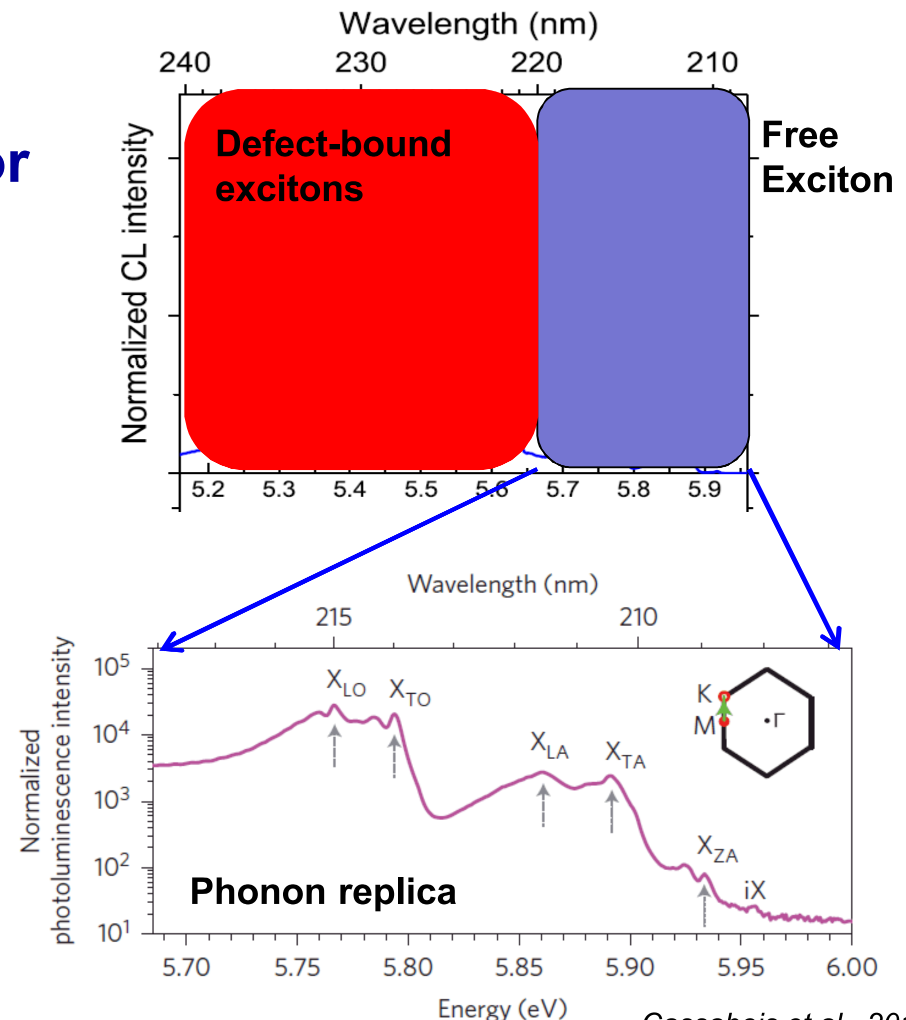
# hBN Photoluminescence

## *hBN PL*

- **Near band edge emission dominated by exciton behavior**
- **Number of phonon replica**
- **Still unclear about direct/indirect nature of hBN**

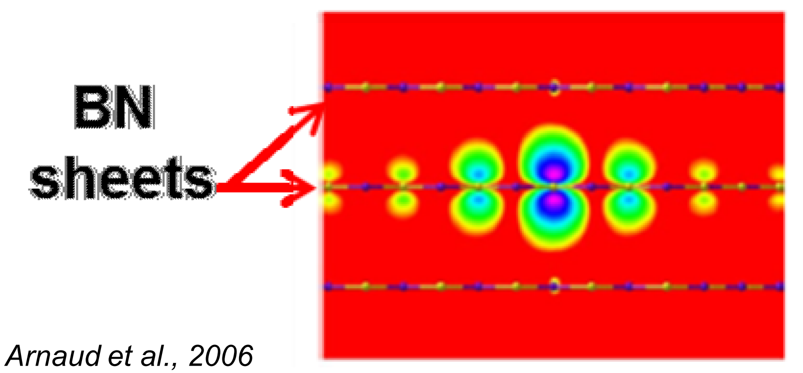
**Bulk BN Low temp CL**

*Pierret, 2014*

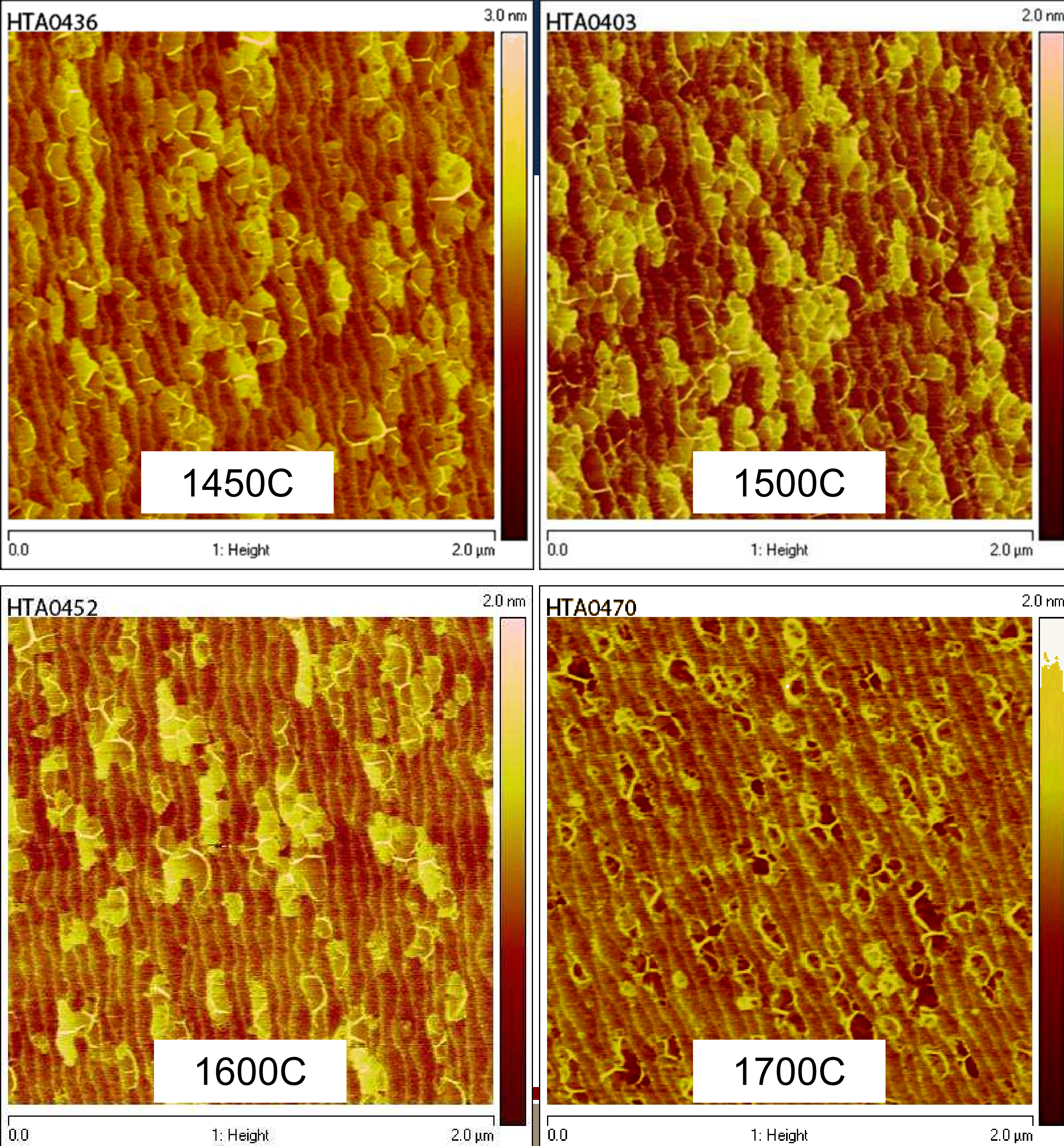



*Cassabois et al., 2016*

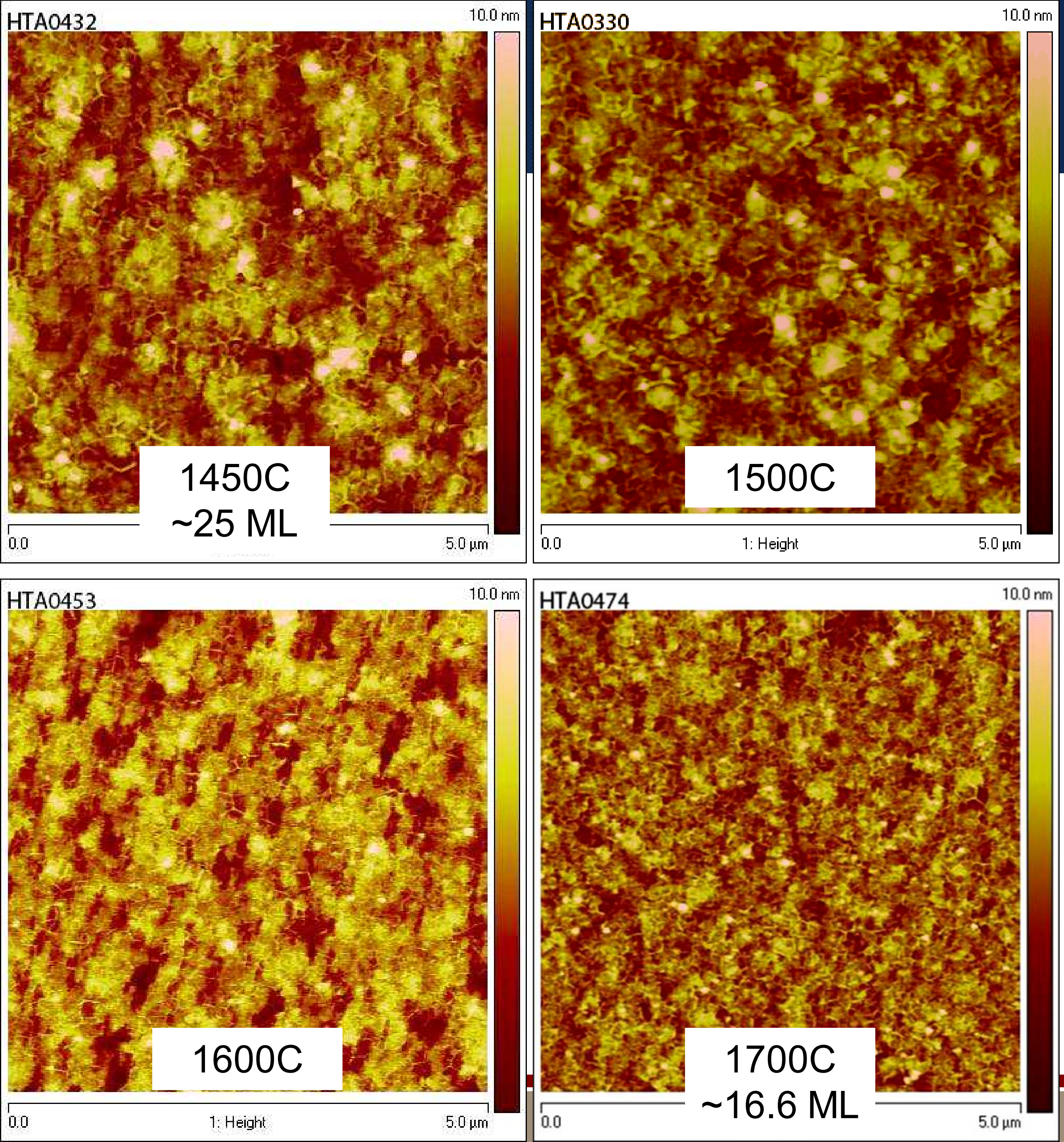
**Exciton probability density (5.78 eV)**




*Arnaud et al., 2006*

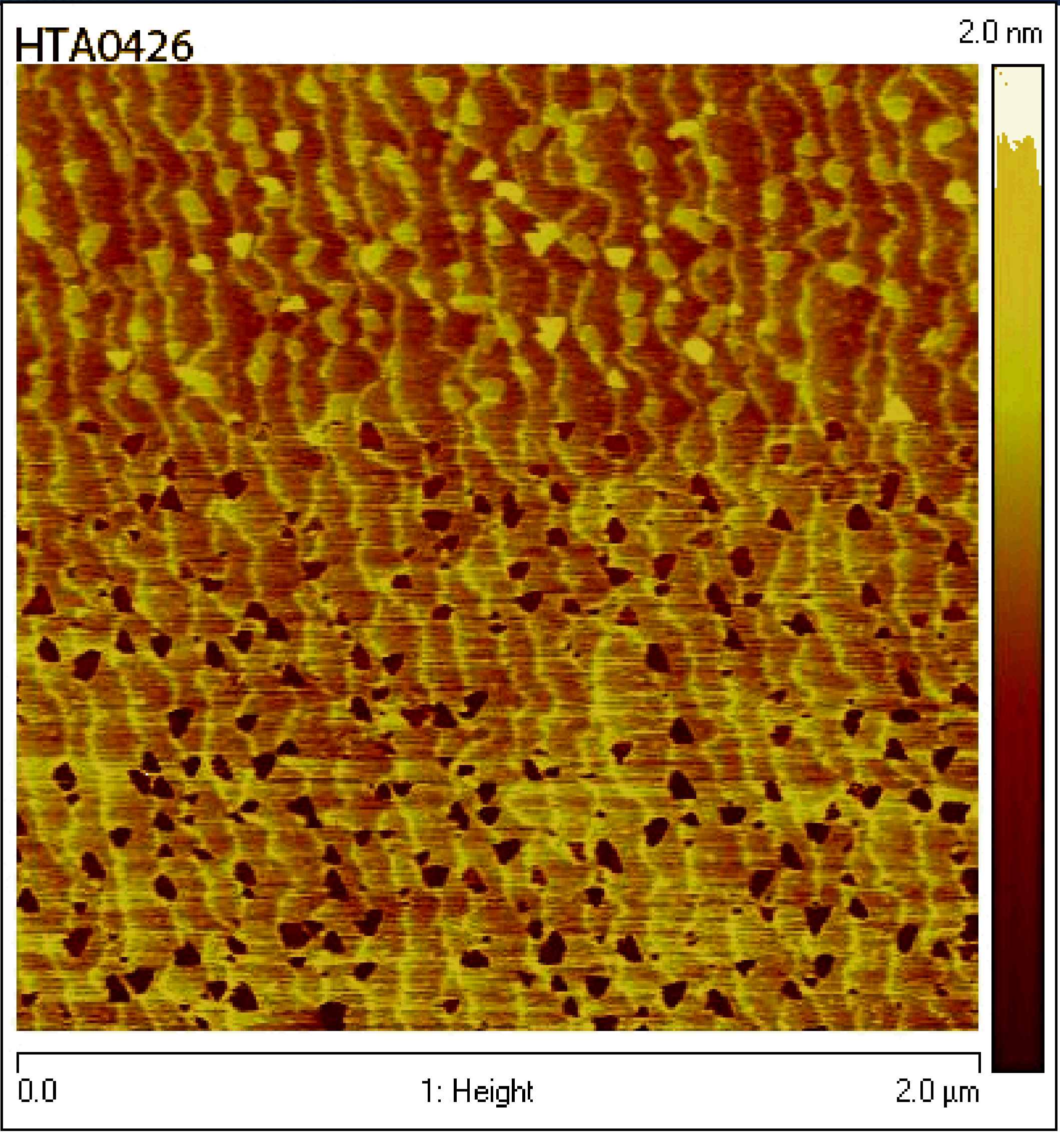



- Get "nuclei" with any of the below:
  - 1450C
  - 60 min at 0.13 umol/min borazine
  - 1500C
  - 5 min at 0.37 umol/min borazine
  - 60 min at 0.13 umol/min borazine
  - 1600C
  - 5 min at 0.75 umol/min borazine
  - 1700C
  - 1 min at 3.6 umol/min borazine

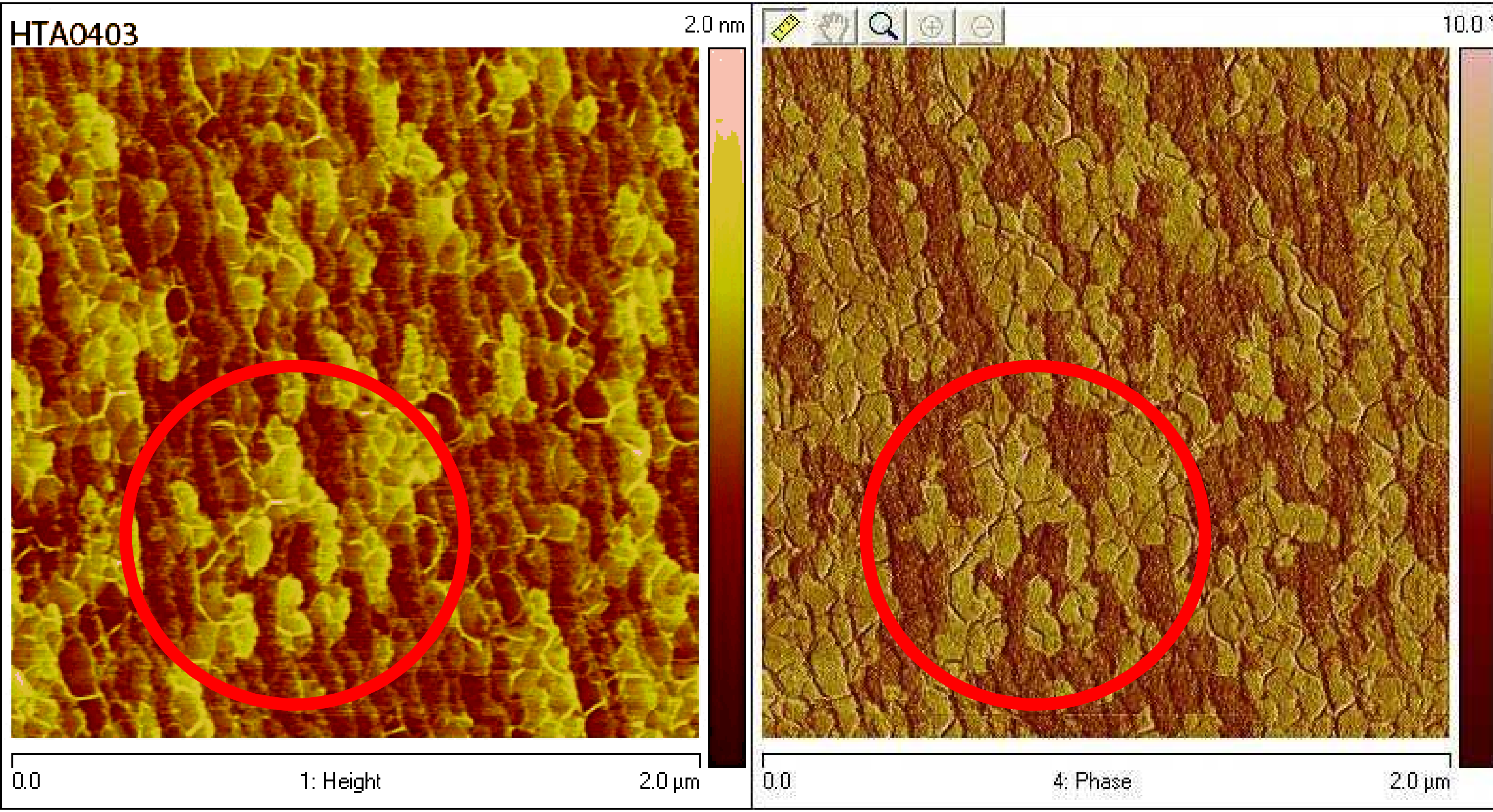



- Get “wrinkles” with any of the below:
  - 1450C
  - 240 min at 0.13 umol/min borazine
  - 1500C
  - 60 min at 0.37 umol/min borazine
  - 1600C
  - 30 min at 0.75 umol/min borazine
  - 1700C
  - 5 min at 3.6 umol/min borazine

# AFM



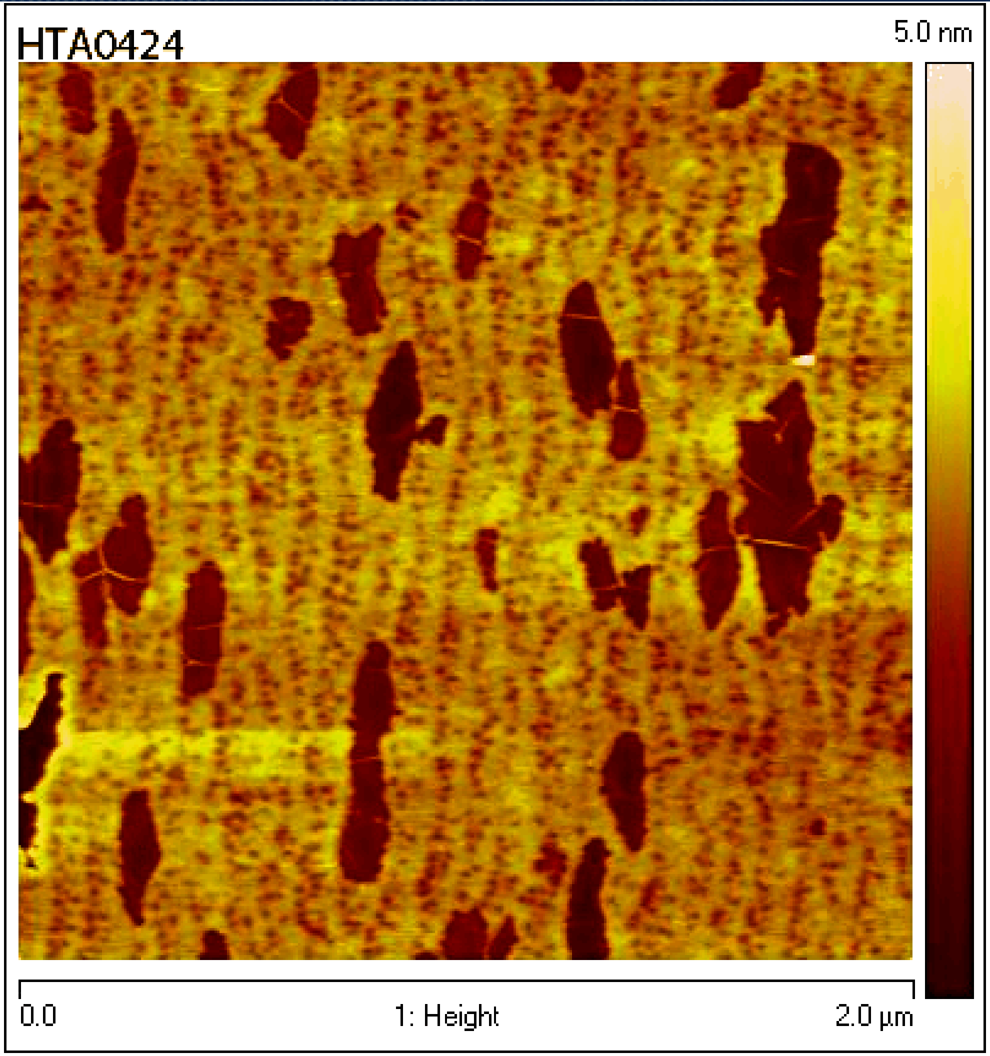
# AFM



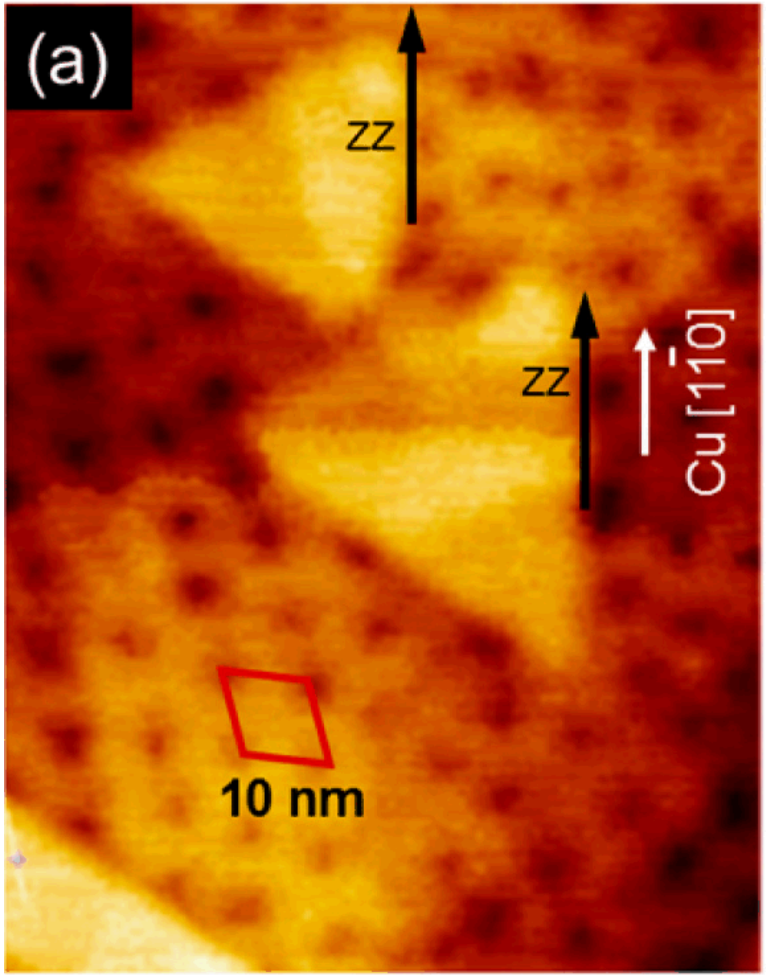

Topograph

Phase Contrast

# AFM

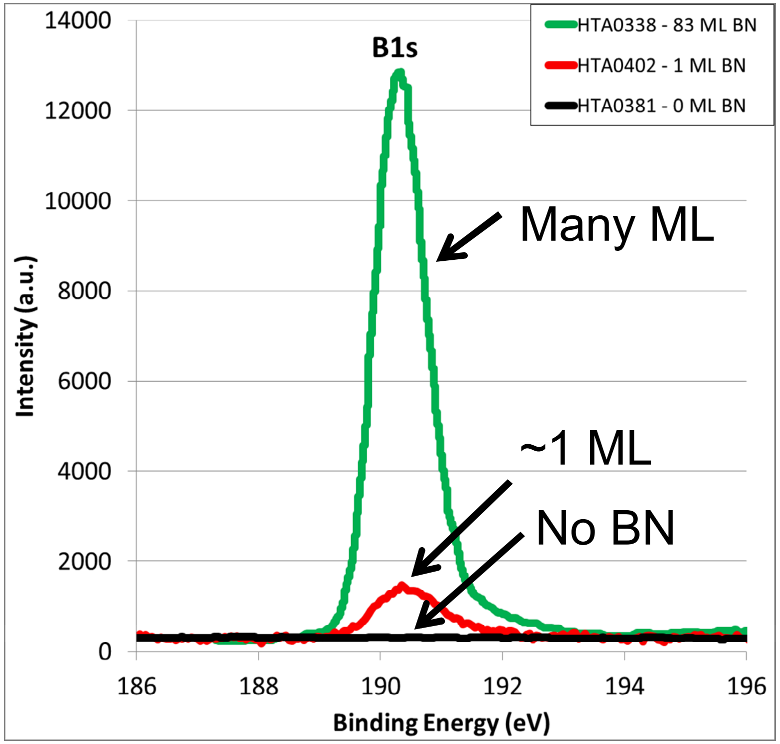


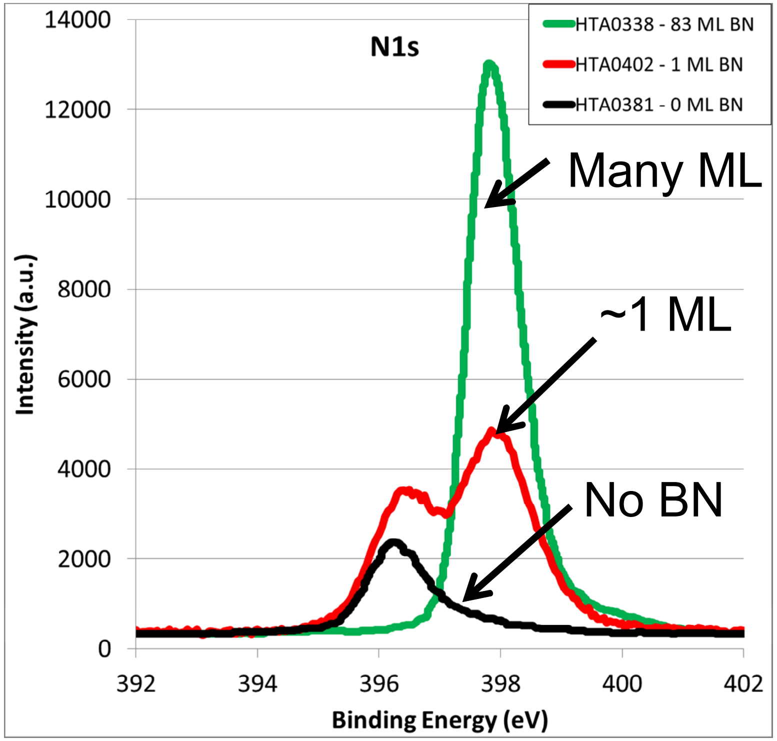

SNL ~2 ML BN




AFRL - Siegel et al.
1 ML with additional ML islands

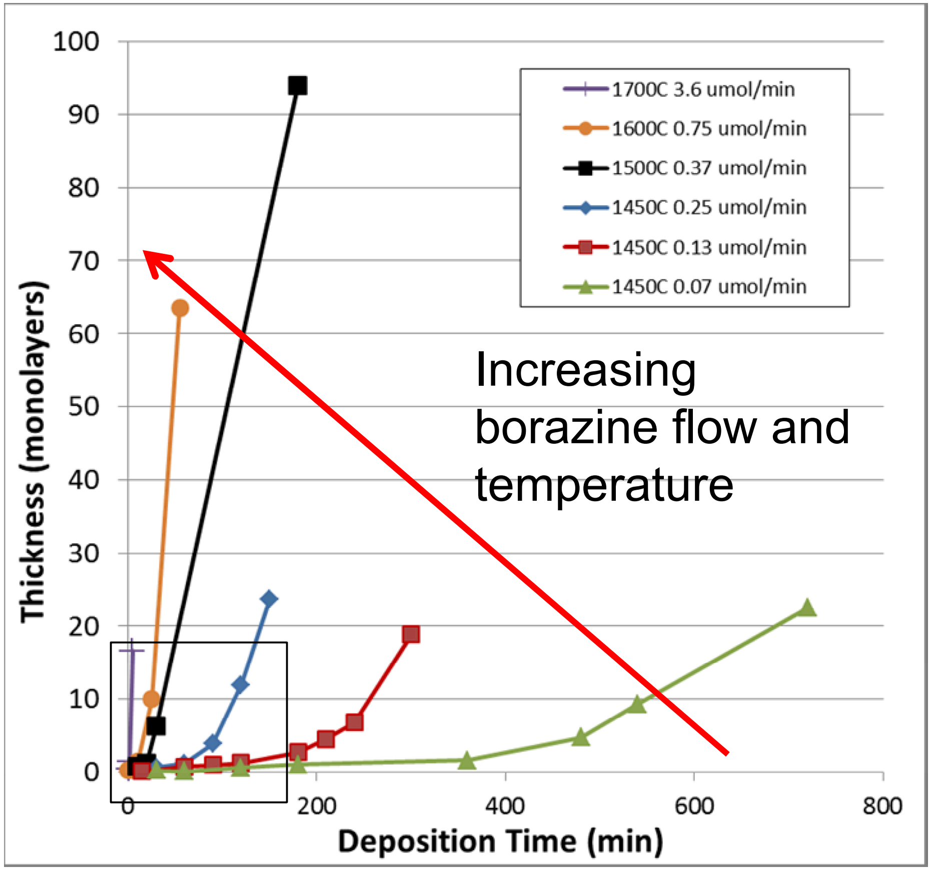
# XPS

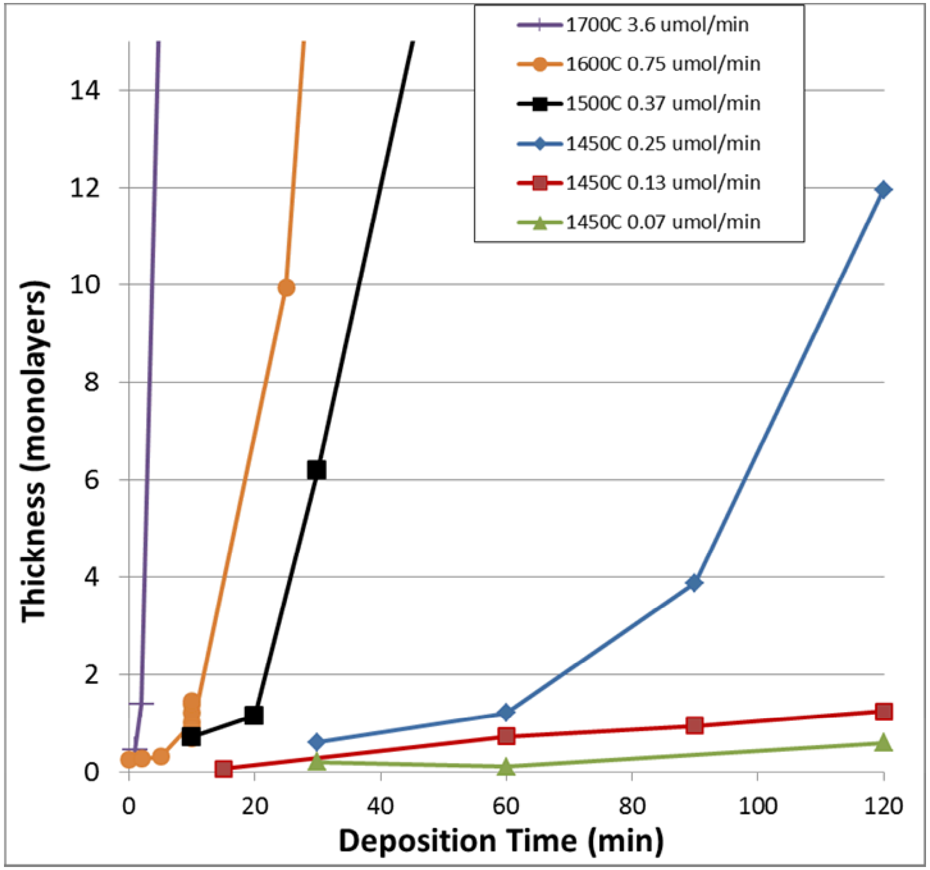



- Thick hBN films B to N ratio ~0.95
- ~1 monolayer hBN appear N rich
- Surfaces exposed to sub-critical borazine flows show N but not B

# Film Deposition

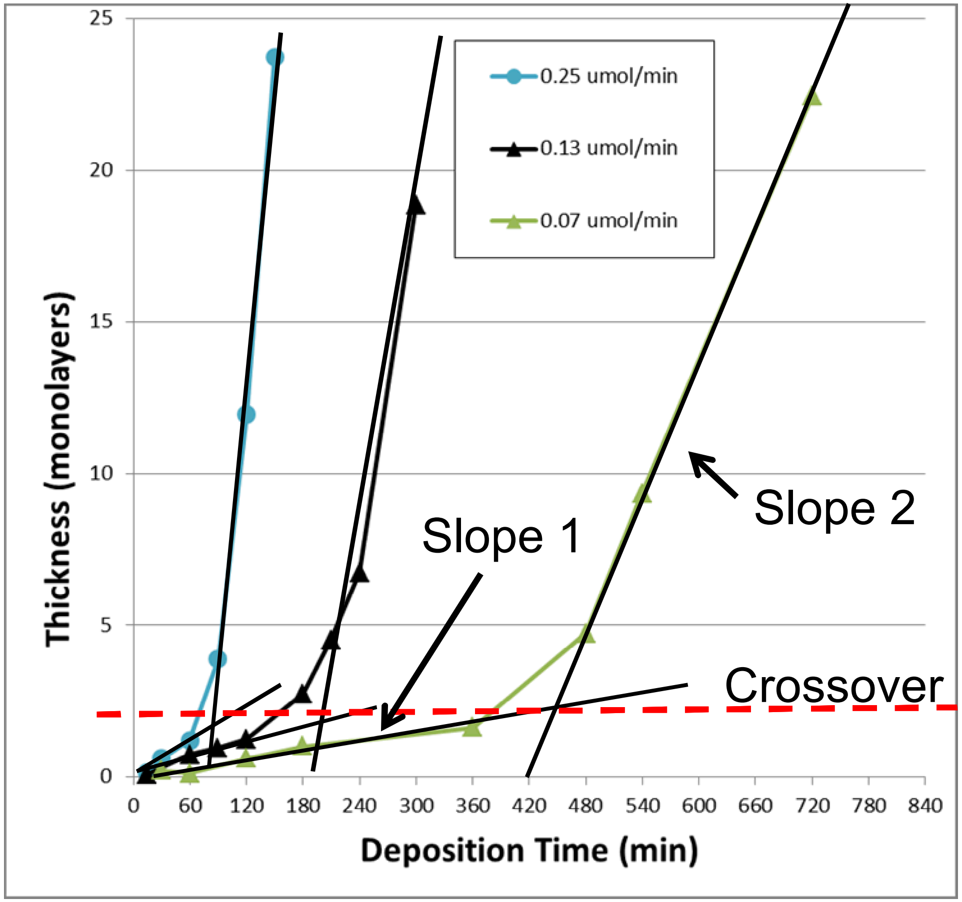


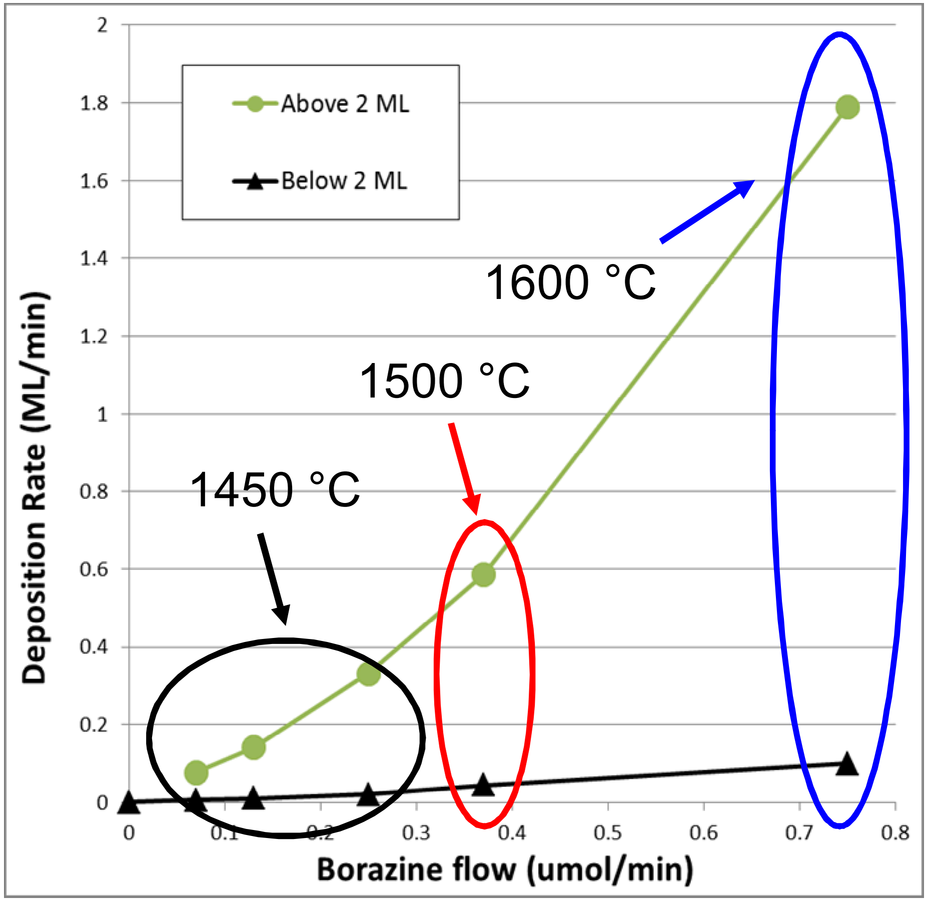




Expanded view of insert to the left

- Deposition rate is not constant with time

# Film Deposition




- Change in deposition behavior at ~2 monolayers
- Sapphire surface acting as an inhibitor?

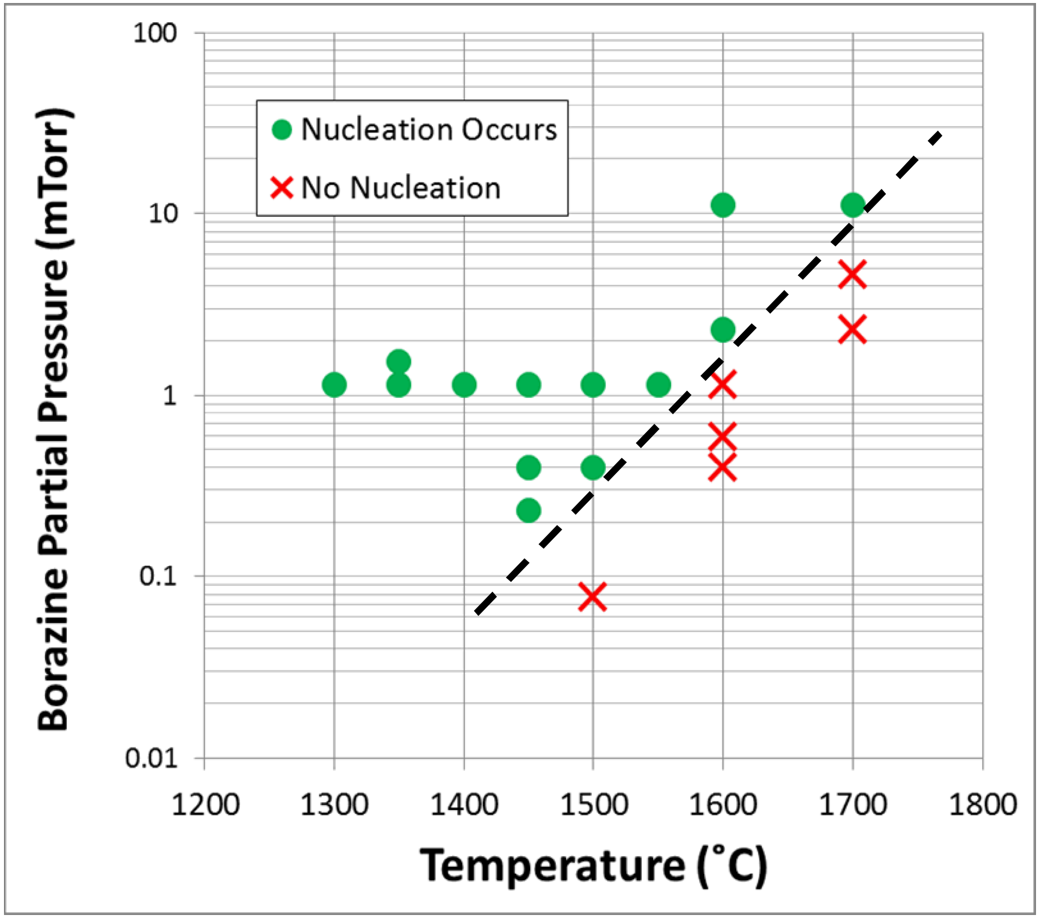
# Separating Nucleation and Growth

## *Nucleation*

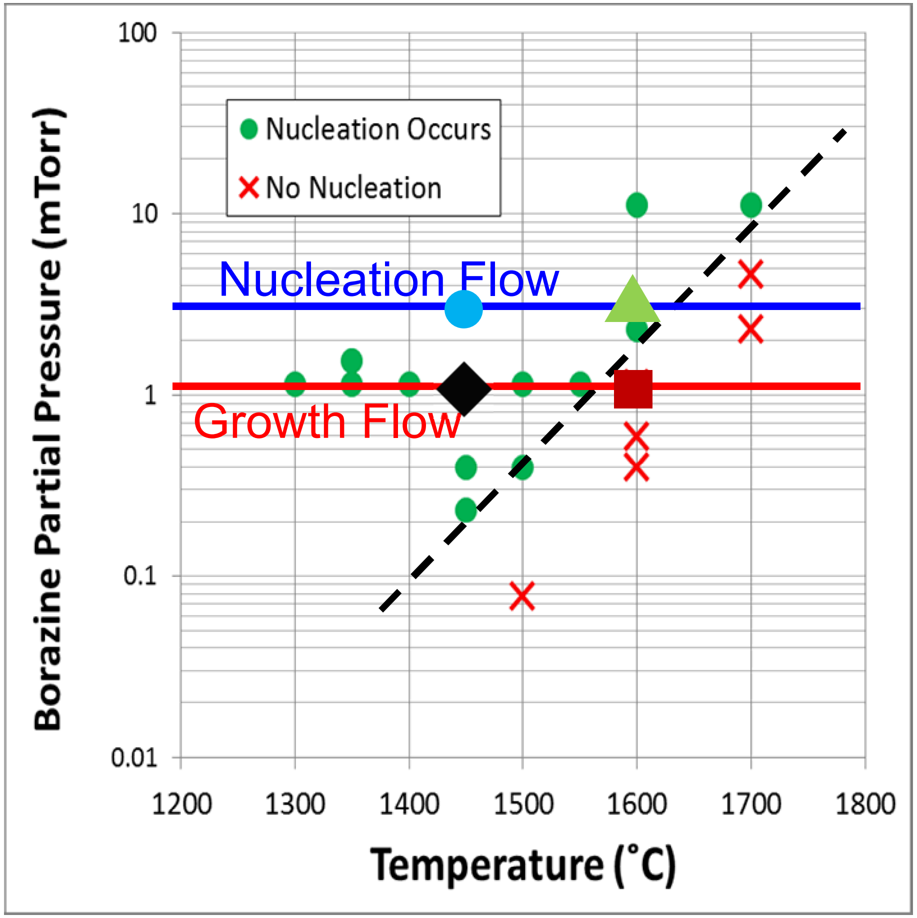
- Threshold determined by supersaturation
- Must over come an energetic barrier to nucleate

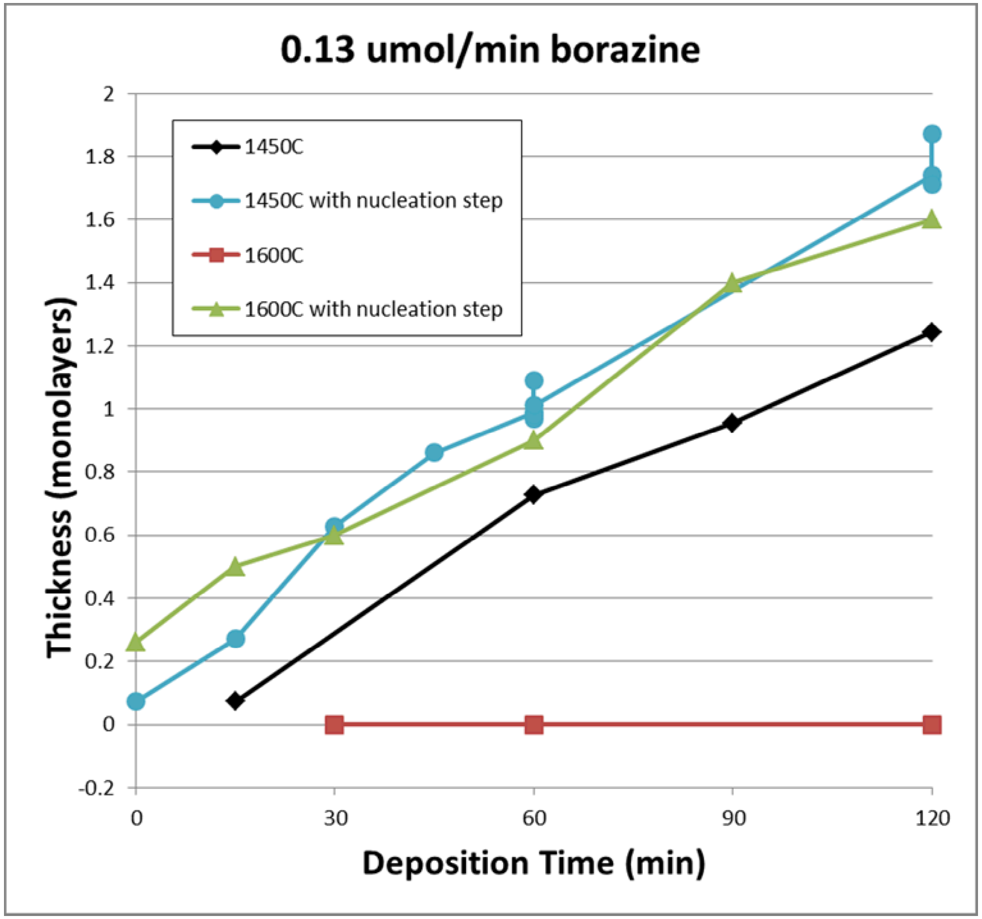
## *Deposition*

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



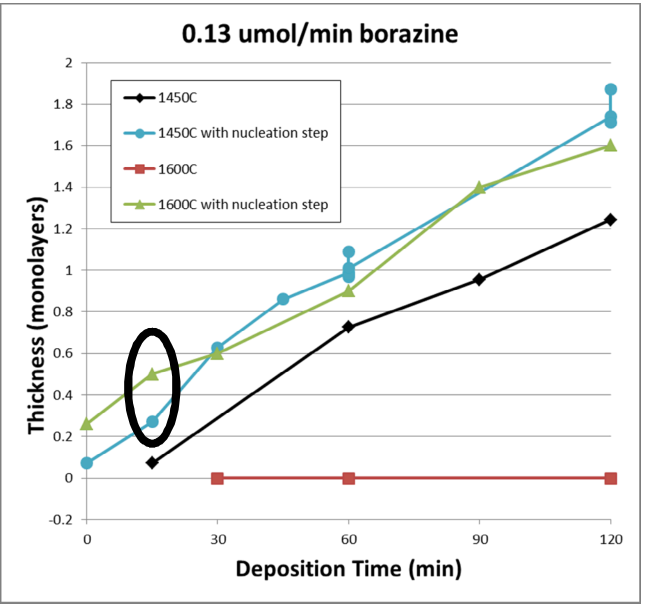
# Separating Nucleation and Growth



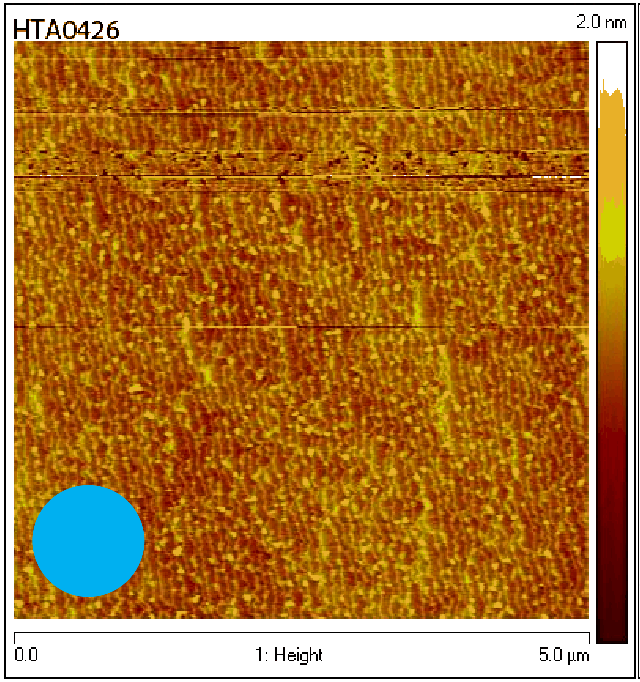




- "Nucleation step" is 5 minutes at 0.37 μmol/min borazine
- Growth at 0.13 μmol/min borazine

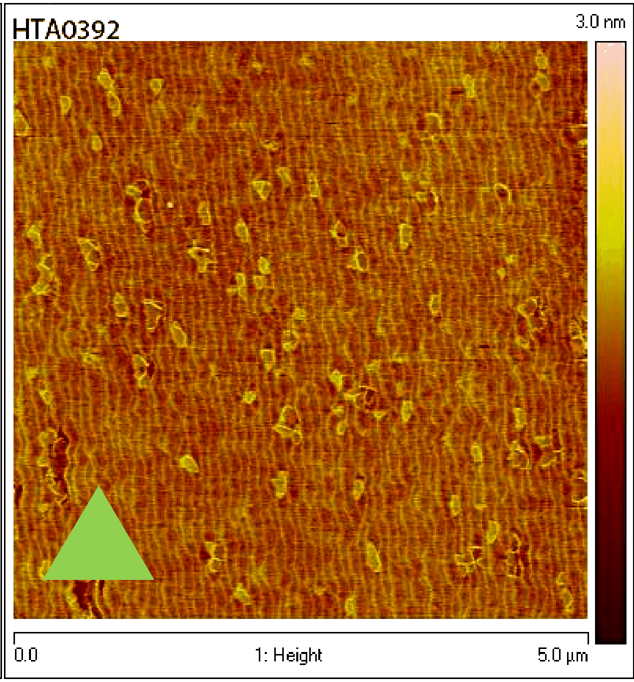
# Nucleation with Temperature




**These are those films!**




1450 ˚C




1600 ˚C

- BN deposition rate does not depend on nuclei density, nuclei size, or deposition temperature