Investigation of Copper Impurities on Silicon Surfaces using X-ray Absorption Near Edge Spectroscopy and Total Reflection X-ray Fluorescence

Andy Singh, Katharina Baur, Sean Brennan, Takayuki Homma¹, Nobuhiro Kubo¹, and Piero Pianetta

Stanford Synchrotron Radiation Laboratory, Menlo Park, CA 94025

¹Waseda University, Shinjuku, Tokyo, Japan

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Motivation: Why Cu on Silicon?

Device degradation

• Cu recently introduced for interconnects
• Cu is a fast diffuser in Silicon
• Contamination Levels \( \sim 10^9 \) atoms/cm\(^2\)

Electrochemistry

• Understand electrochemical nucleation and growth
• Improve silicon cleaning technology
Reaction pathways

**Low pH - reductive**

\[ \text{Cu}^{2+} + e^{-}_{\text{Si}} \rightarrow \text{Cu}^{1+} \]
\[ \text{Cu}^{1+} + e^{-}_{\text{Si}} \rightarrow \text{Cu}^{0} \]

Metallic clusters

**High pH - oxidative**

Si + 2OH⁻ $\rightarrow$ SiO₂ + H₂

Metal incorporated into oxide

In ultra pure water (UPW)?

- Deposition influenced by **O₂ content**, light, defects, etc.
Silicon Wafer surface analysis techniques

X-ray absorption Near Edge Spectroscopy (XANES)
- Incident beam energy scanned through an absorption edge of interest
- Determines chemical state (i.e. oxidation state) of impurities

Total Reflection X-ray Fluorescence (TXRF)
- Incident beam at constant energy
- Useful for determining concentration
- Angle scans can probe location of impurities
Experimental setup at SSRL

TXRF end station at BL 6.2

Wafer handling robot

SPEAR

54 pole Wiggler

Monochromator

Focusing Optics

Fluorescence Detector

Reflected Beam

Si-Wafer with Contaminants

Si-Li
Total Reflection X-ray Fluorescence

- Grazing incidence geometry ($\alpha \sim .10$ degrees)
- High surface sensitivity (30 angstroms)
- Determines **concentration** of impurities
- Detection Limit is $8E7$ atoms/cm$^2$ (i.e. 1 atom in 10 million)
# Sample preparation

**Wafer:**  
p-type Si (100)  (9-18 Ωcm)

**Pre-cleaning:**  
H₂SO₄ : H₂O₂ = 4:1  (120°C, 10 min)  
0.5% HF  (1min)

**Metal source:**  
Cu(NO₃)₂  (10 ppt → 500 ppb)

**Ultra Pure Water:**  
Milli – Q  (18 MΩ)

**Dissolved oxygen control:**  
\( UPW_{deox} : 0.3 \text{ ppm} \)  
\( UPW : 3.4 \text{ ppm} \)
Effect of dissolved oxygen on Cu deposition

- Background consists of scatter in the high energy region and bremsstrahlung in the low energy region
- Concentration determined with a known standard
Trace contamination from Cu spiked UPW

*After 5 min immersion*
Schematic model for Cu species on Si Wafer

10 ppb, oxygenated

Surface oxide containing Cu oxide species

10 ppb, deoxygenated

100 ppb, oxygenated

Cu metallic particle with “native” surface oxide

100 ppb, deoxygenated
X-ray absorption Spectroscopy (XANES)

• Feasibility due to broadband nature of synchrotron radiation
• Low concentrated samples can be measured (detection limit ~ 1E10 atoms/cm²)
• Edge position can identify oxidation state
• Near edge structure probes electronic structure
• SR-TXRF setup is used → Fluorescence Detector measures absorption
• Theoretical predictions difficult, but possible with FEFF8
Copper reference samples

![Graph showing normalized absorption vs energy for Cu, Cu₂O, and CuO](image-url)
Proof of Principle: 100 ppb Cu in HF

Predominantly Cu metal

Cu (0): 78%
CuO (II): 17%
Cu2O (I): 5%

Reducive deposition:

\[ \text{Cu}^{2+} + e_{\text{Si}}^{-} \rightarrow \text{Cu}^{1+} \]

\[ \text{Cu}^{1+} + e_{\text{Si}}^{-} \rightarrow \text{Cu}^{0} \]
40 ppb Cu in UPW

40 ppb Cu in deoxygenated UPW

\[ c(Cu) = 5.4 \times 10^{12} \text{ atoms/cm}^2 \]

Cu (0) : 60%
Cu (I) : 19%
Cu (II): 21%

edge position: 8979.9 eV

40 ppb Cu in oxygenated UPW

\[ c(Cu) = 1.7 \times 10^{12} \text{ atoms/cm}^2 \]

Cu (0) : 38%
Cu (I) : 34%
Cu (II): 28%

edge position: 8980.3 eV

References
40 ppb Cu in UPW, after Air Exposure

$c(Cu) = 5.4 \times 10^{12}$ atoms/cm$^2$

40 ppb Cu in deoxygenated UPW after air exposure

Edge position: 8980.5 eV

Cu (0) : 46%
Cu (I) : 26%
Cu (II): 28%

$c(Cu) = 1.7 \times 10^{12}$ atoms/cm$^2$

40 ppb Cu in oxygenated UPW after air exposure

Edge position: 8980.5 eV

Cu (0) : 39%
Cu (I) : 35%
Cu (II): 28%

$\rightarrow$ stable in air

References
Below the critical concentration: 5 ppb Cu in UPW

first results:

c(Cu) = 9 E10 atoms/cm²

edge position: 8981.2 eV

5 ppb Cu in oxygenated UPW

Data
Fit

Cu (0): 35%
CuO (II): 65%

References
Variation of the angle of incidence

\[ I(\alpha, z) = I_0 \times [1 + R(\alpha) + 2\sqrt{R(\alpha)} \times \cos\left(\frac{2\pi \cdot z}{d} - \phi(\alpha)\right)] \]

- \( \Phi \) : phase shift due to total external reflection
- \( R(\alpha) \) : reflectivity
- \( d = \frac{\lambda}{2\sin\alpha} \)

\( \alpha = 0.05, 0.15, 0.20 \)
Variation of the angle of incidence

Standing waves formed at glancing angles below critical angle

Periodicity of SW modulated by angle

Intensity = f(z, \alpha)

Conc. = f(z)

\[ d = \frac{\lambda}{2 \sin \alpha} \]

\[ Fluorescence \propto \int_0^h I(z) \times C(z) \times dz \]

- Standing waves formed at glancing angles below critical angle
- Periodicity of SW modulated by angle
Assumes square particle (i.e. $C(z)=1$)

Determination of the particle size

Fit yields particle height of 5.4 nm
**Summary**

<table>
<thead>
<tr>
<th>Deoxygenated UPW</th>
<th>Air-saturated UPW</th>
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</thead>
<tbody>
<tr>
<td>• Predominantly, Cu metal deposition</td>
<td>• Deposition of Cu metal and oxides</td>
</tr>
<tr>
<td>• Oxidation in air</td>
<td>• Samples are stable in air</td>
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<tr>
<td>• Particle growth seen by AFM, angle scans</td>
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</table>

**Outlook**

• XANES at lower concentrations → below “flipping point”
• In-situ experiment to remove environmental contamination
• Nucleation & growth experiments - particle size/conc. as a f(time)