The Iodine and Methanol Passivation

Engineering and Basic ScienceApplications

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NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing

ESH Impact of Wafer Cleaning

- **Wafer cleaning, most frequently repeated cycle**

  30% of all processing steps

  25% of all processing time

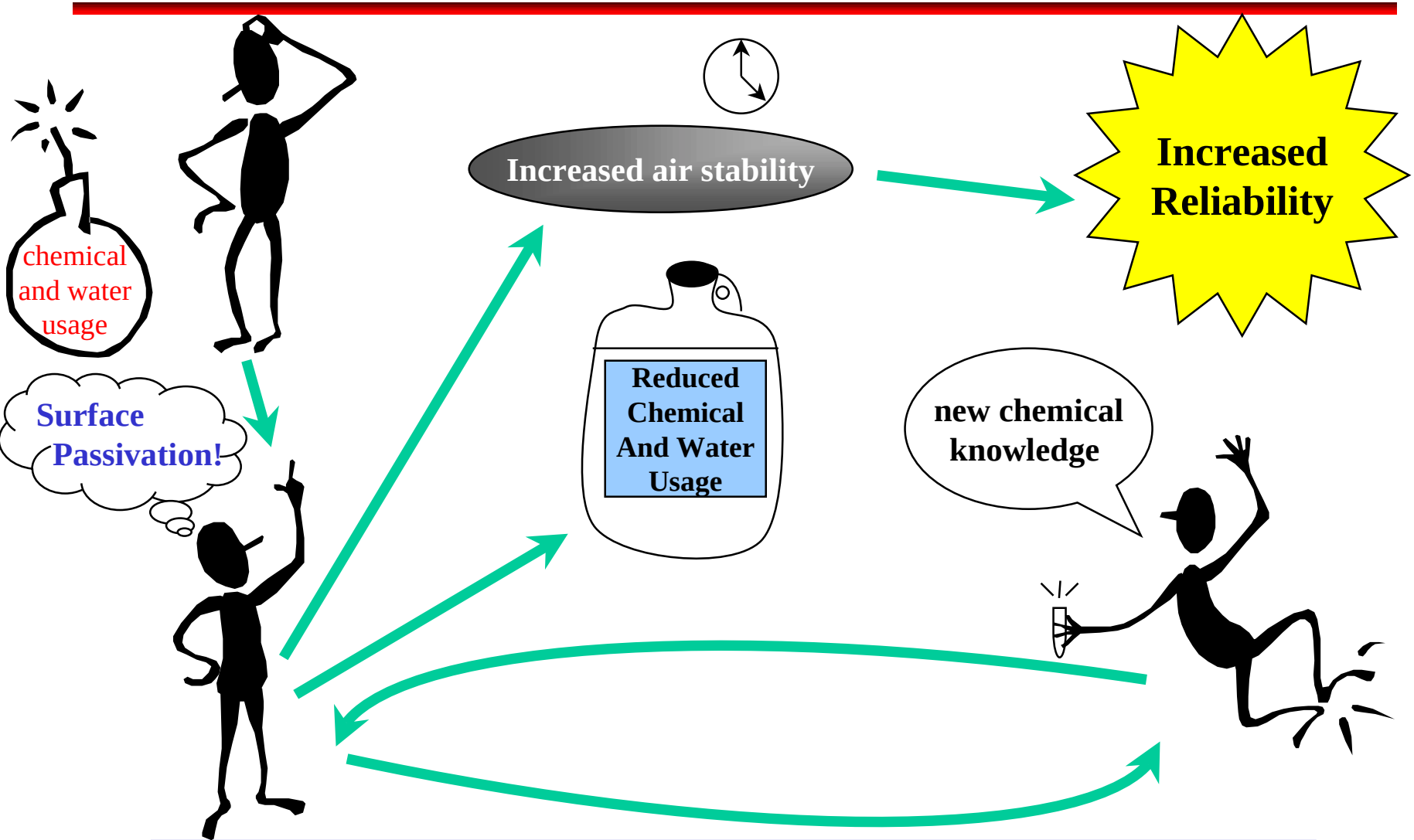
- **↓ cleaning steps =**
  - **↑ throughput**
  - **↓ waste generated**
  - **↓ chemical usage**
  - **↑ $ saved**

Goal:

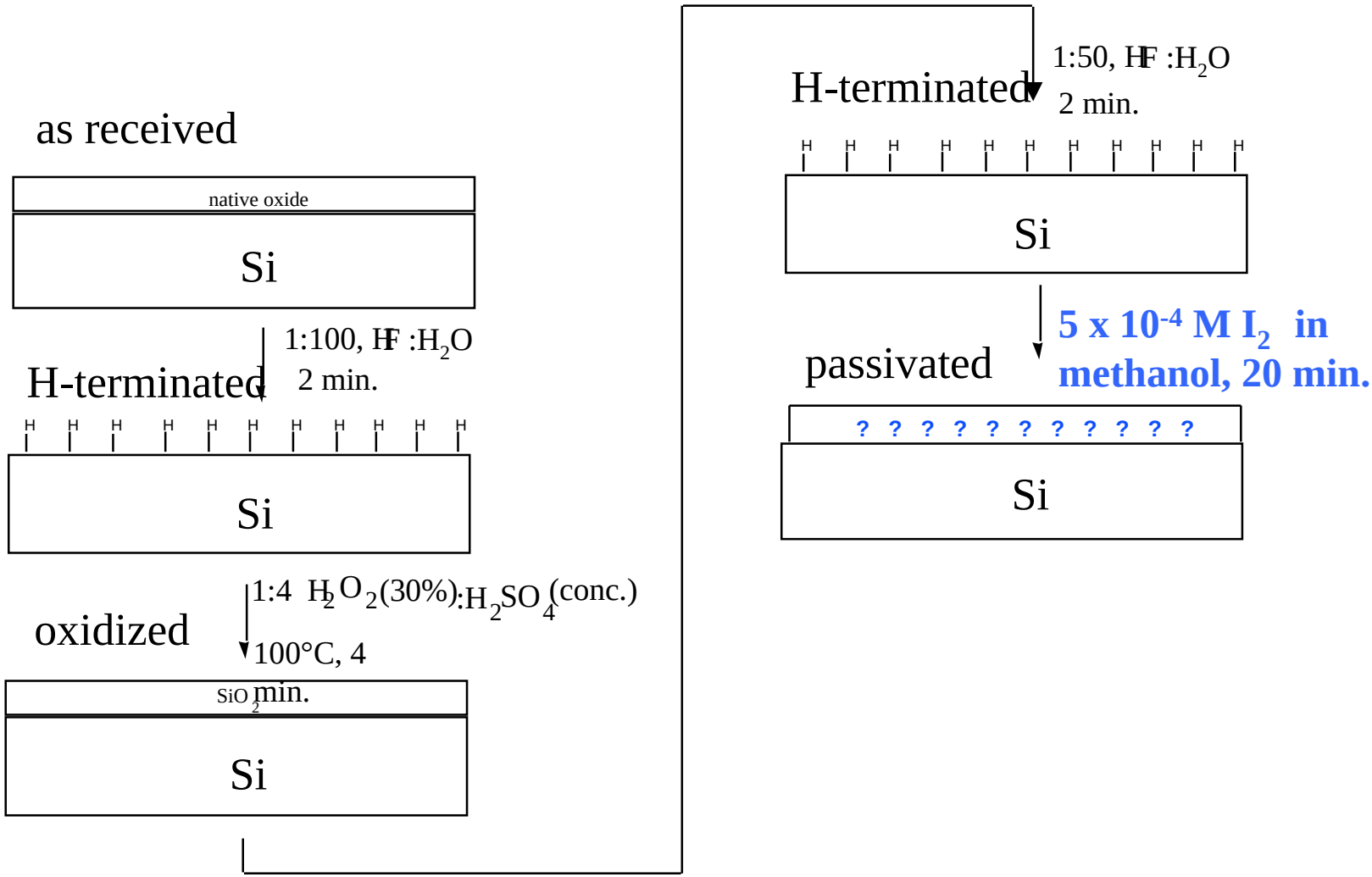
- **Avoid recleaning**
- **Well defined surface**

  → **Clean, reproducible replacement by next solid phase**

Our Strategic Plan



Passivation Method

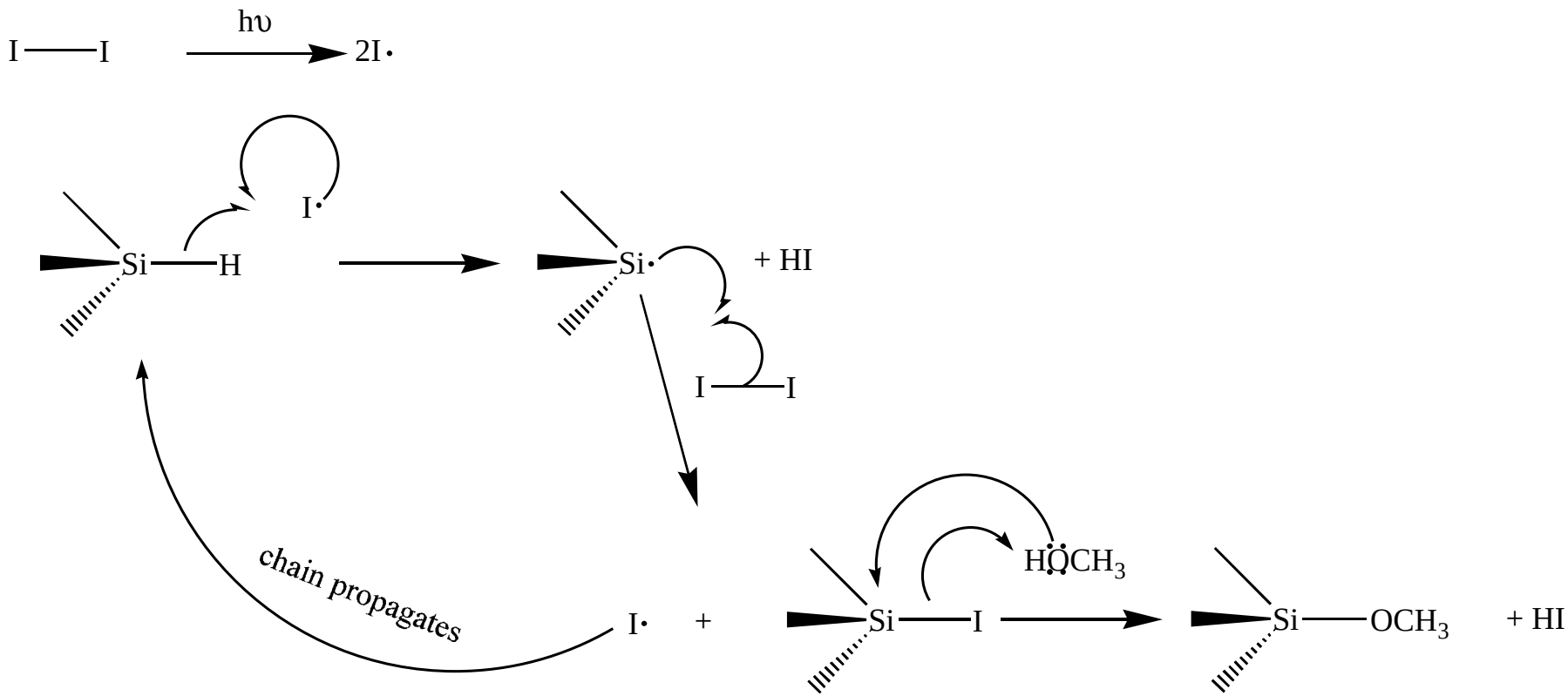


Effective Si Surface Passivation in I_2/Alcohol

Si(100) in:	Lifetime (ms)	Number of unpassivated sites
MeOH/I_2 (5×10^{-4} M)	8	4×10^{9} cm^{-2}
HF(1%)	0.9	4×10^{10} cm^{-2}
HF(49%)	5	7×10^{9} cm^{-2}

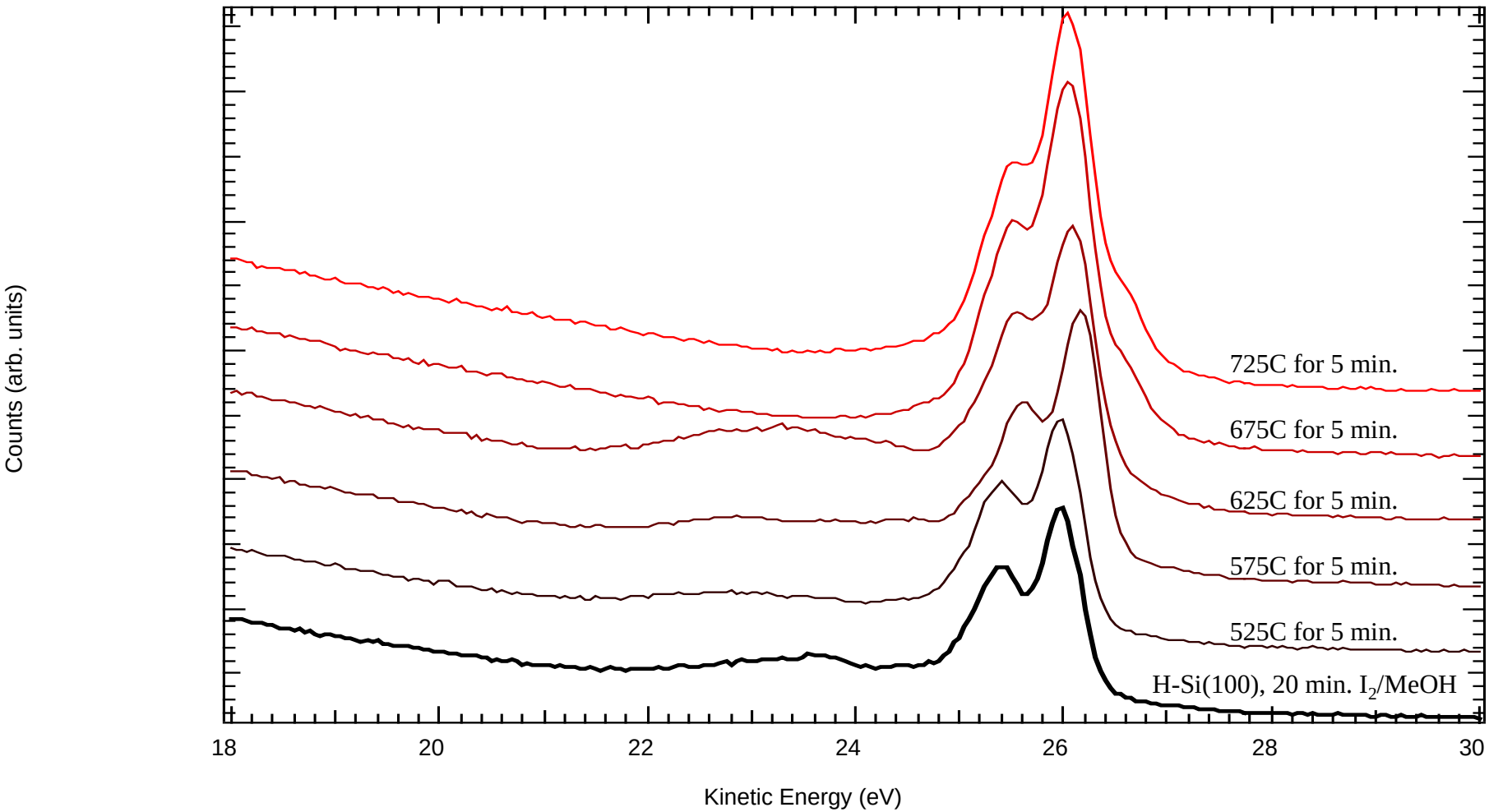
- Methanol/iodine increases the surface quality
- **Unpassivated sites decreased 10X** wrt dilute HF.
- Air stability is also increased.

Proposed Mechanism



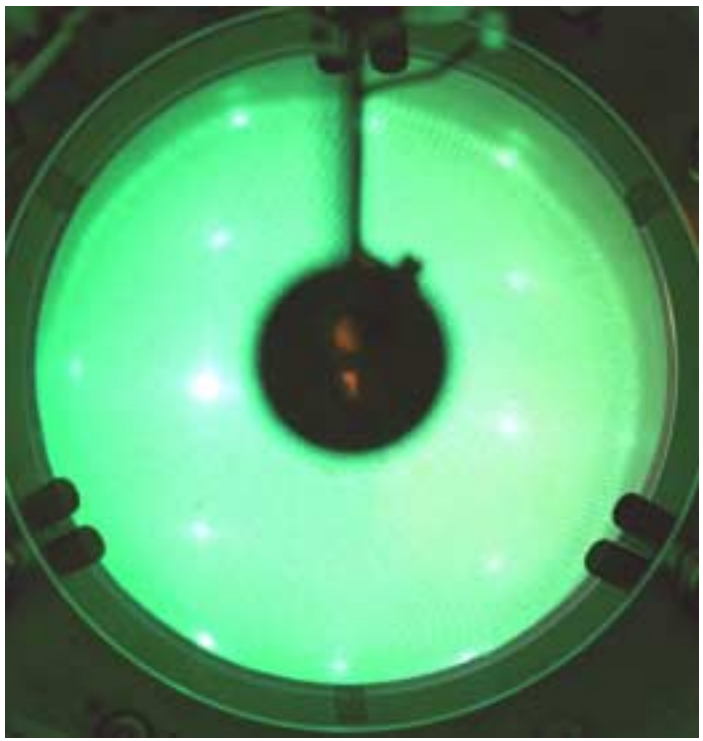
Si2p Core Level Photoelectron Spectra

Temperature Dependence



- Annealing eventually results in the clean Si(100) 2X1 reconstruction.

LEED

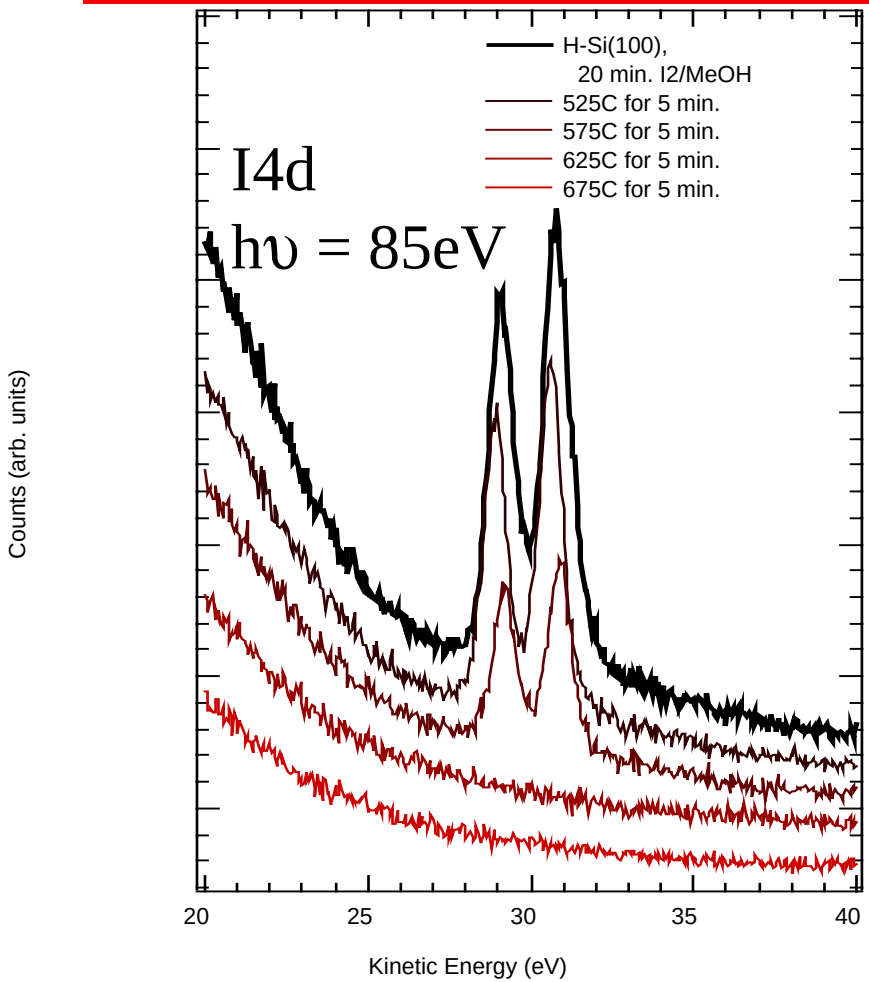


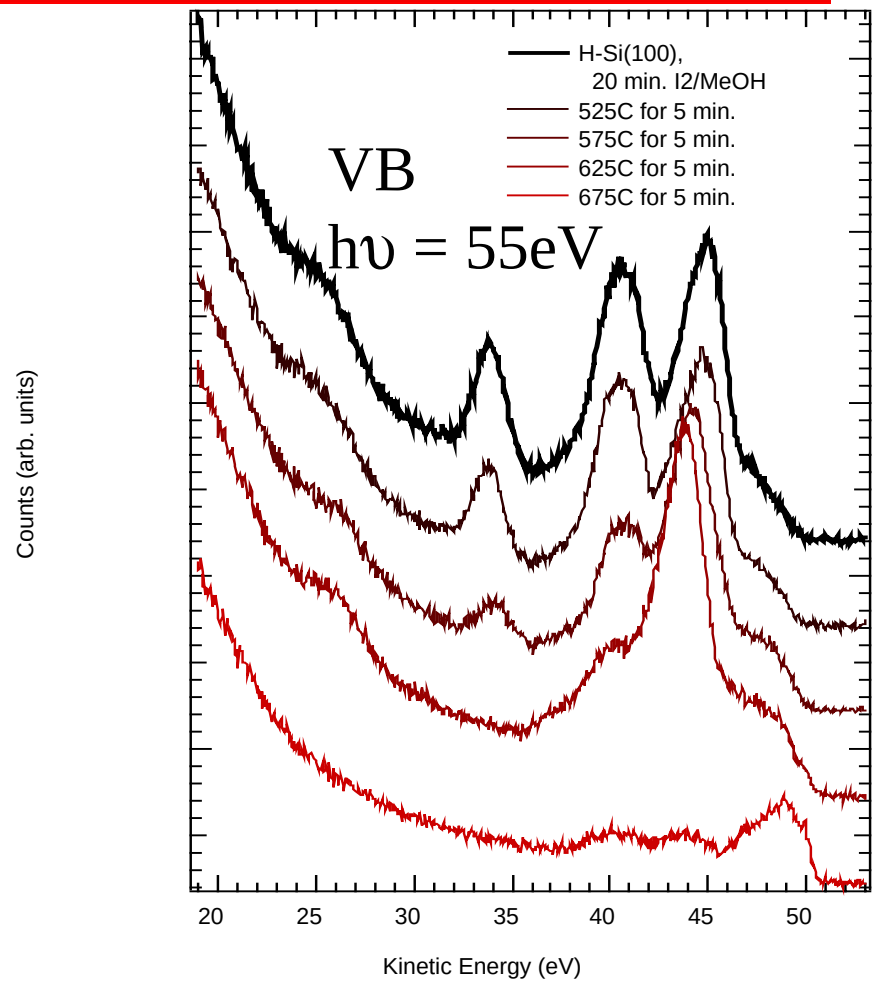
- 2X1 reconstruction after annealing to ~725C is confirmed by LEED.

I_B = 92.6 eV

Photoelectron Spectra

Temperature Dependence



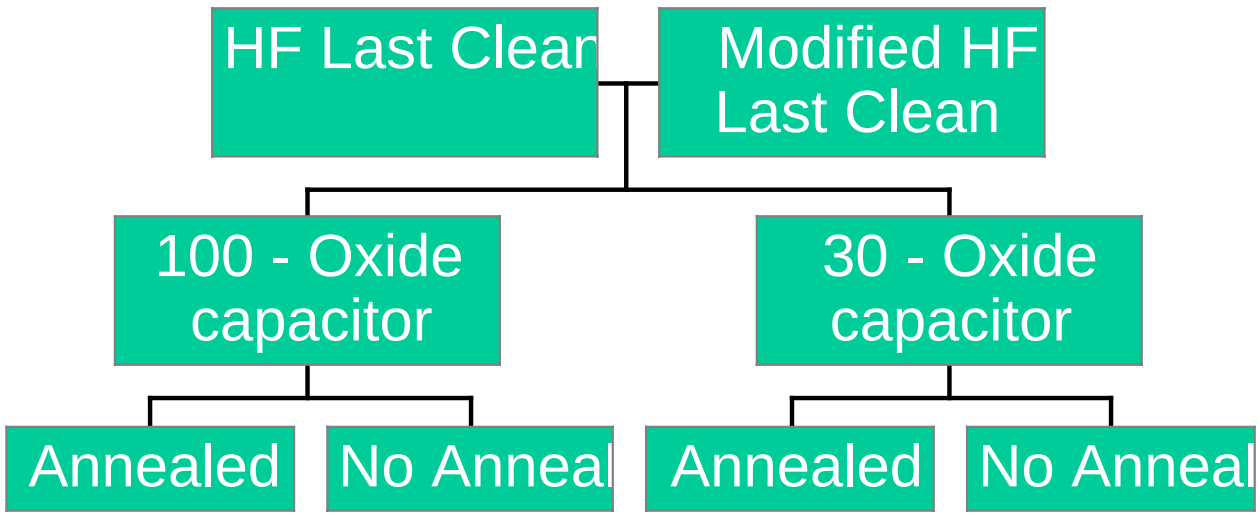


- Iodine disappears by 625C.
- C and O disappear by 675C.

Methoxy Termination Of Silicon During HF last Clean

- Experiments to characterize the integrity and robustness of a methoxy termination from an MOS device standpoint.
- Involves investigating a methoxy terminated surface in the presence of contaminants such as copper, and studying the Si/SiO_2 interface post passivation.
- Goal is to achieve ambient stability and electrical stability by using Methoxy termination in place of Hydrogen termination.

Electrical Stability: MOS Device Characterization



Surface Termination Post Wafer Cleaning

HF Last Clean

- H_2SO_4/H_2O_2 4:1 120C 10min **strip organics**
- DI water rinse
- HCl/ H_2O_2/H_2O 1:1:6 90C 10min **strip alkali ions and metals**
- DI water rinse
- HF/ H_2O 1:50 Room Temp 30sec **strip native and chemical oxides**
- DI water rinse
- Spin Dry

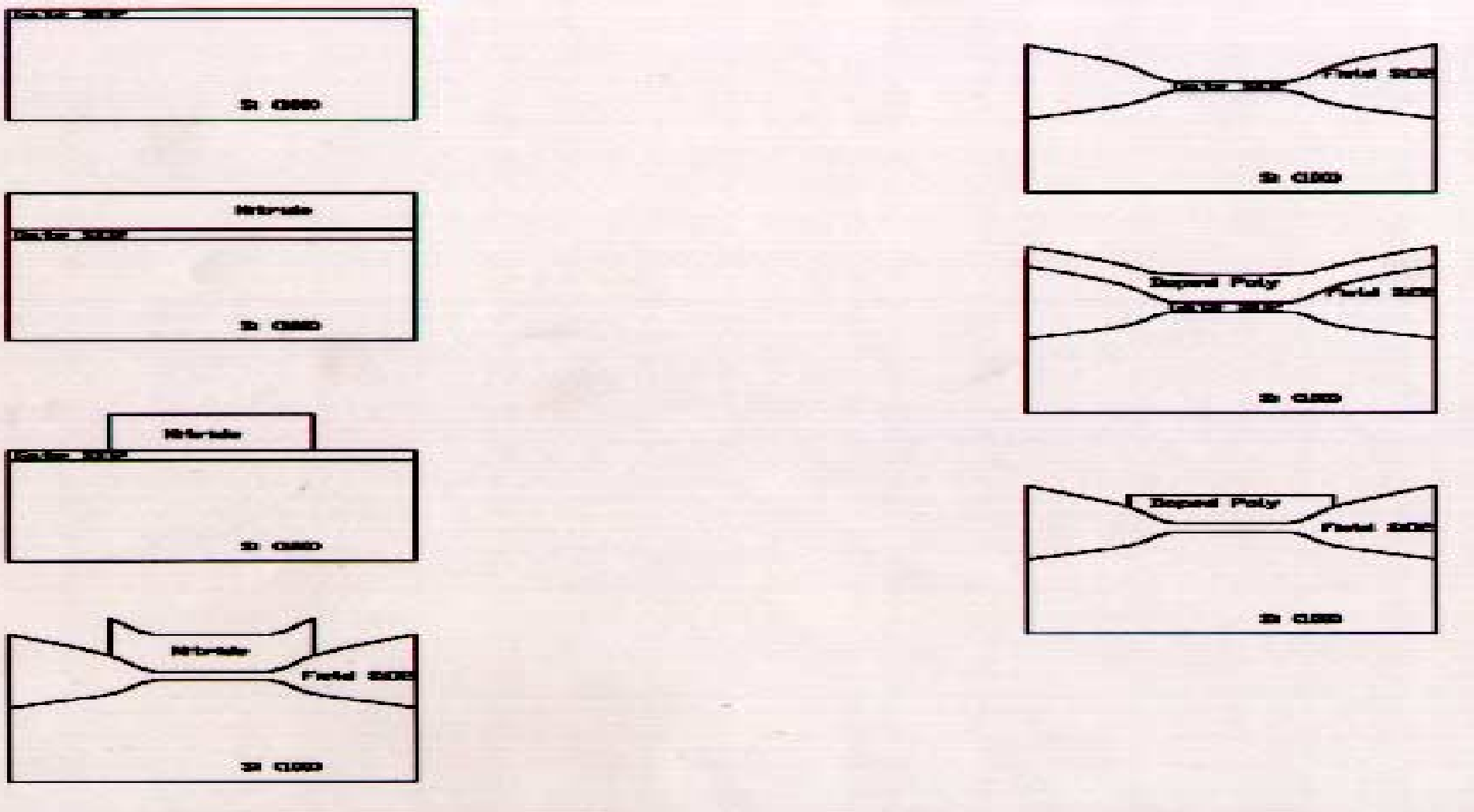
Hydrogen Termination

Modified HF Last Clean

- H_2SO_4/H_2O_2 4:1 120C 10min **strip organics**
- DI water rinse
- HCl/ H_2O_2/H_2O 1:1:6 90C 10min **strip alkali ions and metals**
- DI water rinse
- HF/ H_2O 1:50 Room Temp 30sec **strip native and chemical oxides**
- Methanol Rinse 2min
- Methanol/Iodine 1:2E-5
  Room Temp 20min
- N_2 blow dry

Methoxy Termination

LOCOS MOS Process Flow



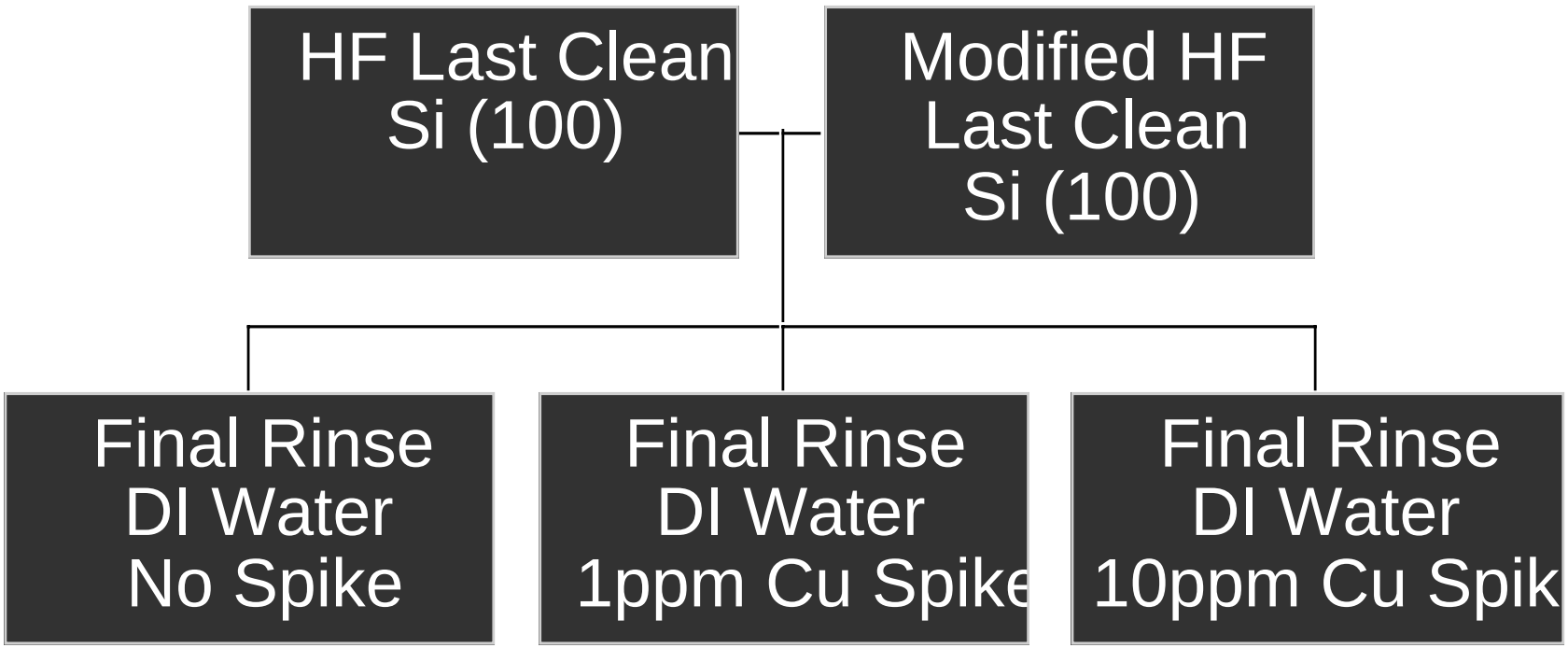
Current Status of Methoxy Project

- An experimental prediffusion clean & Device Fabrication process is established.
- 100 angstrom MOS capacitors are being Fabricated.
- Electrical stability of MOS capacitor structures, will be facilitated by an HP probe station for electrical measurements.
- Leakage Current, C-V measurements, time to breakdown, and breakdown voltages.

Electrical Reliability Measurements

- Will Perform Leakage Current, C-V , time to breakdown, and breakdown field measurements (TDDB).
- GOAL #1: Establish the Methoxy termination as a viable passivation via MOS electrical performance?
- GOAL #2: Potentially determine the Methoxy termination as a superior passivation?

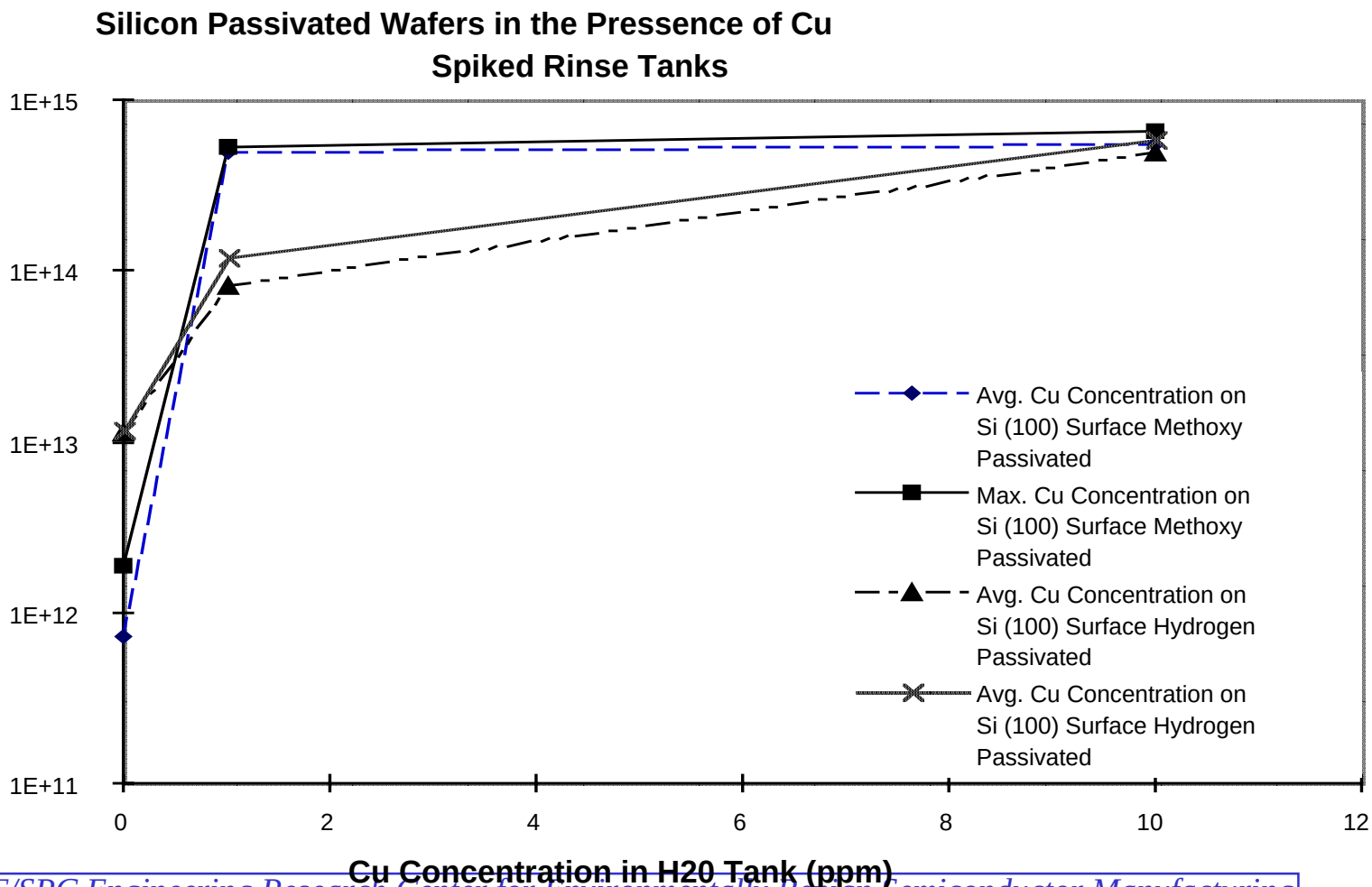
Ambient Stability: Susceptibility to Copper Deposition



Copper Surface Analysis Status

- Through collaboration with HP, TXRF was performed on all Cu spiked and control samples. TXRF is a surface sensitive analytical technique that quantifies amount of Cu on surfaces.

Preliminary Copper Spike Results



Conclusions

- For Lower Concentrations of Cu impurities, Methoxy termination shows an order of magnitude lower level of surface contamination.
- Shows promise of a more robust surface termination in a chemical ambient.
- GOAL #2: Potentially determine the Methoxy termination as a superior passivation?

Future Copper Work

- Need to reproduce this data, and do experiment from .1ppb to 100ppb Cu levels.

- Learn about the chemical bonding environment of Cu in the pressence of the Methoxy molecule through Angle Resolved XPS. Important in trying to achieve an impervious surface termination to impurities?

Gas-Phase Halogens as a Route to Better Surface Passivation

Objectives:

- Use iodine/methanol system as a model to explore analogous halogen/nucleophile systems for decreased environmental impact and more robust passivation

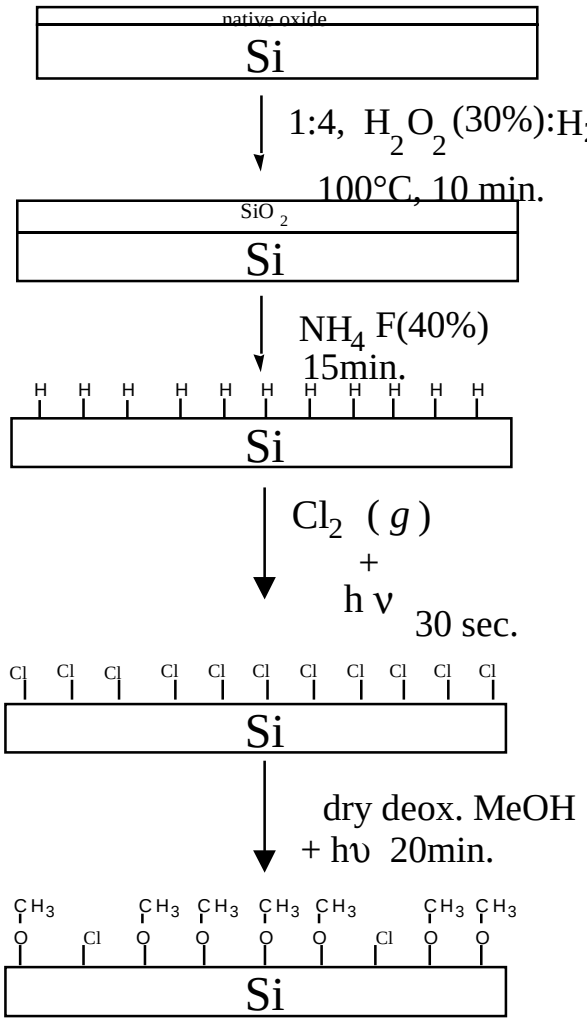
➡ higher efficiency nucleophilic substitution

➡ more aggressive halogens

➡ thermal activation

Aggressive Halogens

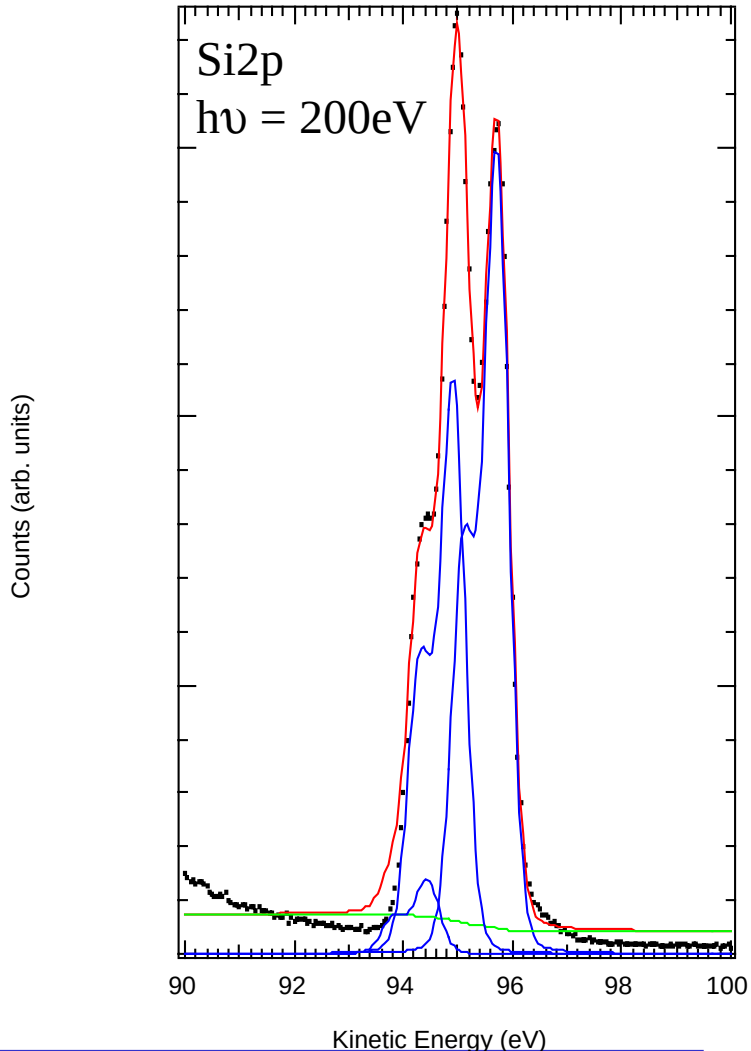
Monomethoxy-Termination of Si(111)



- Gas phase chlorination of H-Si(111)
- Dry, deoxygenated methanol(l) to chlorine-terminated surface

H-Si(111) + Cl_2(g) + hυ

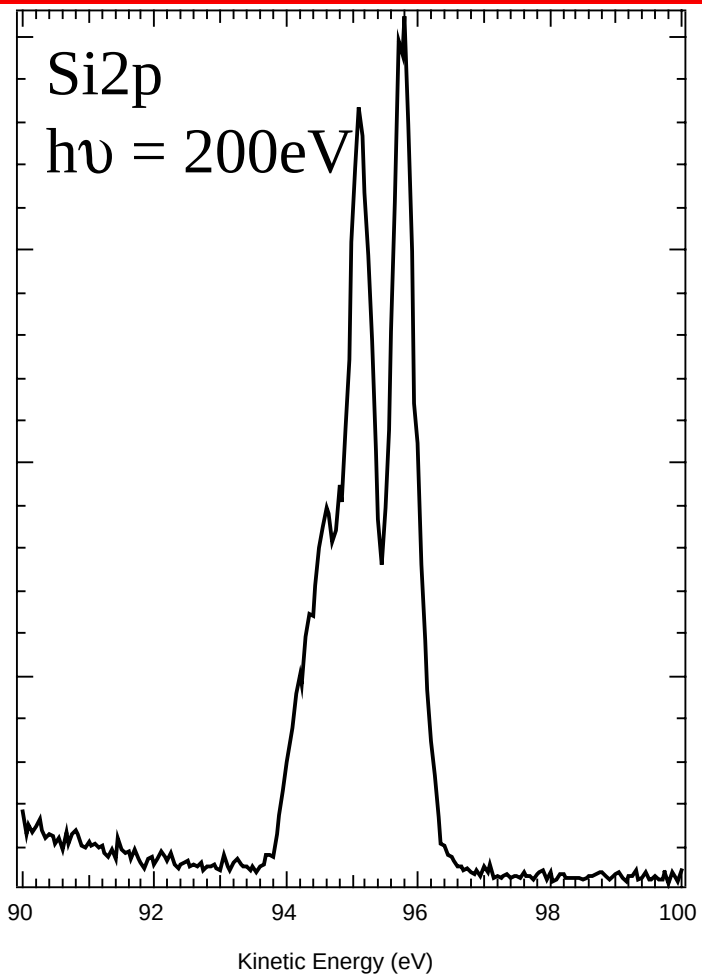
Peak	Kinetic Energy (eV)	Area	Coverage (ML)
B	95.71	12740	
S1	94.91	9107	1.47
S2	94.43	1179	0.17



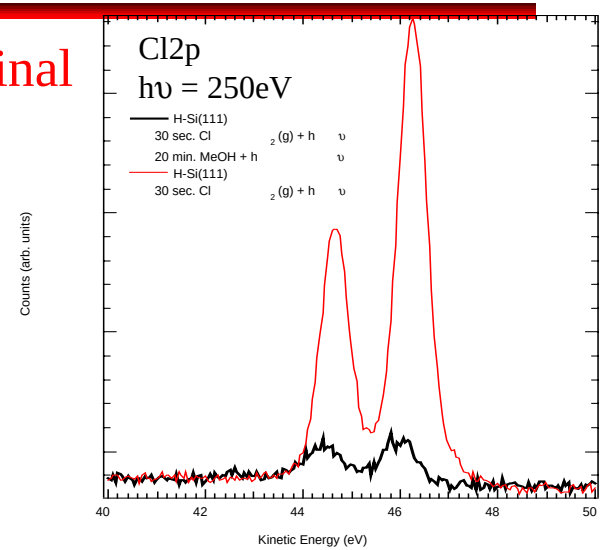
S2 peak could be due to miscut.

Photoelectron Spectra

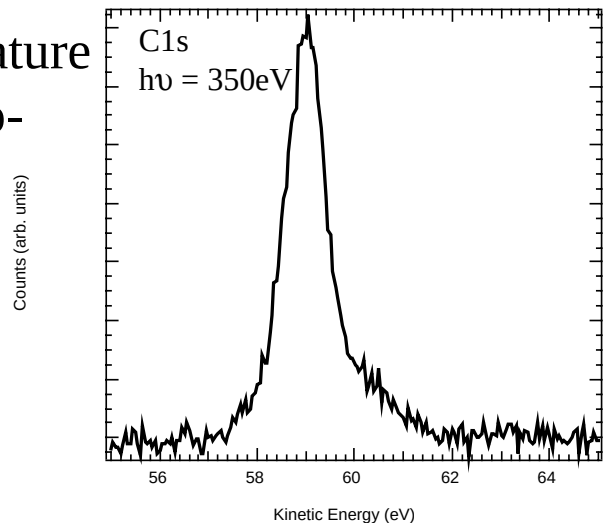
Monomethoxy-Termination of Si(111)



•~12% of original chlorine is left

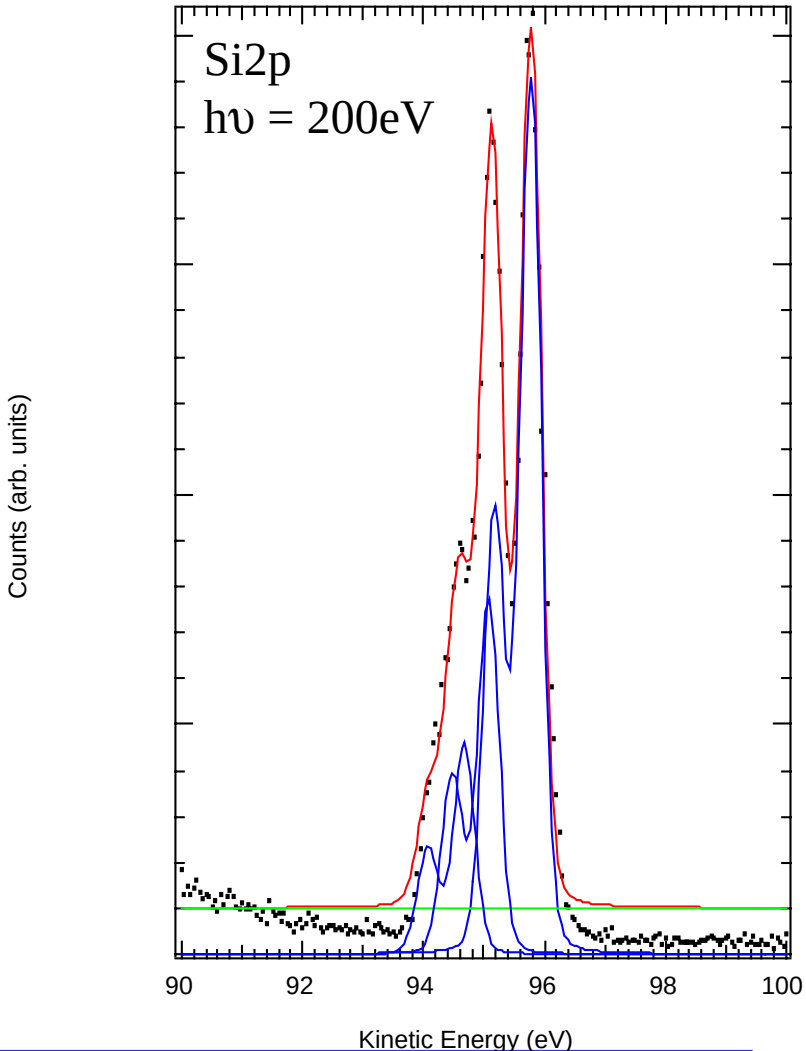


•Sharp C1s feature suggests mono-methoxy-termination.



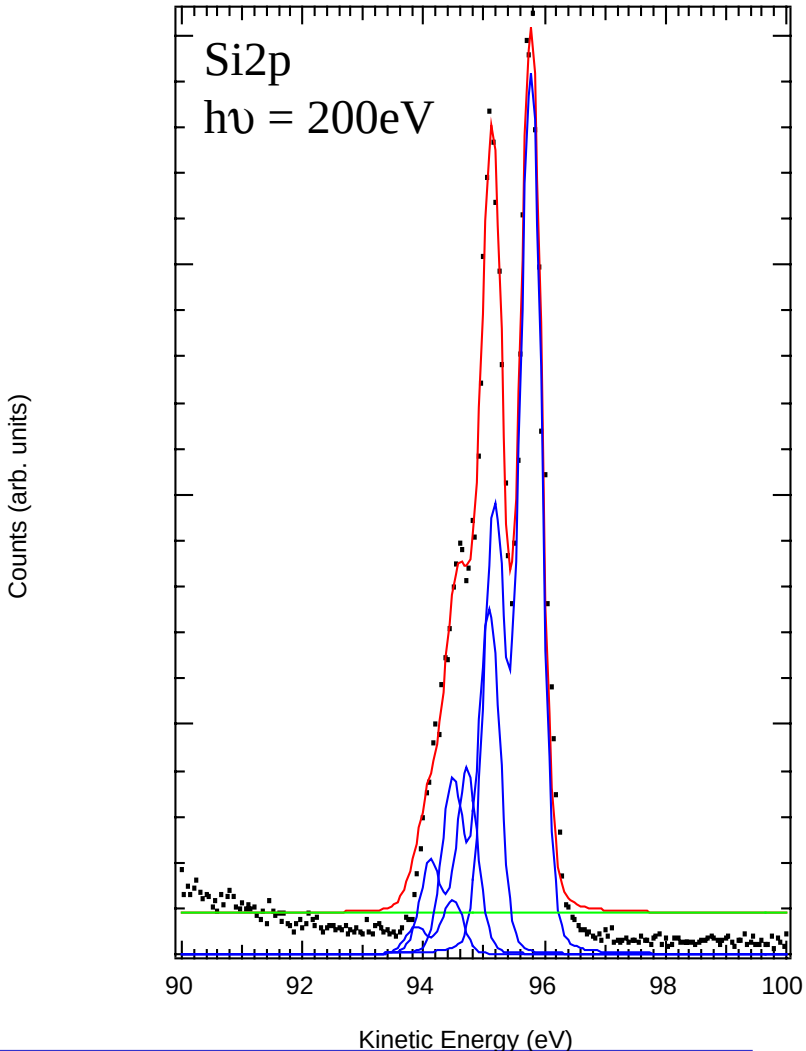
Monomethoxy-terminate Si(111)

Peak	Kinetic Energy (eV)	Area	Coverage (ML)
B	95.77	131160	
S1	95.07	5337	0.91
S2	94.67	3213	0.55



Monomethoxy-terminate Si(111)

Peak	Kinetic Energy (eV)	Area	Coverage (ML)
B	95.77	131156	
S1	95.08	5148	0.87
S2	94.72	2773	0.47
S3	94.48	810.7	0.13



Conclusion

- H-Si(111) exposed to Cl_2 (g), followed by methanol appears to form a monomethoxylated surface.
- This surface would be an ideal model surface for further structural investigations, as well as alternate nucleophilic substitution passivation schemes.
- Halogen-nucleophile systems require further analysis.

Future Work

- Investigate factors affecting monomethoxy-termination of Si(111) with 0.5^{o} miscut crystals(ie. exposure time, temperature dependence, methanol purity).
- Perform structural analysis of methoxy-terminated surface
  - ➡C and O K edge NEXAFS
  - ➡C and O Photoelectron Diffraction