Structure and Electrical Properties of Boron Nitride ALD Grown in a Quasi-static Viscous Flow Reactor

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Robert K. Grubbs
Sandia National Laboratories

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Outline

Motivation

- BN has really attractive properties

Deposition

- Investigate BCl_3 and $B(CH_3)_3$ + NH_3 ALD
- Use quasi-static flow reactor

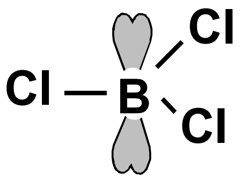
Characterization

- Thickness – Profilometry, optical interference
- Composition – Auger Electron Spectroscopy
- Structure – X-ray Diffraction

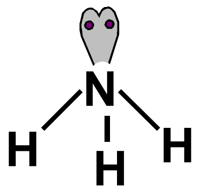
Electrical Properties

- Capacitance measurements
- Current - voltage measurements
- Schottky barrier model

Phases of Boron Nitride



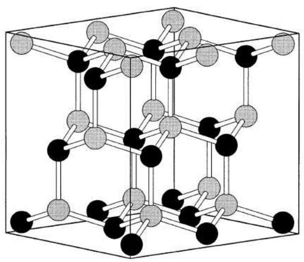
BCl_3 sp^2 hybridized



NH_3 sp^3 hybridized

Cubic

- Lattice sp^3 hybridized
- Excellent high-hardness film
- CVD uses plasma or high pressures

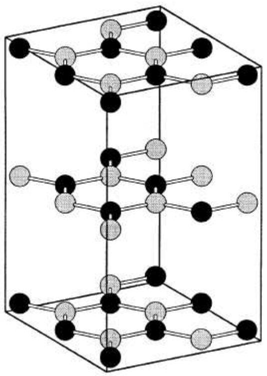


cubic

Hexagonal

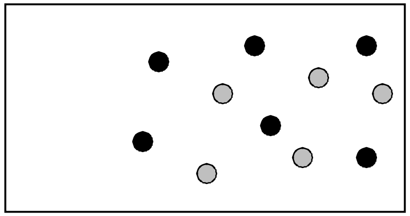
- Lattice sp^2 hybridized
- Excellent thermal conductivity and electrical resistivity
- Ideal lubricant for MEMS devices

hexagonal



Turbostratic

- Lattice mixed sp^3 - sp^2 hybridized
- Potential barrier layer coatings for electronic applications



turbostratic

BN Deposition Chemistry Used
NH_3 and BCl_3 or $B(CH_3)_3$ at T = 480 °C

BN ALD using BCl_3 and NH_3

- Original work performed by Ferguson[1]
- Massive BCl_3 and NH_3 exposures necessary (1×10^8 L)
- Phase of BN not confirmed

BN ALD using $B(CH_3)_3$ and NH_3

- BN more thermodynamically favorable to form than BCl_3
- Silicon processing compatible
- No literature on ALD on $B(CH_3)_3$ and NH_3

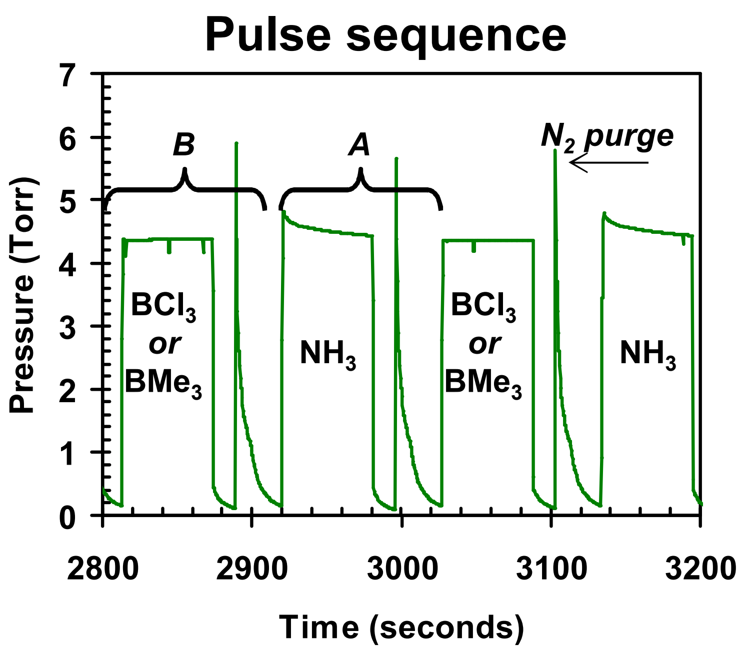
ALD half reactions

A) $B\text{-}Cl^* + NH_3 \rightarrow B\text{-}NH_2^* + HCl$

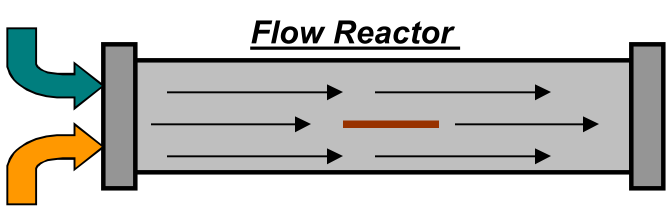
B) $BN\text{-}H^* + BCl_3 \rightarrow BN\text{-}BCl_2^* + HCl$

[1] Ferguson, Weimer and George, Thin Solid Films **413** 16 (2002)

Large Reactant Exposures Obtained using Quasi-static Viscous Flow Reactor



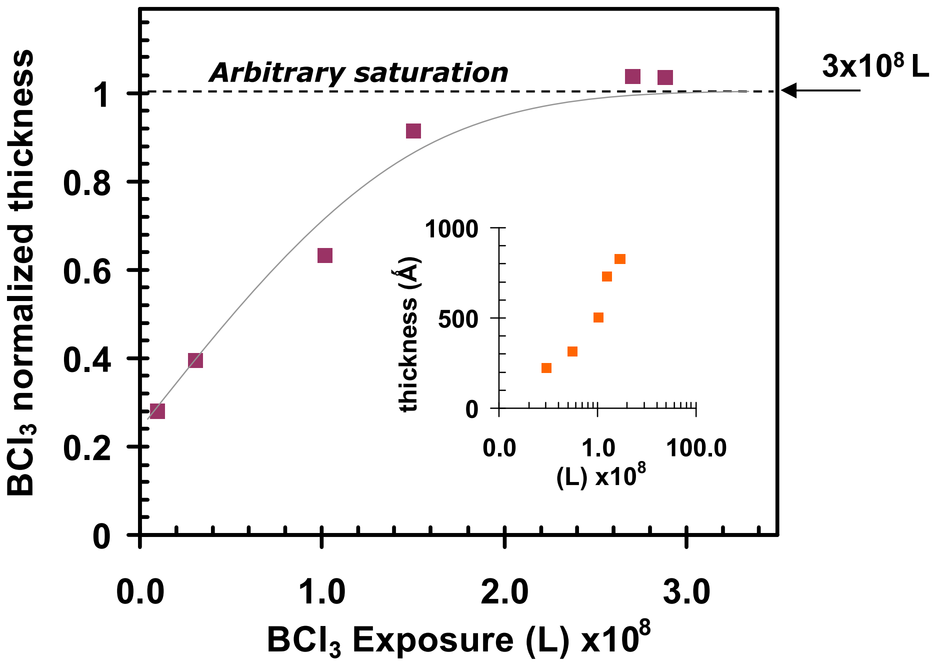
- Need ≈ $1x10^8$ Langmuir exposure for both BCl_3 and NH_3 (1L = $1x10^{-6}$ Torr sec)
- Used a quasi-static[2] flow reactor at T = 480 °C
- Pulse sequence used N_2 purge
- AB cycle time = 212 seconds (1000 AB cycles = 60 hours!)



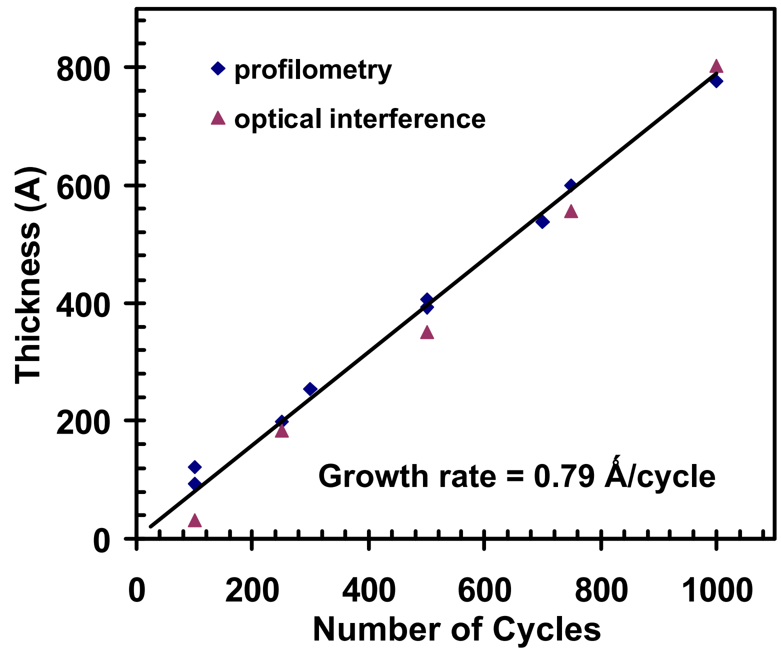
[2] Elam, Routkevitch, Mardilovich and George, Chemistry of Materials, **15** 3507 (2003)

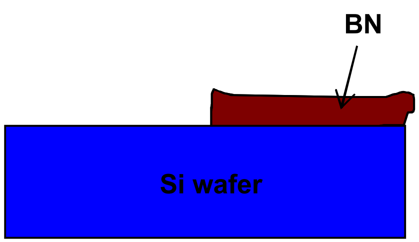
BN thickness Measurements from BCl_3 and NH_3 ALD

Uptake curve



AB cycle growth



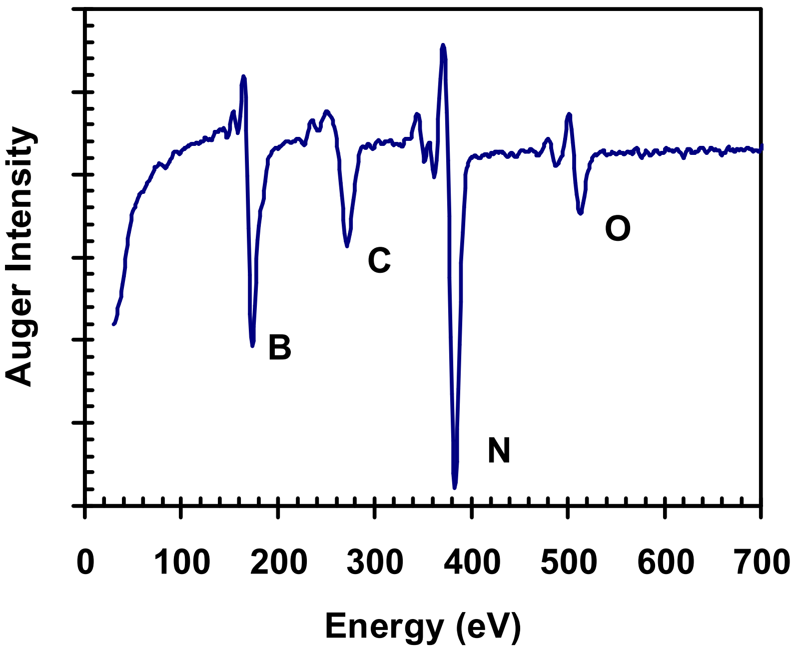


- Si substrate masked with Mo metal
- Film thickness measured using optical interference and profilometry
- Modest changes in exposure affect film thickness

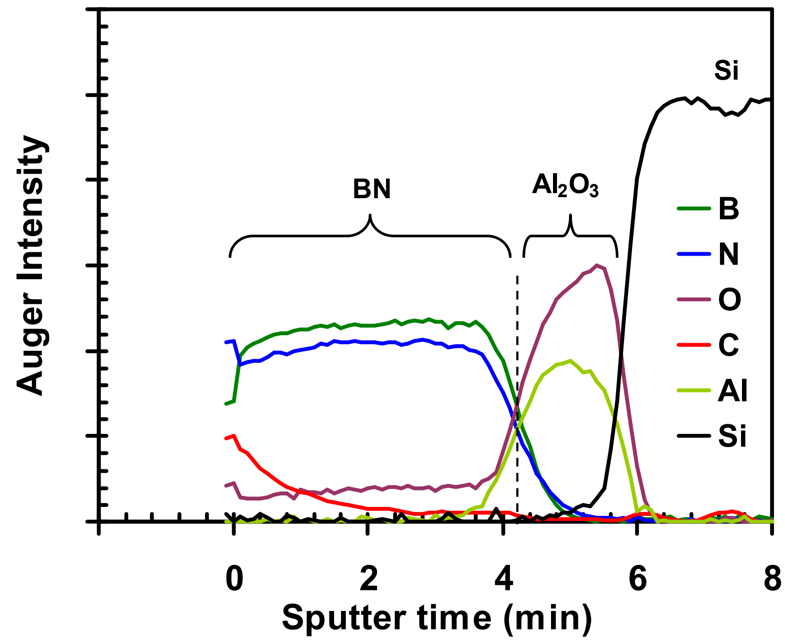
Auger Electron Spectroscopy Confirms the Deposition of BN

BCl_3 + NH_3 ALD

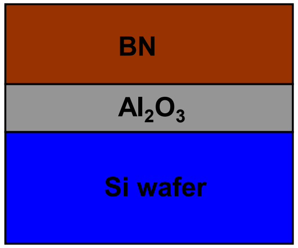
Auger surface spectrum



Auger depth profile

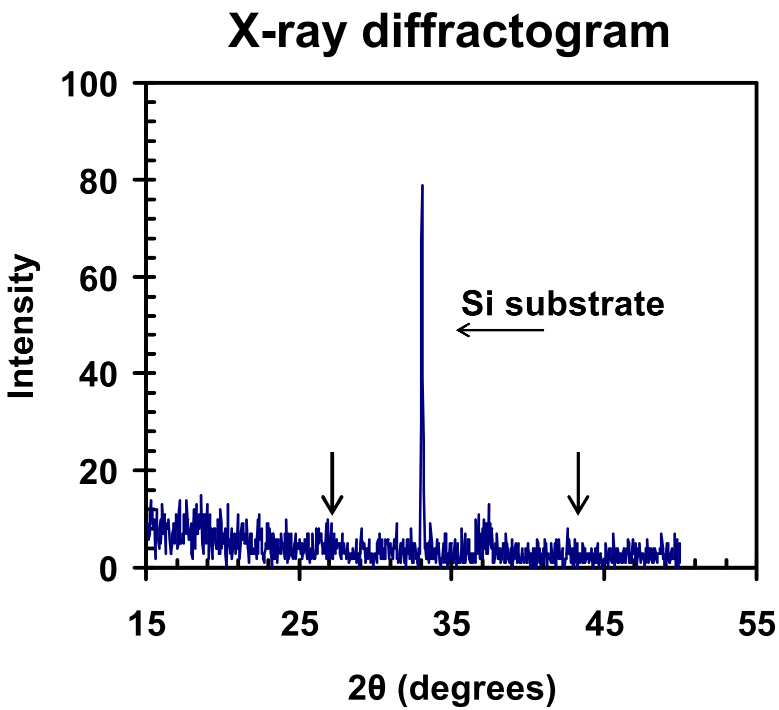


- ALD BN grown on 200 Å of ALD alumina
- Sputter rate is 107 Å /min
- BN films contain C and O



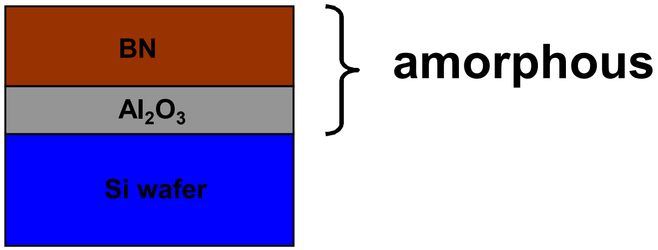
Sample

X-ray Diffraction on BCl_3 + NH_3 BN ALD

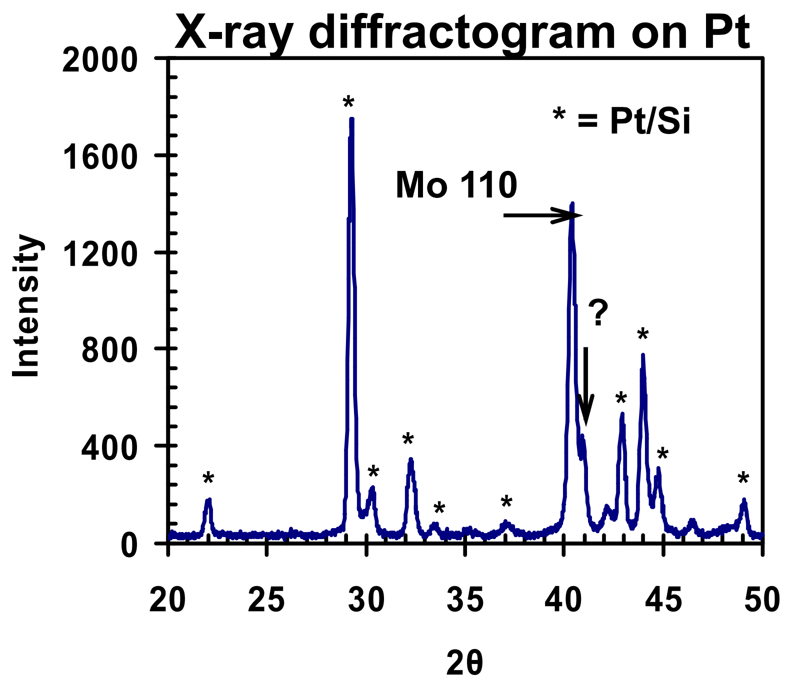


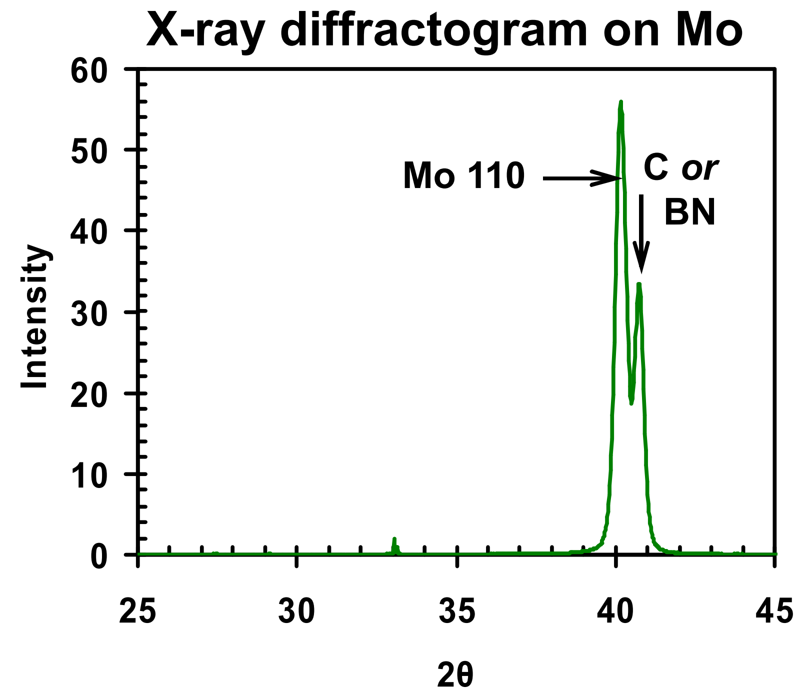
- X-ray diffractogram detected only the crystalline Si Substrate
- Hexagonal BN has x-ray peaks at 2θ = 27 and 42 degrees
- 800 °C anneal showd no conversion to a crystalline phase (Auger confirmed)

Hexagonal BN peaks at 2θ = 27 and 43 degrees

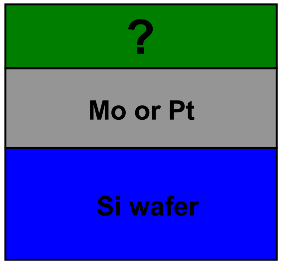


Results From $B(CH_3)_3 + NH_3$ ALD



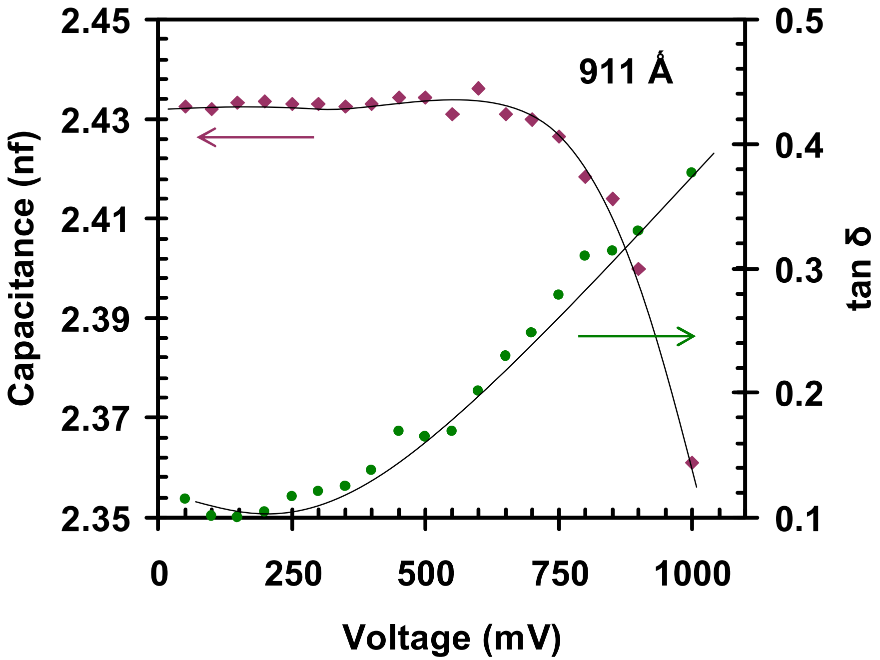


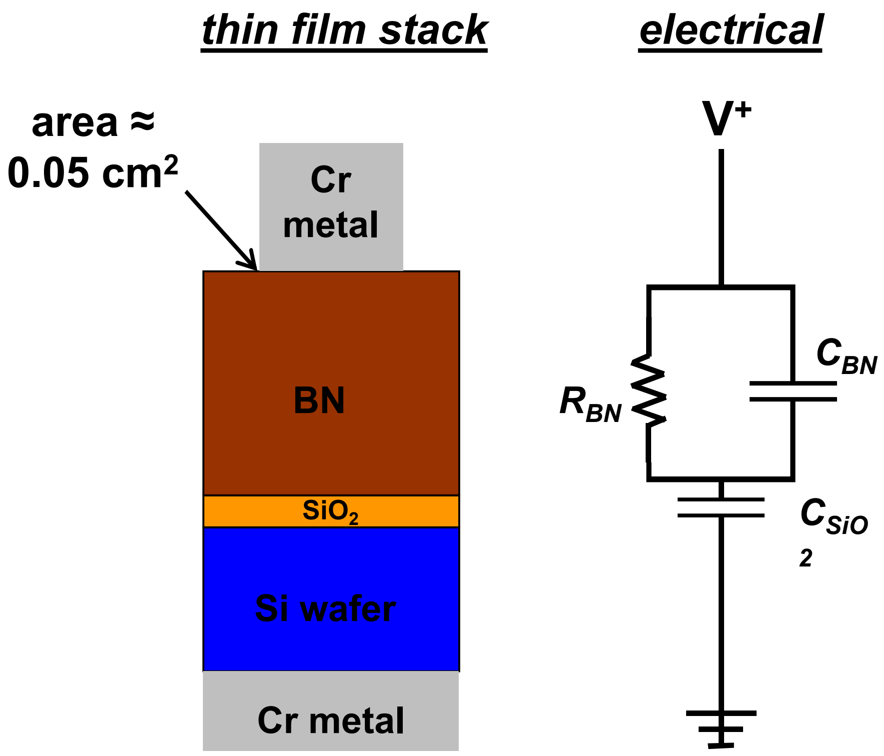
- No evidence of BN on SiO_2 substrates
- High T BN deposition formed Pt/Si alloy
- XRD on Mo sees highly ordered BN or C
- More work needed to be done on $B(CH_3)_3$ and NH_3



BN Thin Film Stack used to Obtain Electronic Properties

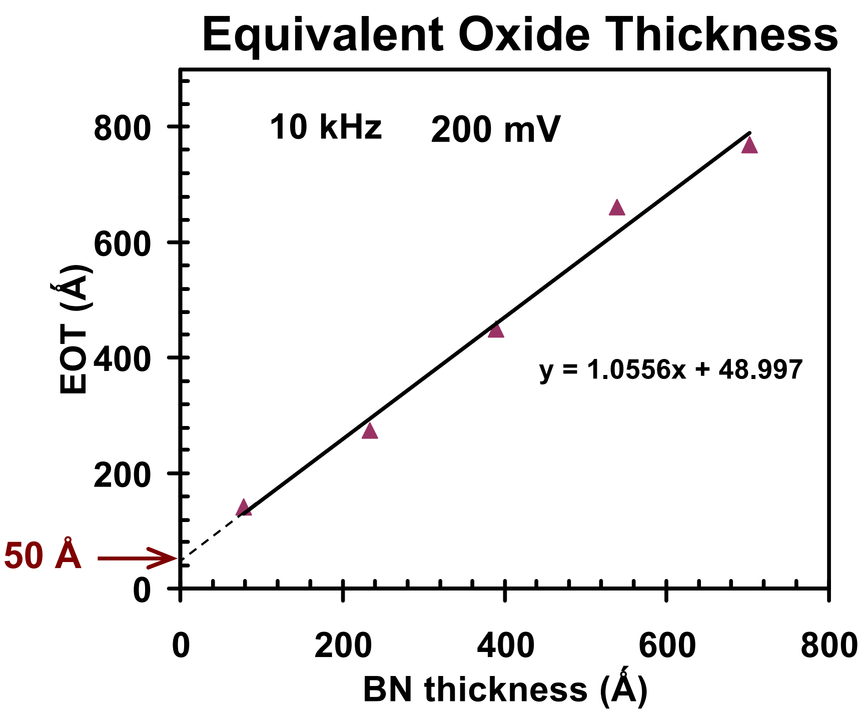
$BCl_3 + NH_3$ ALD



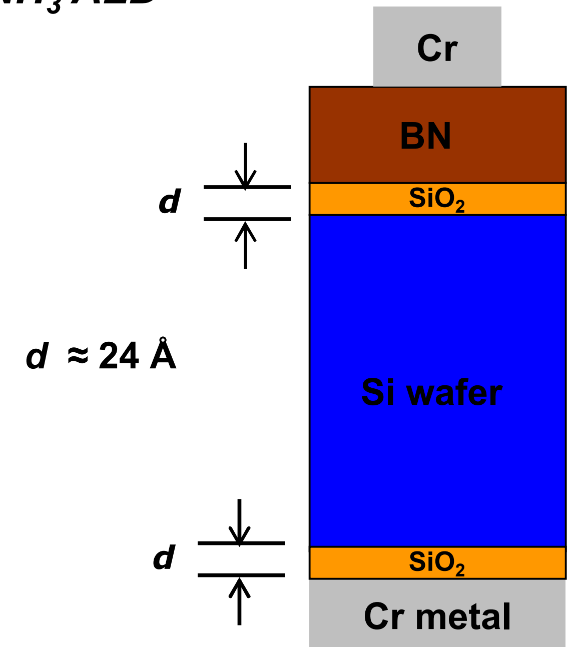


- Substrate degenerately n-doped Si
- Capacitance values measured at low voltages
- Conduction responsible for change in capacitance

Capacitance Measurements Determine the Dielectric Constant of BN



BCl_3 + NH_3 ALD

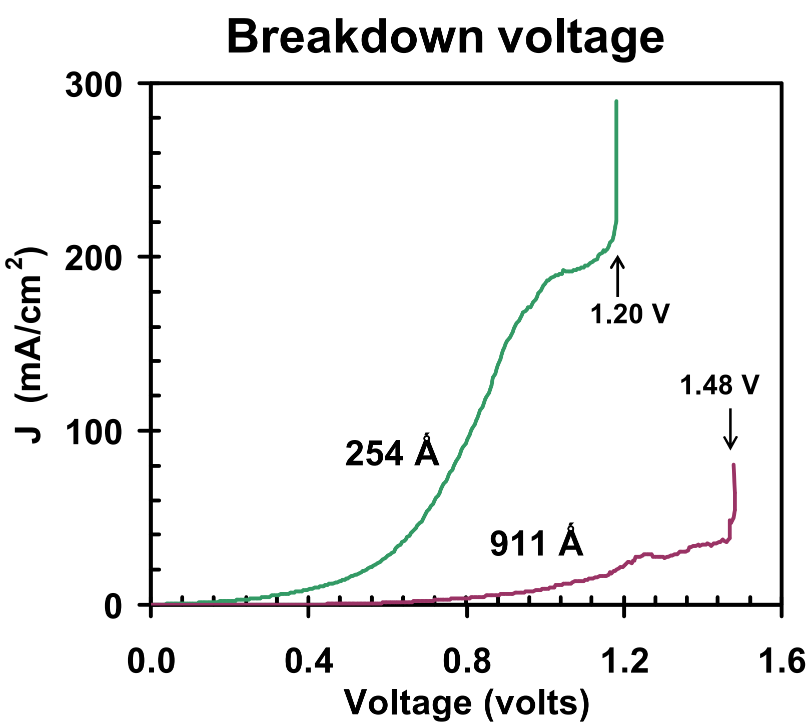


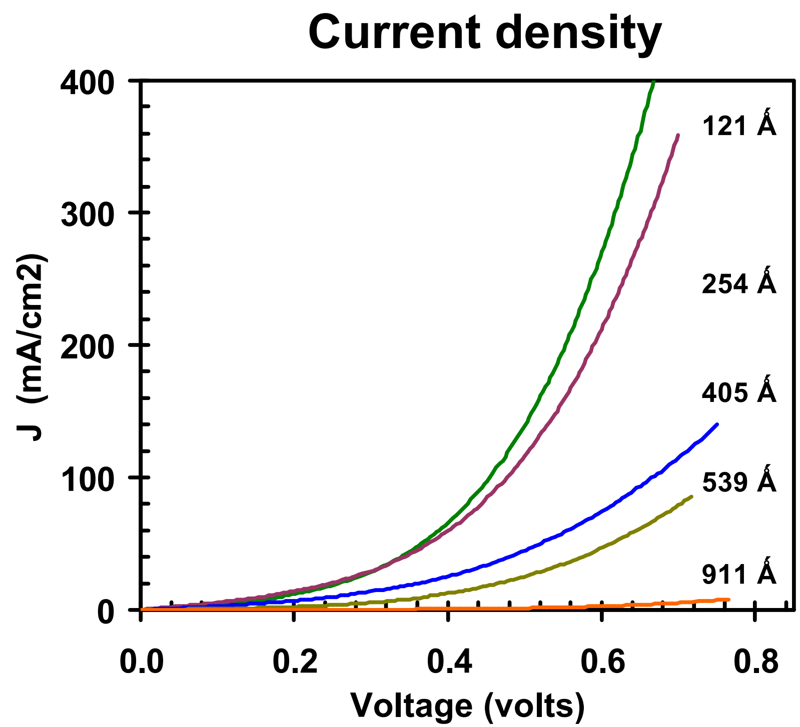
k_{BN} = 3.8

- Intercept determines ≈ 50 Å of SiO_2
- Ellipsometry confirms ≈ 24.3 Å of SiO_2 on each side
- Slope determines the dielectric constant of amorphous BN

Current – Voltage Measurements as a Function of BN Film Thickness

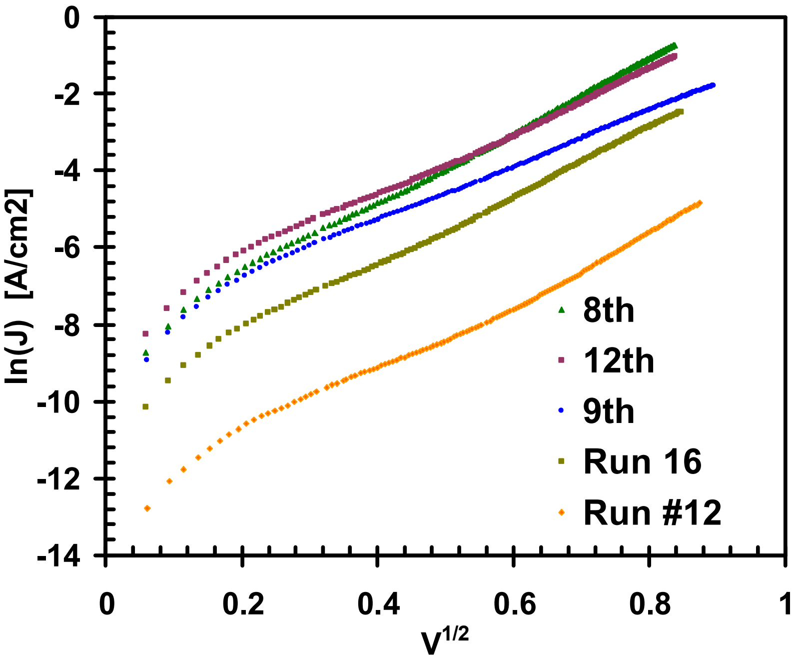
BCl_3 + NH_3 ALD





- **Burn in necessary with 6-10 voltage scans**
- **Typical breakdown voltage ≈ 1 volt**
- **BN film thickness decreases electrical conduction**

Schottky Barrier Emission Describes Conduction

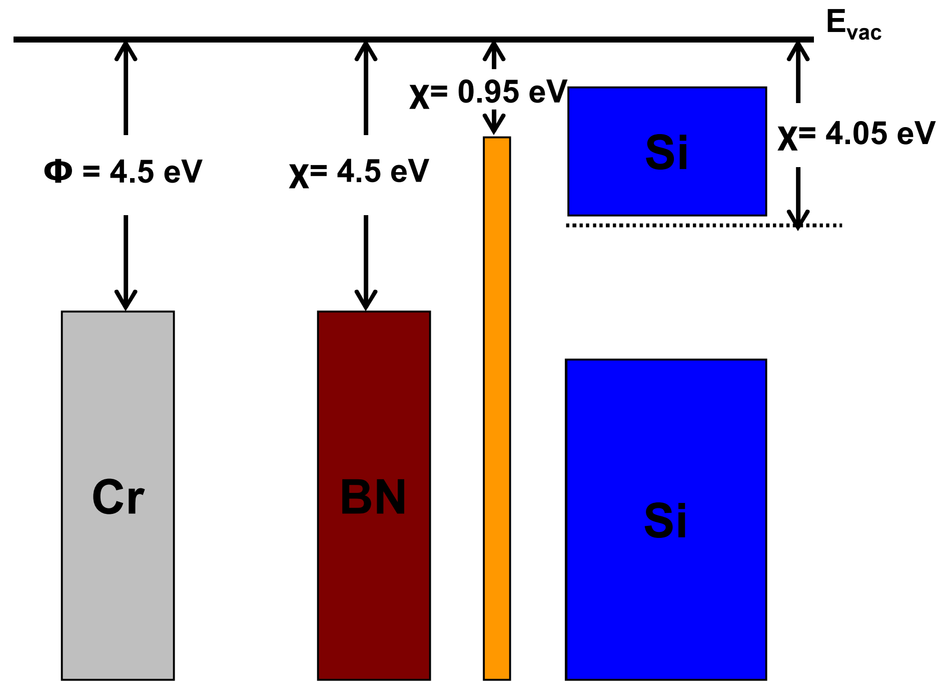


Schottky emission[3]

$$I = \alpha \exp(\beta V^{1/2})$$

$\alpha = (e^3/Kd)^{1/2}/kT$

$\beta = AT^2\exp(\Phi/kT)$



- **Tunneling, Poole-Frankel emission**
- **Temperature dependence experiments**
- **Effective barrier height from intercept = 400 – 600 meV from SiO_2**

[3]Emtage and Tantraporn, Physical Review Letters **8**, 267 (1962)

Conclusions

Thin films of ALD BN grown in quasi-static flow reactor

Growth rate for the BCl3 and NH3 ALD was 0.78 A/cycle at T = 480 C

The amorphous BN films showed no conversion to crystallinity under 800 C anneal

BN ALD using B(CH3)3 and NH3 shows promising results on Mo metal

Dielectric measurements calculated BN dielectric constant k = 3.8

BN film thickness changes electrical conduction by modifying Schottky barrier height of SiO2