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SAND2021-4362C

Solvothermal Chemistry to “Ultradope” Si(100)

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Motivation

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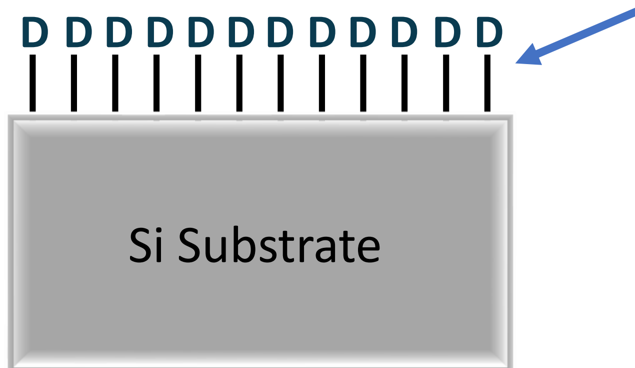
Need: With the advanced state of microelectronics, the development of next generation electronic devices is an enormous challenge.

Atomic Precision chemistry processes allows for "ultradoping" – dopant levels that fundamentally transform electronic structure of Si.



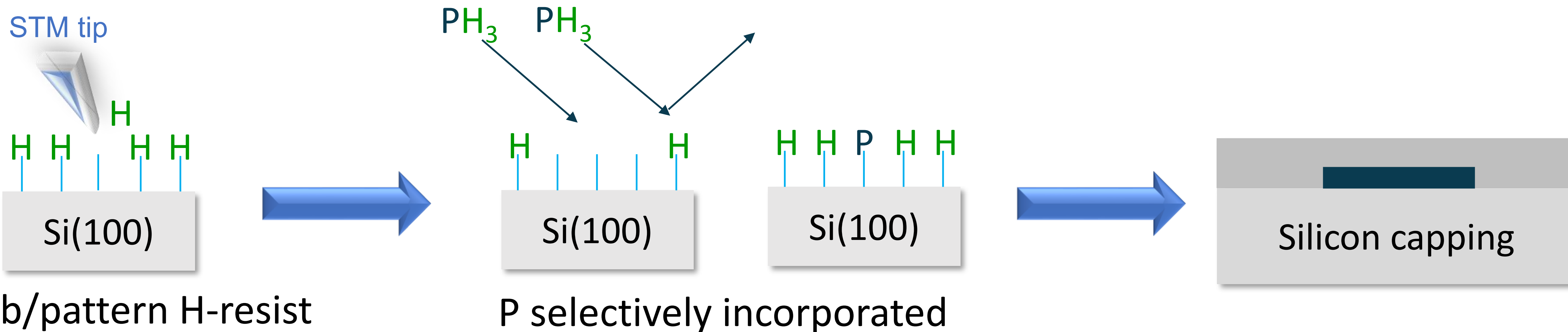
"Ultradoping": Direct dopant-Si chemical bond

	Amount B
Solid solubility	~2e13 cm^{-2}
Ultradoping Chemistry	>~1e14 cm^{-2}

Atomic Precision Advanced Manufacturing

Sandia National Laboratories

Chemistry: Direct dopant-Si bond by removing H, react with bare Si



Ultradoping using STM is limited to UHV process.

- Not scalable
- Only a few working chemistries, took years to develop
- Method is not flexible - hard to try new chemistries

Ward, Elec. Dev. Fail. Anal. vol. 22, pp. 4-10 , 2020.

Traditional Solvothermal Doping

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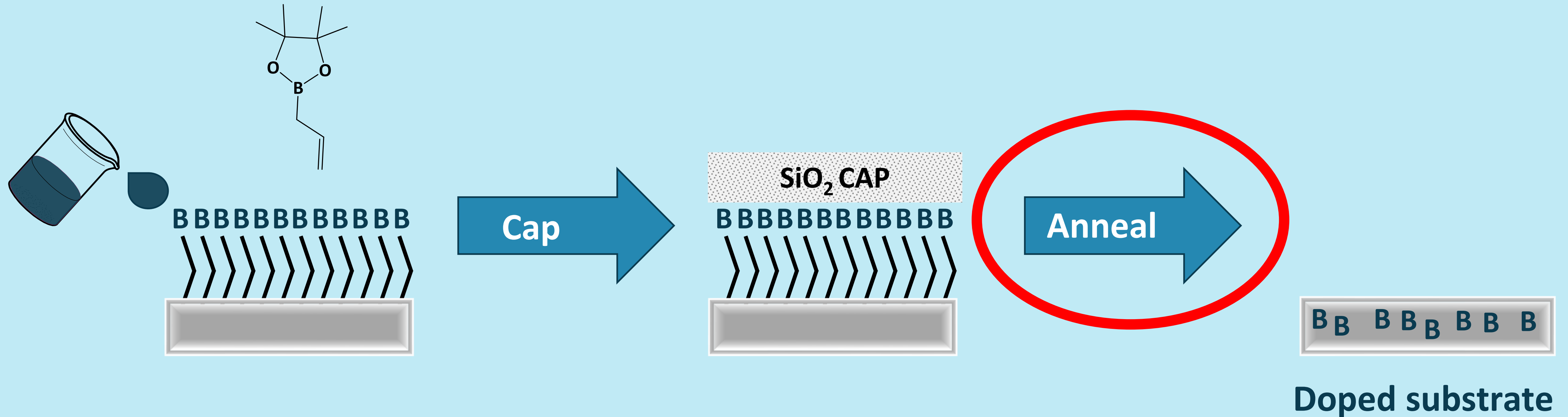

Concentrations achieved by current methods limited by indirect doping → required high temperature anneal, max B ~2e13 cm^{-2}

Ho, J. C. et. al. . *Nat Mater* **2008,** *7* (1), 62-67; L. Ye, A. Gonzalez-Campoet et. Al., *Acs Appl Mater Inter* **2015**, *7*, 27357-27361

Goal – Direct Dopant-Si bond

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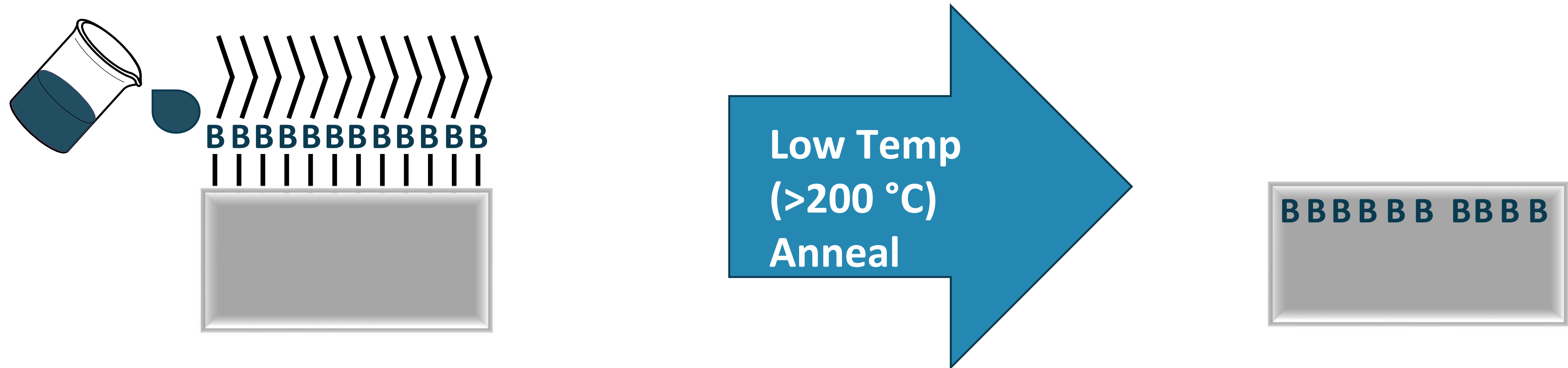

“Ultradoped” delta layer on Si

- Direct Si-dopant bond using solvothermal chemistry
- “Ultradoping” concentrations of dopant

Direct dopant-Si surface solvothermal chemistries have not been well developed and are needed for scalable routes to “ultradoping”.

Preparation for Surface Characterization

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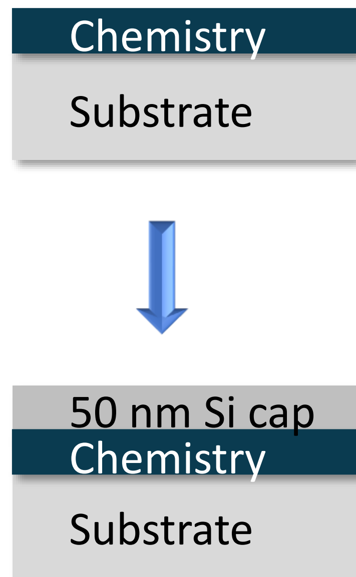
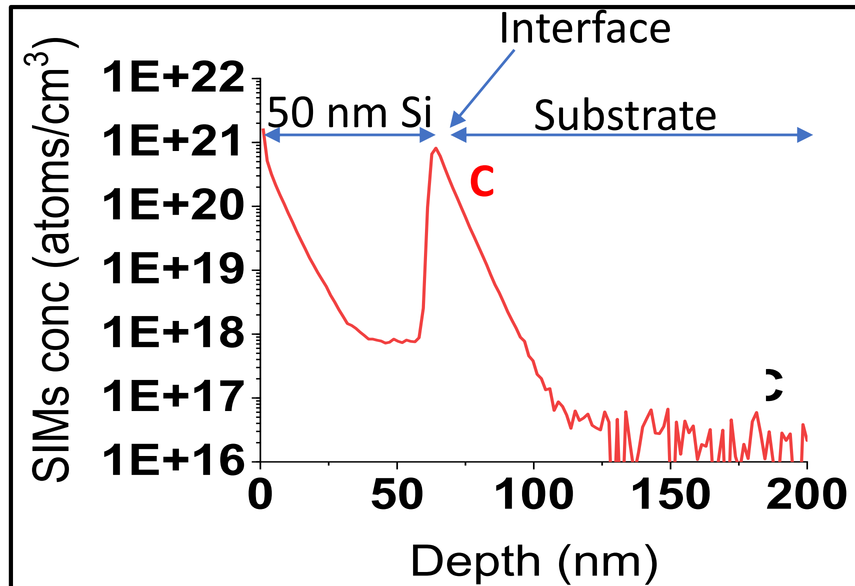
SIMS: Mass Spectrometry

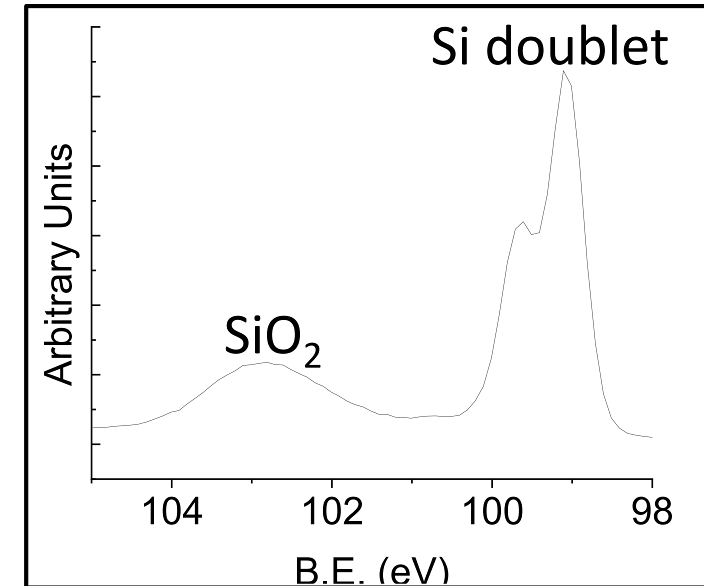
- Depth profile quantification of given element
- Protect interface with cap pre-characterization





XPS

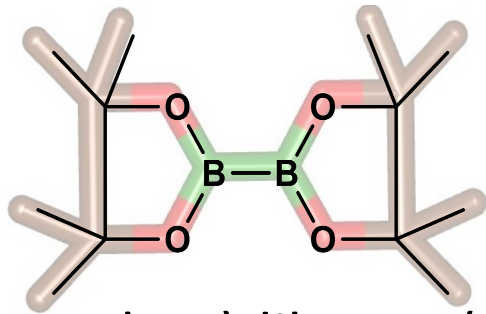
- Highly surface sensitive technique
- Information about chemical species



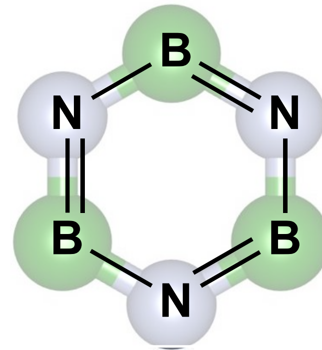
XPS and SIMS are used to analyze and quantify the surface chemistry post-reaction.

Screening Different Chemistries

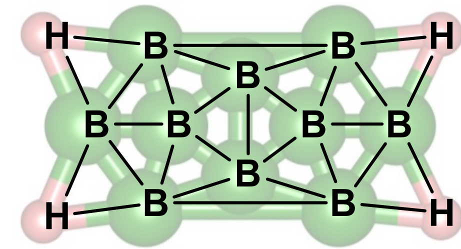
- **To get APAM-like properties, we need to move from traditional Si-C to Si-B bonds.**
- **Need to screen precursors to figure out general rules**
- **Known reactivities – double bonds, B-B bonds, (halides - not today's talk)**



Bis(pinacolato)diboron (B_2Pin_2)

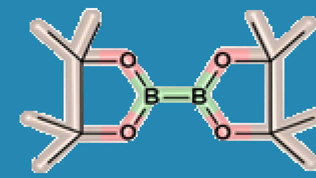


Borazine



Decaborane ($B_{10}H_{14}$)

Bis(pinacolato)diboron (B_2Pin_2)



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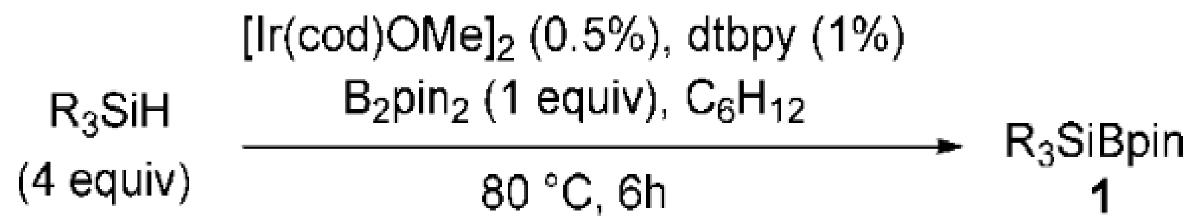
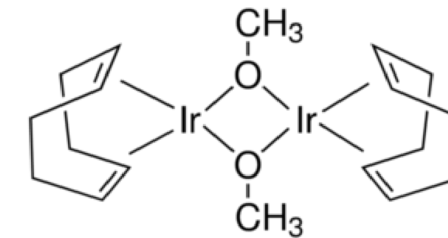
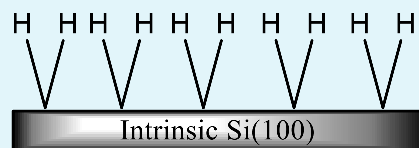
Motivation – Solution phase precedence and stability of Bpin Group



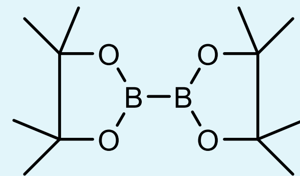


(1,5-Cyclooctadiene)(methoxy)iridium(I) dimer
$[Ir(Cod)Ome]_2$

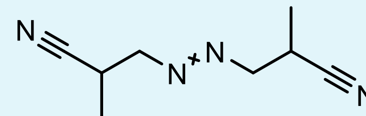
Optimized Surface Reaction (under Ar)



Wet Chemically Prepared H-Terminated Si(100)



Bispinacolatodiboron (B_2Pin_2)

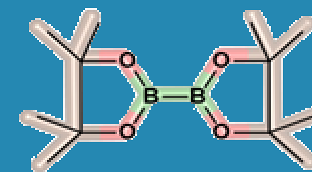


Azobisisobutyronitrile (AiBN) catalyst

Parameter	Optimized Value
Conc.	0.5 mmol/L
Solvent	Benzene
Temp.	140 °C

Boebel, T. A.; Hartwig, J. F.. *Organometallics* **2008,** *27* (22), 6013-6019.

Bis(pinacolato)diboron XPS Results



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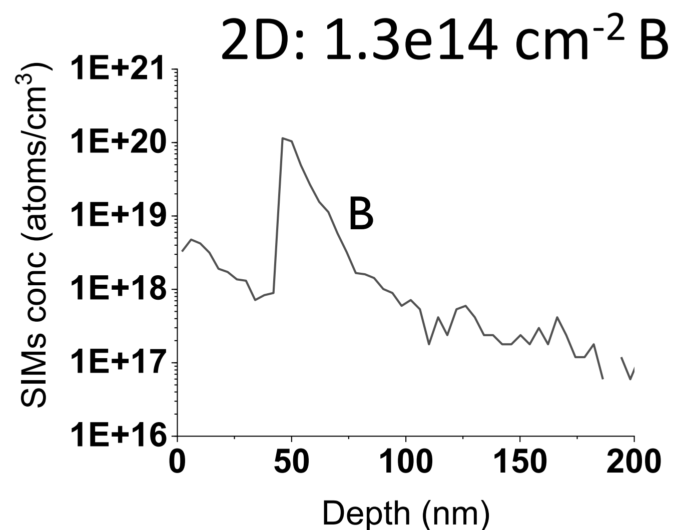
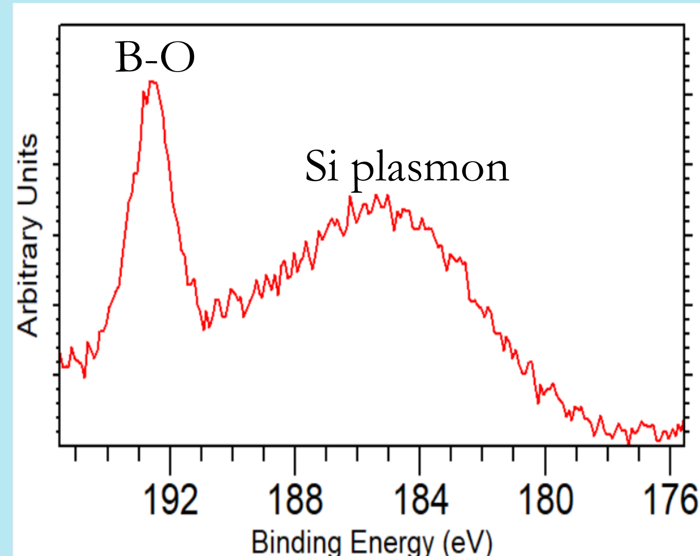
Achievement: B on surface in "Ultradoping" concentration levels (~$1e^{14}$ cm^{-2})

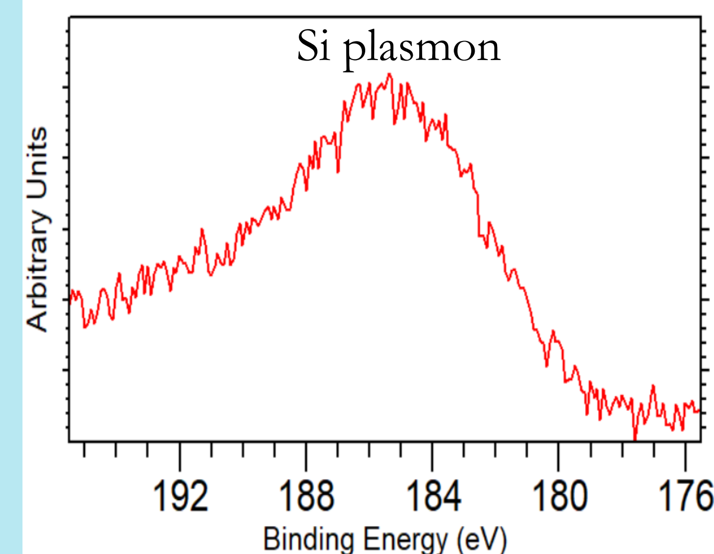
Sample Boron SIMS



Sample Boron XPS



Control Boron XPS



Remaining Question: What is the B_2Pin_2 surface attachment?

Inorg. Chem., 1970, 9 (3), 612; Frederick, E. et al, ChemRxiv, 2021, 10.26434/chemrxiv.13480374.v1

B_2Pin_2 – What is the Surface Attachment?

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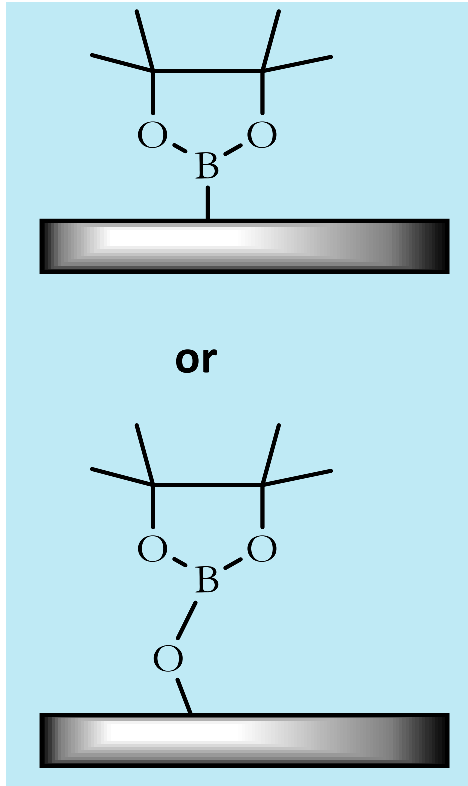
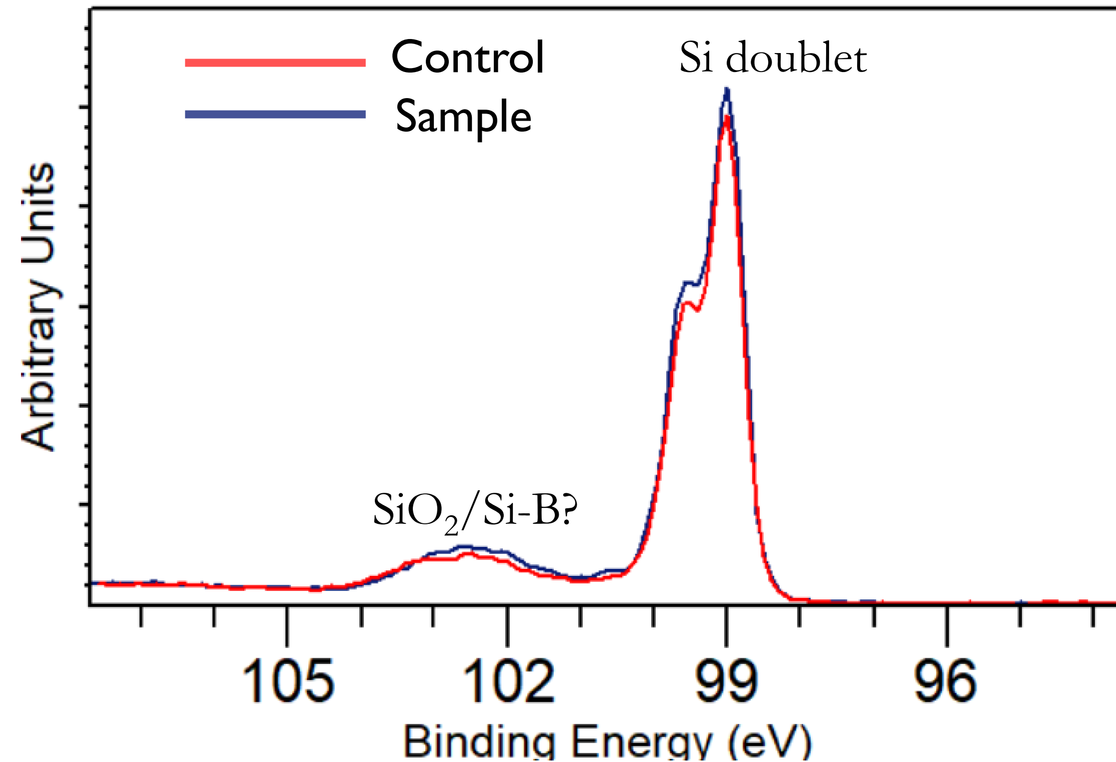


XPS of Silicon Region

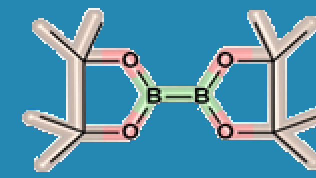


Literature Value for Si-B ranges from 101.9 eV to 103.6 eV

Control and sample have similar peaks in oxide region, cannot confidently attribute to Si-B.

Frederick, E. et al, ChemRxiv, 2021, 10.26434/chemrxiv.13480374.v1; NIST XPS Database, Version 4.1, 2012; http://srdata.nist.gov/xps/

B_2Pin_2 – Catalyst Involvement



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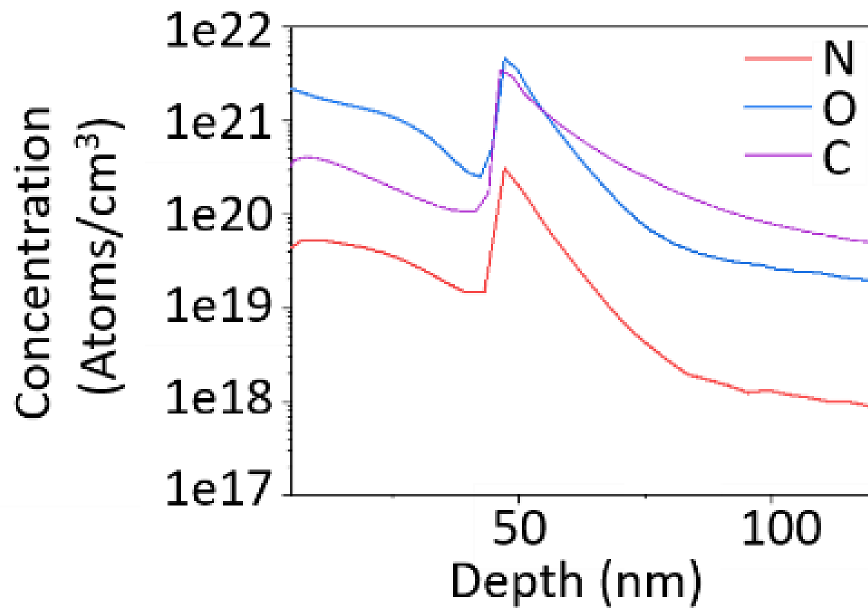
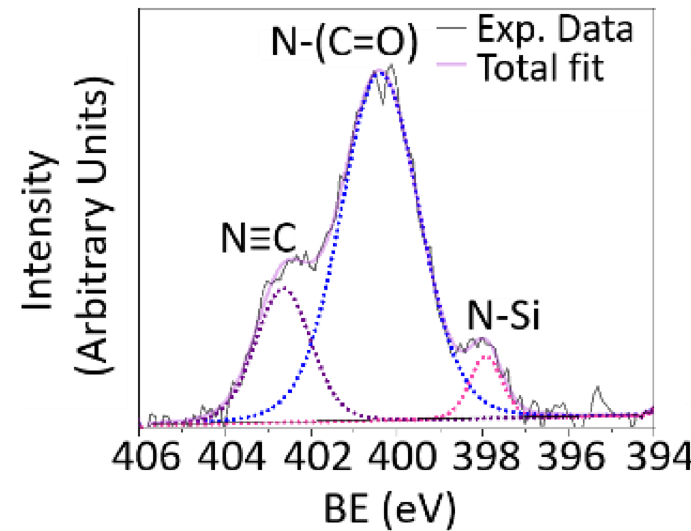
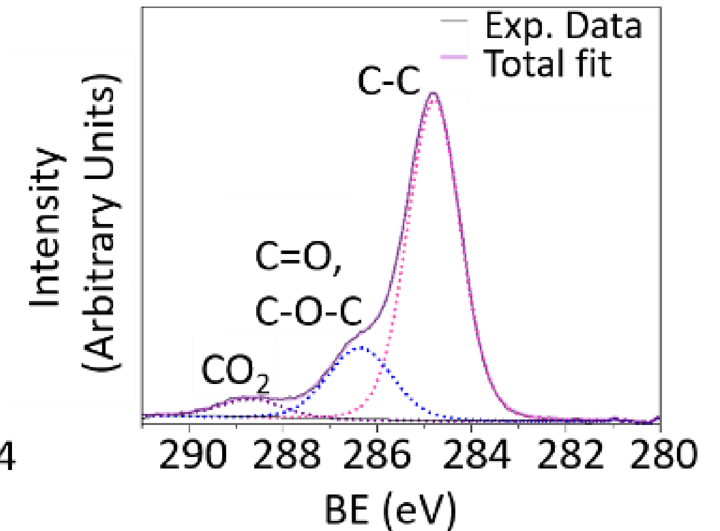
SIMS	N XPS	C XPS

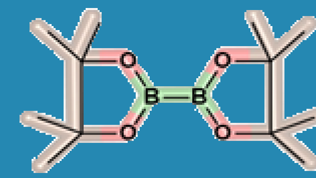






Presence of N and higher levels of O than expected from B_2Pin_2 indicate catalyst is cross-reacting and not benign.

What is the Surface Attachment?



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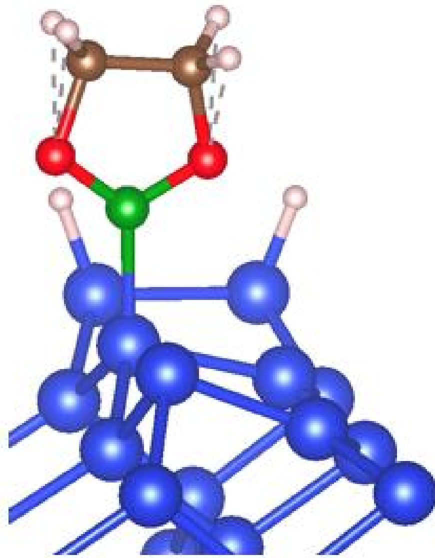
Density Functional Theory (DFT) computations: B_2Pin_2 binds to Si through B

Bonding through B

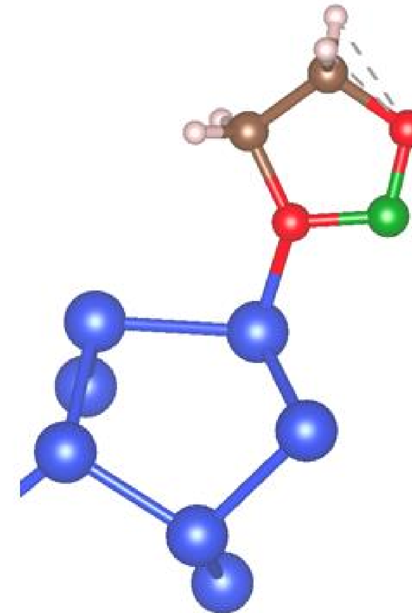
Bare Silicon surface



$E_A = -3.44$ eV

Bonding through O

Bare Silicon surface

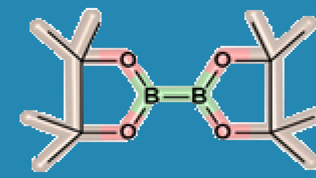


$E_A = -1.84$ eV

(less favorable than B)

Q. Campbell

B_2Pin_2 Takeaways



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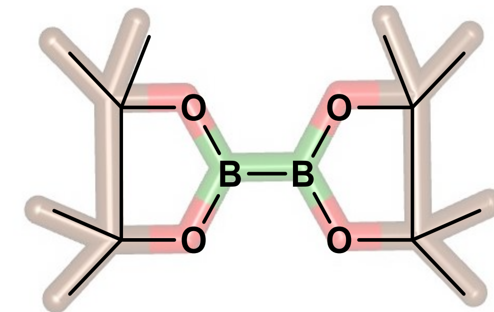
Ultradoping concentrations achieved with solvothermal chemistry – route to scalability

- Experimental confirmation of B-Si tricky - peak overlap
- Catalyst involvement adds further complication
  - side reactions with N, O, C
- DFT indicates bonding preferably B-Si
- We need to eliminate these side reaction:
  - Non-molecular catalysts
  - Other molecules



Bis(pinacolato)diboron (B_2Pin_2)

Trying to Mitigate Side Reactions

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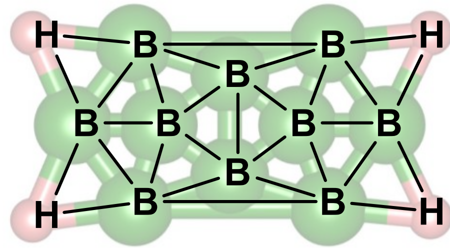
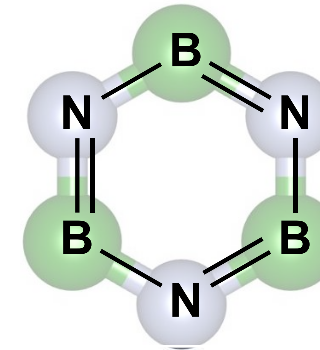
Oxygen free molecules (UHV study – oxygen is higher than expected)
Ran reactions without catalyst
Selected molecules where we expect high reactivity.



Decaborane ($B_{10}H_{14}$)



Borazine

Why Decaborane
- High amount of B
- Reactive B-B bond

Why Borazine?
- polar B-N bond
- ALD precursor

XPS Results from Screening B molecules

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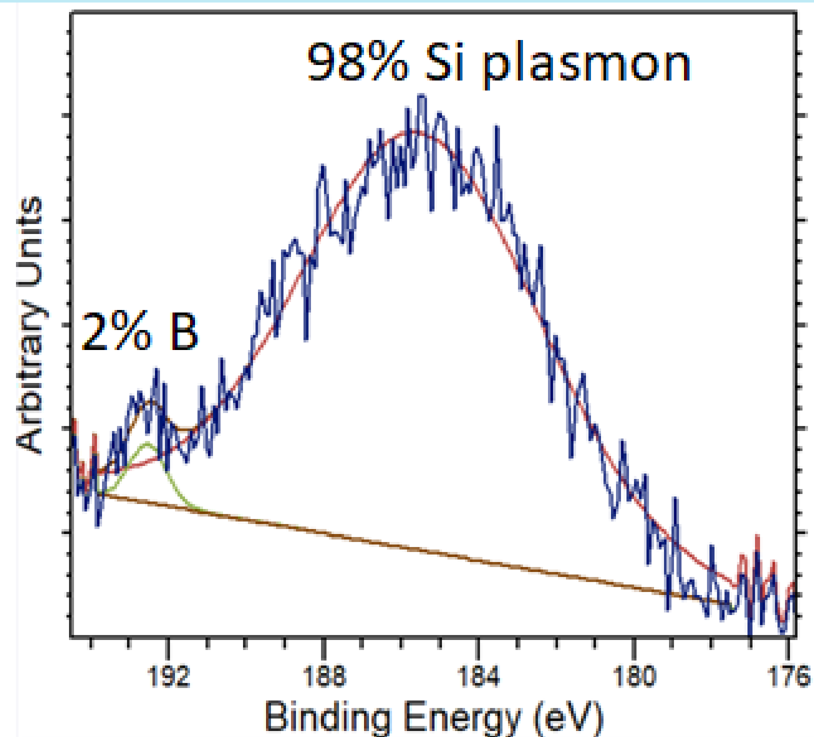
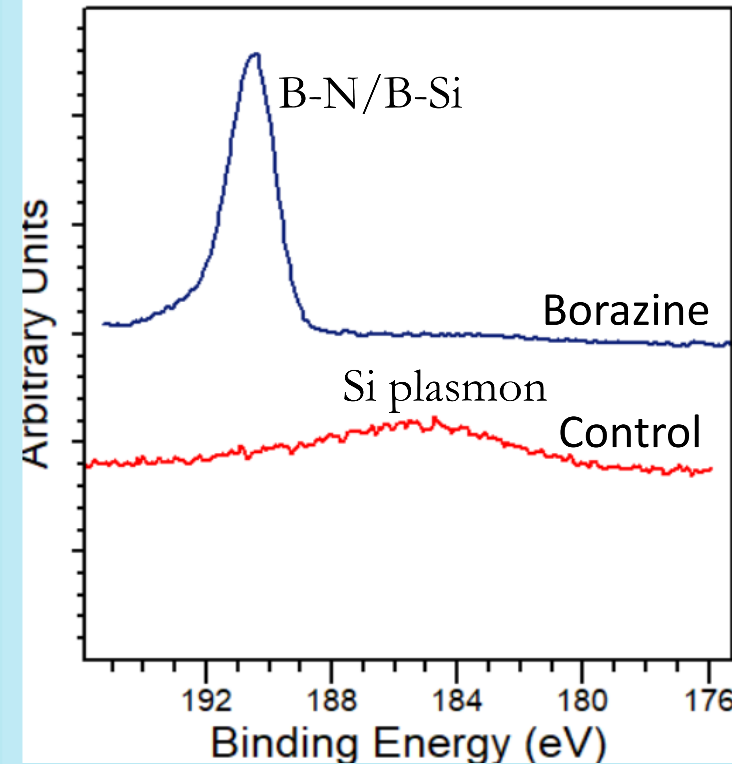
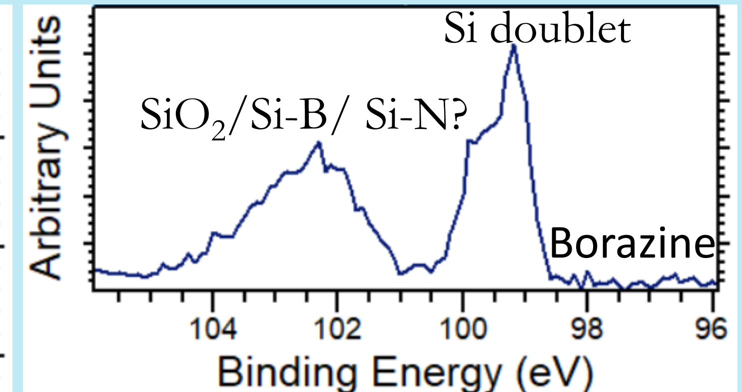
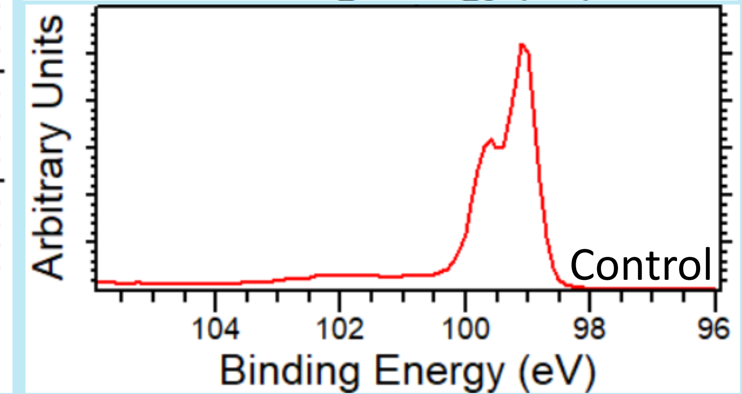
Decaborane
Heated overnight
Little to no B present

Borazine
1 hour, room temp
→ visible, multilayers.

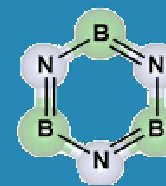








Borazine DFT Computation



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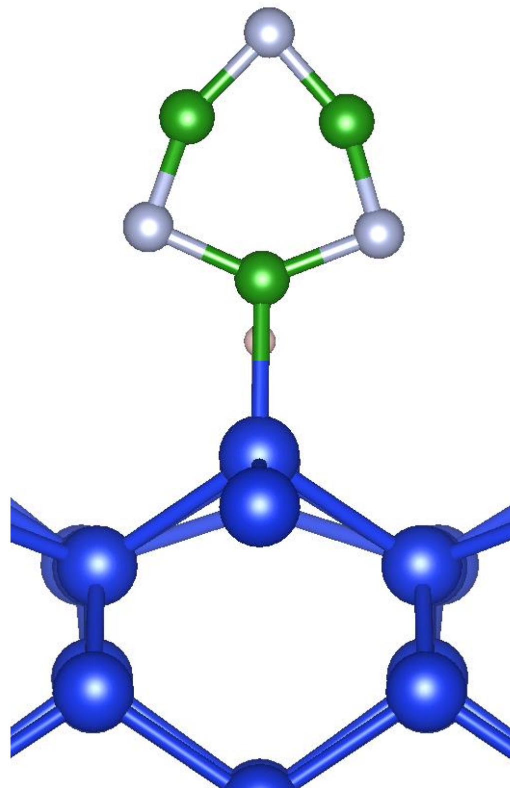
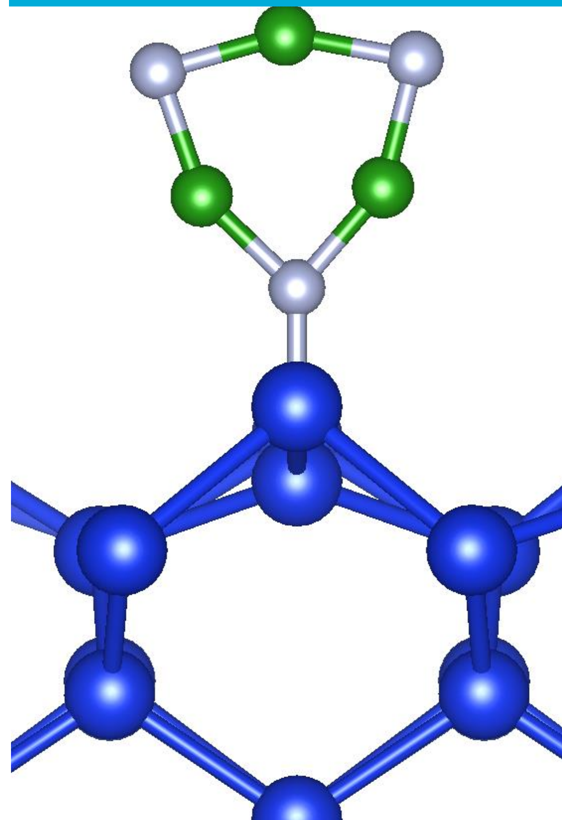
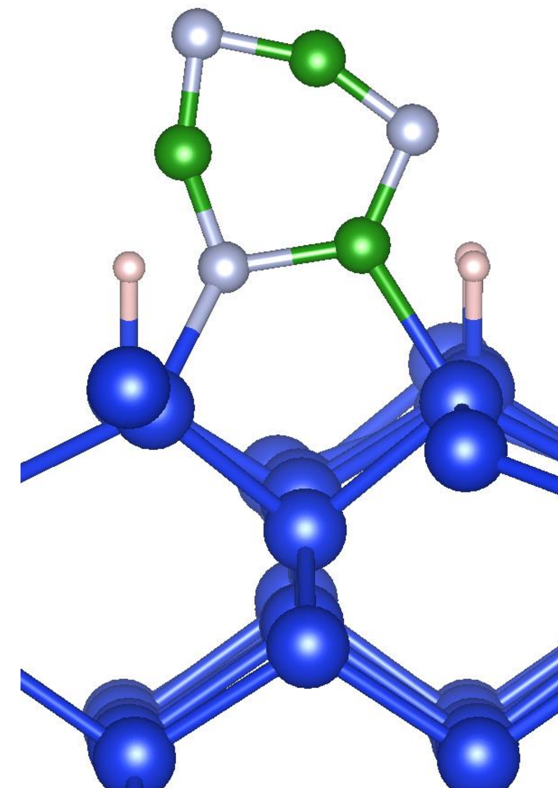
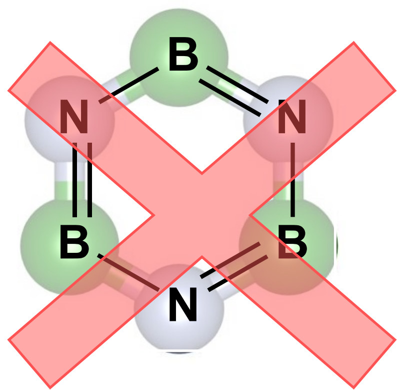
Bonding through B	Bonding through N	Both Bonding
		
Adsorption E = -1.33 eV	Adsorption E = -1.08 eV	Adsorption E = -2.80 eV

Borazine will adsorb to Si through both B and N. Borazine not ideal precursor!

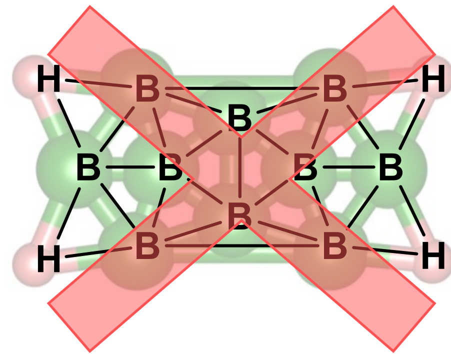
Q. Campbell

Conclusions

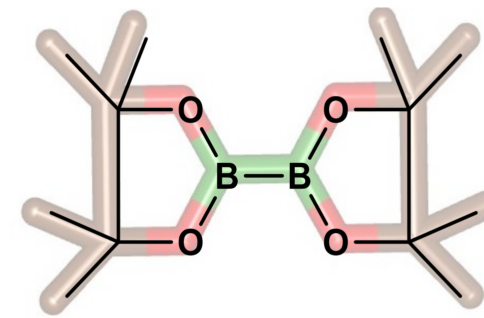
- Ultradoping concentrations of dopants can be reached solvothermally
- Solvothermal reactions enable rapid screening relative to UHV.



Borazine



Decaborane ($B_{10}H_{14}$)



Bis(pinacolato)diboron (B_2Pin_2)

- Nitrogen appears to lead to cross-reactivity/catalysts not benign
- Further exploring halogen substituents, photochemistry

Broad Picture – What's Next?

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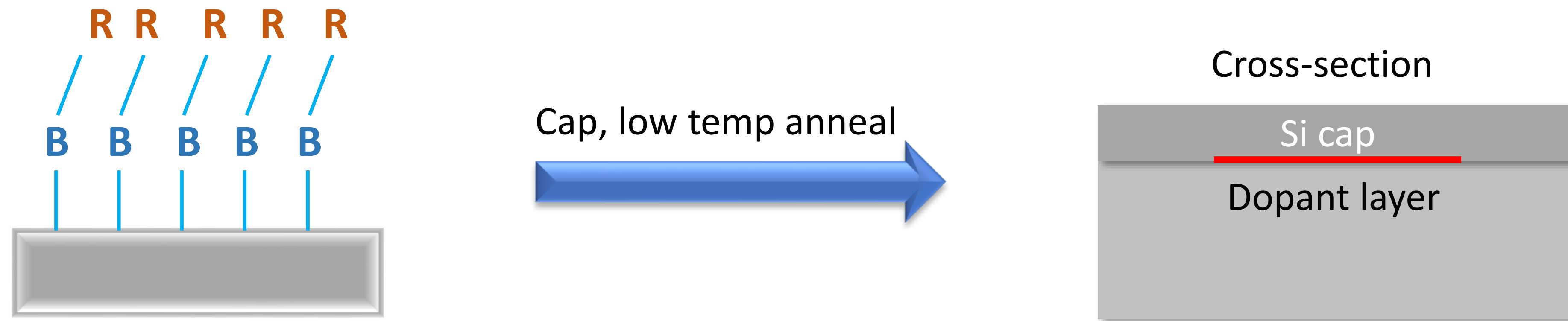
When we add the materials science, do we get something electrically useful?



If inactive – how can we remove scaffolding to get electrical activity?

Thank You

- Shashank Misra
- David Wheeler
- Quinn Campbell
- Igor Kolesnichenko
- Angelica Benavidez
- Evan Anderson
- Scott Schmucker
- Jeff Ivie
- Fabián Pena
- All members of FAIR DEAL

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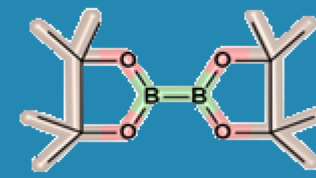
Bis(pinacolato)diboron (B_2Pin_2)



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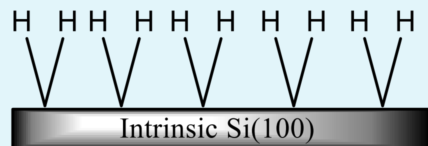
Screened conditions to optimize surface chemistry reaction (under Ar)

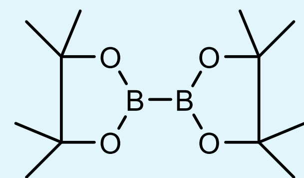
Conc. (mmol/L)	Solvent	Temp. (°C)
0.15	Benzene	80
0.3	Cyclohexane	110
0.5	Dodecane	140
0.8	Mesitylene	

Catalysts		
$[Ir(Cod)Ome]_2$	Azobisisobutyronitrile	Benzoyl Peroxide

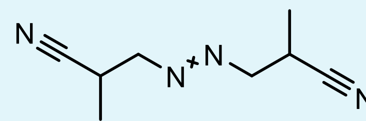
Optimized Reaction



Wet Chemically Prepared H-Terminated Si(100)



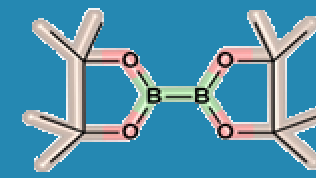
Bispinacolatodiboron (B_2Pin_2)



Azobisisobutyronitrile (AiBN) catalyst

Parameter	Optimized Value
Conc.	0.5 mmol/L
Solvent	Benzene
Temp.	140 °C

B_2Pin_2



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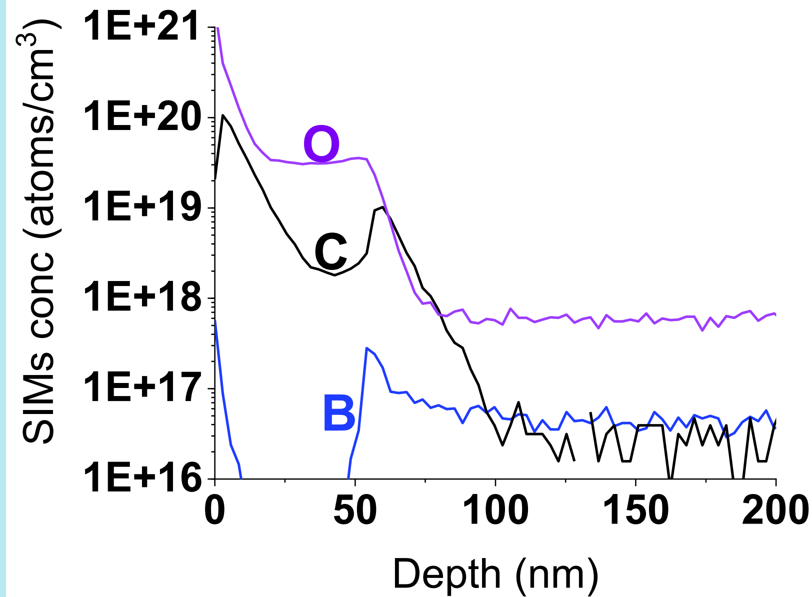
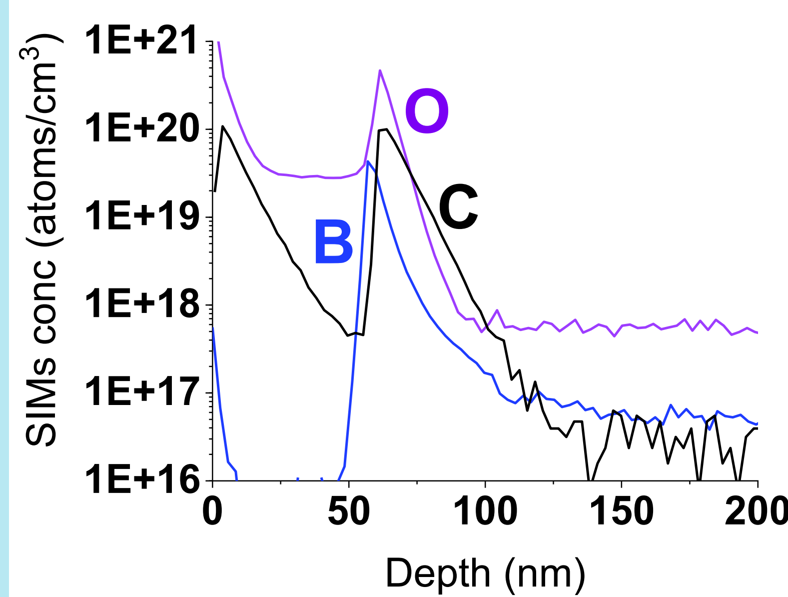
UHV study:

B_2Pin_2 on Si-H	B_2Pin_2 on Bare Si





	C:O ratio
Expected	3:1
Observed	1:4

B adsorbs selectively on bare Si not Si-H. This matches computational results. However, the amount of O is higher than expected.

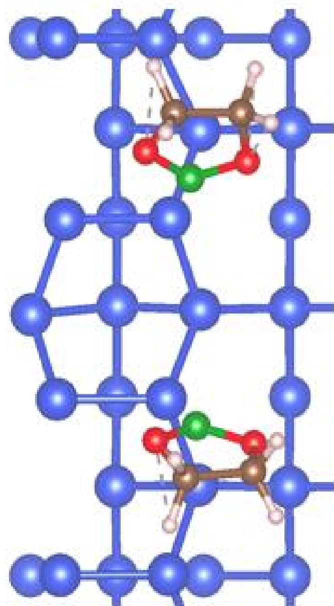
Schmucker, Ivie, Anderson

DFT

Sandia National Laboratories

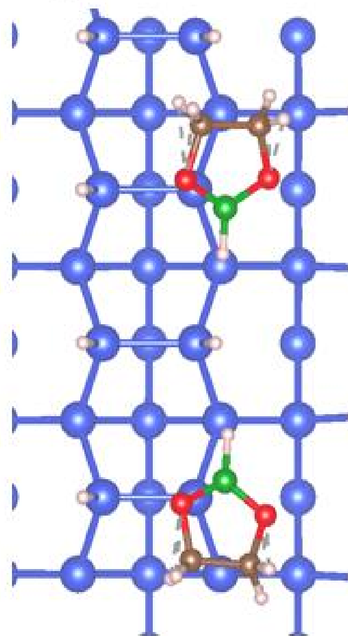
B_2Pin_2 selectively absorbs on bare Si

Bare Silicon surface



$E_A = -1.94$ eV

Hydrogen terminated surface



$E_A = +2.1$ eV

Splitting takes 0.39 eV

BPin fragment preferably removes H