The Iodine and Methanol Passivation

Engineering and Basic Science Applications

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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

  \[ \text{throughput} \]

  \[ \downarrow \text{cleaning steps} = \downarrow \text{waste generated} \]

  \[ \downarrow \text{chemical usage} \]

  \[ \uparrow \text{$ saved} \]

Goal:
- Avoid recleaning
- Well defined surface
  - Clean, reproducible replacement by next solid phase
Our Strategic Plan

- Increased air stability
- Reduced Chemical And Water Usage
- Increased Reliability
- New chemical knowledge
- Surface Passivation!
- Chemical and water usage
Passivation Method

as received

native oxide

Si

H-terminated

Si

1:100, HF : H₂O
2 min.

oxidized

1:4 H₂O₂(30%):H₂SO₄ (conc.)
100°C, 4 min.

Si

H-terminated

Si

1:50, HF : H₂O
2 min.

passivated

5 x 10⁻⁴ M I₂ in methanol, 20 min.

Si
Effective Si Surface Passivation in I$_2$/Alcohol

<table>
<thead>
<tr>
<th>Si(100) in:</th>
<th>Lifetime (ms)</th>
<th>Number of unpassivated sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH/I$_2$ (5 x 10$^4$M)</td>
<td>8</td>
<td>4 x 10$^9$ cm$^2$</td>
</tr>
<tr>
<td>HF (1%)</td>
<td>0.9</td>
<td>4 x 10$^{10}$ cm$^2$</td>
</tr>
<tr>
<td>HF (49%)</td>
<td>5</td>
<td>7 x 10$^9$ cm$^2$</td>
</tr>
</tbody>
</table>

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

\[
\text{I} \rightleftharpoons \text{I} \xrightarrow{h\nu} 2\text{I}^*. \\
\text{SiH} \xrightarrow{\text{I}^*} \text{Si}^* \xrightarrow{\text{HI}} \text{Si}^* + \text{HI} \xrightarrow{\text{I}^*} \text{SiI} \xrightarrow{\text{HOC}_3} \text{SiOCH}_3 + \text{HI}
\]
Si2p Core Level Photoelectron Spectra
Temperature Dependence

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

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

$I_B = 92.6 \text{ eV}$
Photoelectron Spectra
Temperature Dependence

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

- HF Last Clean
- Modified HF Last Clean

100 - Oxide capacitor
  - Annealed
  - No Anneal

30 - Oxide capacitor
  - Annealed
  - No Anneal
# Surface Termination Post Wafer Cleaning

## HF Last Clean
- $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ 4:1 120°C 10min **strip organics**
- DI water rinse
- $\text{HCl}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ 1:1:6 90°C 10min **strip alkali ions and metals**
- DI water rinse
- HF/ $\text{H}_2\text{O}$ 1:50 Room Temp 30sec **strip native and chemical oxides**
- DI water rinse
- Spin Dry

## Hydrogen Termination

## Modified HF Last Clean
- $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ 4:1 120°C 10min **strip organics**
- DI water rinse
- $\text{HCl}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ 1:1:6 90°C 10min **strip alkali ions and metals**
- DI water rinse
- HF/ $\text{H}_2\text{O}$ 1:50 Room Temp 30sec **strip native and chemical oxides**
- Methanol Rinse 2min
- Methanol/Iodine 1:2E-5 Room Temp 20min
- $\text{N}_2$ 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

- HF Last Clean Si (100)
- Modified HF Last Clean Si (100)
- Final Rinse DI Water No Spike
- Final Rinse DI Water 1ppm Cu Spike
- Final Rinse DI Water 10ppm Cu Spike
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

Silicon Passivated Wafers in the Presence of Cu Spiked Rinse Tanks

Cu Concentration in H2O Tank (ppm)

Avg. Cu Concentration on Si (100) Surface Methoxy Passivated
Max. Cu Concentration on Si (100) Surface Methoxy Passivated
Avg. Cu Concentration on Si (100) Surface Hydrogen Passivated
Avg. Cu Concentration on Si (100) Surface Hydrogen Passivated
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 presence 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)

<table>
<thead>
<tr>
<th>native oxide</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1:4, H₂O₂ (30%):H₂SO₄ (conc.)</td>
</tr>
<tr>
<td></td>
<td>100°C, 10 min.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>SiO₂</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NH₄F(40%)</td>
</tr>
<tr>
<td></td>
<td>15 min.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl₂ (g) + hν</td>
</tr>
<tr>
<td>30 sec.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>dry deox. MeOH + hν</td>
</tr>
<tr>
<td>20 min.</td>
</tr>
</tbody>
</table>

- Gas phase chlorination of H-Si(111)
- Dry, deoxygenated methanol(1) to chlorine-terminated surface

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H-Si(111) + Cl₂(g) + hν

<table>
<thead>
<tr>
<th>Peak</th>
<th>Kinetic Energy (eV)</th>
<th>Area</th>
<th>Coverage (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>95.71</td>
<td>12740</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>94.91</td>
<td>9107</td>
<td>1.47</td>
</tr>
<tr>
<td>S2</td>
<td>94.43</td>
<td>1179</td>
<td>0.17</td>
</tr>
</tbody>
</table>

S2 peak could be due to miscut.
Photoelectron Spectra
Monomethoxy-Termination of Si(111)

- Si2p
  \( h\nu = 200\text{eV} \)

- Cl2p
  \( h\nu = 250\text{eV} \)

- C1s
  \( h\nu = 350\text{eV} \)

- ~12% of original chlorine is left
- Sharp C1s feature suggests monomethoxy-termination.

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Monomethoxy-terminate Si(111)

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<th>Area</th>
<th>Coverage (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>95.77</td>
<td>13160</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>95.07</td>
<td>5337</td>
<td>0.91</td>
</tr>
<tr>
<td>S2</td>
<td>94.67</td>
<td>3213</td>
<td>0.55</td>
</tr>
</tbody>
</table>

$\text{Si}2p$
$\hbar\nu = 200\text{eV}$
Monomethoxy-terminate Si(111)

<table>
<thead>
<tr>
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<th>Kinetic Energy (eV)</th>
<th>Area</th>
<th>Coverage (ML)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>95.77</td>
<td>13156</td>
<td></td>
</tr>
<tr>
<td>S1</td>
<td>95.08</td>
<td>5148</td>
<td>0.87</td>
</tr>
<tr>
<td>S2</td>
<td>94.72</td>
<td>2773</td>
<td>0.47</td>
</tr>
<tr>
<td>S3</td>
<td>94.48</td>
<td>8107</td>
<td>0.13</td>
</tr>
</tbody>
</table>

Si$_{2p}$
$\nu = 200\text{eV}$

Counts (arb. units)
Kinetic Energy (eV)
Conclusion

- H-Si(111) exposed to Cl₂ (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° miscut crystals (ie. exposure time, temperature dependence, methanol purity).
- Perform structural analysis of methoxy-terminated surface
  \[ \rightarrow \text{C and O K edge NEXAFS} \]
  \[ \rightarrow \text{C and O Photoelectron Diffraction} \]