Preparation of High Quality Si/SiO_2 Interfaces After Extended Exposure to Ambient Contamination Using Gas Phase Methoxy-Passivation

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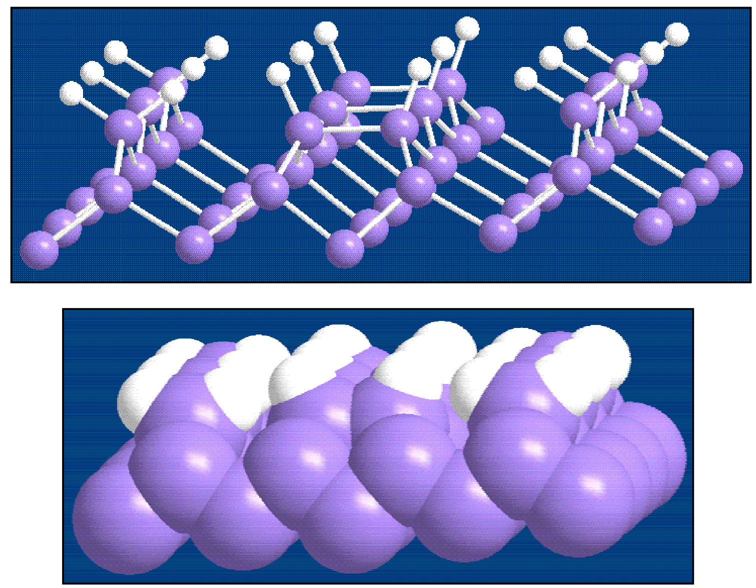
NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing Teleconference
April 21, 2005

Critical Manufacturing of Interfaces

- Pre-gate oxide wafer surface preparation is critical to IC fabrication
- Aqueous F-based chemistries used to terminate Si surface bonds with H
  - Protects against contamination and oxidation
  - < 2 hour staging times limit contamination
- Duplicate cleans to maintain yield
  - Cost in terms of water,chemicals, energy, and time
  - CD loss

http://www-mtl.mit.edu/6152j/sop/oxide.html



Si(100) 3x1 Rearrangement

Environmental Impact

- A fab uses millions of gallons of water a day
- 1 chip = 10 gallons of water
- Wafer cleaning ~25% of the total water usage

Gas phase processing can improve material usage efficiency by 10-100 times

- Electrical power use
  - House uses 1-2 W/ft^2
  - Office Building uses 6-10 W/ft^2
  - Factory uses 20-50 W/ft^2
  - Fab uses 350-375 W/ft^2
    - Air handling ~13% of total

- Decreasing filter requirement from Class 1 would provide savings

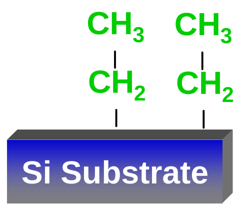
	Electricity Savings
Class 10	25%
Class 100	50%
Class 10,000 w/ mini environments	75%

* Peak electricity numbers, average demand would be ~70% of the listed value.

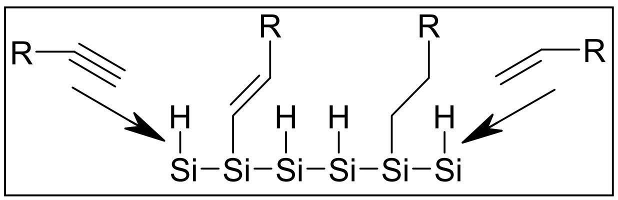
Surface Passivation Strategies

Organic Surface Passivation of Silicon

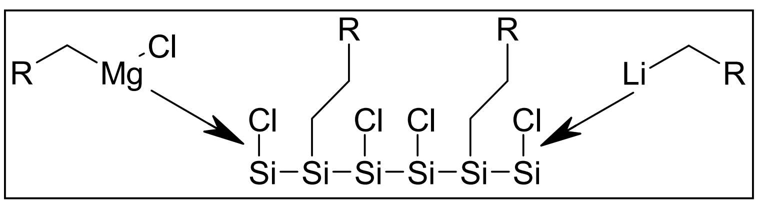
Alkyl Termination



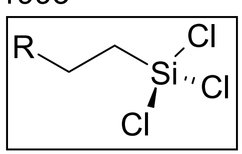
- Alkene and alkyne addition
  - Buriak, *J. Am. Chem. Soc.*, (121) 1999



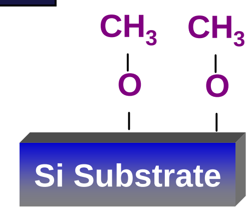
- Alkyl-Grignard & alkyl-lithium reagents
  - Bansal, *J. Phys. Chem. B*, (105) 2001



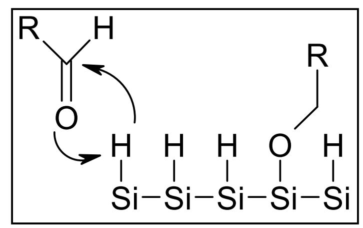
- Pyrolysis of diacyl peroxides
  - Linford, *J. Am. Chem. Soc.*, (115) 1993
- Alkylhalosilane SAMs
  - Chen, *Chem. Mater., (17) 2005*



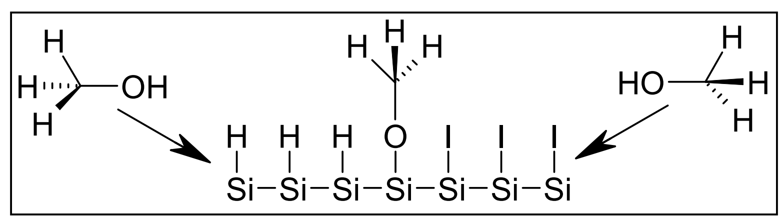
Alkoxy Termination



- Aldehyde addition
  - Boukherroub, *Langmuir,* (16) 2000
  - Effenberger, *Angew. Chem. Int. Ed.*, 37(18) 1998

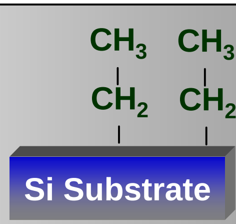


- Alcohol substitution
  - Boukherroub, *Langmuir,* (16) 2000
  - Haber, *J. Phys. Chem. B,* (104) 2000
  - Mo, *ECS Proceedings,* (99-36) 1999



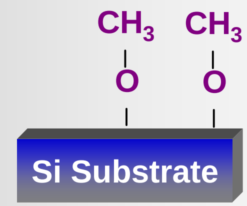
Surface Passivation Strategies

Alkyl Termination



- Si-C linkage is more stable than Si-O-C

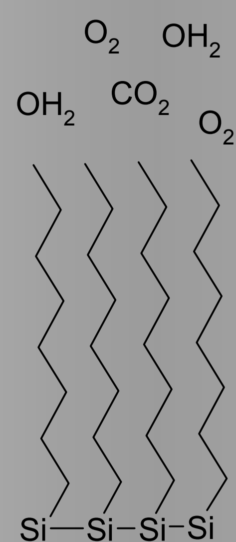
Alkoxy Termination



- Si-O-C bond is less likely to result in silicon carbide formation upon heating

Short Chain

- Smaller physical barrier to reaction
- Higher volatility components
  - –Gas phase synthesis
  - –Gas phase thermal desorption

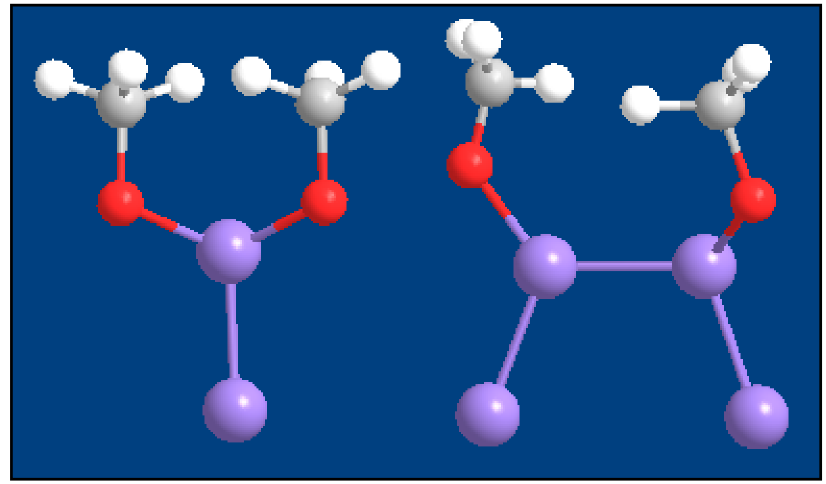


Long Chain

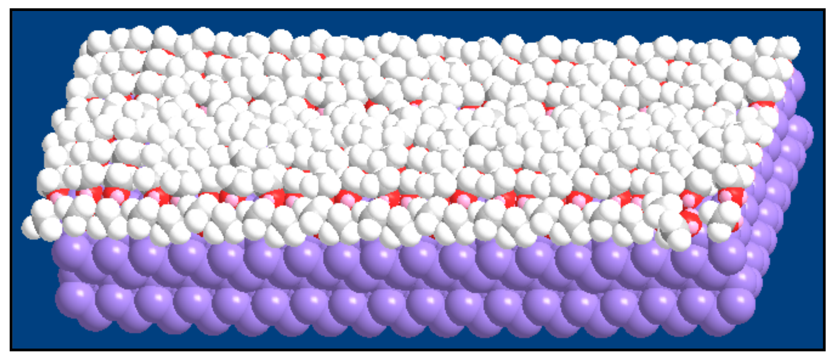
- Large physical barrier to reaction
- Low volatility
  - –Liquid phase synthesis
  - –Difficulties in removing layer

Methoxy Termination

- Rationale for alternatives
  - H presents poor steric barrier to Si surface atoms



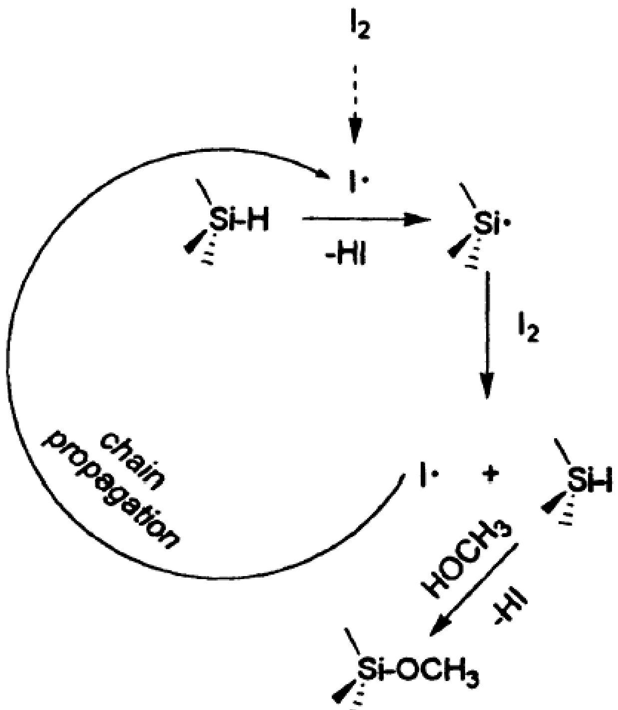
- Methoxy ($-OCH_3$) acts like an “umbrella” and provides a better steric barrier for Si surface atoms



- Methoxy passivation demonstrated using liquid solutions
- Develop gas phase process
  - Decrease water/chemical usage
  - Compatible with current IC processing technology (clustered reactors)

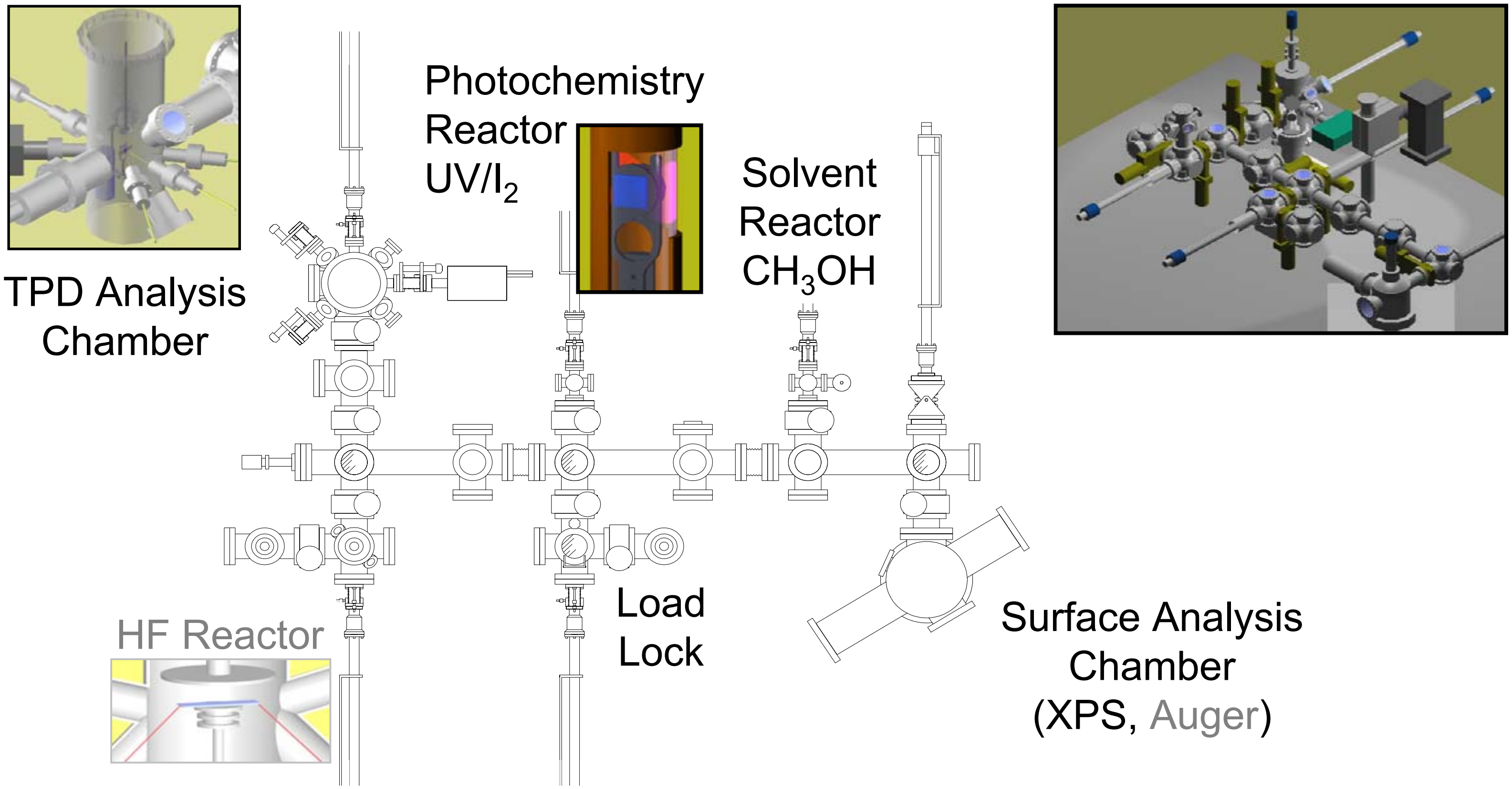
Reactions of Methanol with Silicon

- Thermal reaction of MeOH with Si is slow
  - Reaction occurs first on defects and step edges
    - Most reactive sites
- Higher coverages achieved through oxidative activation
  - Iodine activation
- Conversion to gas phase
  - Light activated iodine adsorption
  - Methanol substitution reaction
- Goal: to increase methoxy coverage and improve surface passivation



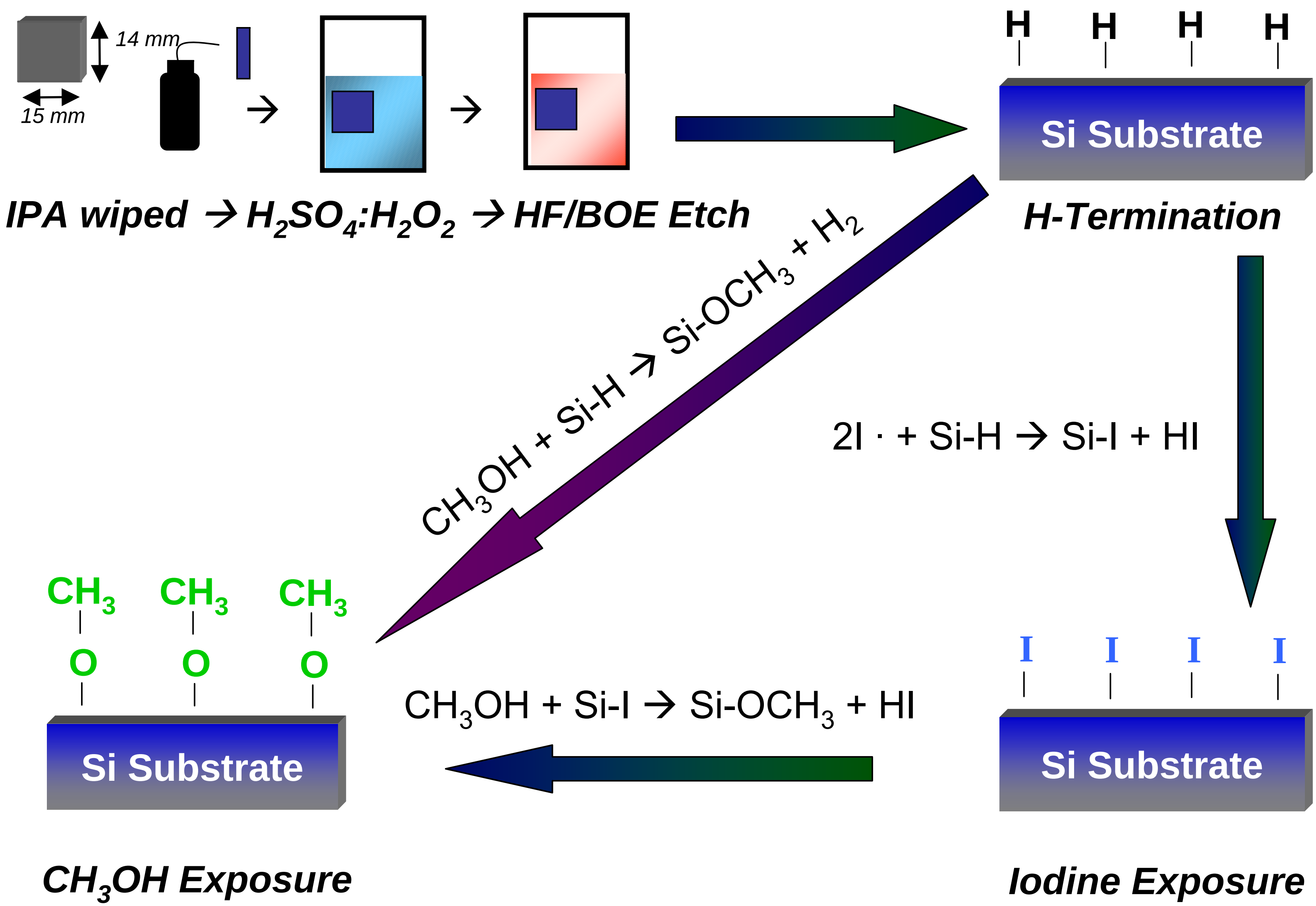
Mo, Burr, and Chidsey et. Al. *Atomic-Scale Mechanistic Study of Iodine/ Alcohol Passivated Si(100).* Electrochemical Society Proceedings Vol. 99-36

Clustered Reactor Apparatus

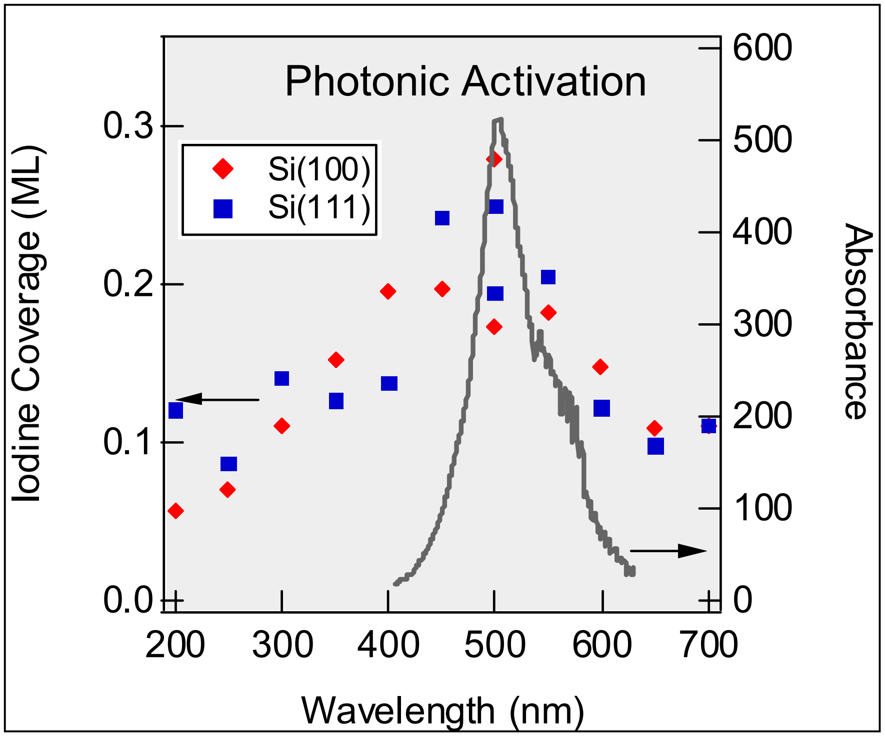


- A vacuum cluster tool provides a clean environment for multi-step processing
- Improved surface passivation can protect the substrate upon removal from the system

Surface Preparation Procedure



Iodine Termination



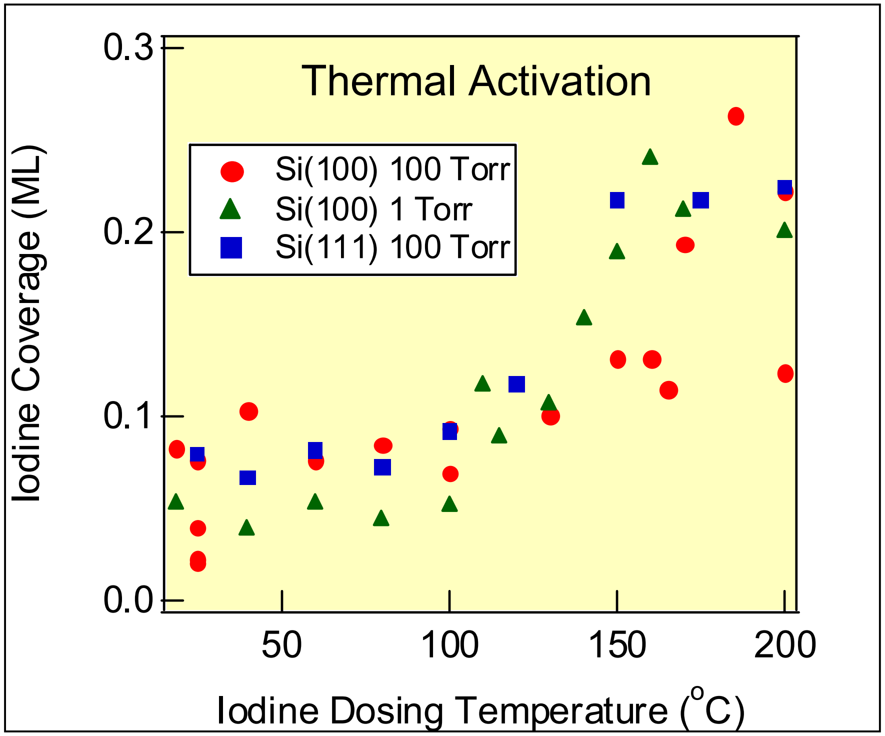
- Tunable iodine coverage
  - 0.05 – 0.28 ML range
- No significant pressure effects
- No significant surface effects

Proposed light-induced mechanism:

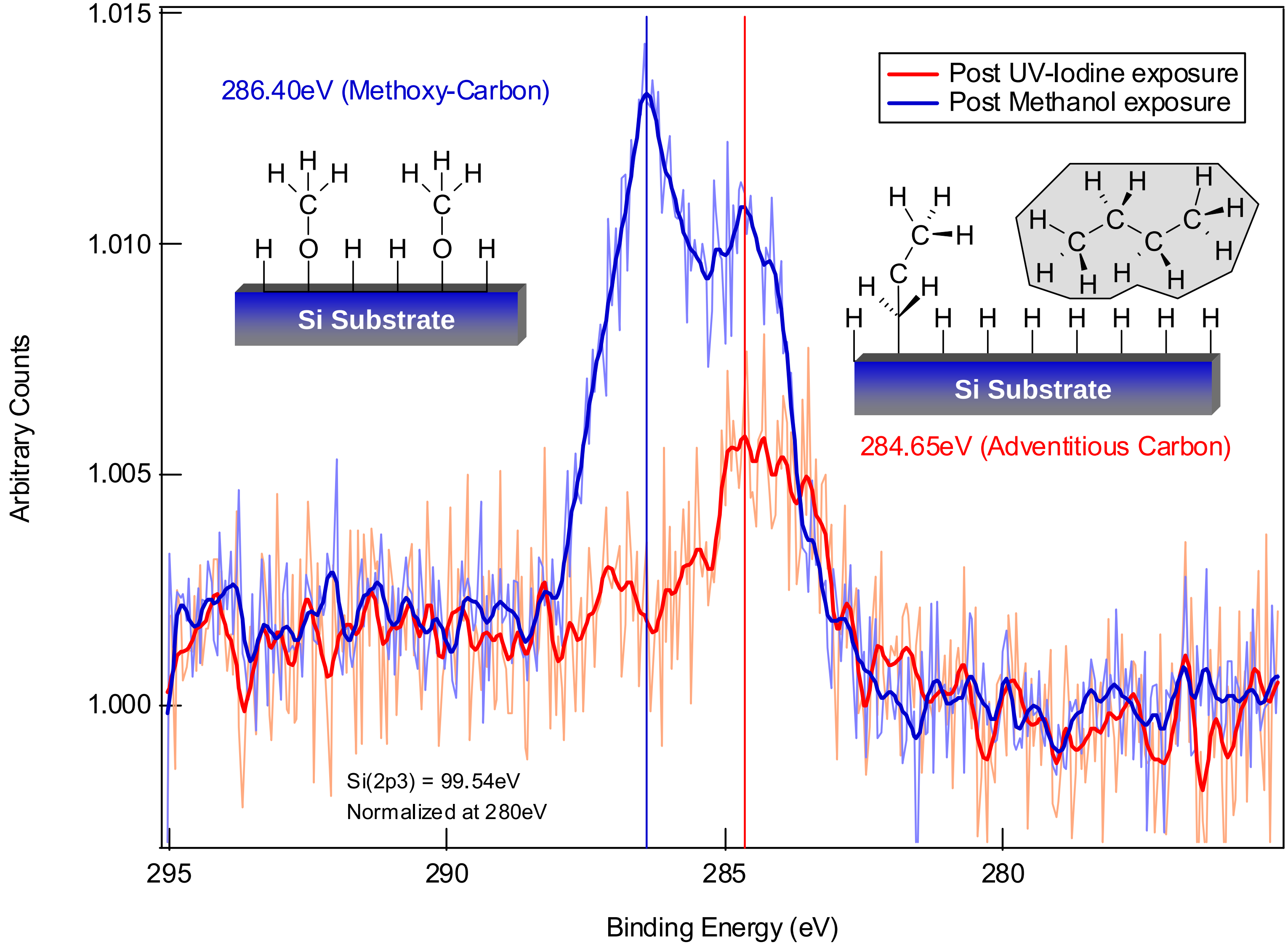
$$I_2 + h\nu \leftrightarrow 2I\cdot$$

$$I\cdot + Si\text{-}H \longrightarrow Si\cdot + HI$$

$$I\cdot + Si\cdot \longrightarrow Si\text{-}I$$



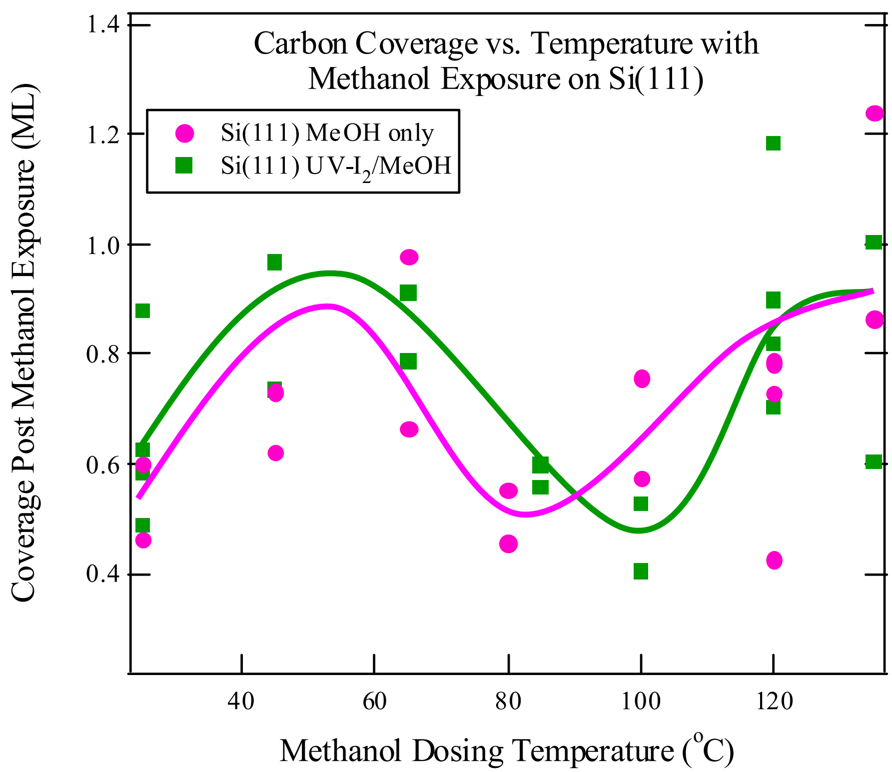
Methoxy Termination

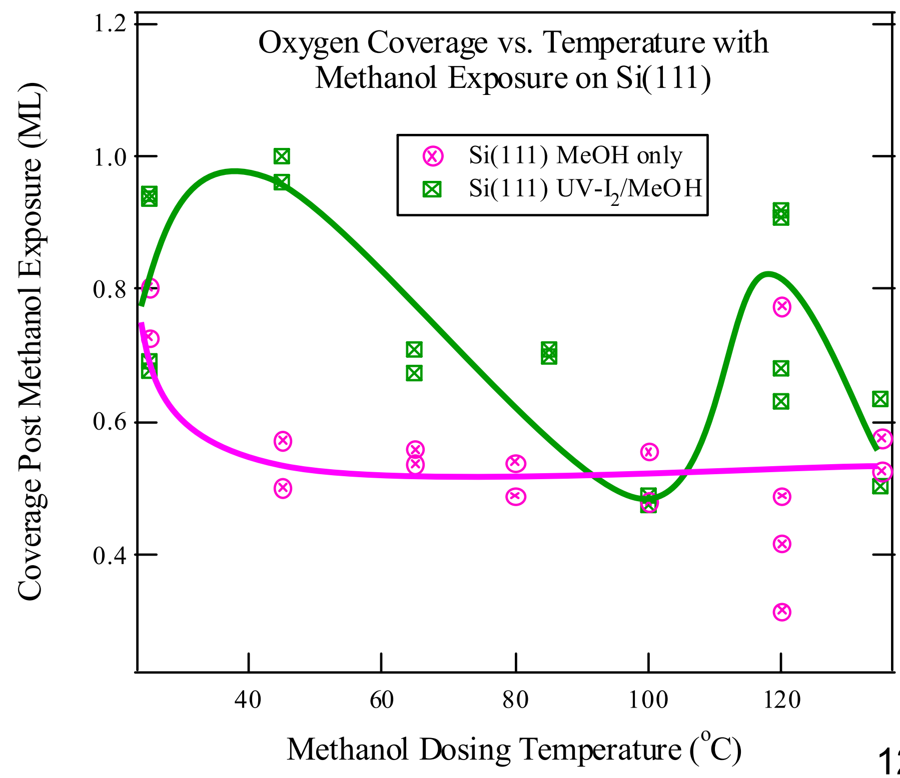


- Methoxy termination detected via a shift in the C(1s) peak of the XPS spectrum

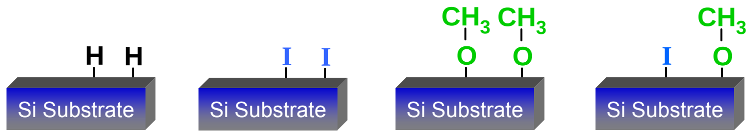
Methoxy Termination

- Parametric investigation
  - T_{MeOH} (25 -135°C)
  - P_{MeOH} (12.5 - 50 Torr)
  - Iodine coverage (0.05 – 0.30 ML)
  - Si(100) and Si(111)
- Maximum methoxy coverage
  - UV-I_2 prepared surface
  - MeOH exposure of 45-65°C or 120°C
  - No difference in crystal face



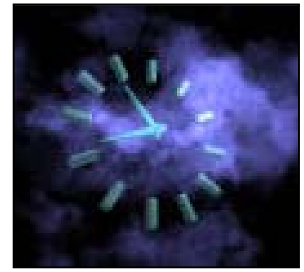


Electrical Testing Procedure



Aging

Exposure to Ambient



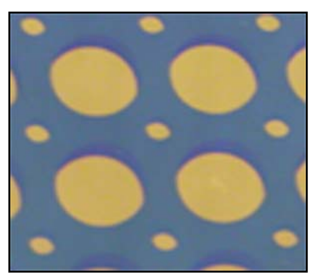
Desorption of passivation layer

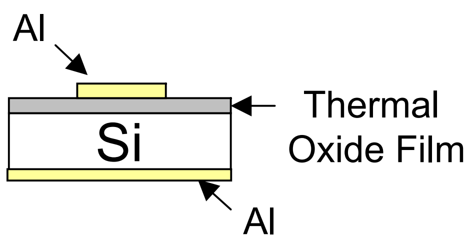
Growth of dielectric layer

Thermal Oxidation (1000 K)

Build capacitor structure

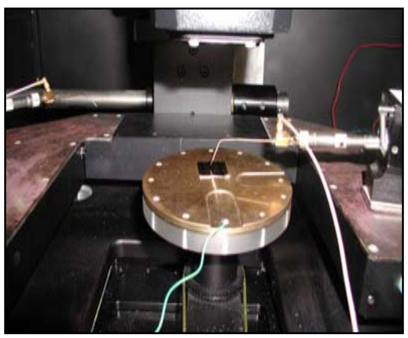
Al Electrode Deposition



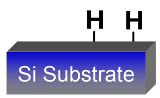


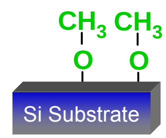
Interface and device quality test

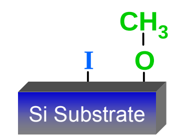
Electrical Testing



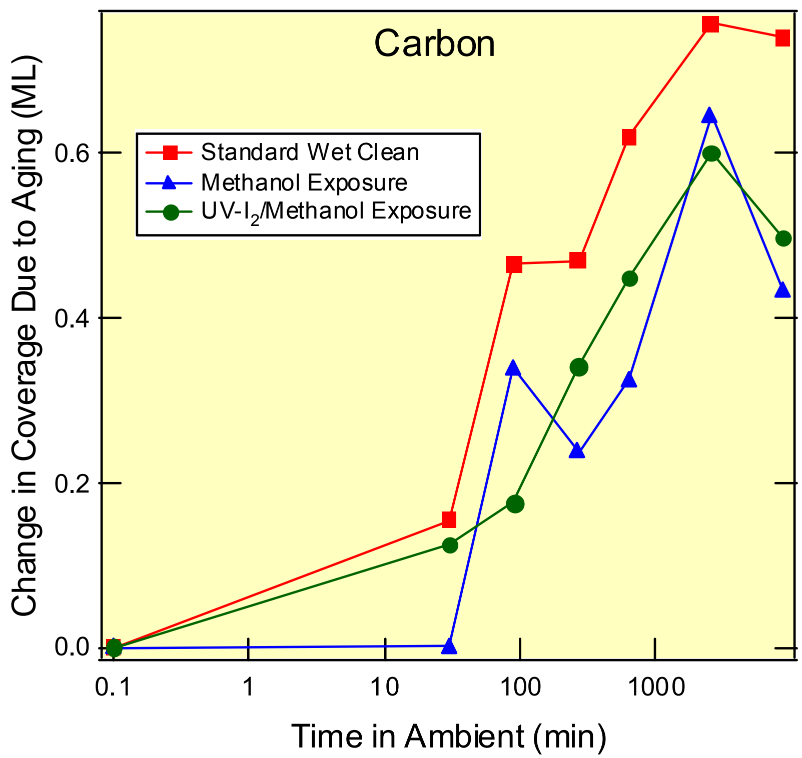
Aging Experiments

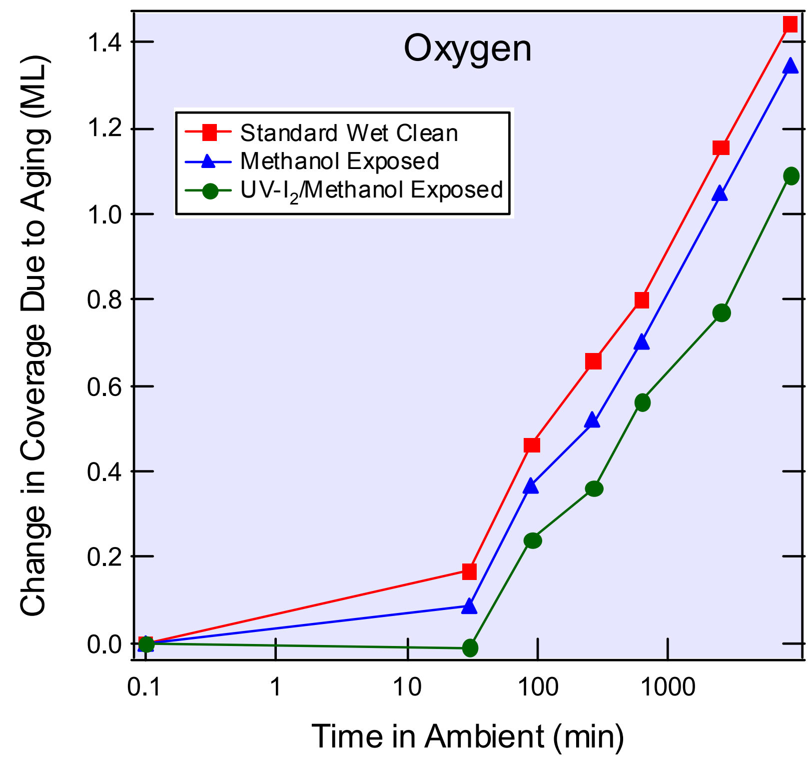






Standard Wet Clean < Methanol Exposure < UV-I_2/Methanol Exposure

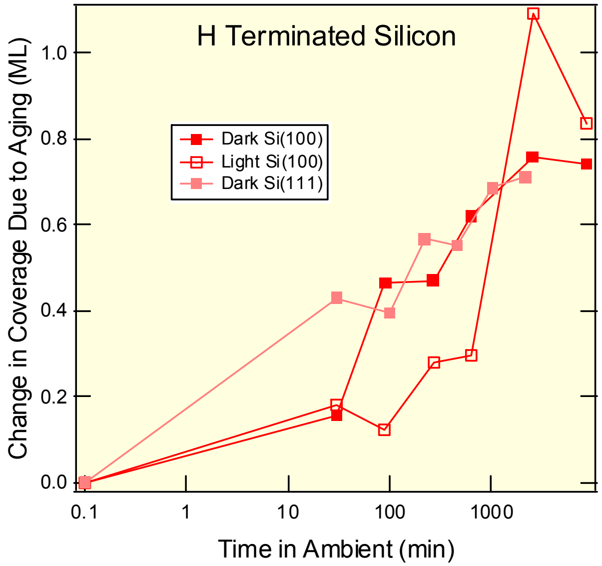




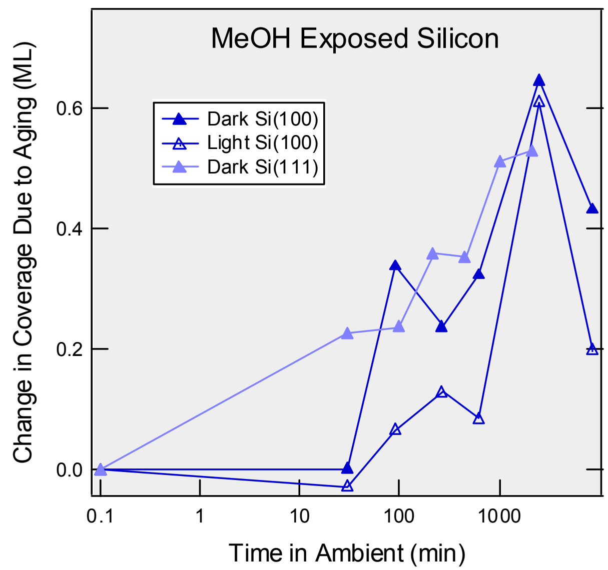
- 30-60% reduction in C

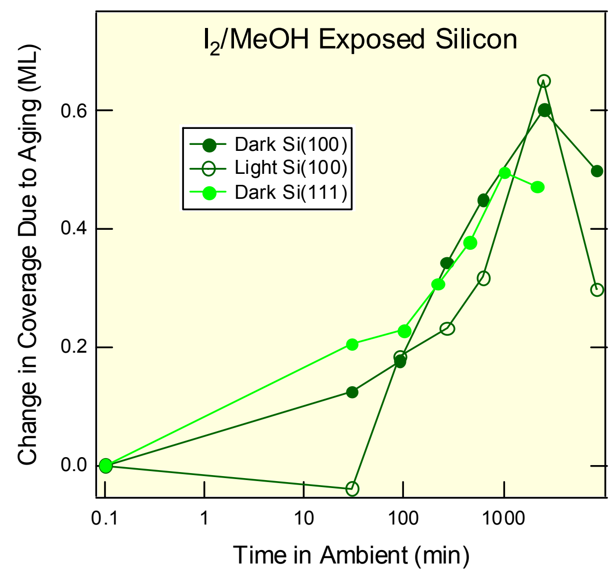
- 50-70% less oxidation within 10 hours
- 10-35% less oxidation after 10 days

Aging Experiments – Carbon Coverage



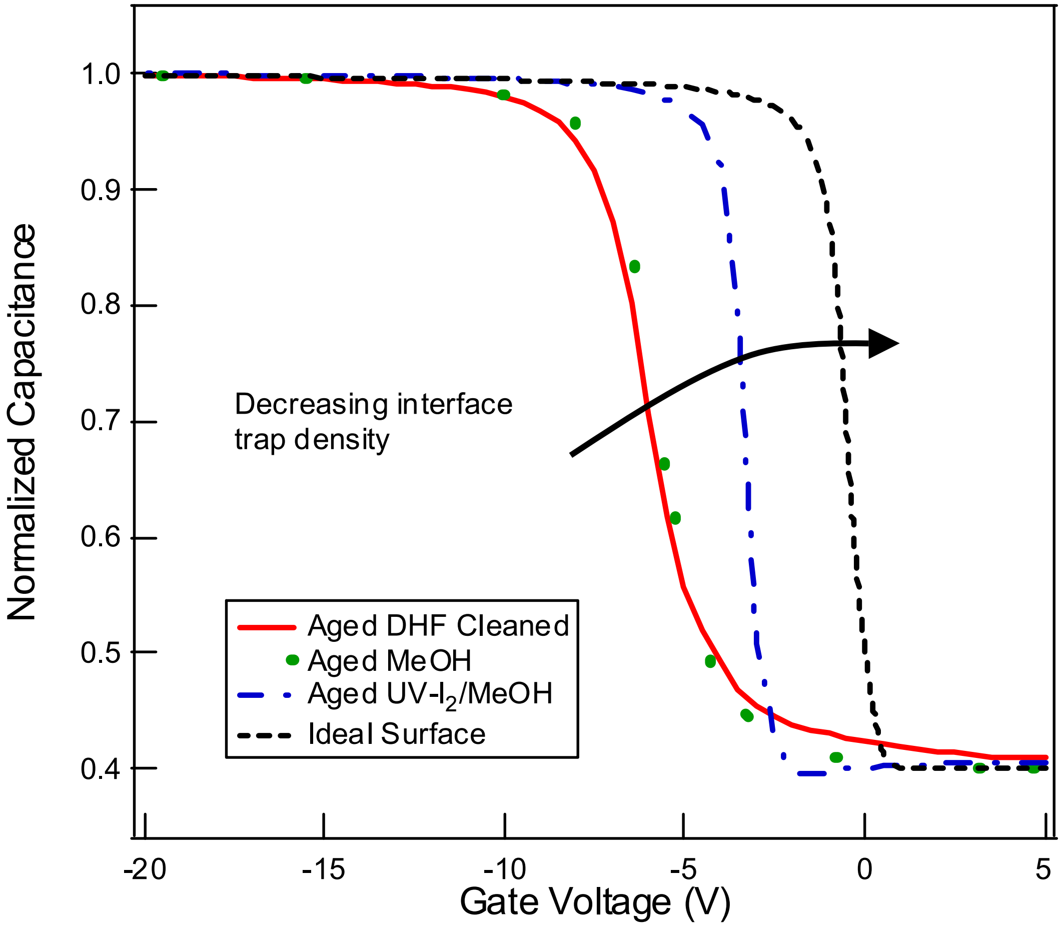
- Performance of three passivation approaches consistent across crystal faces and aging conditions

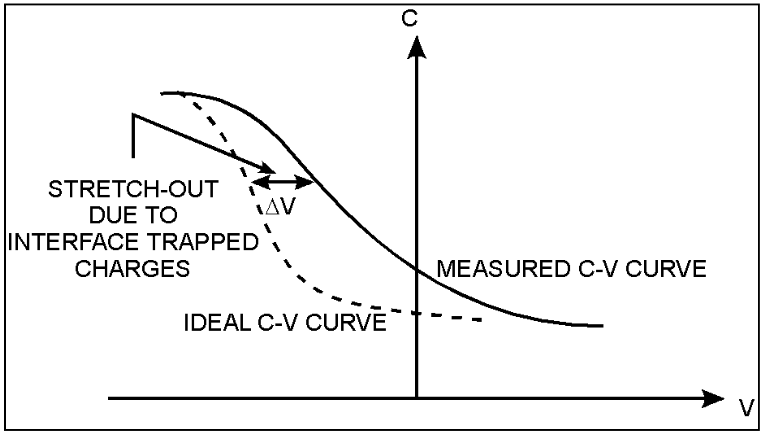




- Si(111) samples had highest C coverage
- Si(100) samples aged with exposure to light had lowest C coverage

Capacitance-Voltage Measurements



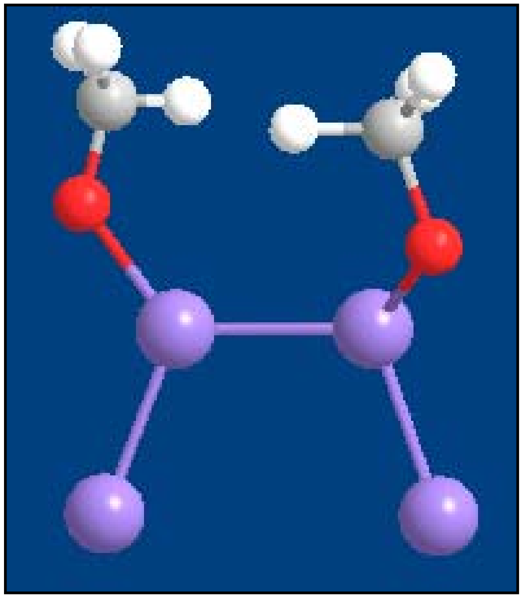


- Interface traps spread the depletion region in a *C-V* curve
- Methoxy-termination maintained a higher Si/SiO_2 interface quality with exposure to air
- In the range of industrial device defect densities (10^9 – 10^{11} cm^{-2})

Summary of Electrical Measurement Results				
	D_{it} (cm^{-2} eV^{-1})	D_{it} % Change compared to I_2/MeOH	Q_{ox} (cm^{-2})	Q_{ox} % Change compared to I_2/MeOH
H terminated	1.9E+11	224%	3.1E+11	98%
MeOH-only	6.7E+10	16%	2.8E+11	79%
I_2/MeOH	5.8E+10	0%	1.6E+11	0%

Summary and Conclusions

- Methods for gas phase methoxy passivation have been demonstrated
  - Decreased chemical usage
  - Compatible with current IC processing technology
- Methoxy passivates Si better than hydrogen atoms
  - I_2/MeOH processing provides the best protection against oxidation over time
- Electrical testing indicates no adverse effects on device performance from adsorbed species
- Utility:
  - Pre-deposition surface quality preservation strategy
  - Passivation for transfer between gas phase cluster tools
  - Protection for additive processing
- Potential to improve device yield and decrease process bottlenecking
- Potential to reduce environmental impact of processing



Acknowledgements

- NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
- SRC Education Alliance/Intel Foundation Master's Scholarship
- Dr. Yoshihide Tada, Dr. Glenn Gale, and Dr. Tomo Ohta, TEL
- Casey Finstad, Gerardo Montaño, Adam Thorsness, Hongbin Zhu, Bo Xie, Shariq Siddiqui, Rachel Morrish