In-Line Detection and Measurement of Molecular Contamination in Semiconductor Processing Solutions

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Outline

- Introduction
  - Why the analysis of molecular contamination is important?

- Discussion
  - Use of the Metara Trace Contamination Analyzer (TCA) for molecular contamination measurement
  - Problem solving examples
    1. A nitrogen-containing compound in $\text{H}_2\text{O}_2$
    2. Organic additives in SC-1
    3. Urea in UPW
    4. Molecular contamination in UPW
    5. Plasticizers in IPA
    6. Sulfur-containing compounds in IPA

- Conclusion
Molecular Contamination Sources

- Process equipment
- Impurities in incoming process chemicals
- Transfer from earlier process steps
- Airborne molecular contamination
- Deliberate addition of organics to process chemicals
  - Surfactants and chelating agents
  - “Proprietary” additives
Gate Oxide Degradation Due To Organic Contamination

* HMDS Monolayer on Oxide

* HMDS = Hexa-methyl-di-silazane

Cumulative Failure (%)

Q_{BD} = Charge-to-Breakdown measurement

“Cost Effective Cleaning and High-quality Thin Gate Oxides”,
### International Technology Roadmap for Semiconductor (ITRS)

(2003 Edition)  
**Table 70a  Surface Preparation Technology Requirements—Near-term**

<table>
<thead>
<tr>
<th>Year of Production</th>
<th>2003</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
<th>2008</th>
<th>2009</th>
<th>Driver</th>
</tr>
</thead>
<tbody>
<tr>
<td>Critical GOI surface metals ((10^{10} \text{ atoms/cm}^2) [F])</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>M</td>
</tr>
<tr>
<td>Critical other surface metals ((10^{10} \text{ atoms/cm}^2) [F])</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>M</td>
</tr>
<tr>
<td>Mobile ions ((10^{10} \text{ atoms/cm}^2) [G])</td>
<td>1.8</td>
<td>1.9</td>
<td>1.9</td>
<td>2</td>
<td>2.2</td>
<td>2.4</td>
<td>2.5</td>
<td>m</td>
</tr>
<tr>
<td>Surface carbon ((10^{13} \text{ atoms/cm}^2) [H])</td>
<td>1.8</td>
<td>1.6</td>
<td>1.4</td>
<td>1.3</td>
<td>1.2</td>
<td>1</td>
<td>0.9</td>
<td>D, %, M</td>
</tr>
</tbody>
</table>

### Surface Carbon

**ITRS 2004 Updated, Table 114a Technology Requirements for wafer environmental contamination control**

<table>
<thead>
<tr>
<th>30% (\text{H}_2\text{O}_2) total oxidizable carbon (ppb)</th>
<th>-</th>
<th>TBD</th>
<th>TBD</th>
<th>TBD</th>
<th>TBD</th>
<th>TBD</th>
<th>TBD</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADD IPA: High molecular weight organics (ppb)</td>
<td>-</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
</tr>
<tr>
<td>ADD 30% (\text{H}_2\text{O}_2): Resin byproducts (ppb)</td>
<td>-</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
<td>TBD</td>
</tr>
</tbody>
</table>
TCA (Trace Contamination Analyzer)
for Metallic, Organic and Molecular Contaminants

<table>
<thead>
<tr>
<th>Trace Contaminant Analysis (TCA) Platform</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Extraction Unit</td>
</tr>
<tr>
<td>Sample Preparation Module</td>
</tr>
<tr>
<td>Electrospray Ionization Interface</td>
</tr>
<tr>
<td>Mass-Analyzer Ion-Trap &amp; TOF</td>
</tr>
</tbody>
</table>

- Cations
- Anions
- Metallics
- Organics
- 24/7

Metara

Characterization and Metrology for ULSI Technology Conference 2005
Example 1: H$_2$O$_2$ Excursion at a Production Fab

- Contaminated H$_2$O$_2$ suspected to cause yield crash at a fab

- Analyses of traditional lab methods show inconclusive results between the “Good” & the “Bad” H$_2$O$_2$ samples
  - ICP-MS (Inductively Coupled Plasma Mass Spectrometry),
  - IC (Ion Chromatography),
  - TOC (Total Oxidizable Carbon)
  - Assay

- Results of TCA showed Intensity of peak at m/z 118 was ~ 20x higher in “bad” sample than in “good” sample
Contaminant found from $\text{H}_2\text{O}_2$ Sample by TCA

Intensity of 118 peak was found to be $\sim 20x$ higher in “Bad” sample.
Identification of Contaminant in “Bad” H₂O₂ Sample

Possible compound: Tri-methyl-glycine

\[
\begin{align*}
\text{CH}_3 & \quad \text{N}^+ \quad \text{CH}_2 \quad \text{C} \quad \text{O}^- \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

m/z = 118.087

\[
\begin{align*}
\text{CH}_3 & \quad \text{N}^+ \quad \text{CH}_2 \quad \text{C} \quad \text{O}^- \quad \text{H}^+ \\
\text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

m/z = 59.074

m/z = 60.082

m/z = 59.074
Contaminant from Ion Exchange Resin

Structure of Ion Exchange Resin

Tri-methyl-glycine

[Chemical structures and equations are shown here, depicting the structure of a contaminant from an ion exchange resin and the tri-methyl-glycine molecule.]
TCA In-Line Monitoring Molecular Contamination in SC-1 (NH₄OH:H₂O₂:H₂O) Bath at a Fab

![Graph showing the ratio of peak areas versus internal standards over time with bath changes indicated.]
### High Organic Content in High Purity H$_2$O$_2$

#### Total Organic Carbon (TOC)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum (Al)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Antimony (Sb)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Arsenic (As)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Boron (B)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Calcium (Ca)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Chromium (Cr)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Gold (Au)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Lead (Pb)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Lithium (Li)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Magnesium (Mg)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Manganese (Mn)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Potassium (K)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Sodium (Na)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Strontium (Sr)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Tin (Sn)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>10 ppt max</td>
</tr>
<tr>
<td>Zinc (Zn)</td>
<td>10 ppt max</td>
</tr>
</tbody>
</table>

#### Problems

- **High Organic Content**
  - 5000 ppb max
- **Low Metallic Content**
  - 10 ppt max
Example 2: Deliberate Addition of Surfactant or Chelating Agents in Baths

- Industrial Trend for Using Diluted Chemistry
  - SC-1 NH4OH:H2O2:UPW from x:1:5 (x = 0.05-3), up to 1:1:500
  - SC2 HCl:H2O2:UPW up to 1:1:1000

- Addition of Surfactant or Chelating Agents in Baths
  - Improve Particle & Metal Removal Efficiency
  - Improve Surface Wetability for Uniform Wafer Surface Preparation
Chelating Agent found from a SC-1 (NH₄OH:H₂O₂:H₂O) by TCA

Possible Formulation:
A Mixture of Compounds with Functioning Groups R-COO⁻ and -(CH₂CH₂)ₙ-O

Chelating agents/surfactants Need to be completely rinsed off from wafer surface
Example 3: TOC (Total Oxidizable Carbon) Excursions at a Fab

- Seasonal TOC excursions at a fab
  - Urea (fertilizer) in UPW (Ultrapure Water) was suspected
  - “No way to confirm suspicions” because “no laboratory methods available to accurately measure low ppb concentrations of urea contamination in water”*

TCA Quantitative Analysis of Urea in UPW

\[(\text{NH}_2)_2\text{COH}^+\]

- **0 ppb Urea**
  - \(m/z = 61.041\)

- **5 ppb Urea**
  - \(m/z = 61.041\)

- **10 ppb Urea**
  - \(m/z = 61.041\)

**DL** = \(3\sigma/m = 0.084\) ppb

\(C = 84\) ppt C, \(n = 6\)
TCA Analysis of Urea by Ratio Technique

1. 0 ppb $^{12}$C Urea + 10 ppb $^{13}$C Urea
2. 5 ppb $^{12}$C Urea + 10 ppb $^{13}$C Urea
3. 10 ppb $^{12}$C Urea + 10 ppb $^{13}$C Urea
Ratio Measurement of $^{12}$C Urea/$^{13}$C Urea

$m/z = 61$ (C12)

$m/z = 62$ (C13)

Ratio of 61/62
TCA Analytical Results of Urea

\[ C_s = C_{sp} \left( \frac{V_{sp}}{V_s} \right) \left( \frac{A_{sp} - Ratio \times B_{sp}}{Ratio \times B_s - A_s} \right) \]

TCA Automatic Quantification

Calculated Results (10ppb C13 Urea Spike)

Accurately Quantified at ppb level

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Example 4: Molecular Contamination in Pre-Gate Cleaning Processes at a Fab

- Yield problems at a Fab
  - Gate oxide breakdown voltage reduction

- Results of TXRF and VPD-ICP/MS
  - No metallic contamination

- Organic or molecular contamination was proposed
  - No significant suspect by routine lab methods
Contaminants Found from HQDR (Hot Quick Dump Rinse) UPW by TCA

- **HQDR UPW_2**
  - (H₃PO₄)H⁺
  - m/z = 98.987

- **HQDR UPW_3**
  - Urea
  - (NH₂)₂COH⁺
  - m/z = 61.040

- **HQDR UPW_4**
  - NMP-H⁺
  - m/z = 100.076

Scale Different
Possible Contamination Sources in Fab

NMP = N-Methyl-2-pyrrolidone (C₅H₉NO m/z = 99.068)

- Photoresist stripper
- Wafer cleaning
- Semi-aqueous defluxing
- Degreasing
- Coatings (polyamide, epoxy, & polyurethane)

H₃PO₄ Incomplete rinse from nitride etching?

Urea Source water, re-cycling or reclaimed water?
TCA In-Line Monitoring Phosphorus Species in SC-1 Bath at a Production Fab

Proposed as $\text{H}_3\text{PO}_4\text{NH}_4^+$ m/z=106.011
Example 5: Phthalate (Plasticizer) Contamination in IPA (Isopropyl Alcohol)

- It has been reported:
  - Dibutyl phthalate (DBP) in high density polyethylene (HDPE) containers leaching into IPA
  - Plasticizers deposit inside the gas nozzles and chamber in a dryer

- Phthalates have deleterious effects on wafers
TCA Analysis of Dioctyl Phthalate (DOP) and Dibutyl Phthalate (DBP) in IPA

![Graphs showing mass spectra for DOP and DBP in different concentrations.]

- **Blank**: DBP H⁺ m/z=279.160
- **5 ppb**: DBP H⁺ m/z=279.160, DOP H⁺ m/z=391.285
- **10 ppb**: DBP H⁺ m/z=279.160, DOP H⁺ m/z=391.285
Example 6: Molecular Contamination in IPA (Isopropyl Alcohol) at a Fab

- IPA from lot 1, 2, 3 suspected causing multiple excursions
- No significant difference between lot 1, 2, 3 and lot 4, 5, 6 by routine lab methods
Contamination Sources from IPA Manufacturing Processes

Isopropyl sulfate is a highly suspect in IPA lot 1, 2, 3

\( \text{propene gas} \)

\[ \text{CH}_3\text{CH}=\text{CH}_2 + \text{H}_2\text{SO}_4 \xleftrightarrow{} (\text{CH}_3)_2\text{CH} \text{O-S-OCH(CH}_3)_2 + (\text{CH}_3)_2\text{CHO-S-O} \]

\( \xrightarrow{\text{hydrolysed with H}_2\text{O}} \)

\[ (\text{CH}_3)_2\text{CHOH} \]

Final Product = IPA

m/z = 139.007
Summary

- Using the TCA we have demonstrated the ability to:
  - Analyze molecular contamination in a variety of process solutions including UPW, SC-1 and IPA
  - Identify specific molecular contaminants
  - Provide quantitative concentration measurement
  - Make measurements in-line and in near real-time
  - Provide process chemistry trends that correlate to Wafer Fab yield problems
Conclusion

- We believe this new measurement capability will:
  - Enable statistically valid real-time process chemistry control decisions
  - Provide advanced warning of excursions
  - Enable chemical specifications and bath life decisions based on process data and yield correlation