Development of a classical force field for the hydroxylated Si surface

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Si-based MEMS devices form hydroxylated surface in presence of $O_2$ and $H_2O$

- Aim to study effects of surface chemistry on protein binding modes
- Need to develop classical force field for Si surface
Oxidation of the Si surface

- Tensile stress development

\[ \Theta = 0.00 \quad g = 0.81 \text{N/m} \]
Oxidation of the Si surface

- Tensile stress development

\[ \Theta = 0.00 \quad g = 0.81 \text{N/m} \]

\[ \Theta = 0.25 \quad g = 0.47 \text{N/m} \]
Oxidation of the Si surface

- Tensile stress development

\[ \Theta = 0.00 \ \ g = 0.81 \text{N/m} \]
\[ \Theta = 0.25 \ \ g = 0.47 \text{N/m} \]
\[ \Theta = 0.50 \ \ g = 0.50 \text{N/m} \]
Oxidation of the Si surface

- Tensile stress development

\[ \Theta = 0.00 \quad g = 0.81\text{N/m} \]
\[ \Theta = 0.25 \quad g = 0.47\text{N/m} \]
\[ \Theta = 0.50 \quad g = 0.50\text{N/m} \]
\[ \Theta = 0.75 \quad g = 0.05\text{N/m} \]
Oxidation of the Si surface

- **Tensile stress development**

  - $\Theta=0.00 \quad g=0.81\text{N/m}$
  - $\Theta=0.25 \quad g=0.47\text{N/m}$
  - $\Theta=0.50 \quad g=0.50\text{N/m}$
  - $\Theta=0.75 \quad g=0.05\text{N/m}$
  - $\Theta=1.25 \quad g=1.28\text{N/m}$
Oxidation of the Si surface

- Tensile stress development

<table>
<thead>
<tr>
<th>Angle (θ)</th>
<th>Stress (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.81 N/m</td>
</tr>
<tr>
<td>0.25</td>
<td>0.47 N/m</td>
</tr>
<tr>
<td>0.50</td>
<td>0.50 N/m</td>
</tr>
<tr>
<td>0.75</td>
<td>0.05 N/m</td>
</tr>
<tr>
<td>1.25</td>
<td>1.28 N/m</td>
</tr>
<tr>
<td>1.50</td>
<td>2.92 N/m</td>
</tr>
</tbody>
</table>
Oxidation of the Si surface

- Mulliken charges
Oxidation of the Si surface

- Mulliken charges

\[ +0.6e^- \]

\[ +0.0e^- \]
Oxidation of the Si surface

- Mulliken charges

\[ +1.2e^- \]

\[ +0.6e^- \]

\[ +0.0e^- \]
Oxidation of the Si surface

- Mulliken charges

\[ +1.8e^-, +1.2e^-, +0.6e^-, +0.0e^- \]
Oxidation of the Si surface

- Mulliken charges
  - $+2.3e^-$
  - $+1.8e^-$
  - $+1.2e^-$
  - $+0.6e^-$
  - $+0.0e^-$
Summary so far

- High tensile surface stress in the native oxide
- Si charges increase linearly with number of O nearest neighbours
- Develop a charge-based classical force field, fit to ab-initio structure and tensile stress
A classical force field

\[ q_{Si} = +0.4 \sum_{O} f(r) \]

\[ q_{O} = -0.4 \sum_{Si} f(r) \]
A classical force field

\[ V_{Si-Si'} = A[Br^{-4} - 1]\exp(\sigma(r - a)^{-1}) \]

\[ V_{ijk} = \lambda \exp[\gamma_1(r_{ij}-d_1)^{-1}+\gamma_2(r_{ik}-d_2)^{-1}](\cos\theta_{ijk}-\cos\theta_0)^2 \]

A classical force field

\[ V_{Si-Si'} = A(q_{Si}, q_{Si'})[Br^{-4} - 1]\exp(\sigma(r-a)^{-1})f(r) + \frac{q_{Si}q_{Si'}}{r} \]

\[ V_{ijk} = \lambda\exp[\gamma_1(r_{ij} - d_1)^{-1} + \gamma_2(r_{ik} - d_2)^{-1}](cos\theta_{jik} - cos\theta_0)^2f(r) \]

A classical force field

\[ V_{Si-O} = \frac{C}{r^9} - \frac{D}{r^4} \exp(-r/b) + \frac{q_{Si}q_{O}}{r} \]

\[ V_{O-O'} = \frac{H}{r^7} - \frac{J}{r^4} \exp(-r/b) + \frac{q_{O}q_{O'}}{r} \]

\[ V_{ijk} = \lambda \exp[\gamma_1(r_{ij} - d_1)^{-1} + \gamma_2(r_{ik} - d_2)^{-1}](\cos\theta_{ijk} - \cos\theta_0)^2 \]

A classical force field

\[ V_{Si-O} = \frac{C(q_{Si})}{r^9} - \frac{D}{r^4}\exp(-r/b) + \frac{q_{Si}q_O}{r} \]

\[ V_{O-O'} = \frac{H}{r^7} - \frac{J}{r^4}\exp(-r/b) + \frac{q_Oq_{O'}}{r} \]

\[ V_{ijk} = \lambda\exp[\gamma_1(r_{ij}-d_1)^{-1}+\gamma_2(r_{ik}-d_2)^{-1}](\cos\theta_{jik}-\cos\theta_0)^2 \]

Hydroxylated surface results

<table>
<thead>
<tr>
<th>Bond length/Å</th>
<th>Bond angle</th>
<th></th>
<th>Bond length/Å</th>
<th>Bond angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ab-initio structure</td>
<td>Classical structure after 50ps MD at 300K</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si-O</td>
<td>Si-Si</td>
<td>O-Si-O</td>
<td>Si-Si-O</td>
<td>Si-Si-Si</td>
</tr>
<tr>
<td>Si⁺⁺</td>
<td>1.64</td>
<td>–</td>
<td>109°</td>
<td>–</td>
</tr>
<tr>
<td>Si⁺⁺⁺</td>
<td>1.65</td>
<td>2.36</td>
<td>109°</td>
<td>109°</td>
</tr>
<tr>
<td>Si⁺⁺</td>
<td>1.67</td>
<td>2.39</td>
<td>109°</td>
<td>108°</td>
</tr>
<tr>
<td>Si⁺⁺⁺⁺</td>
<td>1.70</td>
<td>2.38</td>
<td>–</td>
<td>108°</td>
</tr>
</tbody>
</table>

\[ g = -2.4 \text{N/m} \]

\[ g = -2.0 \text{N/m} \]
Water layering
Water layering

O - H --- O 1.40

O - H --- O 1.41
MEMS Wafer bonding

- Si wafer surface preparation – flat, clean, chemisorbed -OH, H-bonded H₂O

- Room temperature contact – assumed to be H-bonded network between surfaces

- High T annealing – desorbs H₂O and encourages siloxane bond formation
Wafer bonding
Wafer bonding
Wafer bonding
Wafer bonding

0.00ML
Wafer bonding

![Diagram of wafer bonding with force and separation graphs showing 0.25ML values.](image)
Wafer bonding

0.50ML

Forces / nN vs. separation / Angstroms

0.50ML

Total number of H-bonds per H atom vs. separation / Angstroms
Wafer bonding

![Diagram of wafer bonding with force and separation plots.]
Wafer bonding
Wafer bonding

1.50 ML

1.50 ML

1.50 ML
Wafer bonding
Wafer bonding
Wafer bonding
Cells bind to implanted artificial surfaces via extra-cellular matrix proteins, such as collagen.
Conclusions

- Classical force field developed that reproduces the structure, charge distribution and tensile stress of the Si hydroxylated native oxide.
- Used to simulate room temperature hydrogen bonding between Si wafers.
- Future work: continue study of effects of surface chemistry on protein binding to the model Si surface.
**Impurity segregation**

- Do impurities affect the surface electrostatics?

**Phosphorous:**

**Boron:**