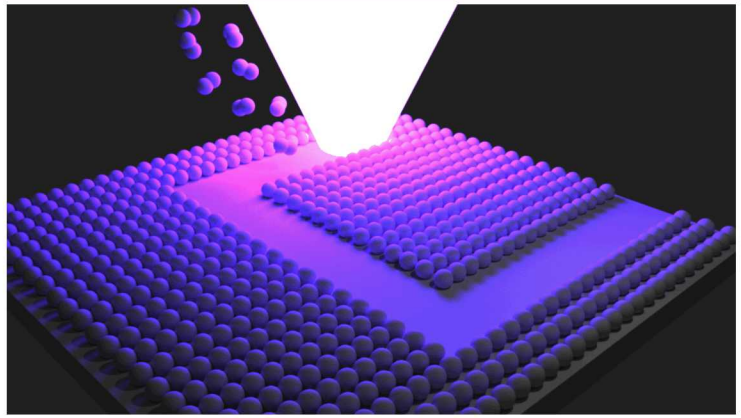
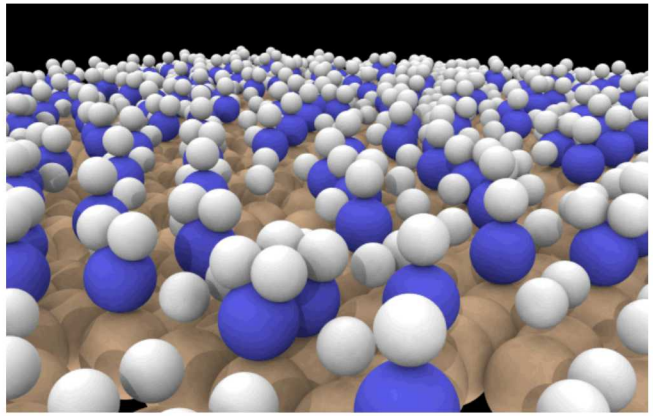
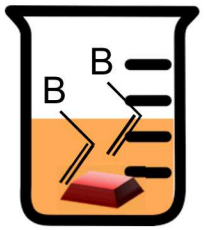
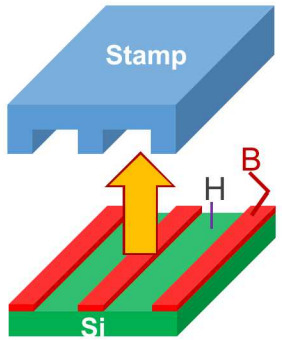
SAND2019-13378PE









FAIR DEAL GC Thrust 4: Application Platform

George T. Wang (Lead), Ezra Bussmann, Robert Butera,
Aaron Katzenmeyer

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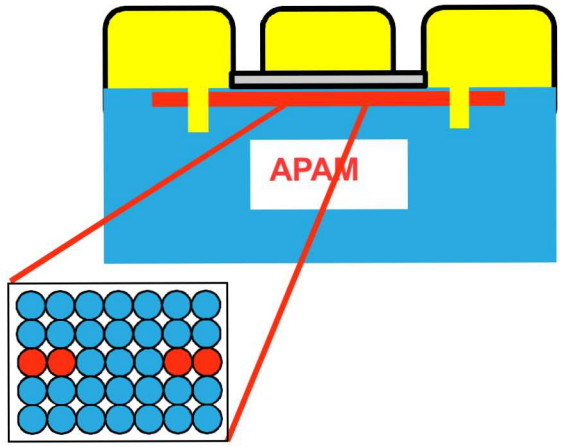
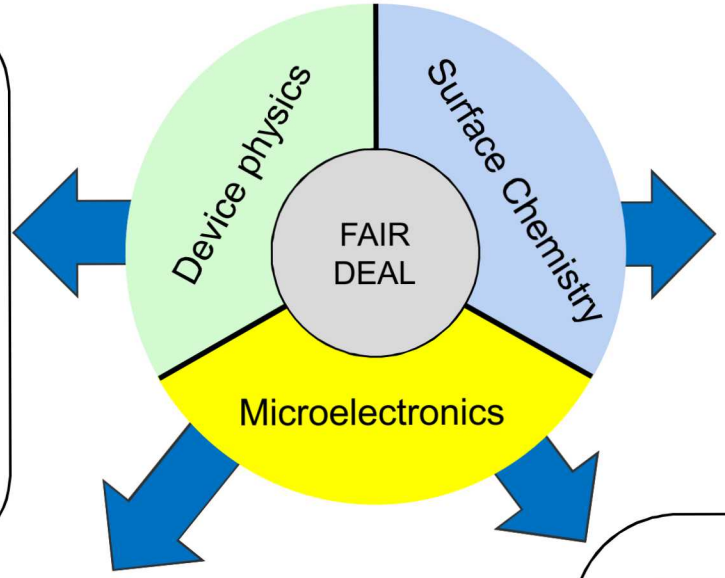
Digital electronics at the atomic limit (DEAL)

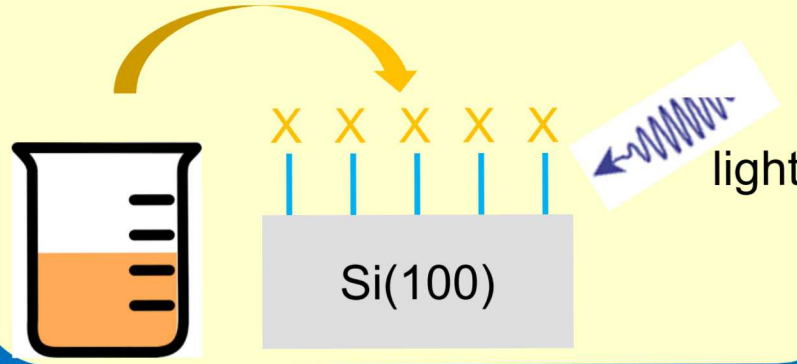
Sandia National Laboratories

Thrust 1: APAM-enabled Devices

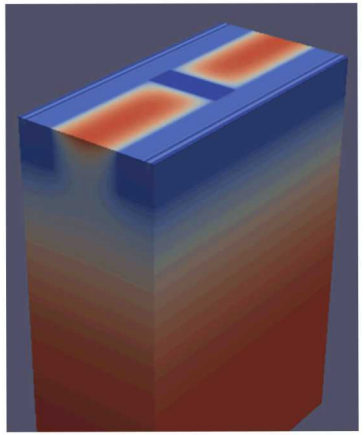




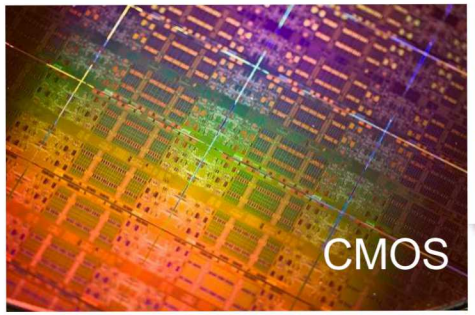
Thrust 4: Application Platform

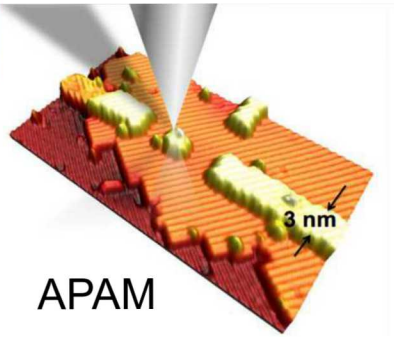


Thrust 2: APAM Modeling



Thrust 3: CMOS Integration

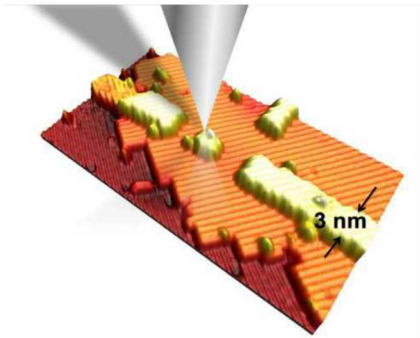




Limitations of APAM state of the art

Application Platform

Sandia National Laboratories



1

Oxide

Silicon

2

Sample clean

× Remove oxide: T > 800°C

3

Hydrogen termination

4

Hydrogen patterning

5

Phosphorus incorporation

× **Patterning in UHV, with STM**
× **Only one proven resist & dopant**

6

Silicon capping

7

source drain

Post-processing

× Limit diffusion: T < 450°C
× Cryogenic operation only

Problems span **surface chemistry**, device physics, microelectronics

Opportunity

Current APAM : STM/UHV
Learning Platform

- **Only one lithography pathway: Slow** STM done in extreme environment (**UHV)**
- **Only one** resist (H) + dopant (PH3) combination in practice -> limited toolkit & devices

APAM "*Application Platform*"

- Rapid lithography
- New atomic resists and dopants
- RT, Non-UHV, processes and chemistries

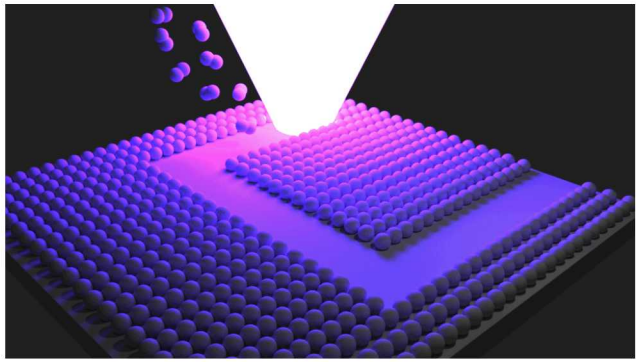
Discovery science to enable new principles & toolkits for atomic scale processes

Thrust 4: APAM Application Platform

Sandia National Laboratories

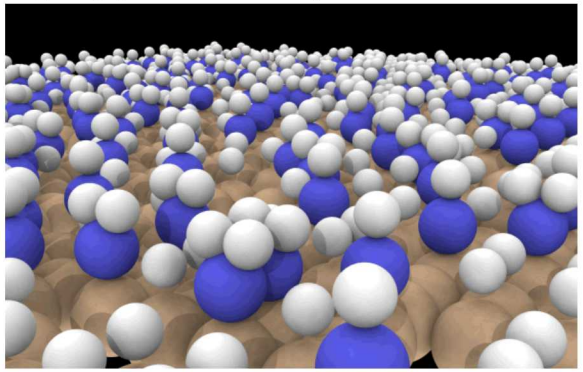
1. Photolithography

Scalable, light-based patterning of atomic resists



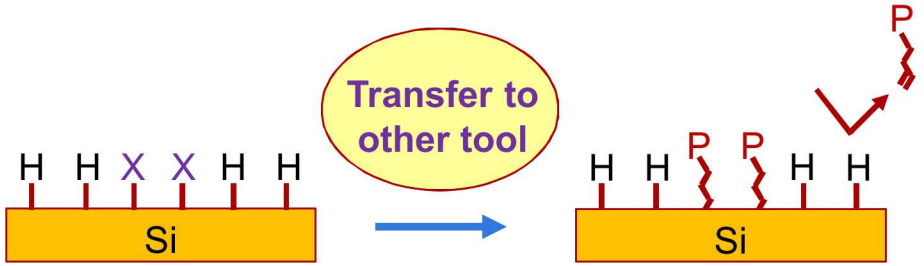
2. Acceptor Doping

p-type APAM processes



3. Alternative Resists

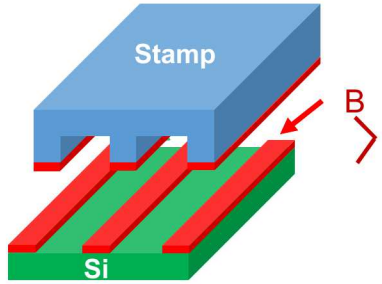
Halogen resists for pattern preservation



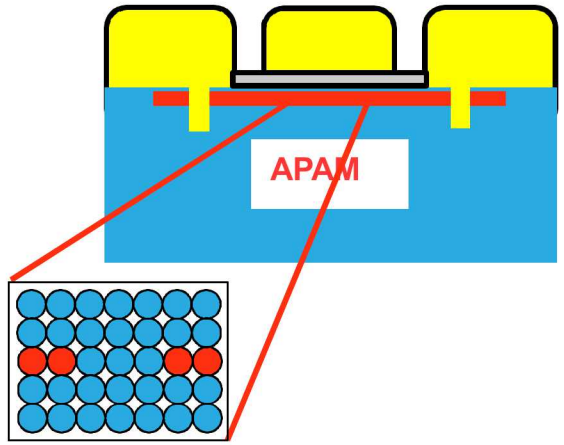
X = Halogen (Cl, Br, or I)

4. Wet Chemistries

Robust and scalable wet surface chemistries for resists and doping



Application Platform - Ties to Exemplars



APAM-MOS:

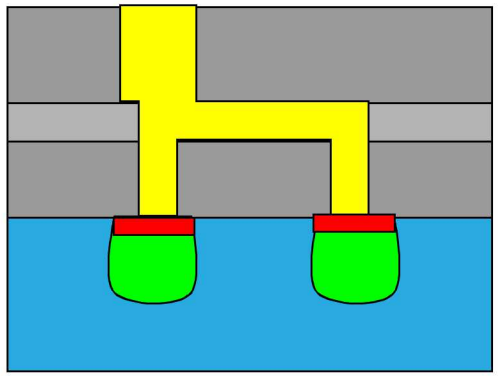
Need:

- Photolithography
- **Acceptor doping**: complementary transistors

Interconnects:

Need:

Acceptor doping:
opposite polarity possible

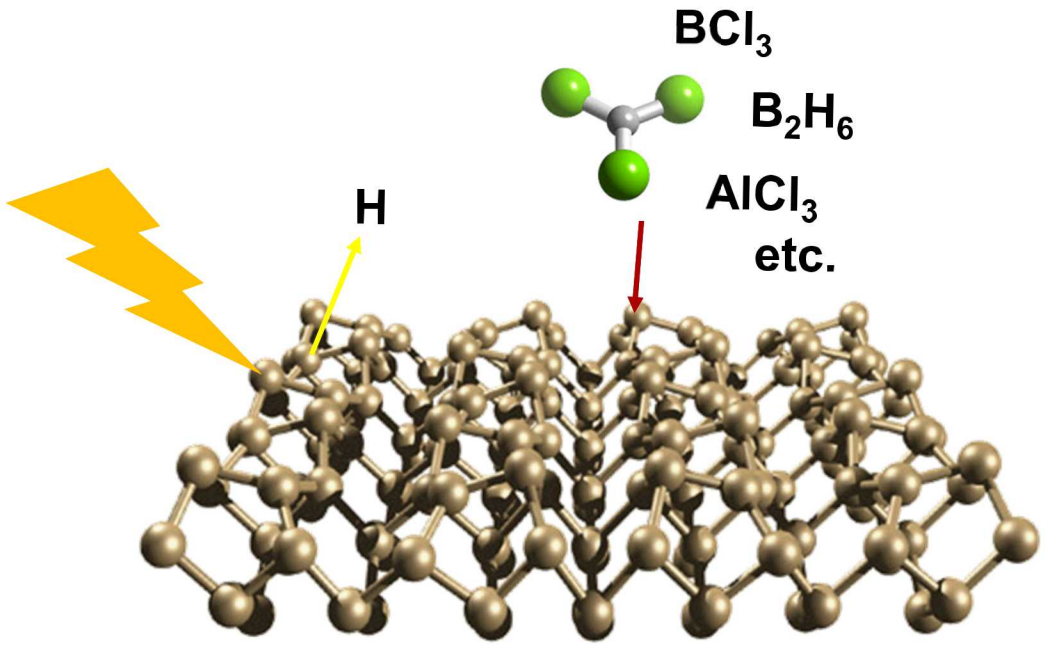


Fingerprint:

Need:

- Photolithography: need large scale patterning
- **Acceptor doping**
- Wet Chemistry

Why is this hard?



Task	Challenge
Photolithography	Desorb H without damaging Si
Acceptor Doping	Discover new surface chemistries that give desired electrical properties
Alternative Resists	Unknown stability and reactivity
Wet Chemistry	Discover new surface chemistries that give desired electrical properties

Application Platform – Team Members

Sandia National Laboratories

Thrust 4 Lead: George Wang
Photolithography: Aaron Katzenmeyer
Acceptor Doping: Ezra Bussmann
Alternative Resists: Robert Butera
Wet Chemistry: George Wang

Surface Science

George Wang
Esther Frederick (PD)
Shashank Misra
Ezra Bussmann
Scott Schmucker
Fabian Pena (PD)
Jeff Ivie

David Wheeler
Tim Lambert
Igor Kolesnichenko (PD)
Robert Butera (UMD)
Kevin Dwyer (UMD, PD)
Andrew Teplyakov (U. Del)
Alex Shestopalov (U. Roch)

Modeling

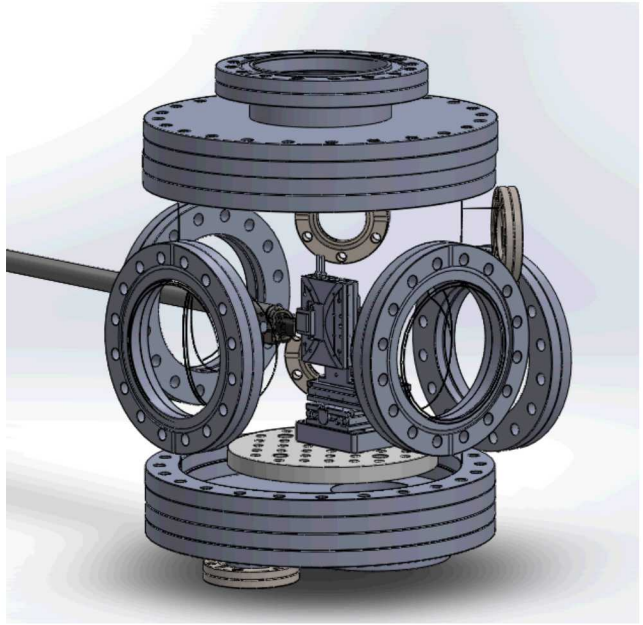
Andrew Baczewski
Quinn Campbell (PD)
Peter Schultz

Fab & Measure

Fab
Dan Ward
DeAnna Campbell
Mark Gunter
Philip Gamache
Electrical
Lisa Tracy
Tzu-Ming Lu
Albert Grine

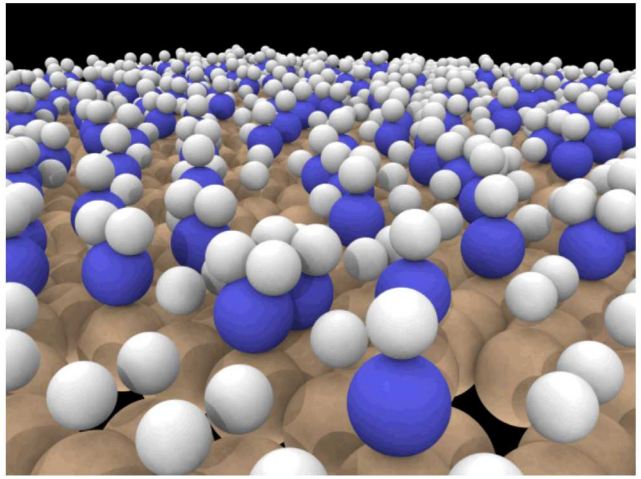
Application Platform – Capabilities

Stand-alone photolithography system



Acceptor doping – experimental infrastructure in place (Sandia, UMD, Zyvex)

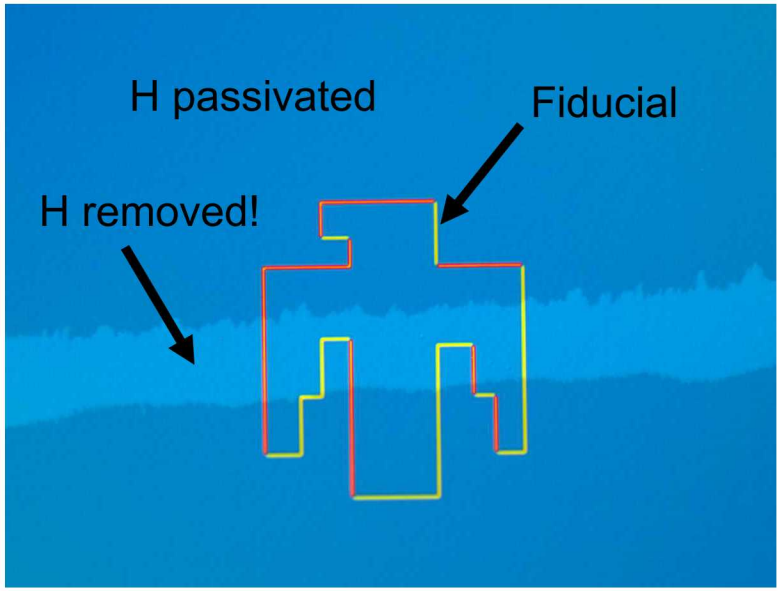
Chemistry modeling toolkit



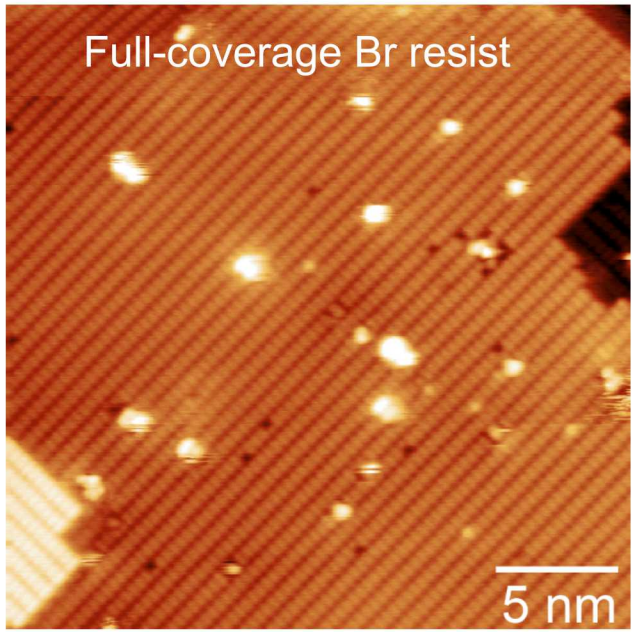
Application Platform – Discoveries

Sandia National Laboratories

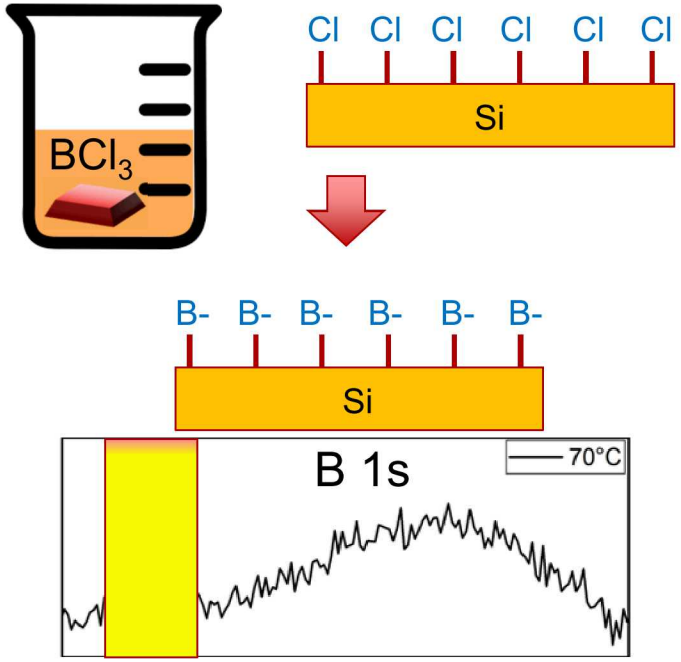
Photolithography demo: H-resist desorption by laser



New halogen (Cl, Br, I) atomic resists and stability determinations



Wet chemical pathway for direct dopant attachment



Application Platform: Metrics and external engagement

Sandia National Laboratories

Written

- White paper submitted (wet chemistry)
- Three journal articles in preparation (Baczewski, Butera, Tepylakov)
- Technical Advance in preparation (photolithography)

Spoken

- Invited talks: DOE Workshop on Atom-by-Atom fabrication (2018, Oak Ridge NL)
- Contributed talks: NM AVS (Best talk award), APS March (2019), Int'l Conf. Electron, Ion, & Photon Beam Tech & Nanofab (2019)…

Collaborations

- Laboratory for Physical Sciences (LPS)
- University of Delaware (Teplyakov)
- University of Rochester (Shestopalov)
- Zyvex Labs

Application Platform – current risk assessment

Successful demonstration!

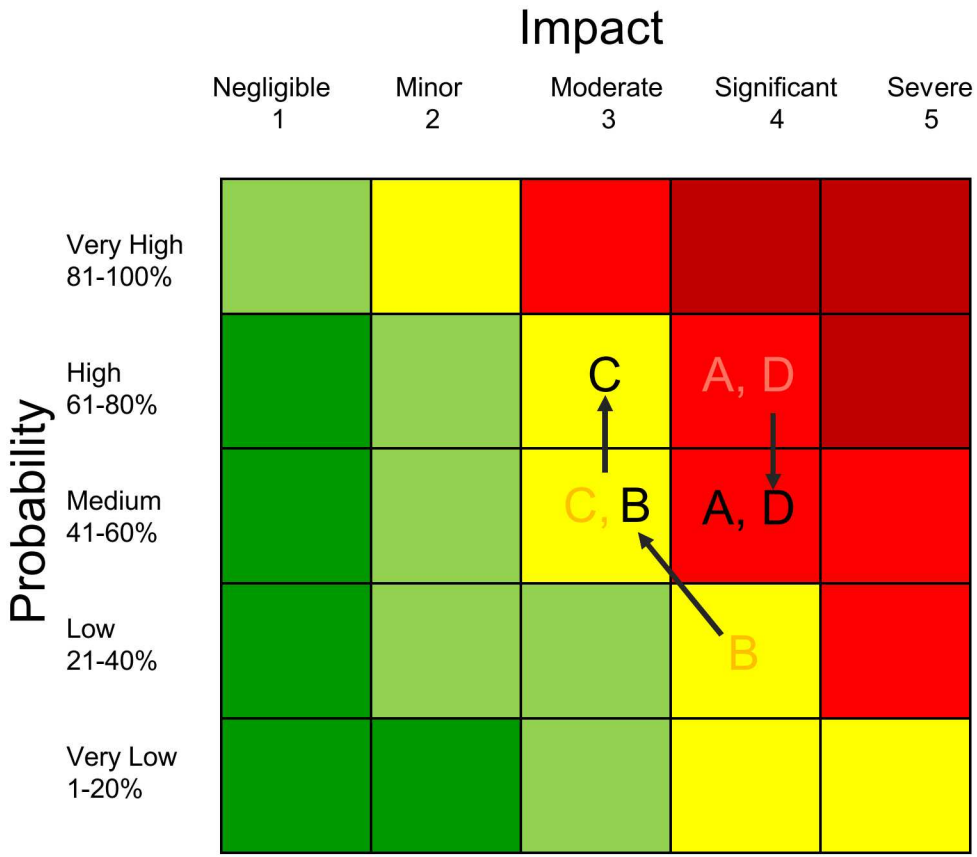
Strategy refocused

Critical Path

Photo-lithography	Alt. Resists & Dopants	Wet Chemistry	Acceptor Doping
A	B	C	D

Question answered, merge with Wet Chemistry

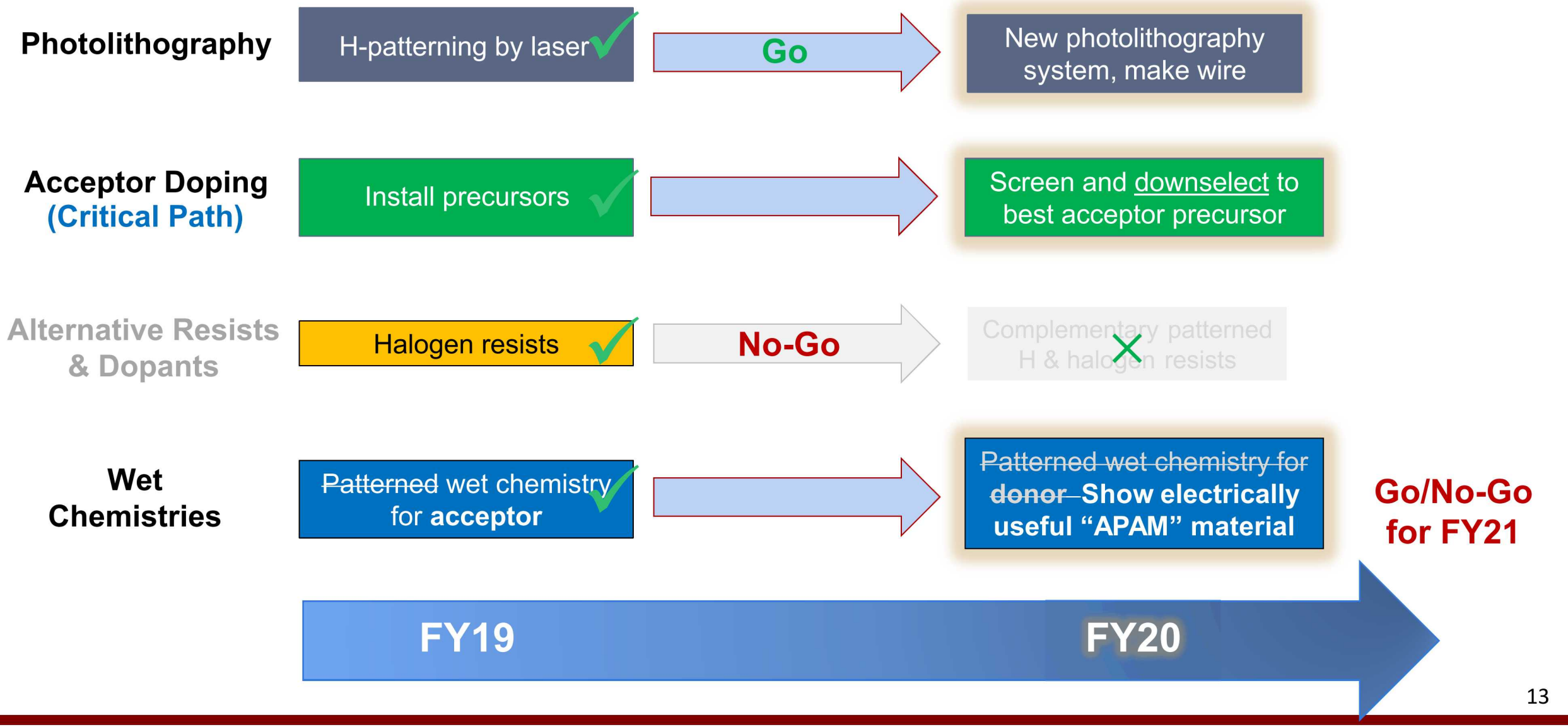
Additional precursors lowers risk



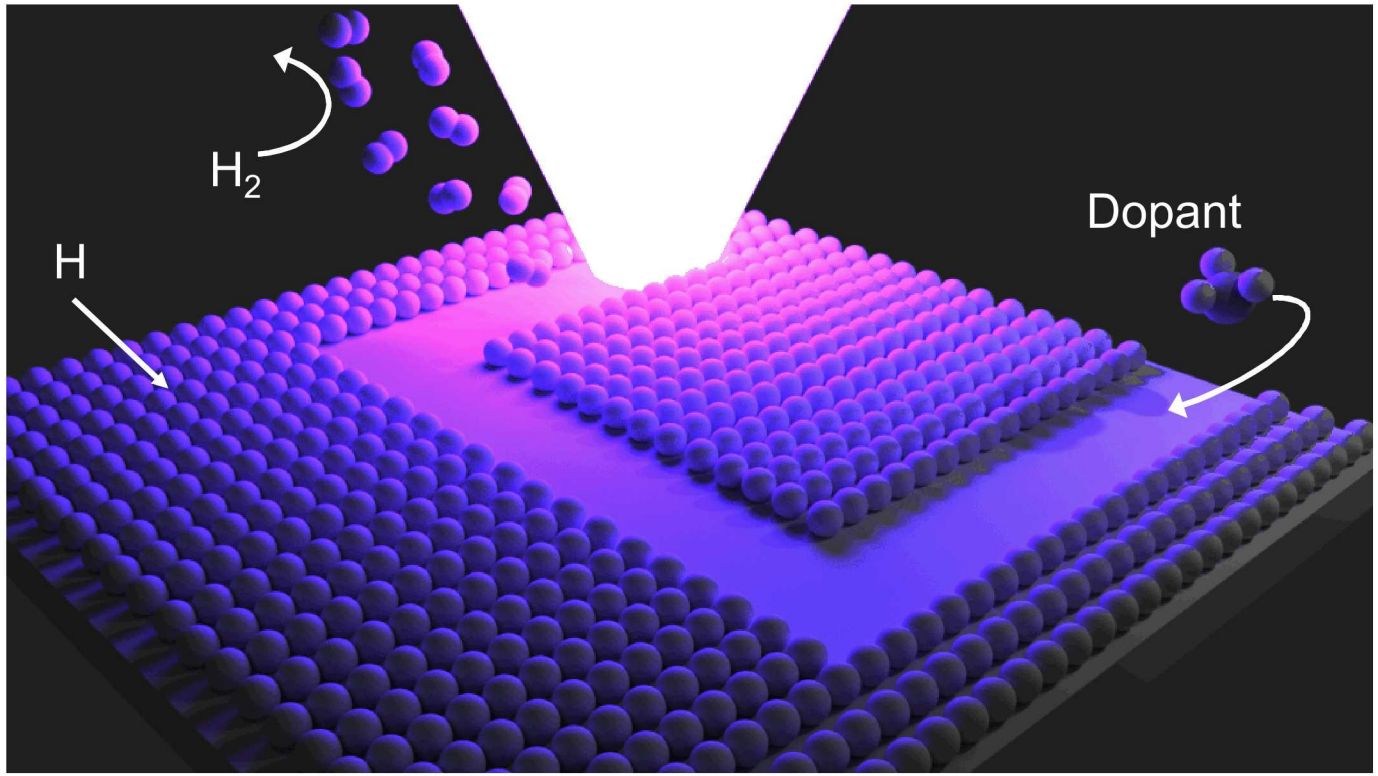
Color key:

- Dark Green – Minimum Risk
- Light Green – Low Risk
- Yellow – Moderate Risk
- Red – High Risk
- Dark Red – Extreme Risk

Thrust 4 Roadmap - FY19 Progress to FY20 Plan



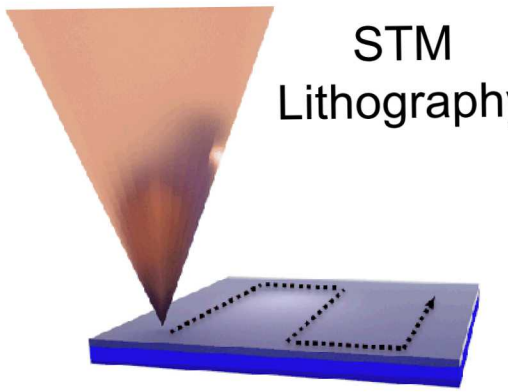
Task 1 – Photolithography



Expedites ***progress throughout GC***
Enables ***basic science and innovation***

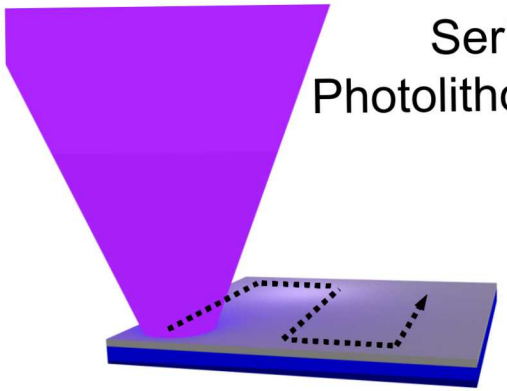
Photolithography vs STM Patterning

Patterning Method	Atomic Resolution	Large Areas	Rapid
Photolithography	x	✓	✓
STM	✓	x	x



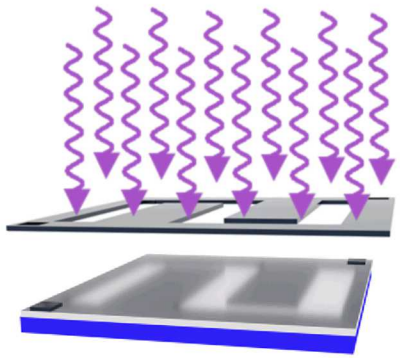
STM Lithography

1 device / day



Serial Photolithography

10 devices / day



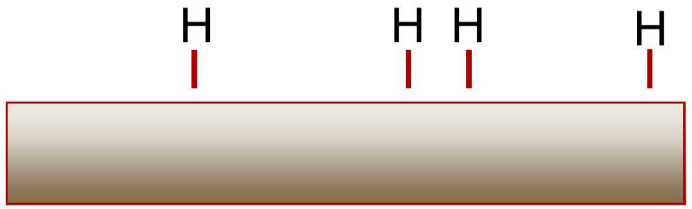
Parallel Photolithography

10^9 devices / day

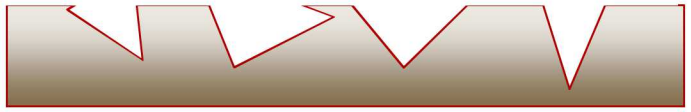
Photolithography - Risks

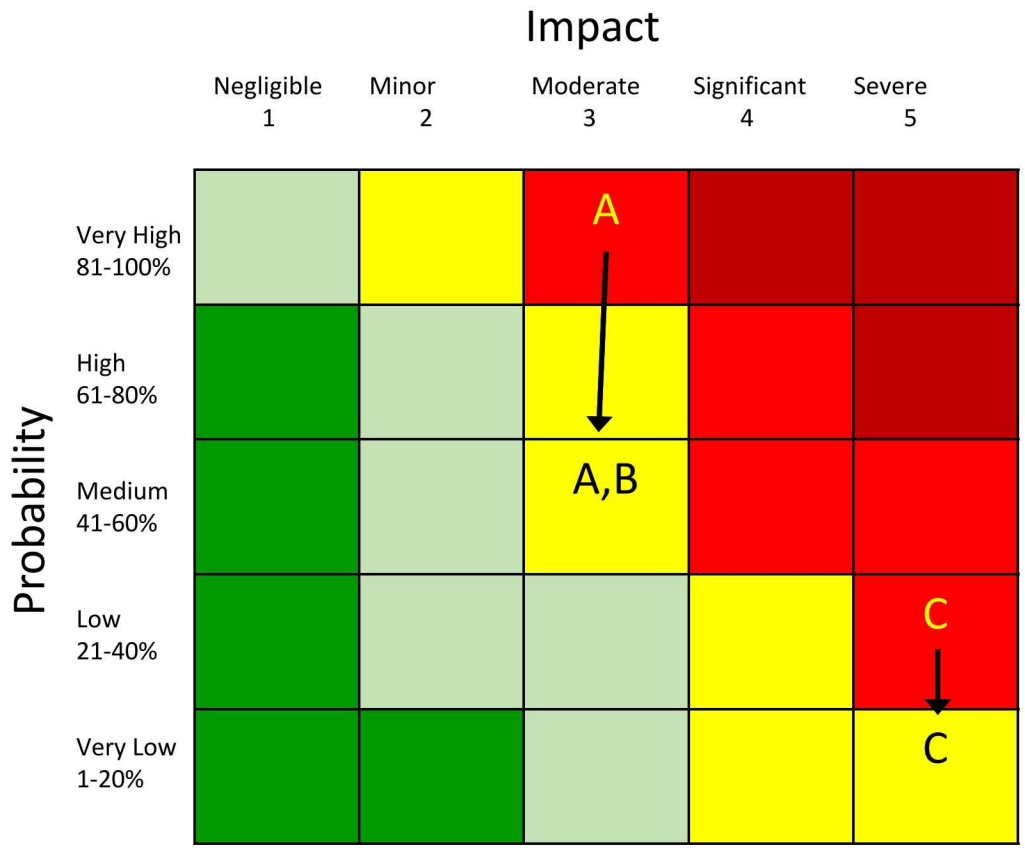
A. Physical mechanism of H photodesorption not understood
   Conflicting literature

B. Quality of device as good as STM?



C. Silicon surface damaged by process
   Catastrophic to fabrication





FY19 – Progress (Theory & Modeling)

Sandia National Laboratories

Numerical model for photothermal heating developed

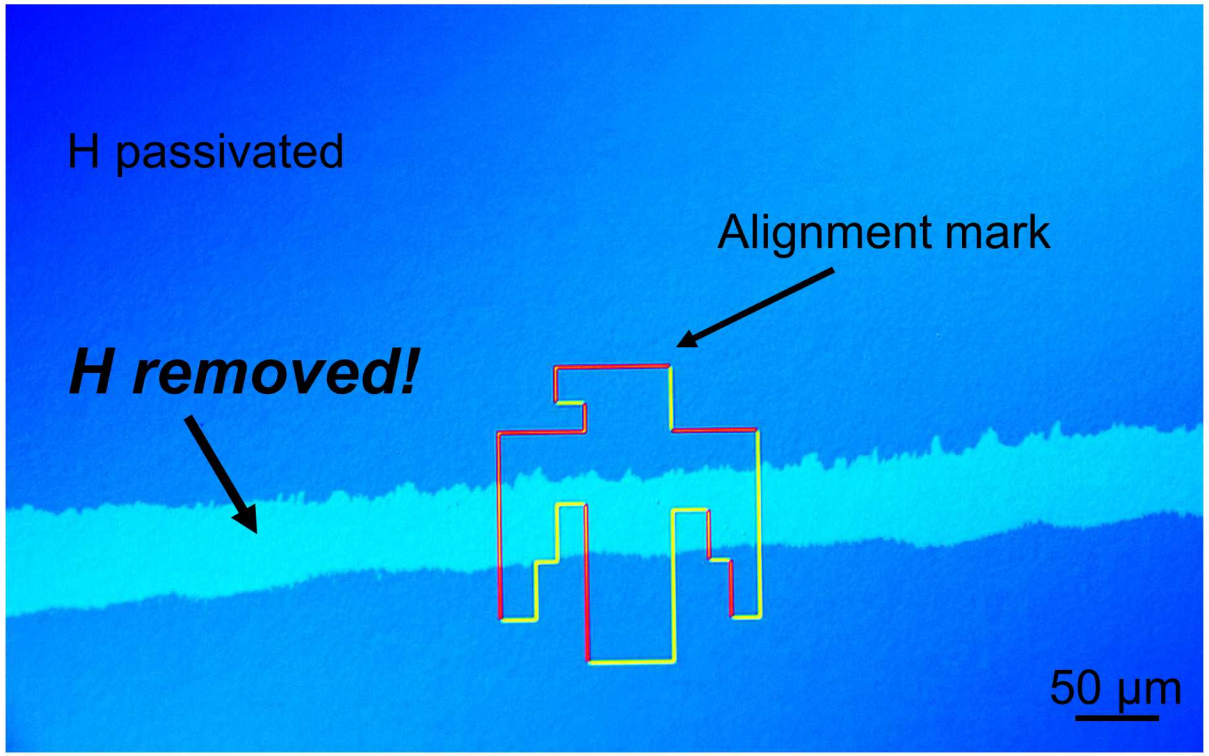
Distilled into a simple analytic expression

Rapidly predicts experimental observation!

$$T_{peak} \approx \frac{2I\left[1-R\right]}{\overline{\kappa}}\sqrt{\frac{D\Delta}{\pi}} + \mathcal{O}\left(\frac{1}{\alpha\sqrt{D\Delta}}\right)$$

FY19 – Progress (Experimental)

Demonstrated H photolithography in UHV!



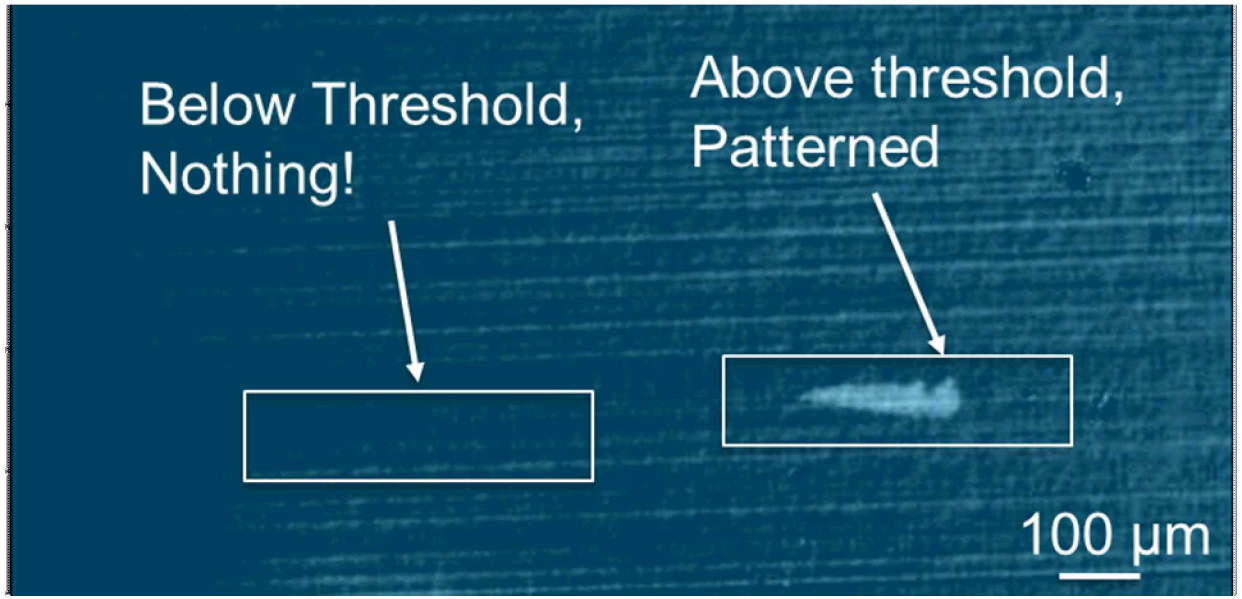
Interference contrast in optical microscope

w/ Summer Intern - Sanja Dmitrovic (University of Arizona)

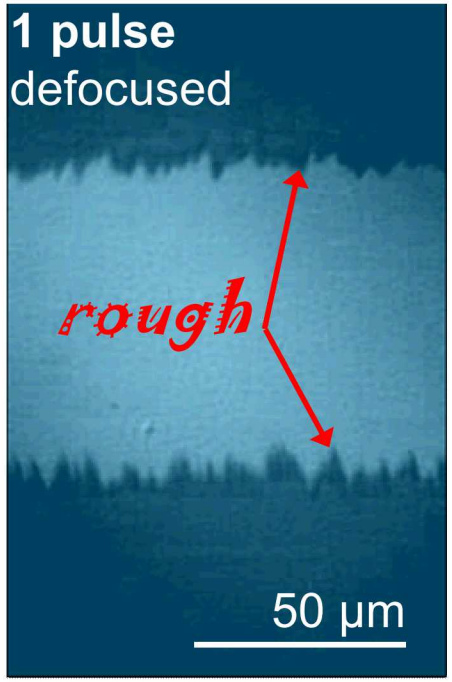
FY19 – Progress (Experimental)

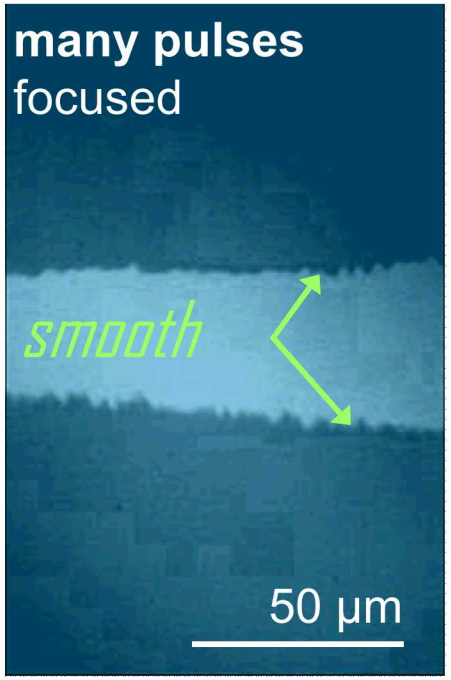
Observed new resist behaviors

Self developing, digital resist



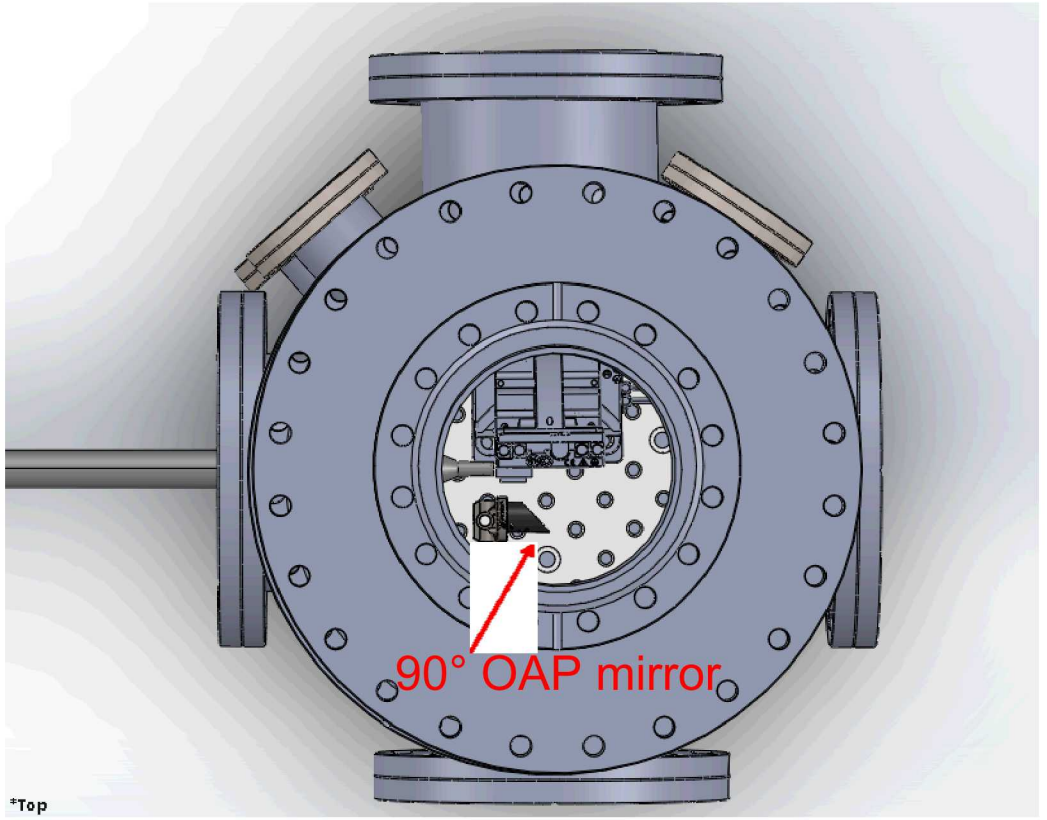
Reduced line-edge-roughness w/out overexposure



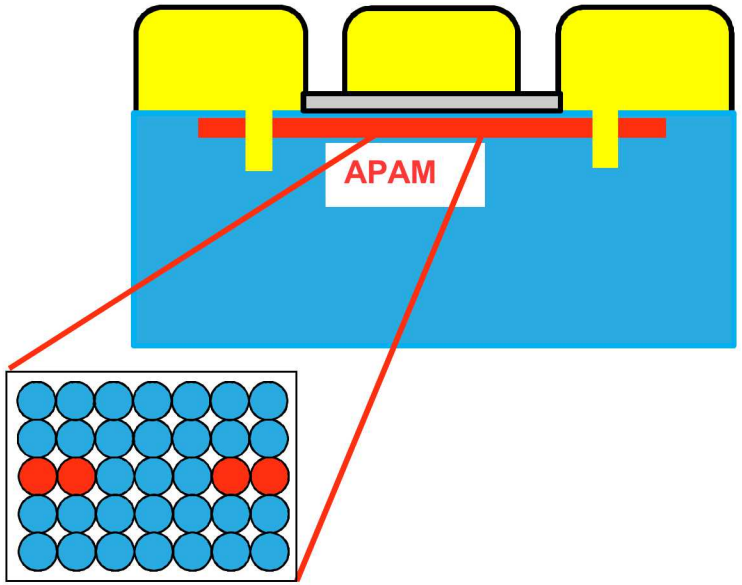


FY20 – Outlook and Improvements

- Next: Demonstrate doping
- New photolithography system
  - Improves accuracy and resolution
- VUV laser ($\lambda \approx 160$ nm)
  - Cleave Si-H bond w/out heating



Task 2 - Acceptor Doping



Current state:

- n-doping only
- Via phosphine (PH_3) & H resist
  (gas phase in vacuum)

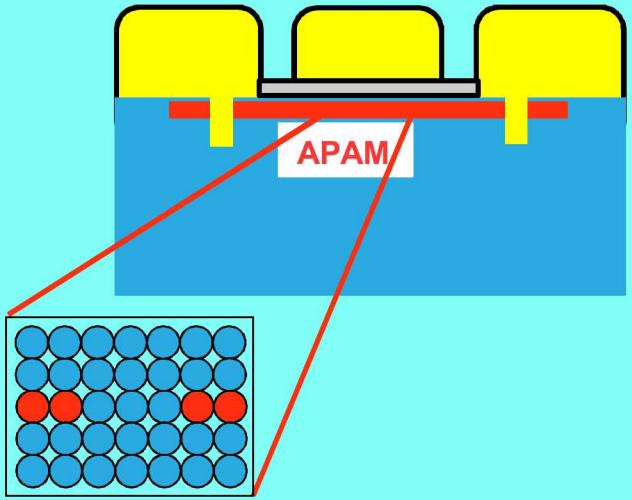
For APAM MOS & other exemplars:

- NEED: acceptor/p-type doping
  (gas phase in vacuum)

Challenge: satisfy two sets of criteria

Sandia National Laboratories

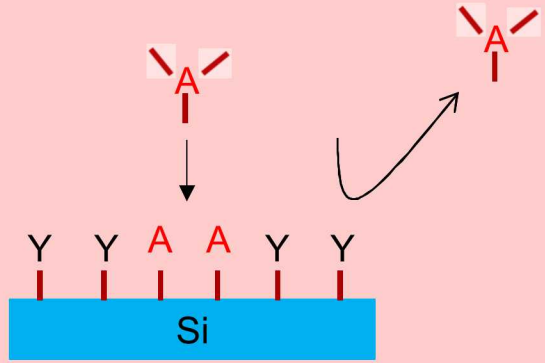
Electronic Performance



- *APAM Doping >> conductive than Si*
  Extreme dopant density, ≥ 10^{14} cm^{-2}
- *Integrate in device process*
  Contact, minimal dopant diffusion

success!

APAM chemistry



- *Selective templated surface chemistry*
  e.g. contrast H >1000:1, T<500C

*** Acceptor doped APAM material meeting all criteria would be world 1st**

Overview of our approach to R&D problem

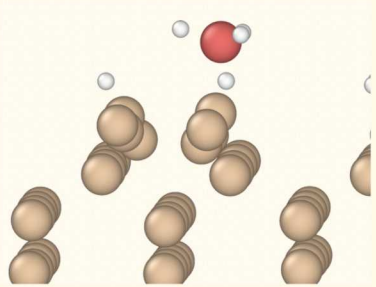
Sandia National Laboratories

1. Identify candidate chemistries & precursors

Acceptor	Hydride	Halide	Organic	~~Amine~~
Boron	B_2H_6 $B_{10}H_{14}$	BCl_3 BF_3 BBr_3	Trimethylboron	Ruled out – poor sticking, attacks H resist
Aluminum	AlH_3	$AlCl_3$	~~Trimethylaluminum~~ Triethylaluminum	
Gallium		$GaCl_3$	Triethylgallium	
…	…	…	…	

2. Prescreen (literature+models)

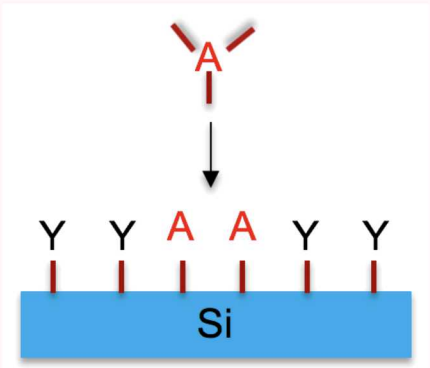
-Is a chemistry/recipe likely to work?

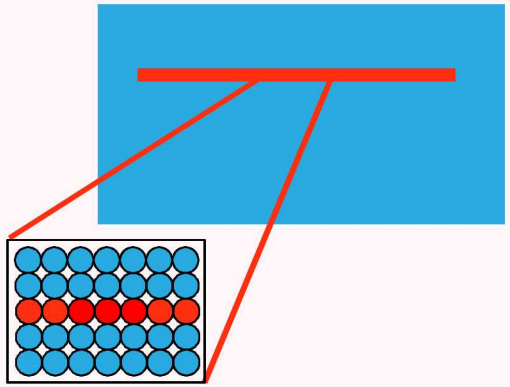


3. Lab tests & recipe development

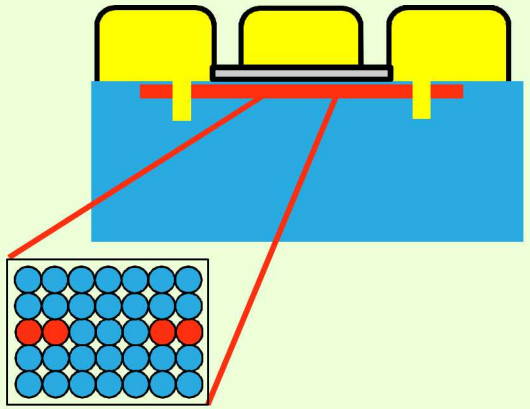
-APAM surface chemistry test

-Materials physical & chemical tests





4. Fab integration - device process



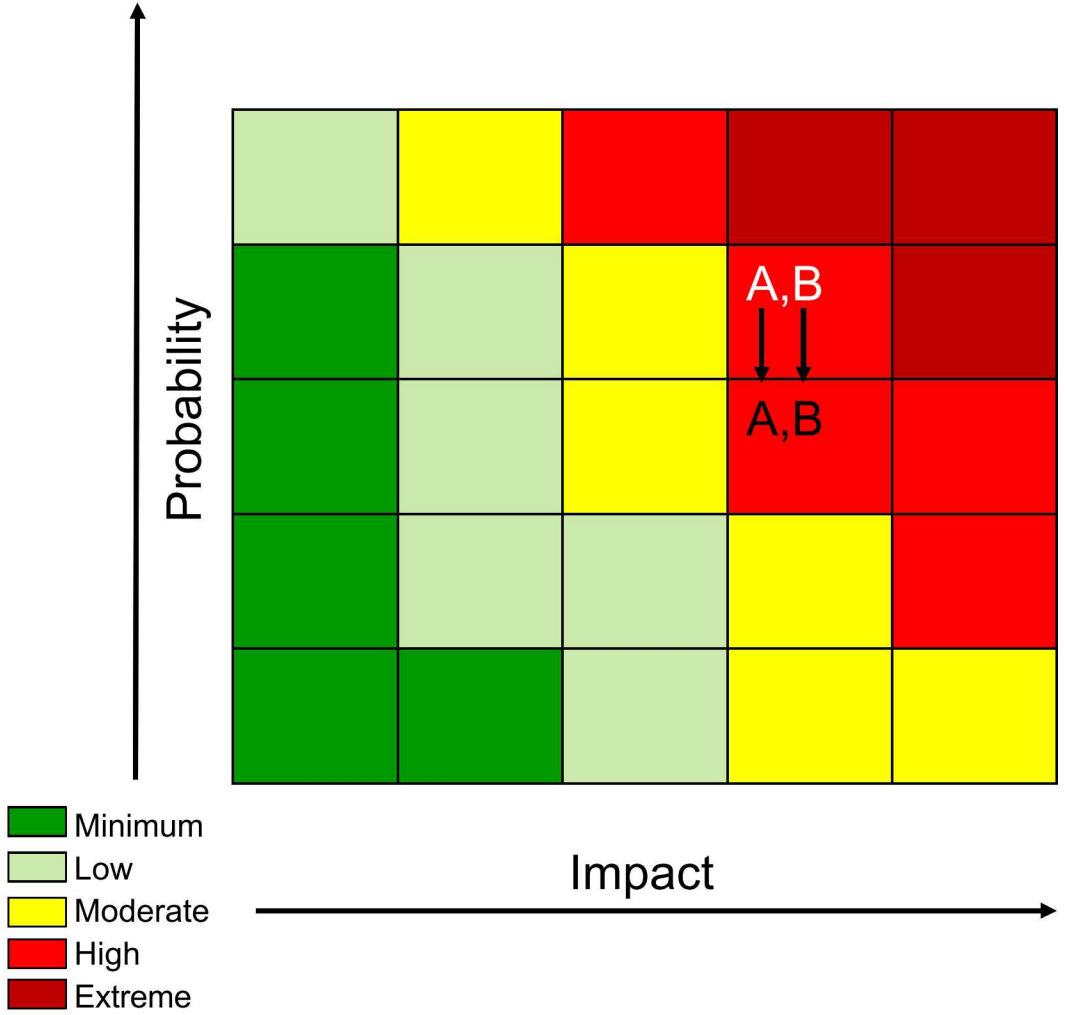
Risks, impact to project, mitigation

Risks

A. Uncertain difficulty to implement lab tests
   → potential delays, time/cost
B. Unable to discover method meeting all requirements
   → cost/risk pushed to other tasks

Mitigations

1. Engage capable partners in surface chemistry tests
2. Use chemical kinetic models to guide experiment



Progress & current status

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1. Identify candidate chemistries & precursors

Acceptor	Hydride	Halide	Organic	~~Amine~~
Boron	B_2H_6 $B_{10}H_{14}$	BCl_3 BF_3 BBr_3	Trimethylboron	Ruled out – poor sticking, attacks H resist
Aluminum	AlH_3	$AlCl_3$	~~Trimethylaluminum~~ Triethylaluminum	
Gallium		$GaCl_3$	Triethylgallium	
…	…	…	…	

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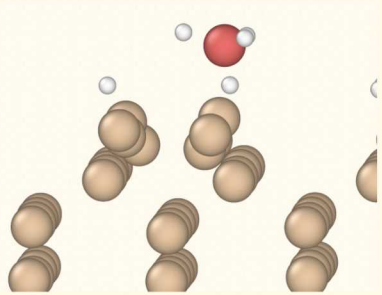
2. Prescreen (literature+models)

-Is a given chemistry likely to work?



BH_3 E_A = -1.90 eV

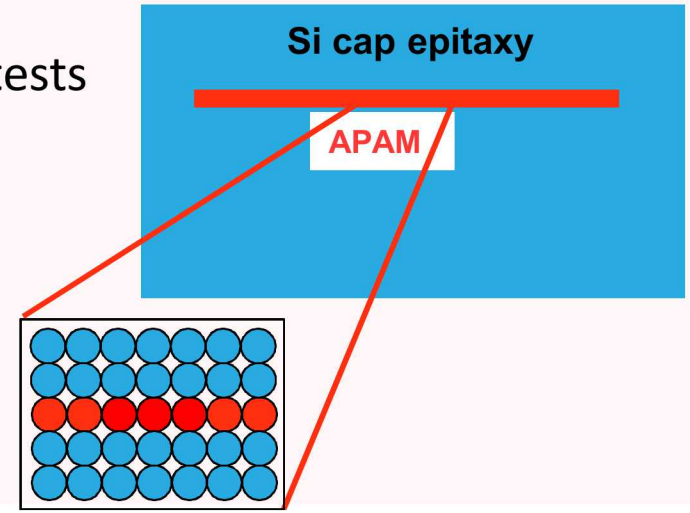
- ❑ We engaged partners to mitigate cost/time/risk
- ❑ We built models now guiding decisions
- ❑ Density functional theory - reaction paths, energetics, and barriers
- ❑ See postdoc Quinn Campbell's poster

Progress & current status

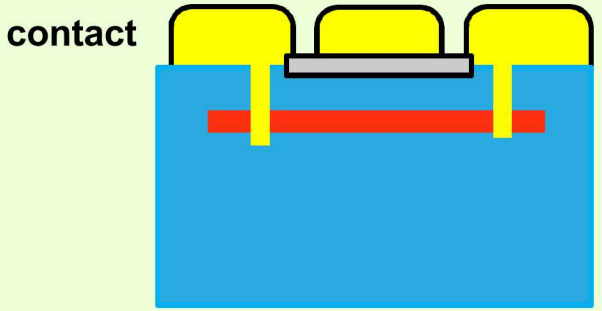
Sandia National Laboratories

3. Lab tests & recipe development

-APAM surface chemistry tests
-Materials physical & chemical tests
-Electronic properties tests



4. Fab integration - device process



❑ **Lab tests & recipe development in-progress**

❑ **ID'd challenges, e.g. electrical contact**
❑ **Solutions in-progress**

FY20 plan

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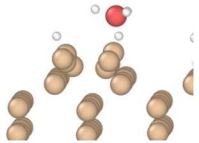
FY 19	FY20 Q1/Q2	Q2	Q3	FY20 Q4

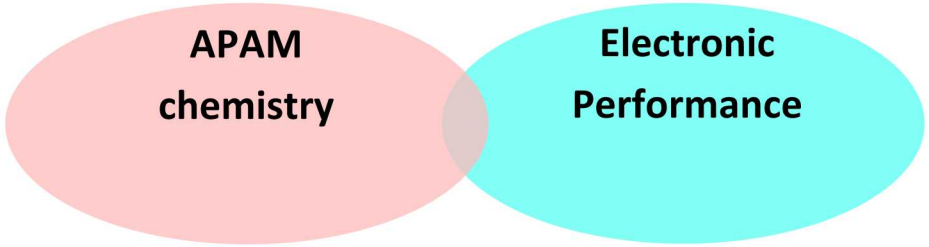
Lab tests & recipe development

Labs set-up & model built



Surface chemistry tests

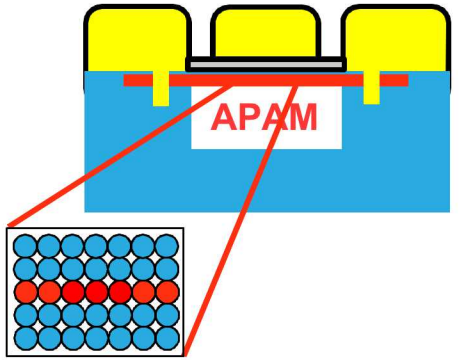
Material Physicochemical test



Material Electronic test

Downselect amongst chemistries- hydride, halide, alkyl

APAM p-doped device e.g. wire



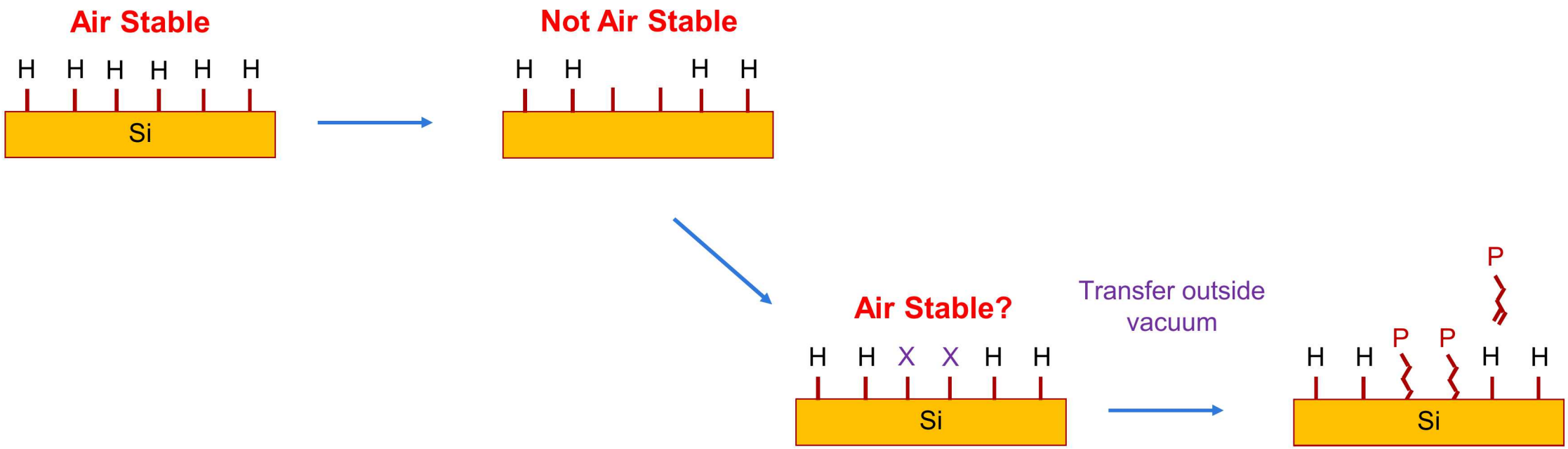
Fab integration

ID integration challenges

Engineer solutions

Task 3 - Alternative Resists

GOAL: Can APAM patterns survive outside of UHV
to transfer between different processing tools?



QUESTION: Are halogen resists stable in air?

Risks

Goal: Alternative and complementary resist and dopant chemistries

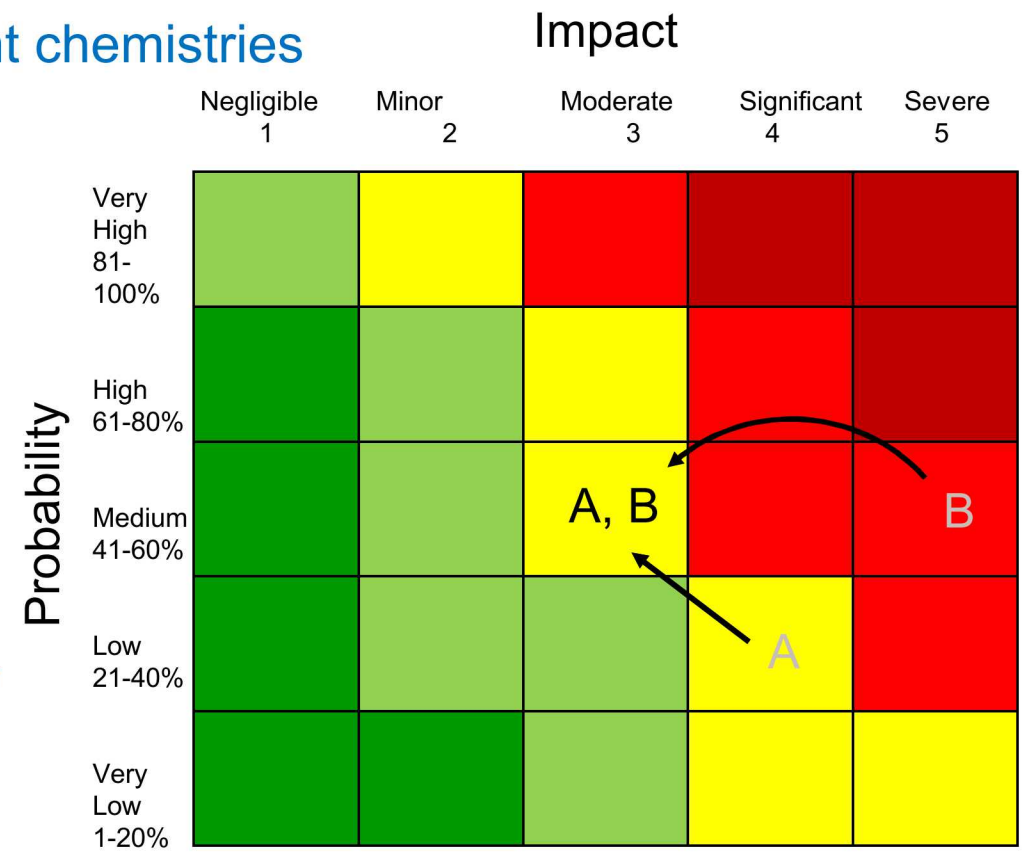
Challenges/Risks:

A. Halogen resist not stable outside UHV

   a. **Stable in N_2**

B. No selective dopant chemistry pathway

   a. **Wet chemical selective chemistry pathway**



Color key:
- Dark Green – Minimum Risk
- Light Green – Low Risk
- Yellow – Moderate Risk
- Red – High Risk
- Dark Red – Extreme Risk

FY19 – Alternative Resists (Cl, Br, and I)

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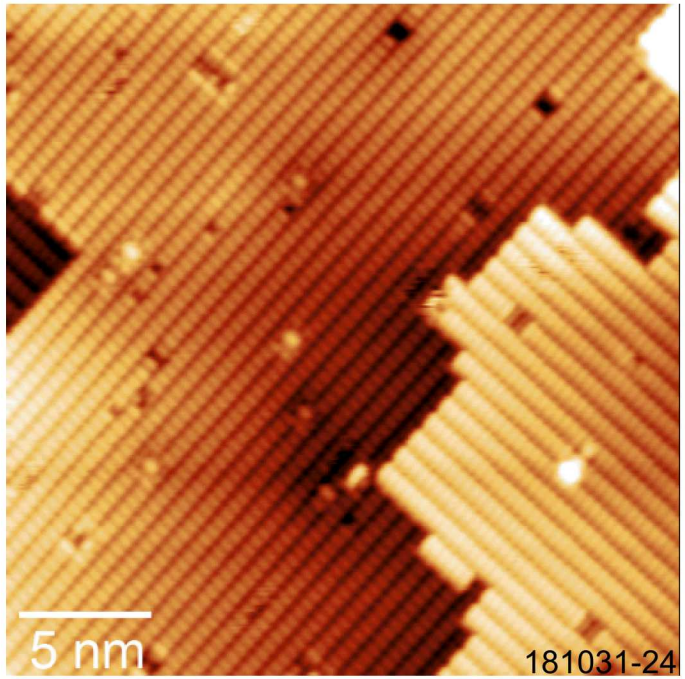
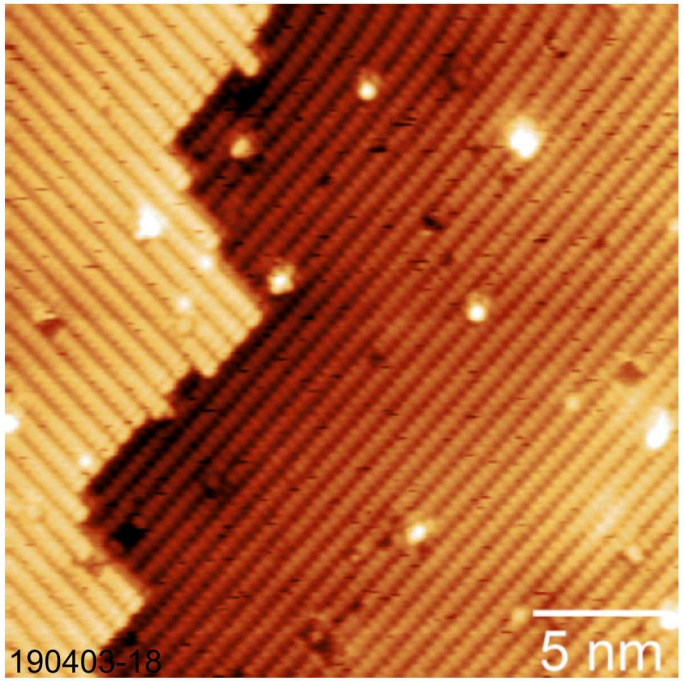
Full Cl Passivation



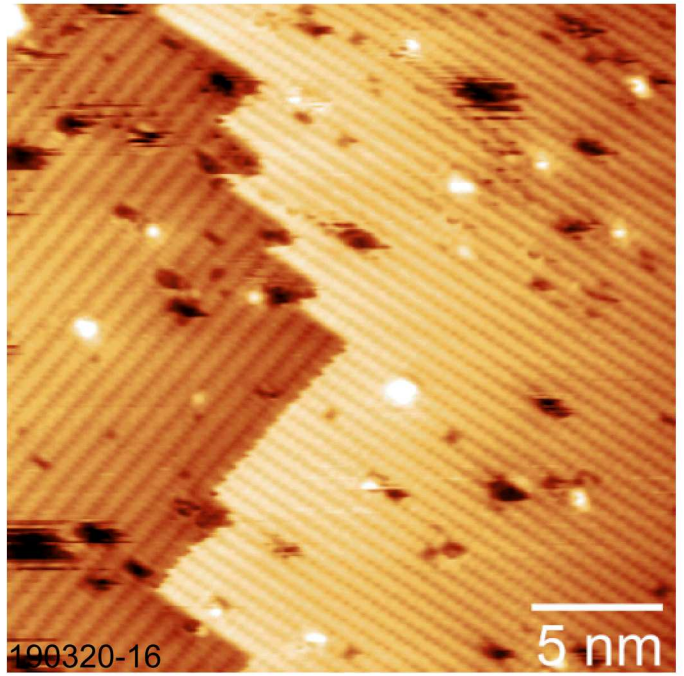
-1.7V, 0.7nA

Full Br Passivation



-1.7V, 0.4nA

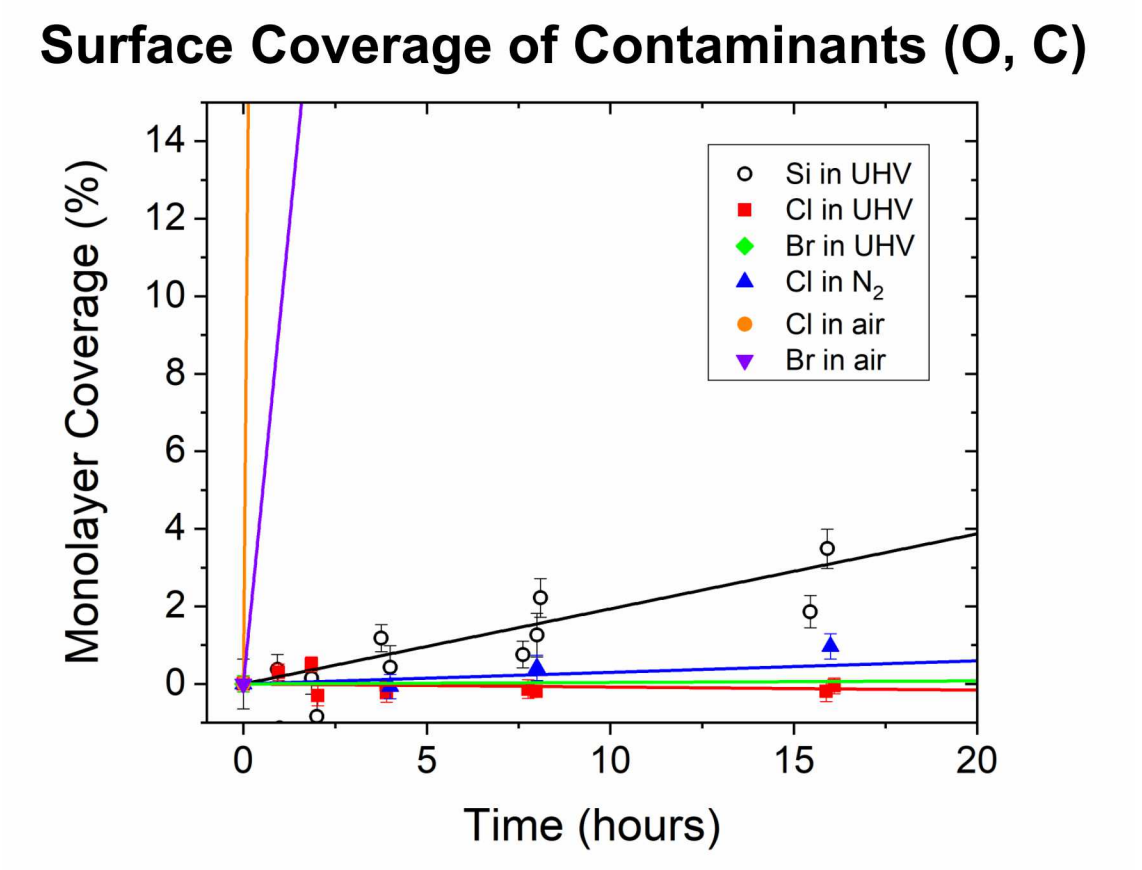
Full I Passivation



-1.7V, 0.5nA

First observation complete iodine passivation

FY19 – Stability of Halogen Resists



- ***All*** halogen resists contaminated by air exposure
- ***All*** halogen resists stable in N_2 for hours

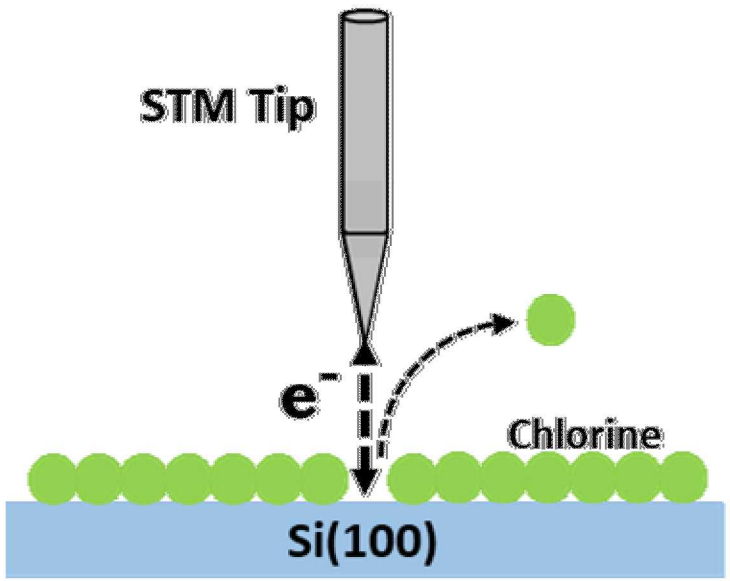
FY20 – Impact & Outlook

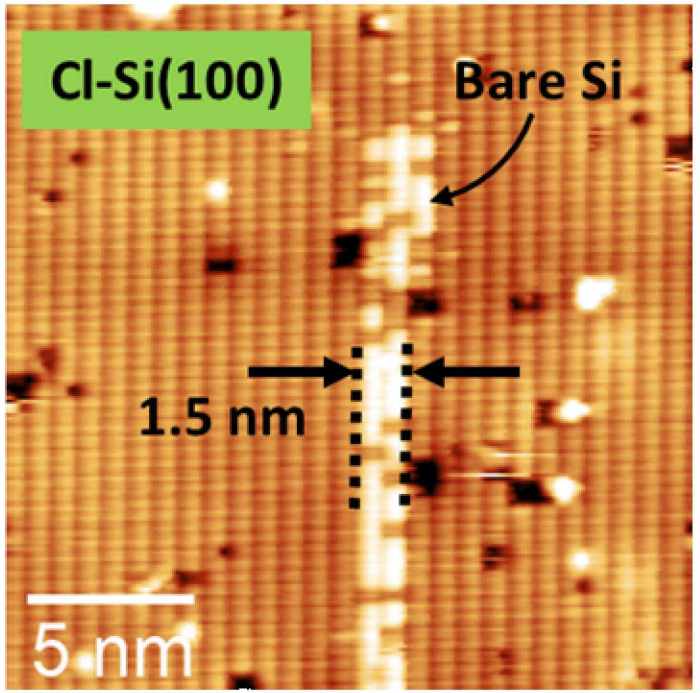
- Fabricated Cl, Br, and I resists
  - First observation of complete iodine passivation
- Determined stability of halogen resists:
  - ***Not stable*** in air, but…
    - ***stable*** in N_2 → *Suitable for wet chemistry pathway*
- Patternable halogen resists in UHV: Cl, Br, I

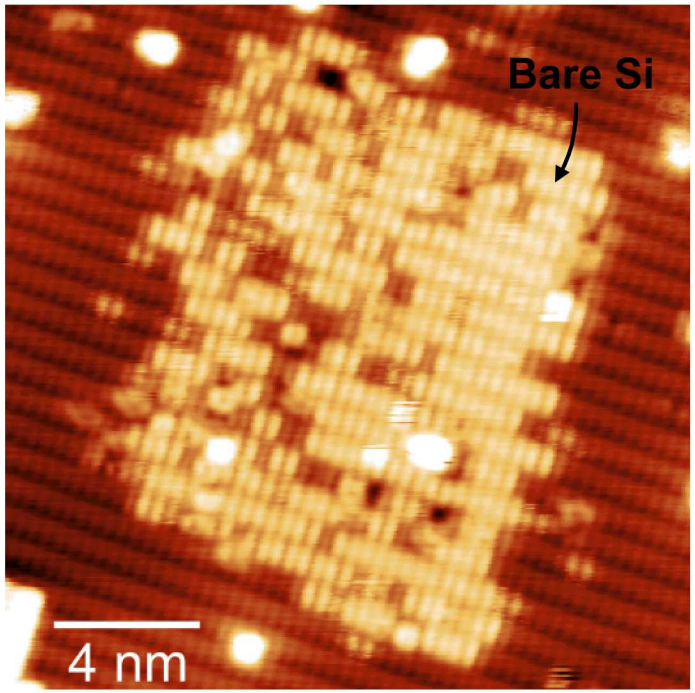
FY20: Merge complimentary resists with Wet Chemistry Task

- ***Re-allocate resources to acceptor doping task.***

Alternative Resists for Acceptor Doping



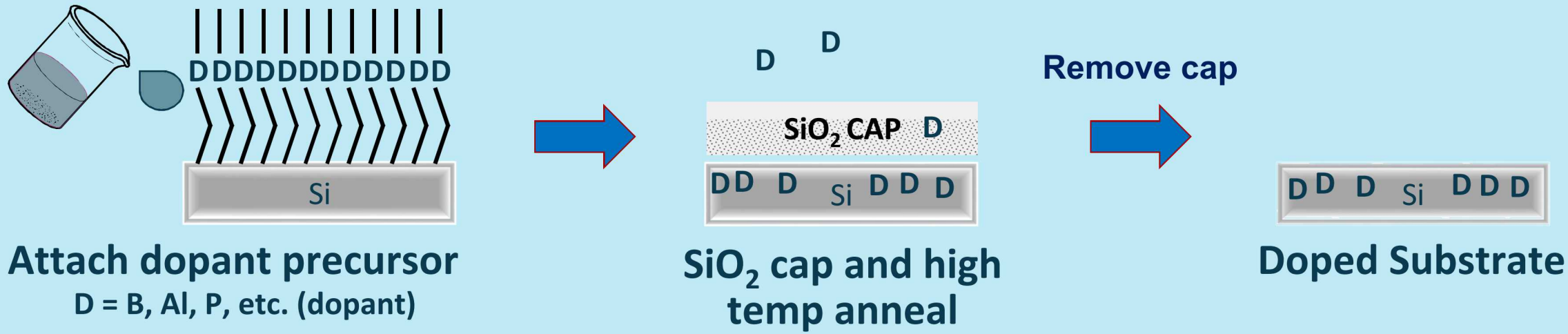




Patternable halogen resist expands available acceptor chemistry

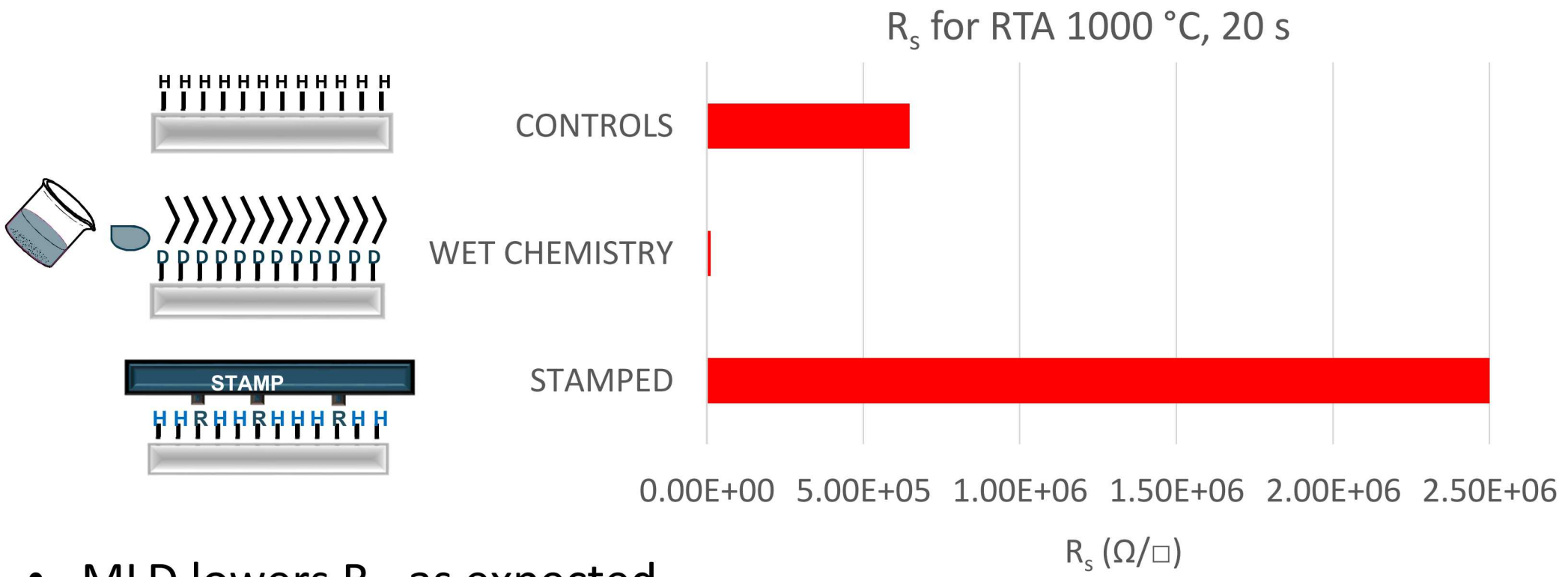
Task 4 - Wet Chemistry

Goal - Develop a scalable wet-chemistry method to dope Si(100) with high active dopant concentration & desirable electronic properties.



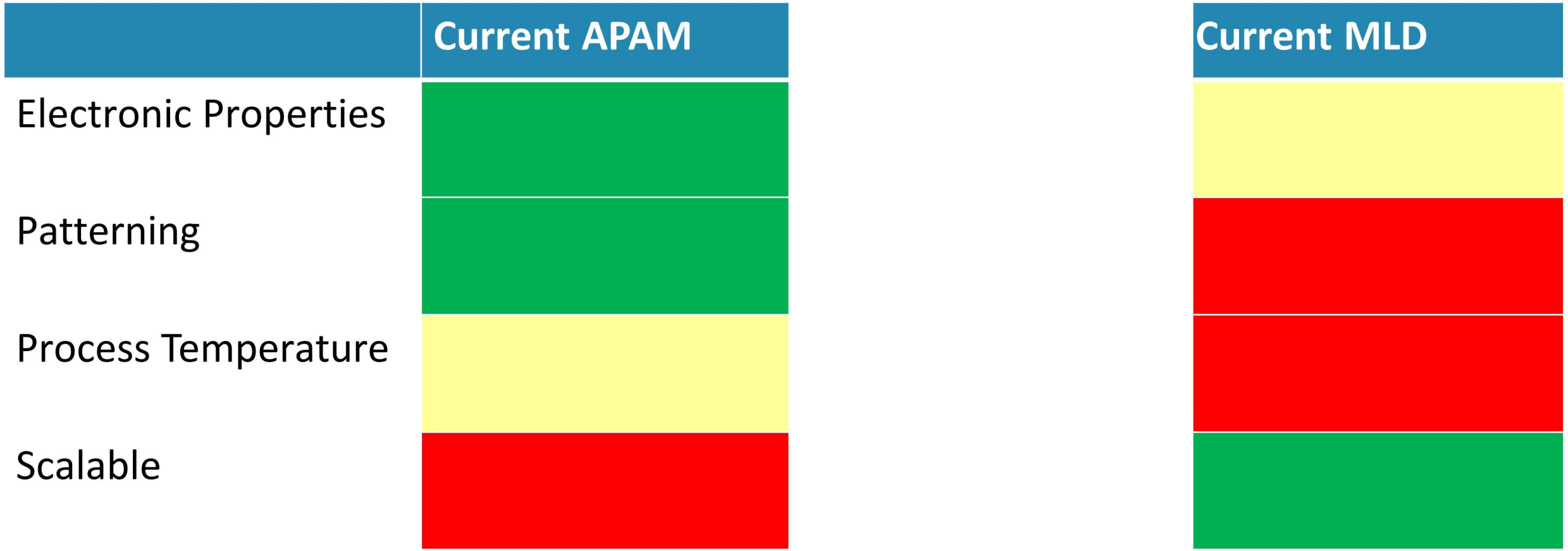
"Monolayer Doping (MLD)" (Javey, 2007) allows for a large variety of dopant attachment chemistries via organic functionalization of the silicon surface.

FY19 - Hines/Javey MLD Chemistry



- MLD lowers R_s, as expected
- Stamping made R_s worse than undoped control
- Lowest achievable experimental R_s = 1.3E+04 Ω/□, Javey reported R_s = 2.0E+03 Ω/□
- MLD doesn't meet "APAM-like" target goal: <500 Ω/□

Filling in the Gaps



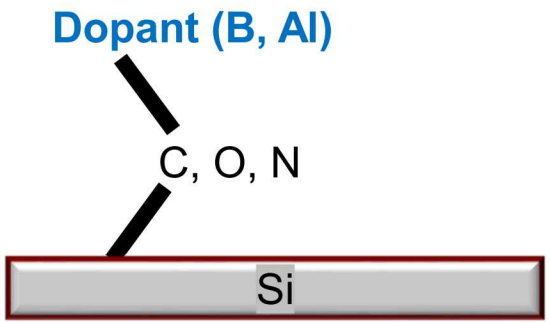
Goal – Discover a scalable, low temperature process to dope Si(100) to achieve material with "APAM-like" properties (e.g. very high doping).

Impact

Problem: Current SOTA MLD chemistry has not produced "APAM-like" doping levels

Hypothesis: Si-C bonds require high temperature annealing to break, resulting in diffusion-limited doping (i.e. current fab processes) instead of desired surface delta doping

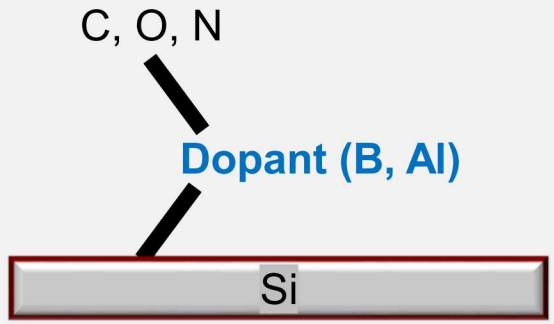
Current MLD chemistry



Indirect dopant attachment (e.g. Si-C-B) limits doping to solid solubility

FY20

Desired MLD chemistry

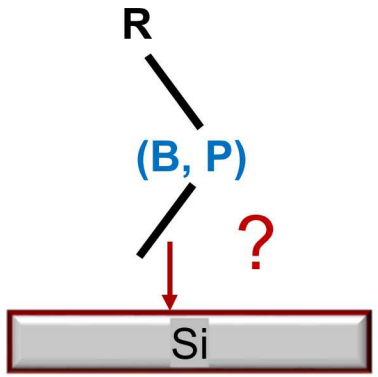


New strategy: Direct Si-dopant bond

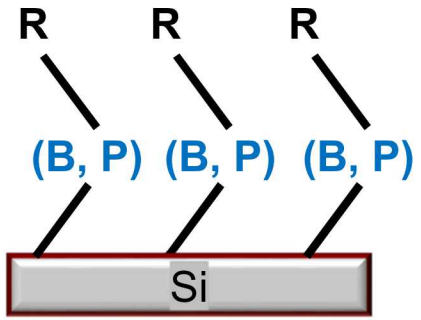
But: Little precedent for direct Si-dopant bond formation and stability on Si(100) surface

FY20 New approach: challenges

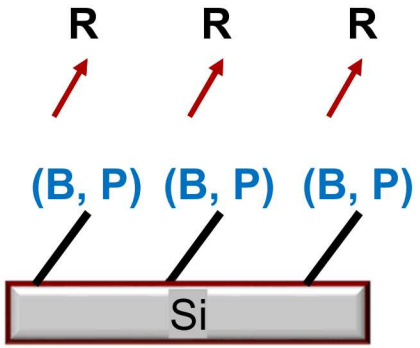
Discover direct dopant-Si wet chemistries



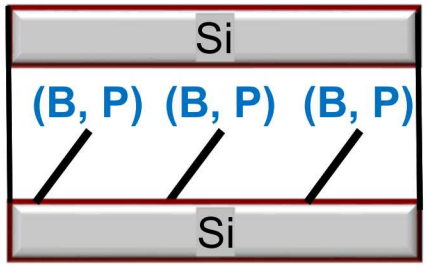
Optimize for high density dopant attachment



Remove ligands & contaminants



Capping & electrical characterization



Risks Assesment

Goal: Scalable wet chemical processes for dopant attachment resulting in APAM-like electrical properties

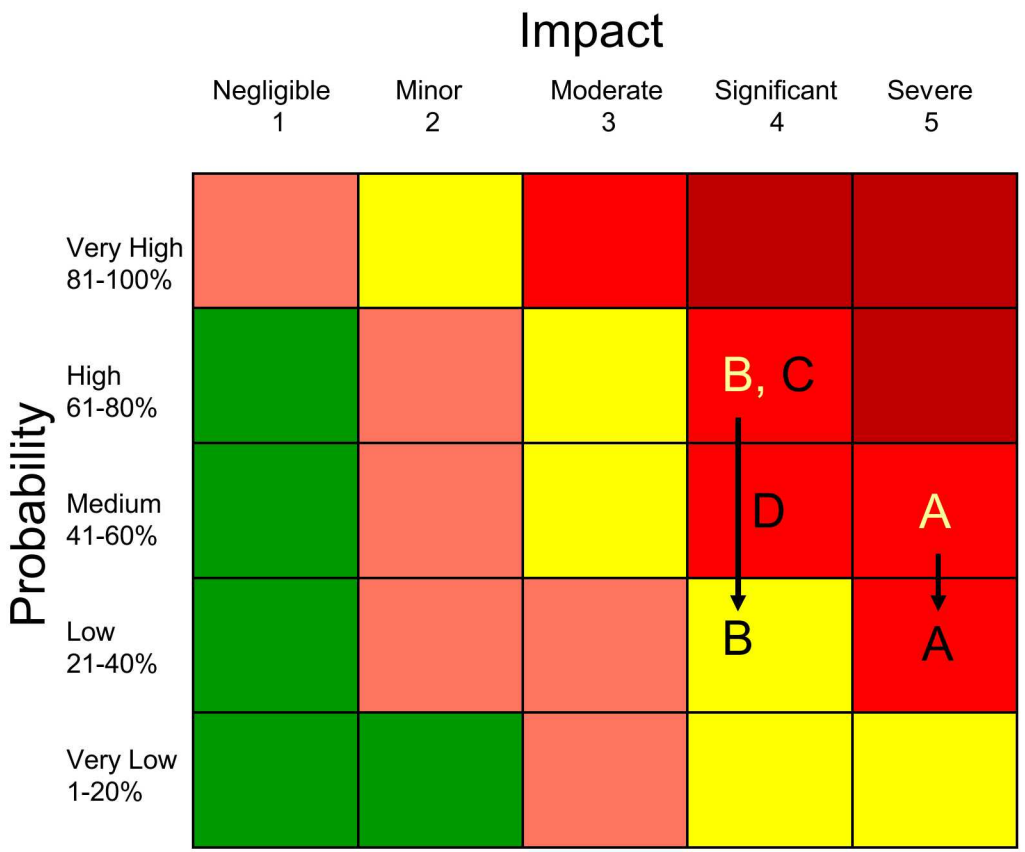
Challenges/Risks:

A. No stable direct dopant attachment chemistries

B. Low yield of dopants attached

C. Unable to remove ligands/impurities (C, O, etc.)

D. No clean Si capping process



Color key:
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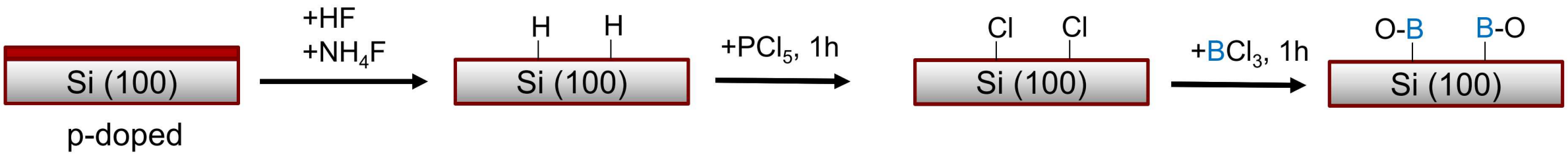
- Light Green – Low Risk
- Yellow – Moderate Risk
- Red – High Risk
- Dark Red – Extreme Risk

Demonstration of wet-chemical Si-B formation

w/U. Delaware and UMD/LPS

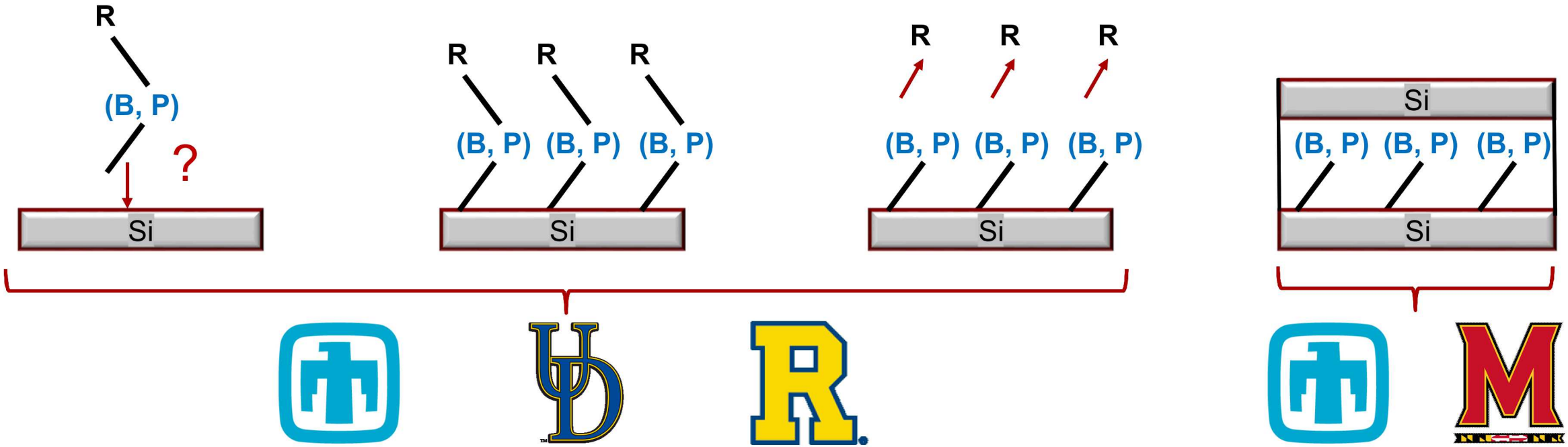


- **Showed direct Si-B formation possible by wet chemistry**
- B incorporation with high ~1-4x10^{14} cm^{-2} density
- Need to mitigate high C & O levels
- Selective to Cl-Si over H-Si – compatible with standard patterned H resist?
- **IMPACT/SYNERGIES -** Acceptor Doping Task: result leads to BCl_3 doping in UHV, other suitable precursors for UHV dosing may be discovered

FY20: Leverage external collaborators

Many scientific and technical challenges to overcome!

Discover direct dopant-Si wet chemistries → **Optimize for high density dopant attachment** → **Remove ligands & contaminants** → **Capping & electrical characterization**



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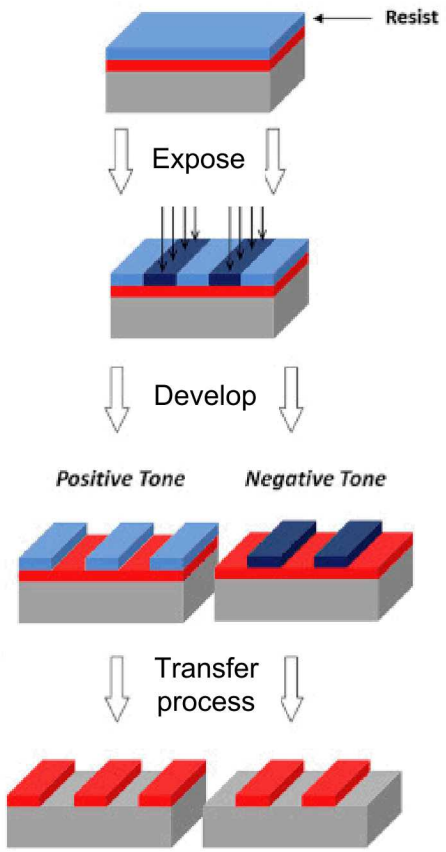
Backup & Previous EAB Slides

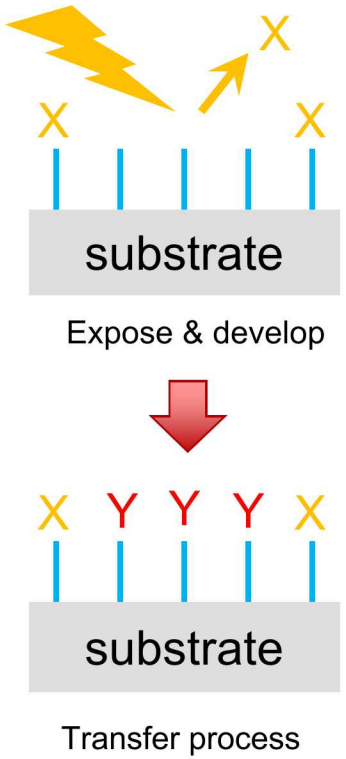
Atomic scale processing - opportunity



Traditional etch process

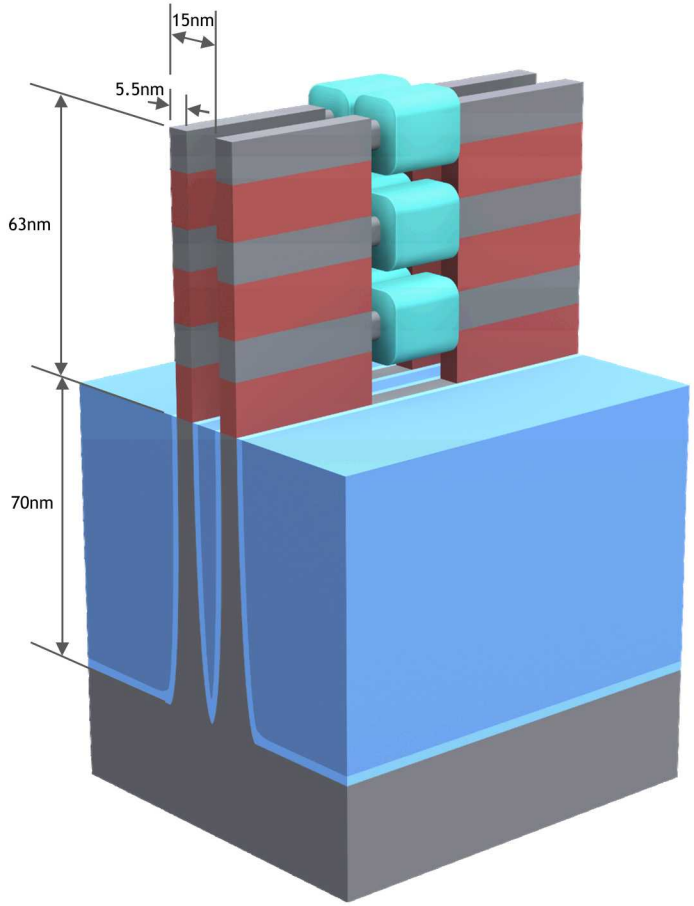
Scaling limitations

Unexplored, new phase space



Area selective chemistry

Obviate limitations?



R. Arghavani estimates

Parameters	I_{ON} (mA/μm) @ $V_{GS}=V_{DS}=0.7V$
Si FinFET (H_{FIN}=37nm)	0.630
1 NW GAA	0.286
2 NW GAA	0.525
3 NW GAA	0.576
Si FinFET (H_{FIN}=54nm)	0.690

Compare to APAM: over 2 mA/ μm (cryogenic)!

Produces material that defies expectation

Thrust 4 – milestones (backup slide)

- Photolithography Task (Lead: Katzenmeyer)
- Q1: Fabricate large area patterned sample via photodesorption of H with Hall density within 1/5 of a full-dose delta layer.
- Q2: Determine depassivation dose range and associated line edge roughness (via SMIM)
- Q3: Determine conductivity for 2 um wide photopatterned wire with new system
- Q4: Determine better mode for H photolithography (thermal vs. photodissociation) based on sheet resistance and line-edge roughness of P-doped regions

- Acceptor Doping (Lead: Bussmann)
- Q1: Performers demo APAM acceptor chemistries in-vacuum
- Q2: Demonstrate test chip for acceptor Hall bars with acceptor implant proxy, for both B and Al.
- Q3: Down-select to best acceptor precursor with >5e13 cm-2 carrier density and conductivity > 0.1 mS/sq.
- Q4: Implement down-selected process at Sandia

- Wet Chemistry Task (Lead: Wang)
- Q1: Show wet chemical acceptor and donor doping chemistries on H- and Cl- terminated Si
- Q2: N/A
- Q3: Go/no-go: Determine if wet chemistry doping processes can produce >5e13 cm-2 carrier density and conductivity > 0.1 mS/sq.
- Q4: Implement down-selected process at Sandiaa

FY19 – Stability of Halogen Resists

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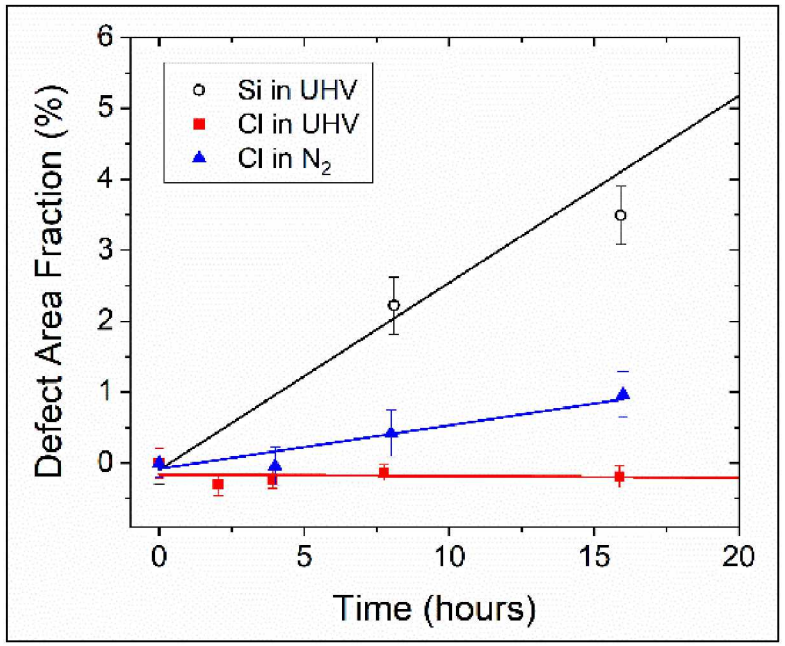
Back up slide

Stability in N_2 (STM)



- All halogen resists stable in N_2 for many hours
- Halogen resists show oxidation and carbon contamination in air
  - *Br is most stable, comparable to H resist(?)*