

Characterization of Organic Monolayers Attached to Si(111) via Ultraviolet Irradiation

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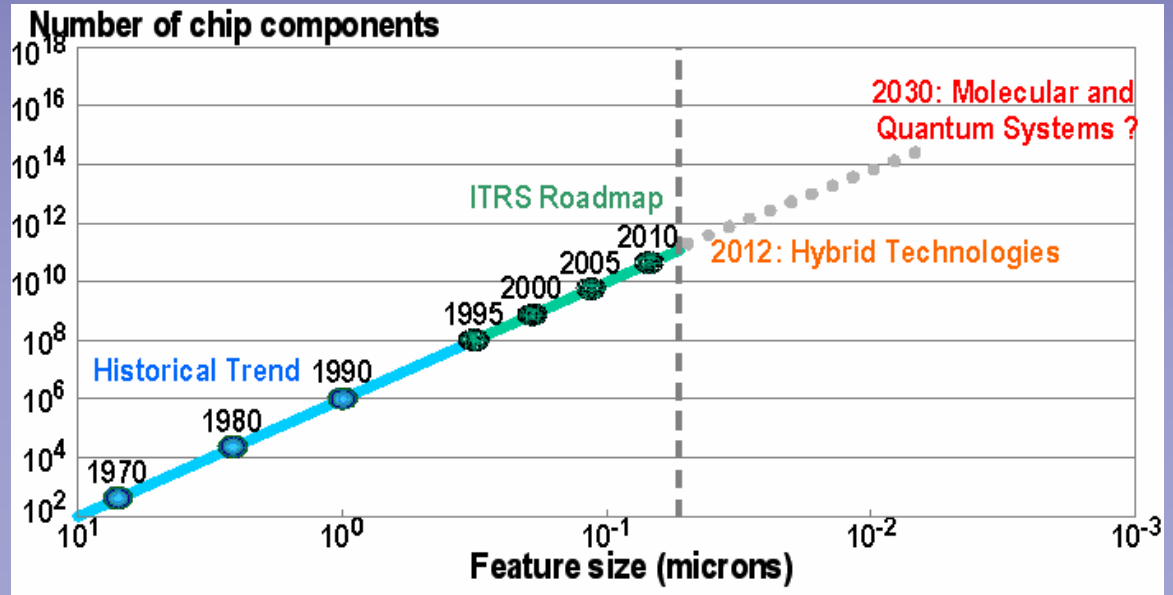
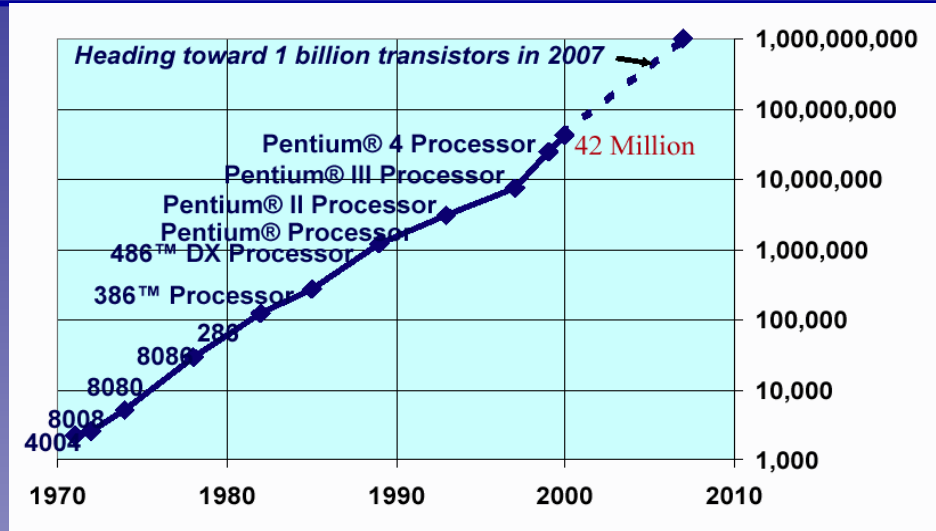
NIST



Electronics and Electrical Engineering Laboratory
Semiconductor Electronics Division
Gaithersburg, MD 20899

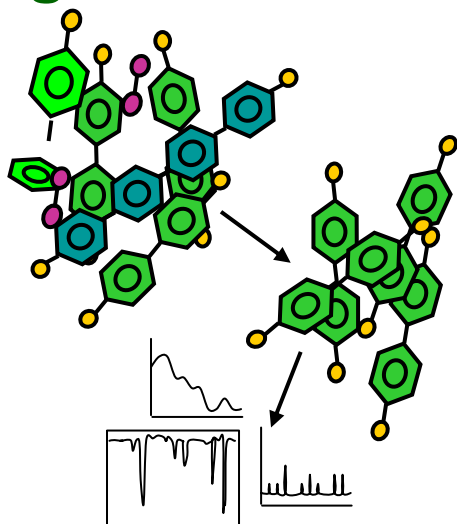
Motivations (Big Picture)

- Nanoelectronics next revolution in technology
- Smaller, faster devices
 - Moore's Law
 - Alternative Technologies



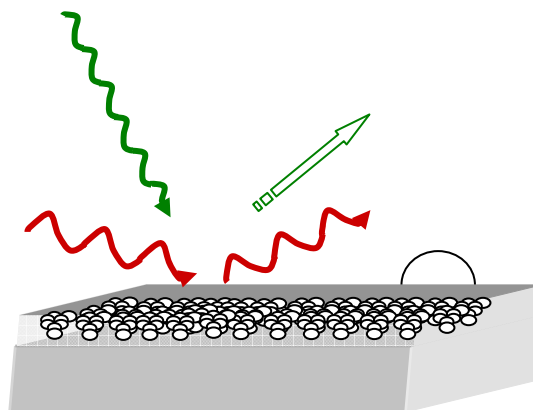
Molecular Electronics

Organic Molecules



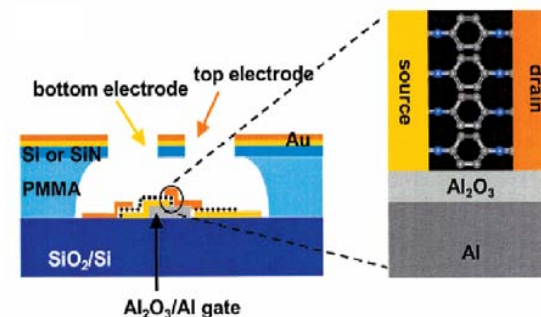
Synthesis, purification, and characterization of molecules is necessary to remove impurities.

Characterization



Characterization of the organic monolayer and device components performed to understand charge transport mechanisms.

Device Physics



The molecule-device structure must be designed and characterized both structurally and electrically.

Motivations

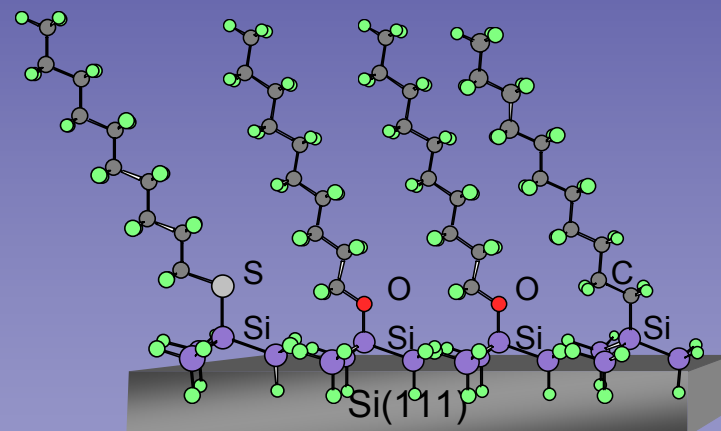
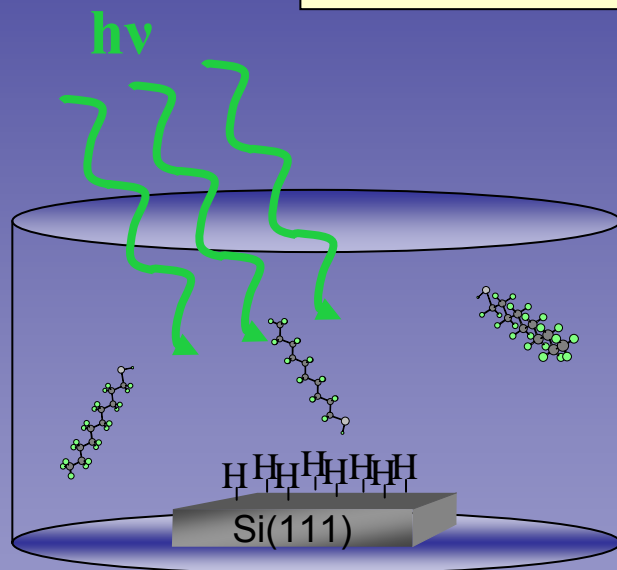
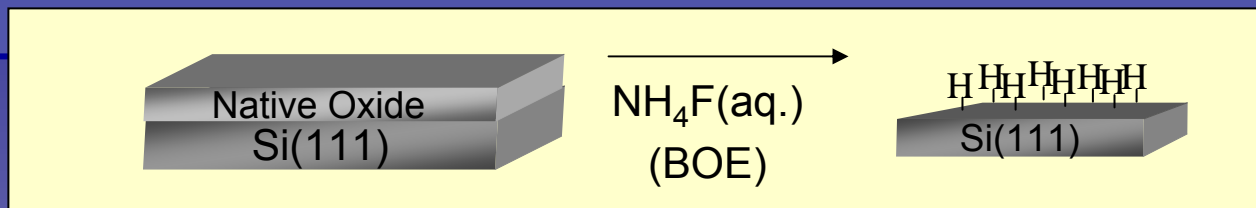
(Small Picture)

- Develop enhanced understanding of attachment processes
- Well understood surface modification and manipulation techniques
- Organic monolayer films helping to improve CMOS devices and develop the field of molecular electronics

Outline

- Attachment and characterization
- Results
 - Establish functional group favorability
 - Determine n- or p-type doping dependence
 - Obtain a strong understanding of the reaction mechanism driving attachment process
- Conclusion and future research

Ultraviolet Irradiation

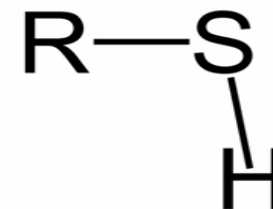
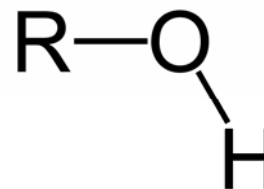
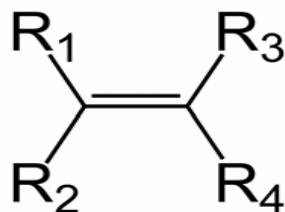
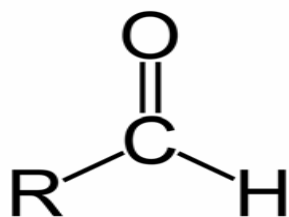


Aldehyde

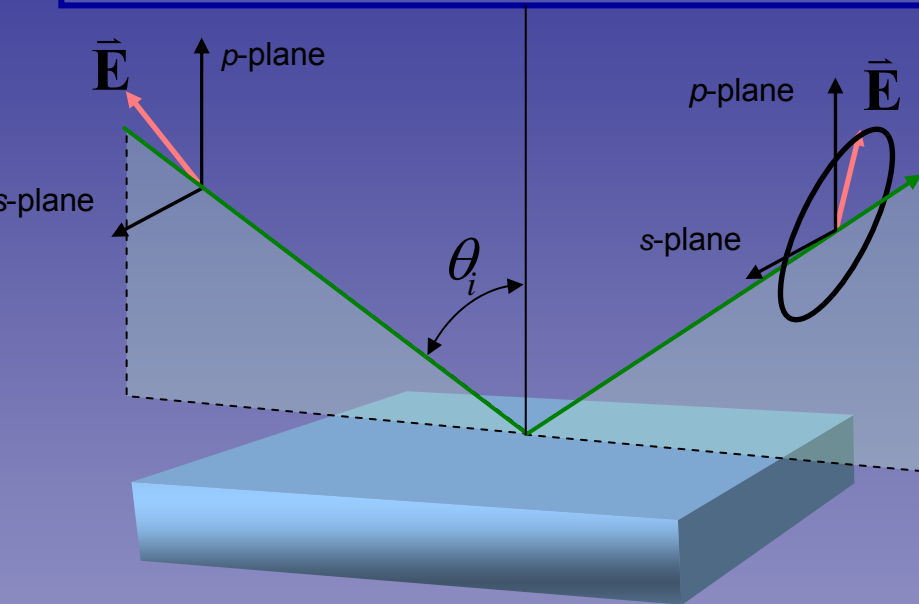
Alkene

Alcohol

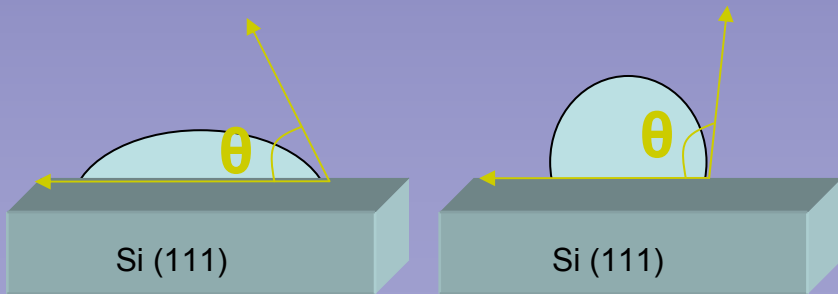
Thiol



Characterization of Monolayers



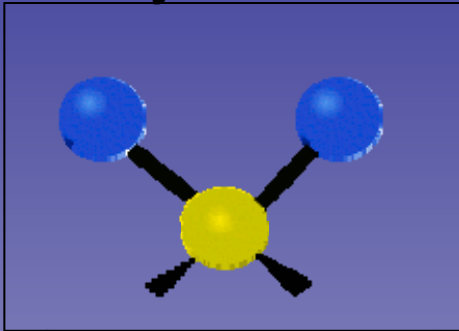
- **Ellipsometric Thickness**
 - Spectroscopic Ellipsometry
 - Multiple reflections cause changes in polarization parameters ψ and Δ
 - Curve fitting used to correlate changes to monolayer thickness



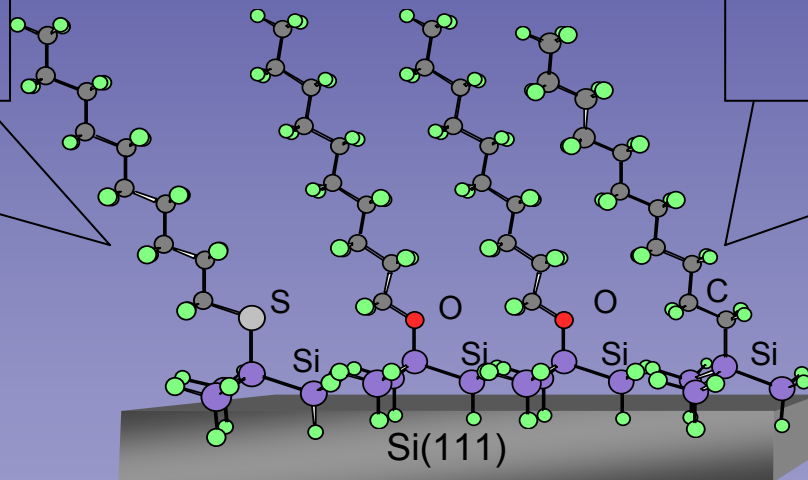
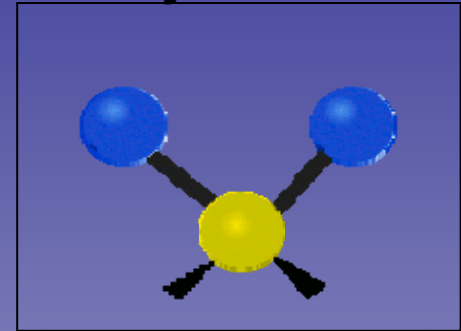
- **Hydrophobicity**
 - Contact Angle
- Measured with respect to the substrate on inner side of droplet
 - Native oxide is hydrophilic
 - Organic monolayers are hydrophobic

Characterization of Monolayers

Symmetric

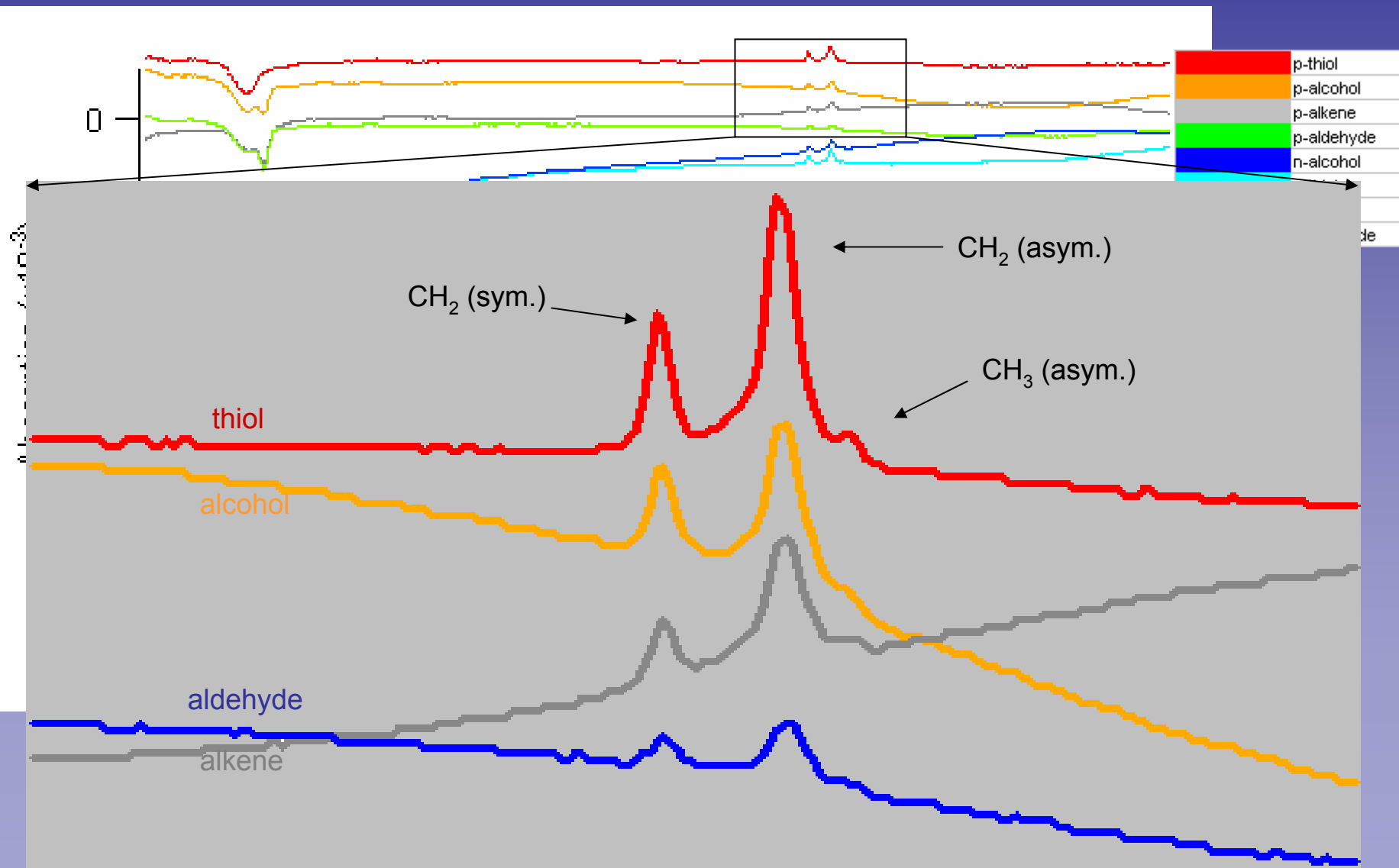


Asymmetric



- **Absorption Intensities**
 - Fourier Transform Infrared (FTIR) Spectroscopy
- IR beam, incident at near-Brewster's angle
 - Induces CH₂ stretches of the aliphatic chains
- Referenced to SiO₂ and SiH surfaces

Absorptions



n- vs. p-type Doping Dependence

aldehyde	
p-type	n-type
87.04 ± 6.03	89.23 ± 5.71

alkene	
p-type	n-type
96.59 ± 3.18	96.76 ± 3.52

alcohol	
p-type	n-type
98.92 ± 3.03	99.03 ± 2.25

thiol	
p-type	n-type
97.30 ± 6.15	97.82 ± 4.43

- Day-to-day averages, CA
 - All p- / n-type averages fall well within 1 standard deviation
 - Alcohol and thiol groups slightly favored

aldehyde	
p-type	n-type
1.57 ± 0.40	1.57 ± 0.32

alkene	
p-type	n-type
1.58 ± 0.19	1.65 ± 0.26

- Day-to-day averages, SE
 - All p- / n-type averages fall well within 1 standard deviation
 - Alcohol and thiol groups strongly favored

alcohol	
p-type	n-type
1.77 ± 0.30	1.68 ± 0.29

thiol	
p-type	n-type
1.87 ± 0.47	1.93 ± 0.34

n- vs. p-type Doping Dependence

	aldehyde	
	p-type	n-type
p-pol	0.074 ± 0.005	0.075 ± 0.009
s-pol	0.082 ± 0.021	0.096 ± 0.032

	alkene	
	p-type	n-type
p-pol	0.094 ± 0.021	0.089 ± 0.012
s-pol	0.089 ± 0.051	0.111 ± 0.049

	alcohol	
	p-type	n-type
p-pol	0.106 ± 0.014	0.100 ± 0.016
s-pol	0.130 ± 0.073	0.138 ± 0.058

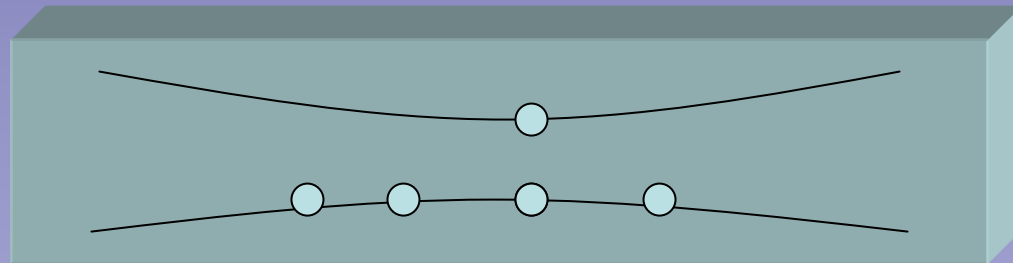
	thiol	
	p-type	n-type
p-pol	0.110 ± 0.038	0.095 ± 0.045
s-pol	0.205 ± 0.159	0.185 ± 0.132

- Day-to-day averages, FTIR
 - All p- / n-type averages fall well within 1 standard deviation
 - Strong favorability of alcohol and thiol groups

n- vs. p-type Doping Dependence Summary

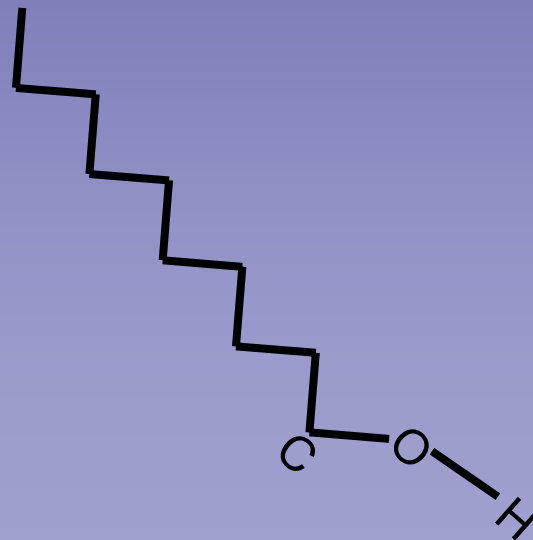
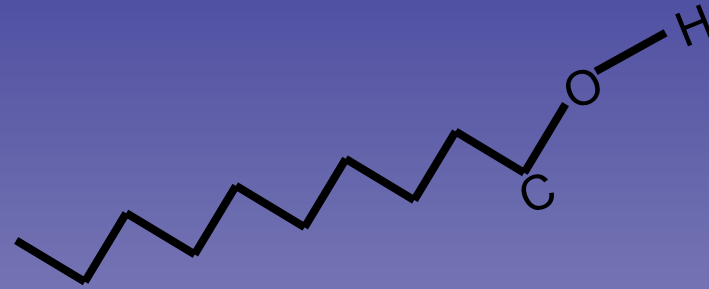
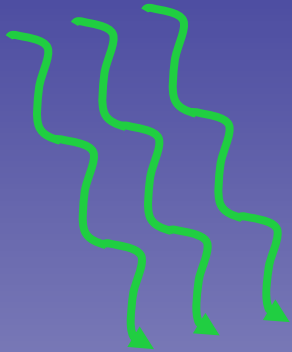
- 32 samples examined
 - 16 n-type and 16 p-type
- They day-to-day averages were compared for p- and n-type doped wafers
 - All p- / n-type averages were within one standard deviation of each other
- Determined there is NO doping dependence for the dopant levels in this study
 - Cannot exclude any dopant-dependence for highly doped wafers
- Showed favorability to the thiol and alcohol functional groups
 - Slightly favored over alkene
 - Strongly favored over aldehyde

Surface Driven Reaction

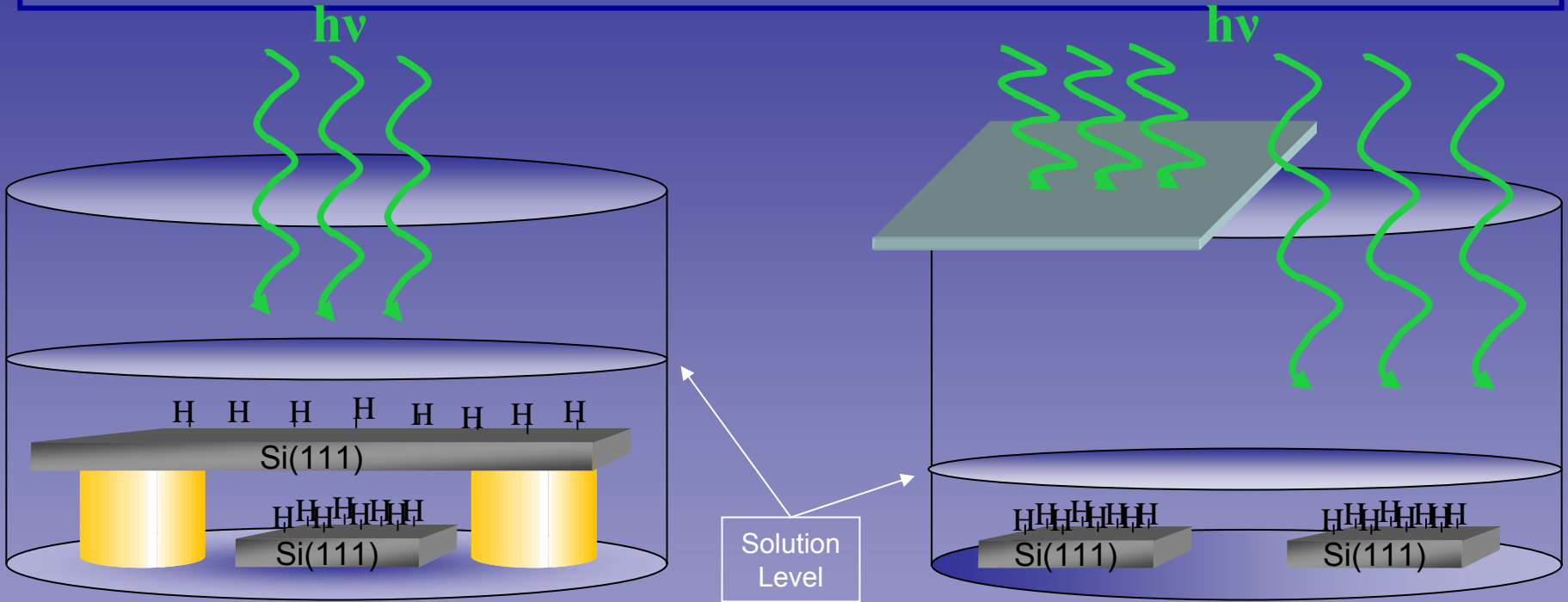


Solution Driven Reaction

$h\nu$

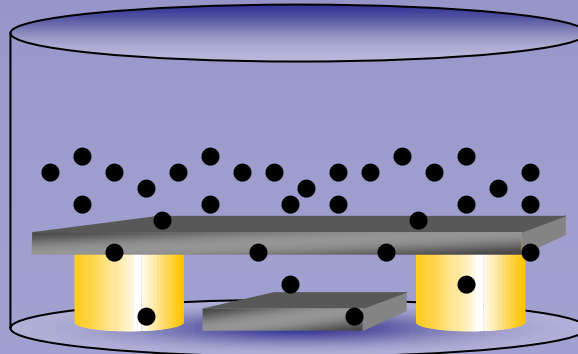


Reaction Mechanism Schematics



-Radical densities decrease with depth of solution

-Short lifetimes do not allow for solution agitation



What's Driving the Reaction?

- Evidence of solution driven reaction
 - Favorability of the thiol and alcohol groups suggest solution driven reaction
 - Absence of doping dependence suggests solution driven reaction
 - Experimental data leads to no clear evidence towards either reaction mechanism
 - » Decrease from limitations of radical lifetime?
 - » Decrease from absence of UV light?

Conclusion

- For low doping, no p- / n-type dependence
- UV irradiation favors thiol and alcohol functional groups
- Preliminary data suggests solution driven reaction during molecular attachment

Future Research

- p- / n-type doping dependence (highly doped)
- Alternative schematics to explicitly determine reaction mechanism
- Deposition of metal onto organic monolayer
 - Electrical Characterization
- Development of CMOS devices and molecular electronics

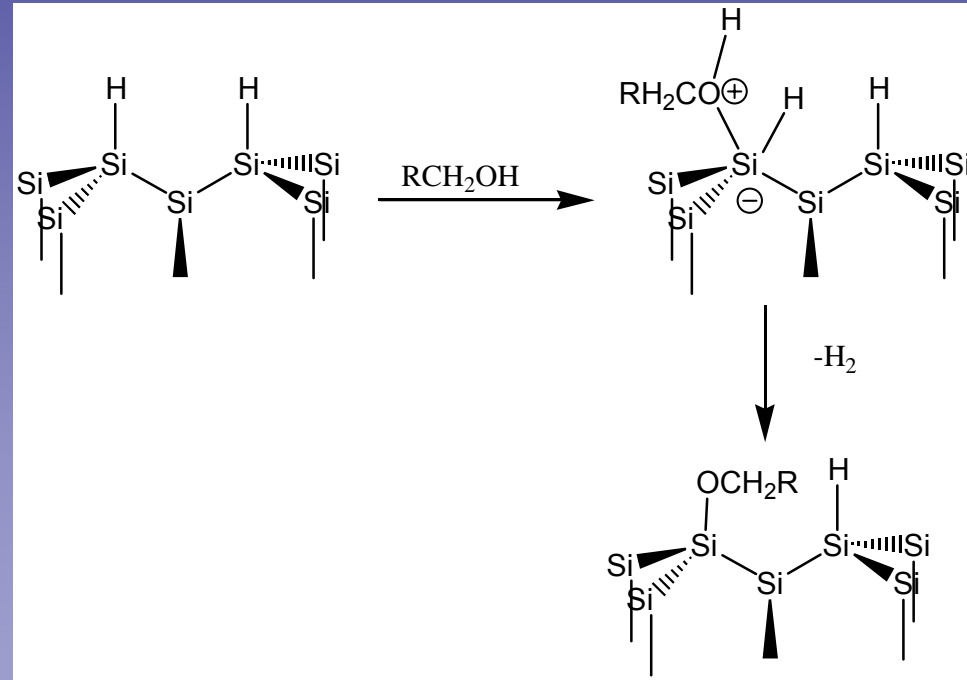
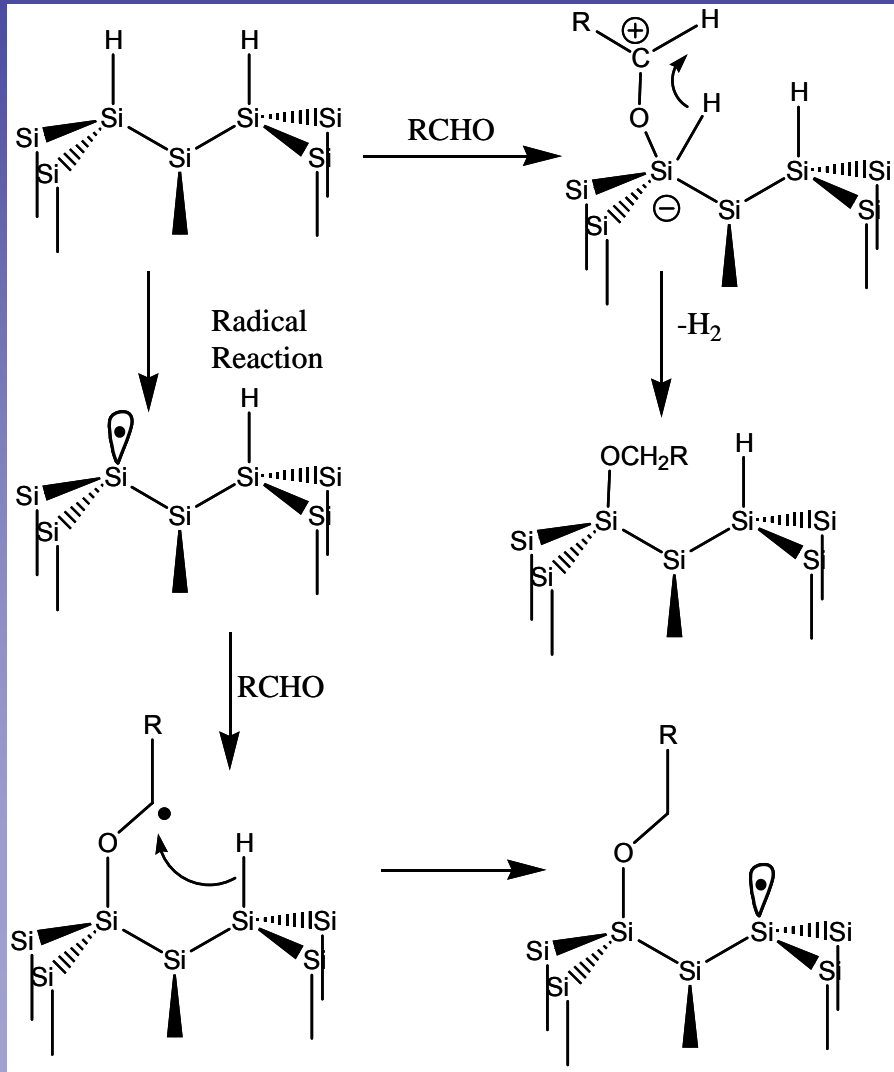
Acknowledgments

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- **AIP and SPS Crew**
- **SPS Interns**

Questions



Extras

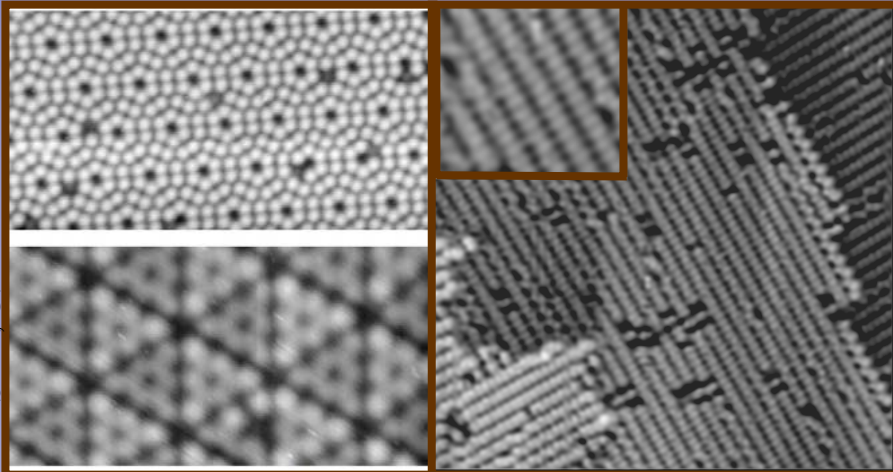


Advantages of Silicon

- Strong bond energies
- Existing microelectronics, devices, and manufacturing
- Substrate flexibility

Si(111)-7x7

Si(100)-2x1



D Sarid, U. of Arizona

RJ Hamers, U Wisconsin-Madison

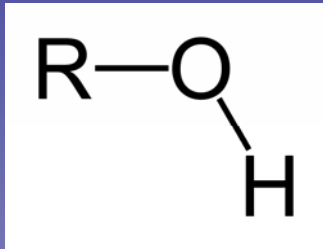
Typical Bond Energies (kJ/mol) (eV)

Au-S	125-146	1.3-1.5
Si-S	226	2.3
Si-C	369	3.8
Si-O	368	3.8

J. M. Buriak, *Chem. Rev.*, 102(5), 1271 (2002)

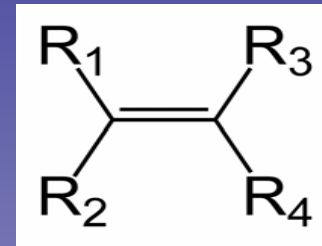
Functional Groups

Alcohol



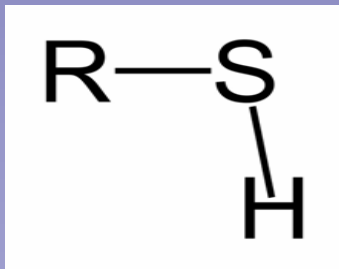
Characterized by the OH functionality

Alkene



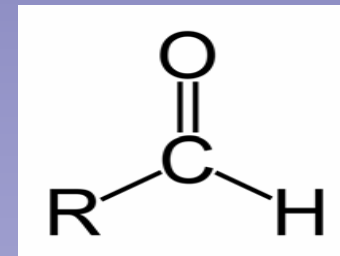
Characterized by the double bonded carbon functionality

Thiol



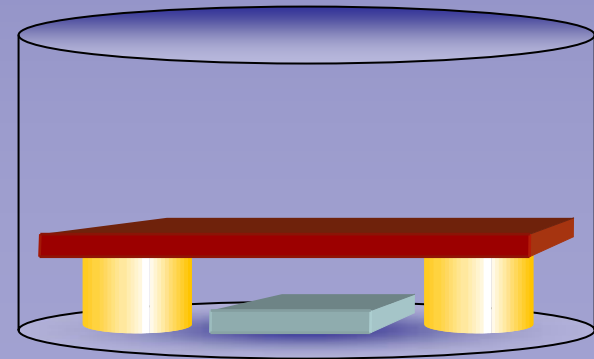
Characterized by the SH functionality

Aldehyde



Characterized by the C double bonded O functionality

NIST



NIST

