

Effects of Temperature and Ammonia on MOCVD Hexagonal BN



LABORATORY DIRECTED RESEARCH & DEVELOPMENT

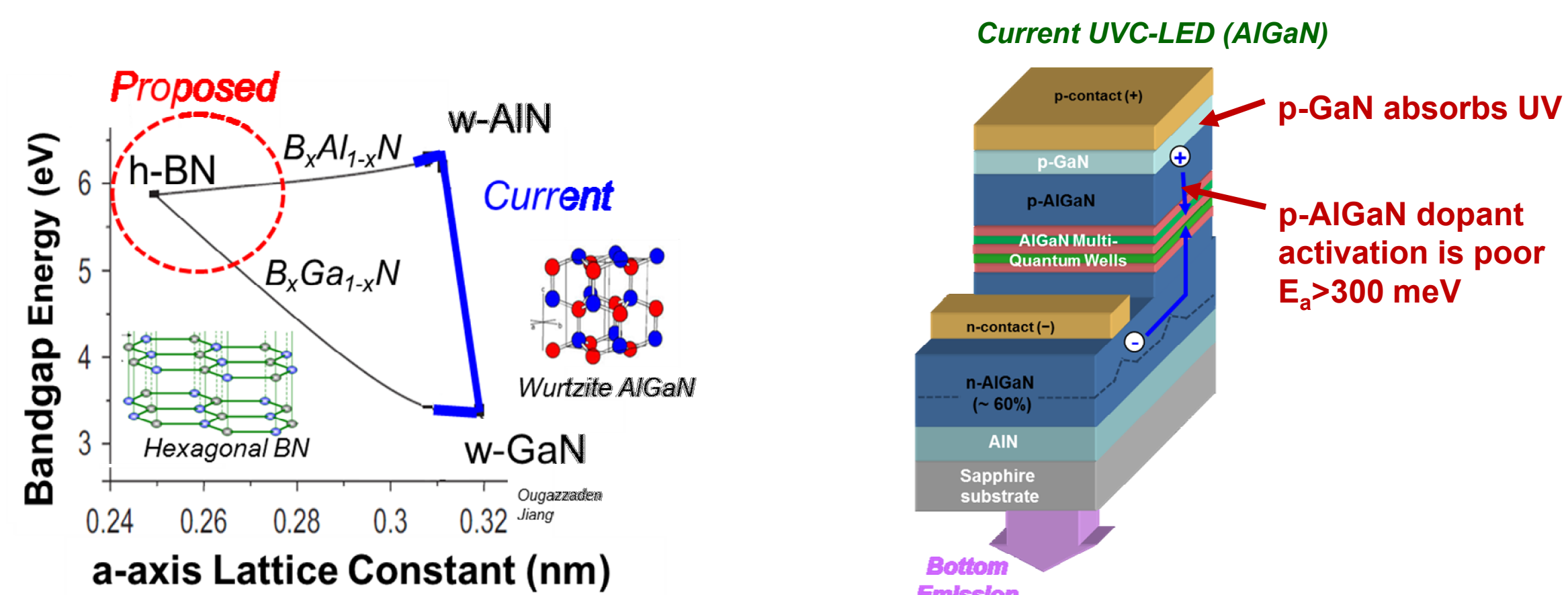
Sandia National Laboratories

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Challenge

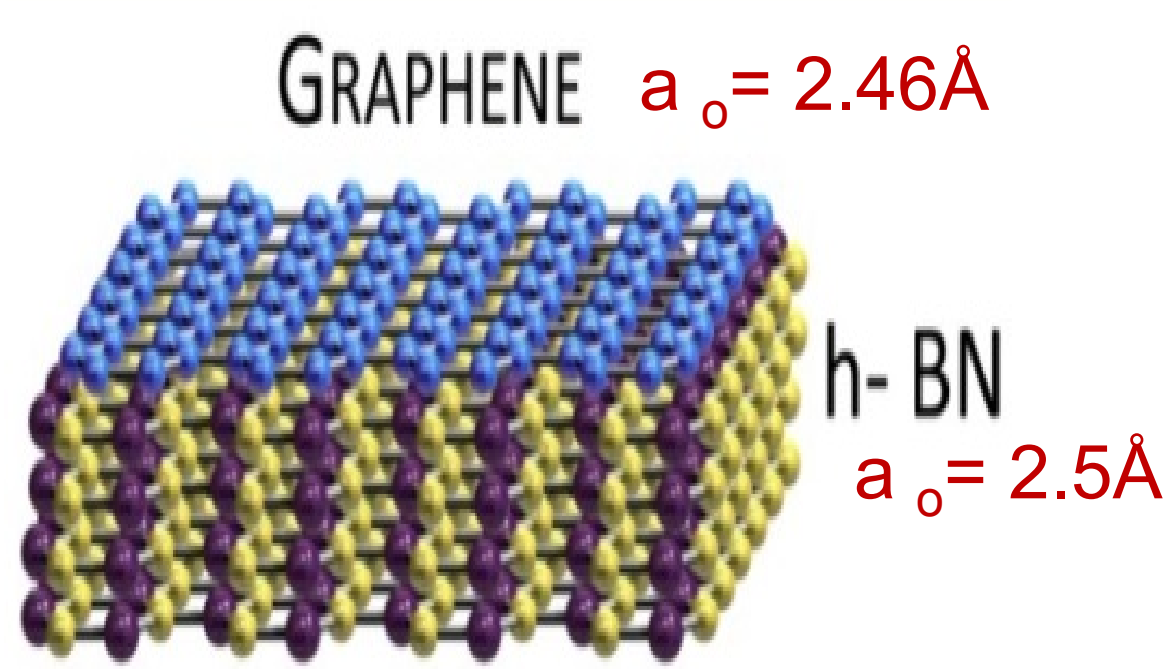
Why MOCVD hBN:

- Hexagonal Boron Nitride (hBN) is a wide bandgap (~6 eV) semiconductor of interest both for use in optoelectronic devices as well for use in 2-D heterostructures.
- Bulk hBN not available at a wafer scale
- 2-D BN heterostructures most commonly fabricated by film transfer



hBN alloys for lattice matching and bandgap tuning

p-hBN as UV transparent contact layer could improve efficiency

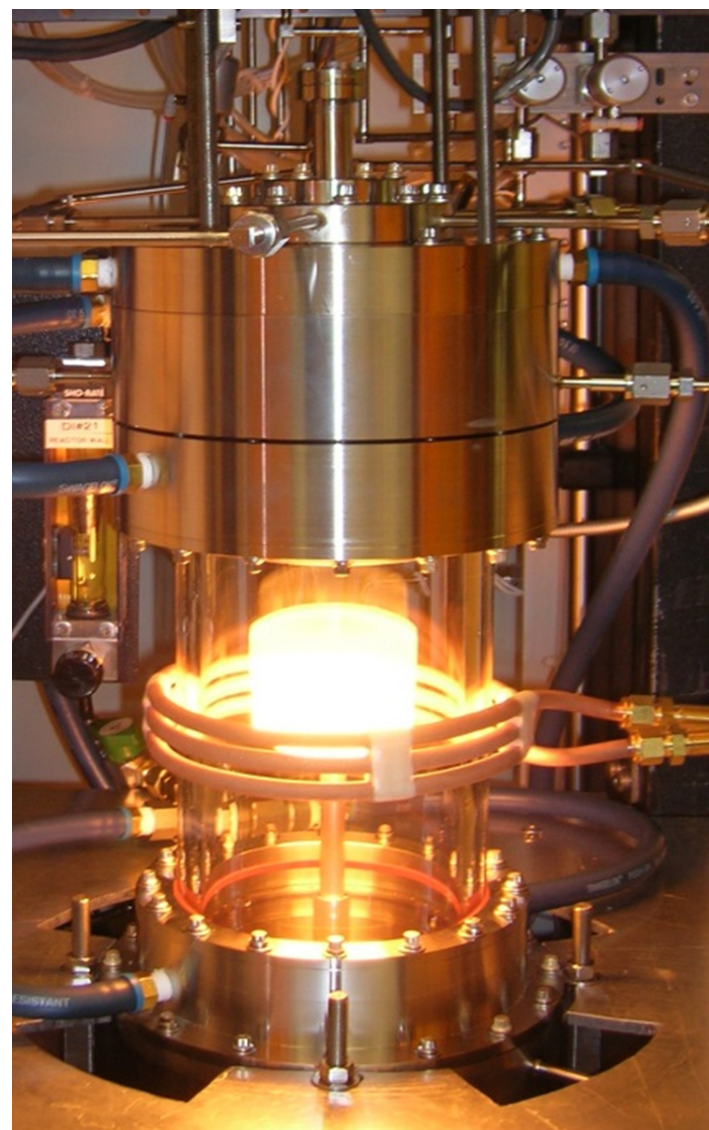


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hBN is isoelectric and isostructural with graphene making an excellent substrate and encapsulant

Graphene/hBN heterostructures with tunable optical response through moiré potential

Film Deposition



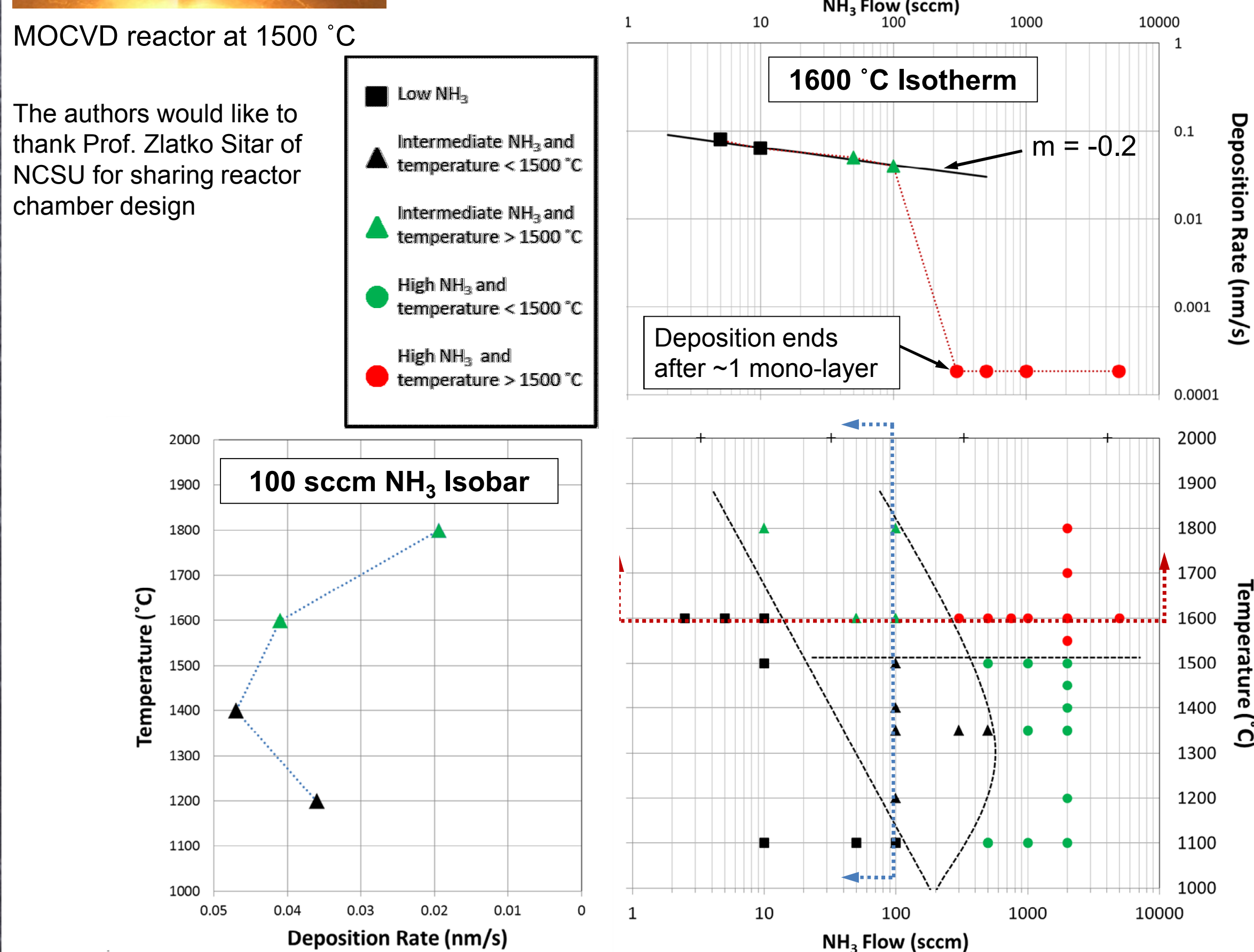
MOCVD reactor at 1500 °C

Deposition:

- Cold walled rf-heated high temperature reactor (up to 1800 °C)
- Triethylboron (TEB) and ammonia as source gases
- Deposition on c-sapphire wafers
- Typical operation deposition conditions:
 - 50 Torr
 - N₂ diluent gas and carrier gas
 - Plots below are for 22 μmol/min (~0.5 sccm) TEB flow

Summary of deposition behaviors:

- 3 different deposition behaviors with different ammonia flows
 - Discolored boron sub-nitride at low ammonia flows
 - Multi-layer stoichiometric hBN at intermediate ammonia flows
 - Self-limiting BN deposition at high ammonia flows
- Different photoluminescence behaviors above and below 1500 °C

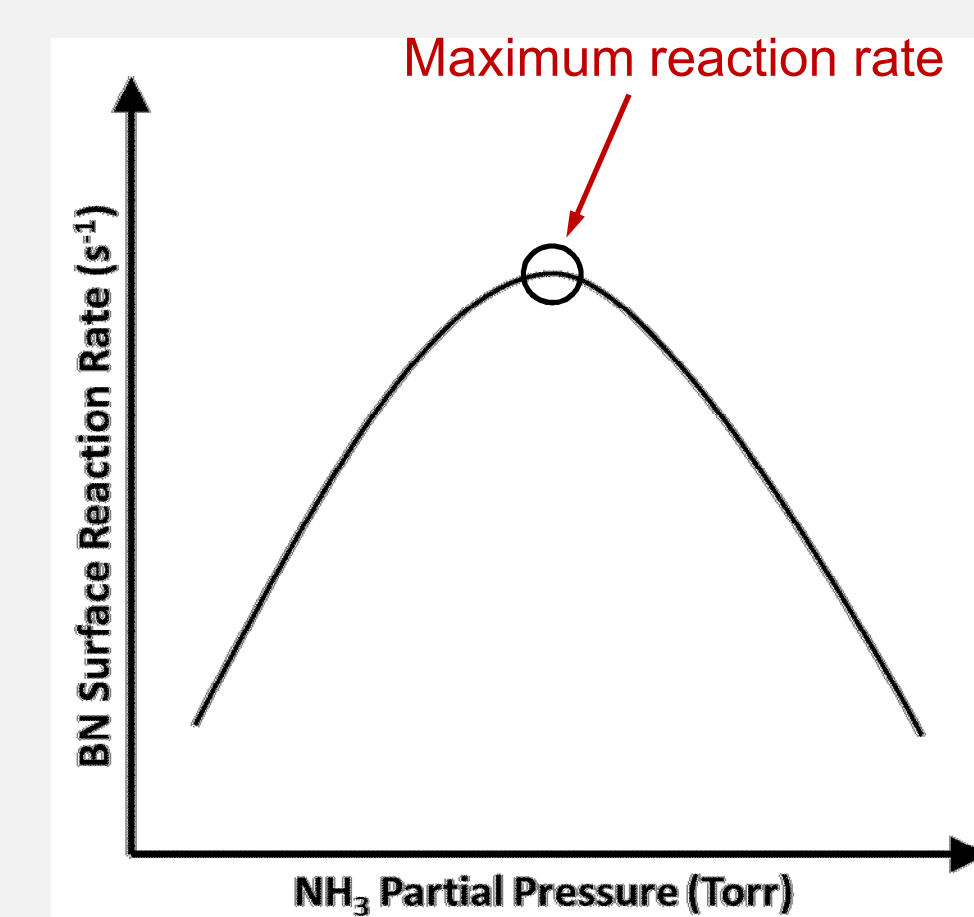
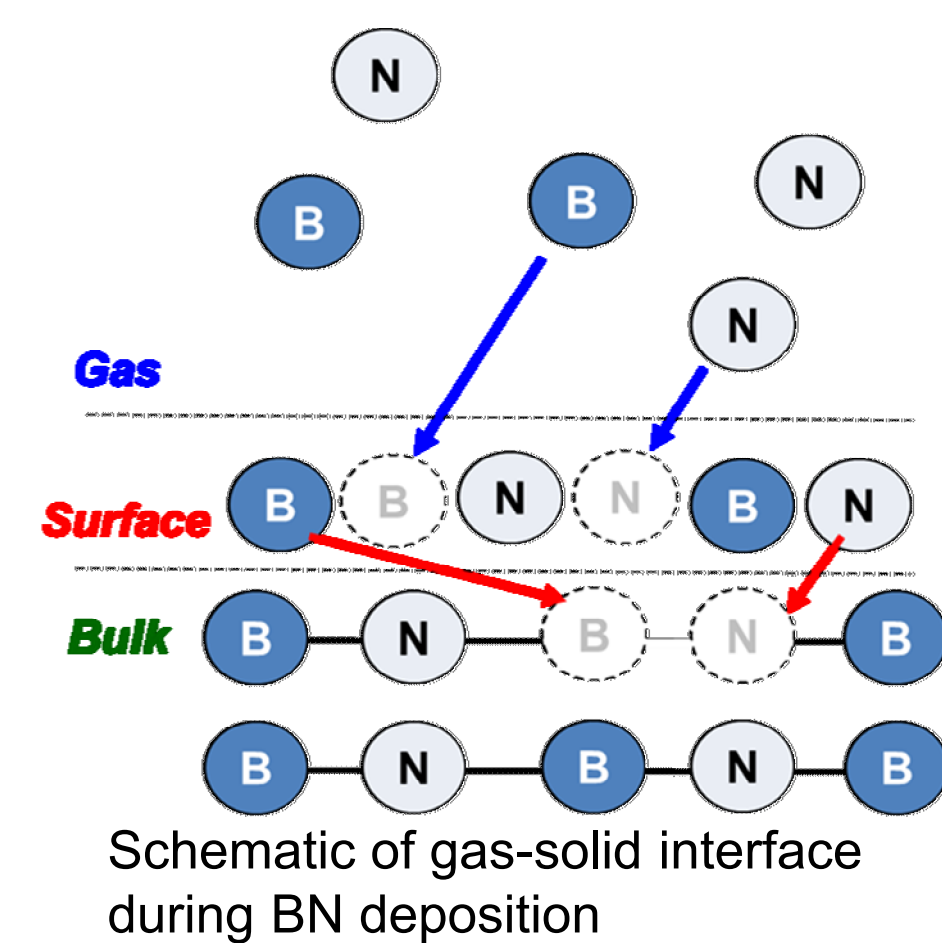


The authors would like to thank Prof. Zlatko Sitar of NCSU for sharing reactor chamber design

Deposition Model

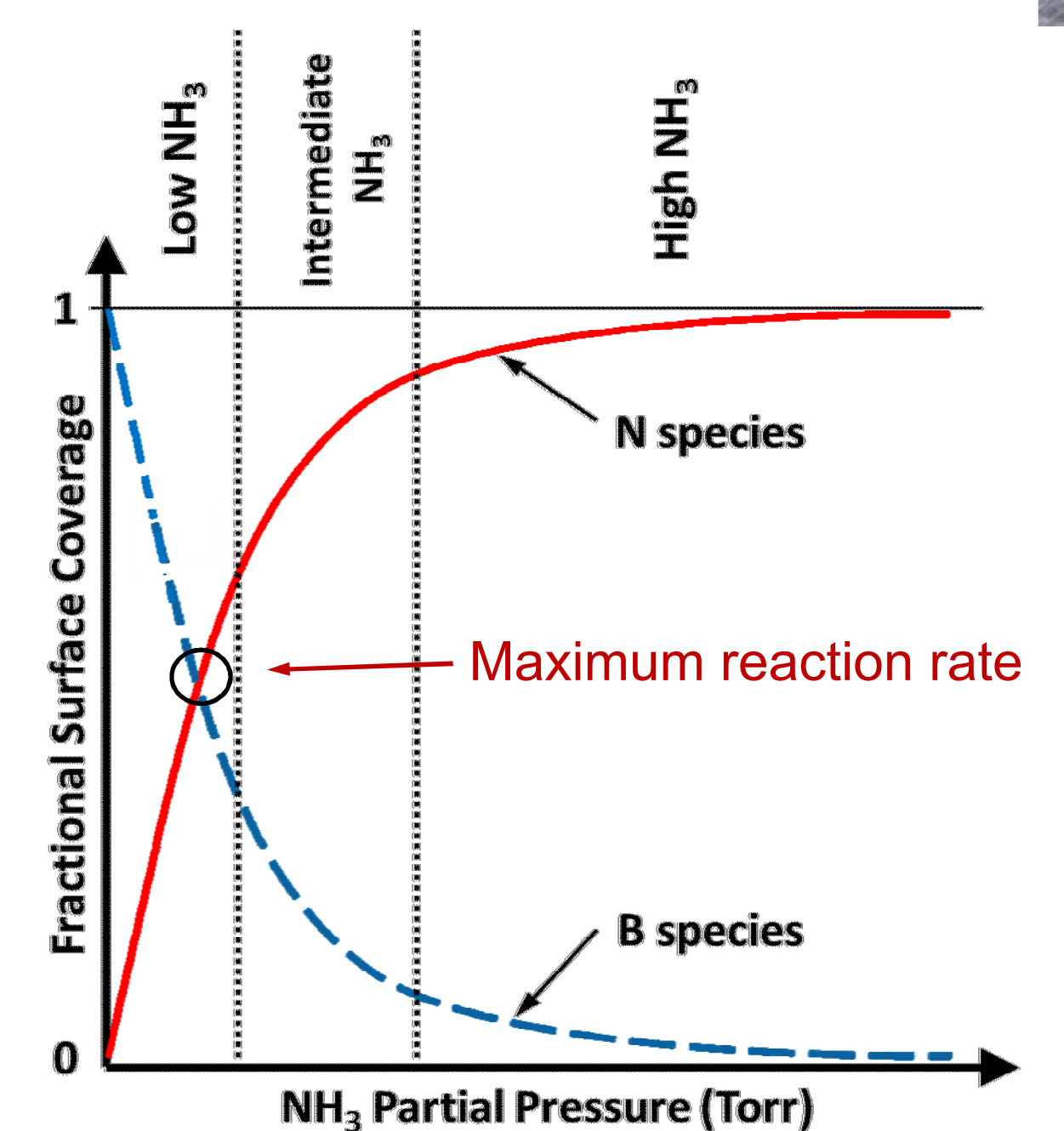
Model:

- hBN deposition behavior can be explained with a Langmuir-Hinshelwood (LH) surface reaction
 - B and N species compete for finite surface sites
 - Excess surface coverages of either species can limit reaction rate



$$R = k_r [B_s] [N_s] = \frac{k_{rxn} k_B k_N p_B p_N \Gamma^2}{(1 + k_B p_B + k_N p_N)^2}$$

Expected LH type reaction rate



Expected surface coverage for LH behavior with our experimental ammonia flow regimes overlaid based on deposition behavior

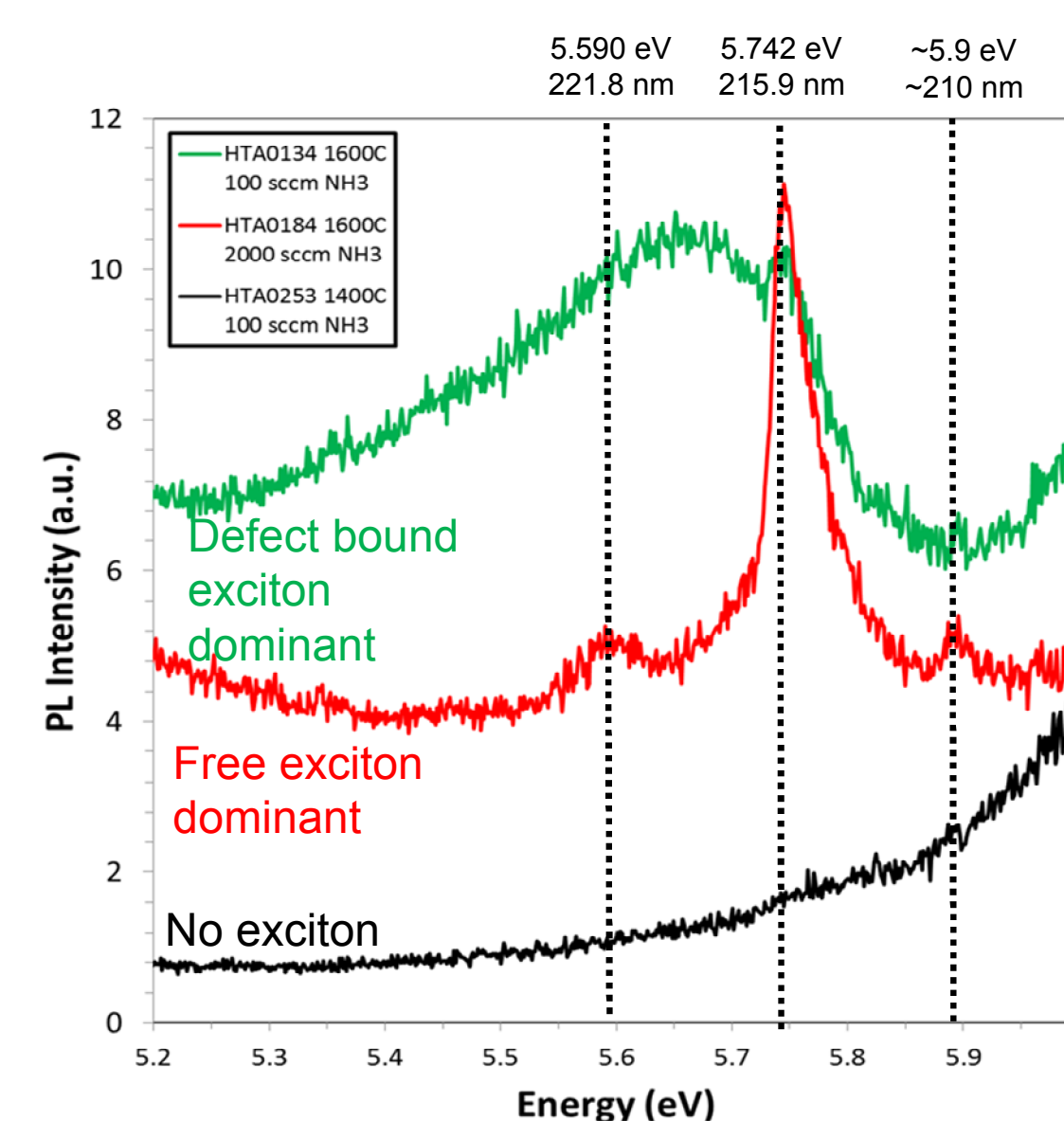
Photoluminescence

Characterization:

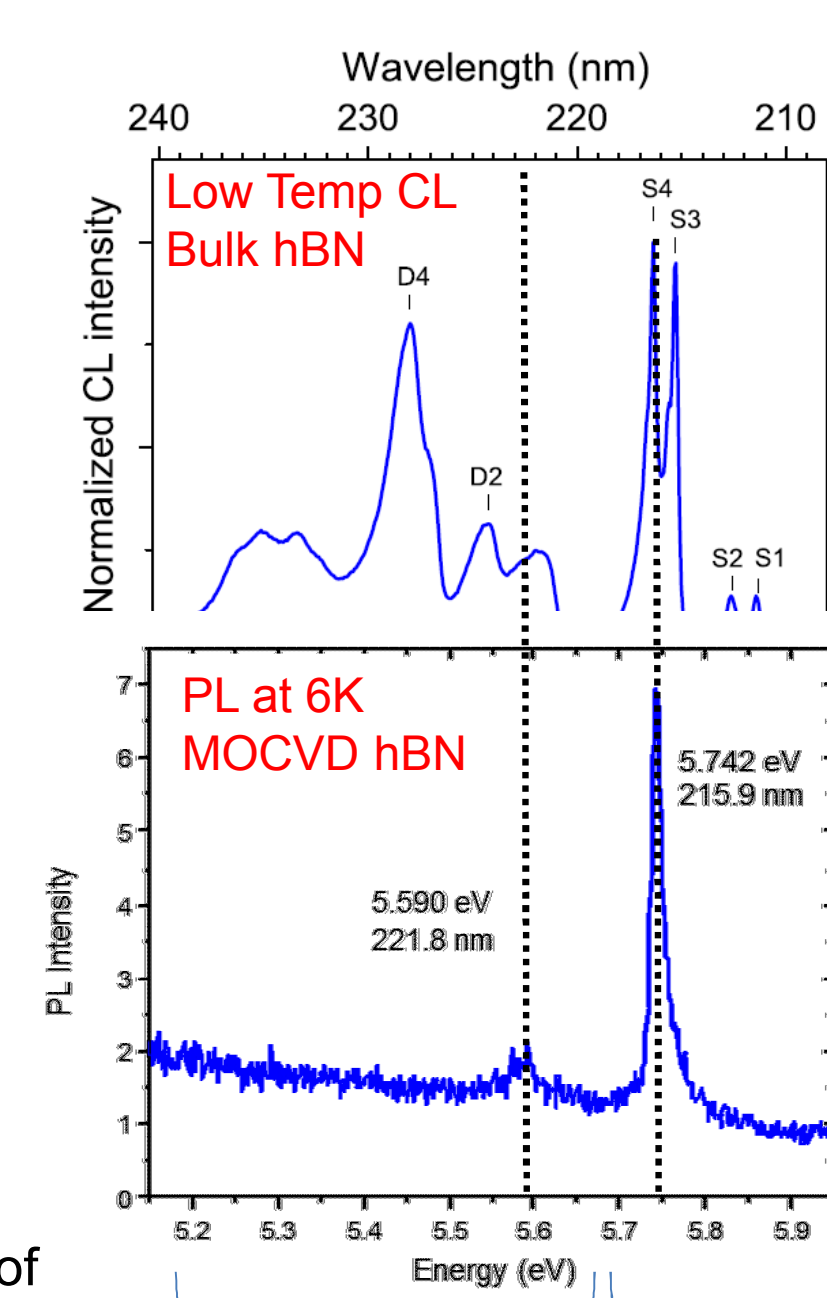
- 197 nm excitation source using a 4th harmonic Ti:sapphire laser
- Photoluminescence (PL) spectra taken at room temperature and ~6K

Influence of deposition conditions:

- Temperature and ammonia flow during deposition determine PL
- PL behavior can be categorized into 3 behavior types
 - No exciton emission - Low ammonia samples regardless of temperature and intermediate ammonia samples deposited at T < 1500 °C
 - Defect bound exciton dominant - Intermediate ammonia samples deposited at T > 1500 °C and high ammonia samples deposited at T < 1500 °C
 - Free exciton dominant - High ammonia samples deposited at T > 1500 °C



Representative room temperature PL spectra of the three types of PL behavior. Colors correspond to the markers of the plot opposite illustrating where films with such PL behavior can be deposited.



Bulk hBN from Pierret et al. Phys Rev B 2014

High Temp High ammonia MOCVD hBN from this work

Defect Bound Excitons Free Excitons