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

Andrew J. Stokes
University of Wisconsin – La Crosse

Researching Advisor:
Dr. Christina A. Hacker, Ph.D.

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

![Graph showing trend in number of chip components over time.](image)
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

Native Oxide Si(111) → NH₄F(aq.) (BOE) → Si(111)

hv

Aldehyde

\[
\begin{array}{c}
\text{R} \\
\text{C} \\
\text{H}
\end{array}
\]

Alkene

\[
\begin{array}{c}
\text{R}_{1} \\
\text{C} \\
\text{C} \\
\text{R}_{2} \\
\text{R}_{3}
\end{array}
\]

Alcohol

\[
\begin{array}{c}
\text{R} \\
\text{O} \\
\text{H}
\end{array}
\]

Thiol

\[
\begin{array}{c}
\text{R} \\
\text{S} \\
\text{H}
\end{array}
\]
Characterization of Monolayers

• **Ellipsometric Thickness**
  - Spectroscopic Ellipsometry
  - Multiple reflections cause changes in polarization parameters $\psi$ and $\Delta$
    - 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

- **Absorption Intensities**
  - Fourier Transform Infrared (FTIR) Spectroscopy
  - IR beam, incident at near-Brewster’s angle
    - Induces CH$_2$ stretches of the aliphatic chains
  - Referenced to SiO$_2$ and SiH surfaces
Absorptions

- thiol
- alcohol
- aldehyde
- alkene

- CH$_3$ (asym.)
- CH$_2$ (sym.)
- CH$_2$ (asym.)
### n- vs. p-type Doping Dependence

#### Aldehyde

<table>
<thead>
<tr>
<th></th>
<th>p-type</th>
<th>n-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>aldehyde</td>
<td>87.04 ± 6.03</td>
<td>89.23 ± 5.71</td>
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</table>

#### Alkene

<table>
<thead>
<tr>
<th></th>
<th>p-type</th>
<th>n-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>aldehyde</td>
<td>96.59 ± 3.18</td>
<td>96.76 ± 3.52</td>
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</tbody>
</table>

#### Alcohol

<table>
<thead>
<tr>
<th></th>
<th>p-type</th>
<th>n-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>aldehyde</td>
<td>98.92 ± 3.03</td>
<td>99.03 ± 2.25</td>
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</table>

#### Thiol

<table>
<thead>
<tr>
<th></th>
<th>p-type</th>
<th>n-type</th>
</tr>
</thead>
<tbody>
<tr>
<td>aldehyde</td>
<td>97.30 ± 6.15</td>
<td>97.82 ± 4.43</td>
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</table>

#### Alcohol

<table>
<thead>
<tr>
<th></th>
<th>p-type</th>
<th>n-type</th>
</tr>
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<tbody>
<tr>
<td>aldehyde</td>
<td>1.57 ± 0.40</td>
<td>1.57 ± 0.32</td>
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#### Thiol

<table>
<thead>
<tr>
<th></th>
<th>p-type</th>
<th>n-type</th>
</tr>
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<tbody>
<tr>
<td>aldehyde</td>
<td>1.58 ± 0.19</td>
<td>1.65 ± 0.26</td>
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</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th></th>
<th>aldehyde</th>
<th>alkene</th>
<th>alcohol</th>
<th>thiol</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>p-type</td>
<td>n-type</td>
<td>p-type</td>
<td>n-type</td>
</tr>
<tr>
<td>p-pol</td>
<td>0.074 ± 0.005</td>
<td>0.075 ± 0.009</td>
<td>0.106 ± 0.014</td>
<td>0.110 ± 0.038</td>
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<tr>
<td>s-pol</td>
<td>0.082 ± 0.021</td>
<td>0.096 ± 0.032</td>
<td>0.130 ± 0.073</td>
<td>0.205 ± 0.159</td>
</tr>
<tr>
<td></td>
<td>0.089 ± 0.012</td>
<td>0.094 ± 0.021</td>
<td>0.138 ± 0.058</td>
<td>0.185 ± 0.132</td>
</tr>
</tbody>
</table>

- 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

hv

\[ \text{Chemical structure diagram} \]
- 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

• Dr. Christina Hacker, Ph.D.
• Semiconductor and Electronics Division, NIST
• Dr. Lee Richter, Ph.D.
• AIP and SPS Crew
• SPS Interns
Questions
Advantages of Silicon

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

Typical Bond Energies

<table>
<thead>
<tr>
<th></th>
<th>(kJ/mol)</th>
<th>(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au-S</td>
<td>125-146</td>
<td>1.3-1.5</td>
</tr>
<tr>
<td>Si-S</td>
<td>226</td>
<td>2.3</td>
</tr>
<tr>
<td>Si-C</td>
<td>369</td>
<td>3.8</td>
</tr>
<tr>
<td>Si-O</td>
<td>368</td>
<td>3.8</td>
</tr>
</tbody>
</table>


D. Sarid, U. of Arizona
RJ Hamers, U Wisconsin-Madison
Functional Groups

**Alcohol**
Characterized by the OH functionality

![Alcohol](image)

**Thiol**
Characterized by the SH functionality

![Thiol](image)

**Alkene**
Characterized by the double bonded carbon functionality

![Alkene](image)

**Aldehyde**
Characterized by the C double bonded O functionality

![Aldehyde](image)