Gas phase surface preparation using ultraviolet-activated chlorine

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Outline

• Motivation for Gas Phase Surface Preparation
  – Processing
  – Environmental Safety and Health (ESH)
• Background Information: UV/Cl$_2$
• Experimental Setup and Preliminary Results
• Future Plans
• Summary
### Front End Cleaning Steps

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Application</th>
<th>Liquid Phase</th>
<th>Gas Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organics</td>
<td>• Post- RIE</td>
<td>• O₂ Ash</td>
<td>• UV- O₃</td>
</tr>
<tr>
<td></td>
<td>• Ion Implant</td>
<td>• SPM (Piranha)</td>
<td>• UV- Cl₂</td>
</tr>
<tr>
<td></td>
<td>• Rework</td>
<td>• Ozonated Water</td>
<td>• Moist O₃</td>
</tr>
<tr>
<td>Oxide</td>
<td>• Pre-gate</td>
<td>• Dilute HF</td>
<td>• HF/ vapor</td>
</tr>
<tr>
<td>Particles</td>
<td>• Post- CMP</td>
<td>• APM (SC- 1) + megasonics</td>
<td>• Cryogenic Aerosol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• APM (SC- 1) + brush scrubbing</td>
<td>• Laser</td>
</tr>
<tr>
<td>Metals</td>
<td>• Post- RIE</td>
<td>• HPM (SC- 2) + chelating agents</td>
<td>• UV- O₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• UV- Cl₂</td>
</tr>
</tbody>
</table>
Motivation — Gas Phase Cleans

- No surface tension effects
  - Vapors penetrate sub-0.1 micron features (year 2005)

- No contamination from liquid bath

- Cluster tools
  - Wafer protected from atmosphere
  - Tool footprint in fab
  - Single wafer processing
Sources of Metallic Contamination

- Photoresist
- Reactive Ion Etching (RIE) (plasma etching)
- Oxygen Ashing
- Replace HPM (SC-2) with UV/Cl₂

SEM of 0.5 μm Feature After RIE

CD = 0.5 μm
AR = 2.5
HDP Source, post-RIE, before ashing
PR / TEOS
International Technology Roadmap for Semiconductors -- Metal Concentration Goals

Table 21 1999 Short Term Surface Preparation Technology Requirements

<table>
<thead>
<tr>
<th>Year of Introduction</th>
<th>2001</th>
<th>2002 130 nm</th>
<th>2003</th>
<th>2004</th>
<th>2005 100 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Front End of Line (A)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Critical surface metals (at/cm²)</td>
<td>≤6x10⁹</td>
<td>≤4.4x10⁹</td>
<td>≤3.4x10⁹</td>
<td>≤2.9x10⁹</td>
<td>≤2.5x10⁹</td>
</tr>
<tr>
<td>Metal atoms per Si(100)</td>
<td>1:323,000</td>
<td></td>
<td></td>
<td></td>
<td>1:770,000</td>
</tr>
<tr>
<td>Solutions Exist</td>
<td>Solutions Being Pursued</td>
<td>No Known Solution</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Critical Surface Metals: Fe¹,⁴, Ca, Co, Cu¹,³,⁴, Cr⁵, K¹, Mo, Mn, Na¹, and Ni¹,²,⁴


NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
Water Conservation

- Replacing 1/3 of wet cleans with dry cleans saves 216 million gallons of UPW or 324 million gallons of municipal water per year.
  - 1500 8”-wafers/day and 2000 gallons UPW per 8”-wafer
  - Wet cleans consume ~60% of UPW
  - 1.5 gallons of municipal water per 1 gallon UPW
  - (Mendicino, et al, 1999)
Chemical Usage Reduction

- Chemicals, Materials, and Equipment Management -- Reduced Consumption of Chemicals
  - Elimination of sulfuric acid by 2004

- Dry Cleans can reduce chemical consumption by 1000 times (Chang, et al, 1999).

- Reduced consumption = less waste disposal
Energy Conservation

- At 50 kWh/1000 gallons of UPW (Mendicino, et al, 1999), saving 216 million gallons of UPW conserves 10.8 million kWh of electricity.
- At $0.045/kWh, this saves $486,000/year.
- Gains need to be measured against increased usage of vacuum pumps and heaters.
International Technology Roadmap for Semiconductors -- ESH Targets

• Workplace Protection -- Reduced Worker Exposure to Hazardous Fumes
  – “Isolate workers from chemicals and byproducts during operation” in 2001
  – “Reduced chemical usage in clean processes” by 2005
  – “Novel rinse/clean methods that reduce water and chemical usage” by 2011

• All fumes/vapors contained within vacuum chamber

• Thrust B, Wafer Cleaning Resource Consumption for Front End 0.13 µm CMOS Device Process Flow Project
Background Information—UV/Cl$_2$ Metal Removal

- Gas-phase photolysis (250-400 nm)

\[ 340 \text{ nm} \rightarrow 3.6 \text{ eV} \]

- Surface photolysis

Cl-Cl bond = 2.5 eV
Project Objectives—UV/Cl$_2$ Metal Removal

• Removal mechanism
  – Volatile products
  – "Lift-Off"
  – Metal-silicon-chlorine complex

• Reaction mechanism and products
  – Gas-phase or surface photolysis
  – Substrate and dopants
  – Oxide thickness
  – Contaminant and its concentration
  – Surface termination and other adsorbed species

• Monochromatic UV source
# Thermochemistry

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G_{\text{rxn}} (250^\circ\text{C})$</th>
<th>$P_{\text{sub}} (250^\circ\text{C})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. $\text{Cu} + \text{Cl(g)} \rightarrow \text{CuCl}$</td>
<td>-219 kJ/mol</td>
<td>$4\times10^{-5}$ Torr</td>
</tr>
<tr>
<td>2. $\text{Cu} + 2\text{Cl(g)} \rightarrow \text{CuCl}_2$</td>
<td>-322 kJ/mol</td>
<td>$4\times10^{-7}$ Torr</td>
</tr>
<tr>
<td>3. $\text{CuCl}_2 \rightarrow \text{CuCl} + \frac{1}{2} \text{Cl}_2(g)$</td>
<td>67.4 kJ/mol</td>
<td></td>
</tr>
<tr>
<td>4. $\text{Cu}_2\text{O} + 2\text{Cl(g)} \rightarrow 2\text{CuCl} + \frac{1}{2} \text{O}_2(g)$</td>
<td>-307 kJ/mol</td>
<td>$4\times10^{-5}$ Torr</td>
</tr>
<tr>
<td>5. $\text{CuO} + \text{Cl(g)} \rightarrow \text{CuCl} + \frac{1}{2} \text{O}_2(g)$</td>
<td>-112 kJ/mol</td>
<td>$4\times10^{-5}$ Torr</td>
</tr>
</tbody>
</table>
UV Reactor Schematics

**Reactor**
- 5 - 50 sccm Cl₂ flowrate
- Pressure (100 - 1000 mTorr)
- Temperature (21 - 300°C)
- 1000-Watt Xe arc lamp (~250 mW/cm² at sample)

**Future Plans**
- Install Monochromator
- Residual Gas Analyzer (RGA) to identify reaction products
- UV/O₃ for carbon removal
Integrated Processing Apparatus

- UHV SSC reactor
- Photochemistry reactor
- Load Lock
- HF/Vapor Phase Etching Reactor
- Ultra High Vacuum Surface Analysis Chamber
Experimental Procedure

**Pre-deposition**
- Clean sample in piranha
- Immerse in 49% HF
- Repeat

**Copper Deposition**
- 1% HF solution
- 5 ppm Cu (from CuSO\(_4\)·5H\(_2\)O)
- 2 to 5 minutes
- Rinse and blow dry with N\(_2\)

**Dice wafer into 3/4 x 3/4 inch pieces**
**Mount on sample holder**

**Pre-copper removal XPS scan**

**Copper Removal with UV/Cl\(_2\)**

**Post-copper removal XPS scan**
Preliminary Results, UV/Cl₂ Copper Removal

- Experimental Conditions
  - Nominally 21°C
  - Reactor pressure 300 mTorr, 30 mTorr Cl₂

- Results
  - CuCl₂ at room temperature
    \[ \text{Cu} + 2\text{Cl}(g) \rightarrow \text{CuCl}_2 \]
  - No significant removal of copper
Preliminary Results, UV/Cl$_2$ Copper Removal

- **Experimental Conditions**
  - Reactor pressure 300 mTorr, 30 mTorr Cl$_2$

- **Results**
  - High temperature induced formation of CuCl
  - Chemical shift stronger than expected
  - Copper concentration decreased
  - Unable to achieve total removal, even after two additional 1-hour cleans
Future Plans

- Calibrate reactor temperature
- Calibrate XPS for copper concentration
- Complete Removal of Copper
  - Higher Cl$_2$ concentration
  - Low temperatures (100°C or lower)
- Oxide wafers
- Integrated Processing
- Look for wavelength dependence
  - Removal and reaction mechanisms
  - Removal efficiency
  - Oxidation state of metal chloride surface species
- Verify conclusions with TXRF
- Other metals
Preliminary Results, Carbon Removal

XPS spectra showing decrease in carbon signal during copper removal experiment.

• Experimental Conditions
  – nominally 150°C
  – Reactor pressure 500 mTorr, 147 mTorr Cl₂
  – 90 minute reaction time.

• Results
  – Carbon signal decreased.
  – Inconsistent carbon removal

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Summary

• ITRS goals
  – Reduced consumption of Water, Energy, and Chemicals
  – Reduced worker exposure

• Processing benefits
  – Cluster Tools
  – Clean small features

• UV/Cl₂ Metal Removal
  – Nickel, copper, iron, sodium, potassium, calcium, chromium, and zinc
  – Reaction and removal mechanisms
  – Monochromatic light source

• Carbon Removal
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