PFOS Management in
Semiconductor Manufacturing

Beatrix Pichl
ESH Director Europe
Texas Instruments
Who we are
Cleanroom Environment
Role of PFOS in SC Manufacture
Human exposure
Environmental Exposure
SCHER Report
EU PFOS Use Data
PFOS Substitution
Summary of Risk
Semiconductors are at the heart of the modern economy

2004 electronics industry revenues of US $1.24 trillion achieved overall revenues of US $5.0 trillion. When added together, this accounts for approximately 10 percent of the overall global economy.
Who we are

Semiconductors worldwide sale
US $213 billion in 2004
Employees: 225,000 people in the United States 86,000 in Europe
est. 500,000 people employed worldwide in 2003

Data source:
SIA 2005 Annual Report entitled “2020 is Closer Than You Think,” the EECA-ESIA 2005 Competitiveness Report,
SIA at http://www.sia-online.org/home.cfm;
EECA-ESIA at http://www.eeca.org/esia.htm;
SEMI at http://www.semi.org/
Basic Steps in Semiconductor Manufacturing

- Oxidation
- Photolithography
- Doping (Ion Implantation/diffusion)
- Thin Film Deposition
- Etching
- Metallization
- CMP

15-30 Iterations
PFOS and Semiconductor Manufacturing

- Semiconductor manufacturing is highly complex
- As circuit features get ever smaller, specialty chemicals like PFOS become ever more critical
- Semiconductor uses of PFOS include:
  - Photoacid generators (PAGs) that increase the sensitivity of photoresist to allow etching images smaller than wavelength of light
  - Anti-reflective coatings (ARCs) that prevent blurred images caused by surface reflections
  - Use in developers: commitment to phase out by end of 2006
- PFOS is not incorporated in endproducts

PFOS provides unique chemical functionality that makes advanced semiconductors possible
Photo resist is spun on the wafer in an enclosed robotically controlled piece of equipment.
PFOS Human Exposure in Cleanroom Environment

Based on the survey results from the May 2005 study at Sematech and similar surveys at numerous other semiconductor facilities over the past four years, airborne exposure levels to PFOS in photolithographic areas of semiconductor fabrication facilities appear very low (i.e., nondetectable) and more than two orders of magnitude below the manufacturer’s exposure guideline (i.e., 0.1 mg/m³).

Source:
International SEMATECH Manufacturing Initiative, Technology Transfer #05094683A-TR, November 2005: A Summary of Analytical Methods and Industrial Hygiene Sampling Results Relating to Airborne concentrations of Perfluorooctane Sulfonate (PFOS) in Semiconductor Industry Photolithography Applications
SC Manufacture: Cleanroom Suits and Personal Protective Equipment (PPE)

PPE worn during:
- Normal process
- Equipment cleaning
- Maintenance and repair
PFOS Environmental Exposure
PFOS waste streams

- Two primary wastestreams generated:
  - Waste water: from rinsing and developing steps ca. 17% of total waste stream; EU 2002: 43 kg/a from essential = critical uses
  - Waste solvent: captured and disposed of by high temperature incineration is standard industry practice
Scientific Committee on Health and Environment SCHER Report (Feb 05):
“Opinion on ‘RPA’s report ‘Perfluorooctane Sulphonates: Risk reduction strategy and analysis of advantages and drawbacks

Recent review of PFOS uses in Europe concluded: a further examination of the 2004 data reveals that PFOS and PFOS-related substance emissions from the European semiconductor industry in 2002 represented only 0.45 percent of all PFOS emissions in Europe.

This compares to metal plating, which is by far the highest emitter at 94 percent, followed by fire fighting foams at 5.4 percent.

“The contribution of the confirmed on-going industrial/professional uses to the overall risks for the environment and for the general public are probably negligible with regard to the sectors…[including] semiconductor industry…”
1. The term PFOS is reserved strictly for the C8 homologues of the PFAS family.
2. Percentages are applied to the revised input. For example, the resist quantity to wastewater is calculated by taking 7% of the input value (44.9 kg) and 50% of the resulting number = 1.57 kg.
3. PFOS inputs reflect actual ESIA and SEMI member company survey data for calendar year 2002.
4. The ESIA and SEMI surveys were conducted independently from one another. Values used in the mass balance represent the high-end estimate from either survey.
5. A Destruction Removal Efficiency (DRE) value of 99.99% is used for incineration to determine amount of annual emissions to the environment estimated through that technology.
   Note: This is a conservative DRE number considering that this number is used for destruction as a recycled fuel in boilers and most of the material is likely incinerated at 99.9999% DRE.
6. In blue: changes made in comparison with last version.
7. In pink: numbers still to be optimized.

**SYNOPSIS 2002**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total input PFOS</td>
<td>435.9 kg</td>
</tr>
<tr>
<td>Total PFOS incinerated</td>
<td>196.5 kg</td>
</tr>
<tr>
<td>Total PFOS release to wastewater</td>
<td>238.4 kg</td>
</tr>
</tbody>
</table>

**In case of no PFOS developer use:**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total estimated potential release</td>
<td>43.38 kg PFOS/Yr</td>
</tr>
<tr>
<td>Total amount PFOS used</td>
<td>240.9 kg PFOS/Yr</td>
</tr>
<tr>
<td>Total estimated amount incinerated</td>
<td>196.52 kg PFOS/Yr</td>
</tr>
<tr>
<td>% PFOS incinerated</td>
<td>82%</td>
</tr>
</tbody>
</table>
PFOS Substitution

• Ongoing industry effort – semiconductor industry in partnership with chemical and equipment suppliers
• “Critical” vs. “non-critical” uses: based on availability, or expected availability, of functionally-adequate substitutes – are there functional substitutes in specific applications?
• Non-critical uses virtually eliminated – remaining applications (PAGs and ARCs) – have no readily-available substitutes
• Finding and qualifying substitutes for all critical uses:
  • Is extremely complex
  • Is process-, technology-, and company-specific
• Therefore, if possible to replace, will take many years – and it will require invention
• Industry already moved away from PFOS use where feasible substitutes exist in non critical applications

PFOS alternatives are not “drop-in” replacements
Summary
PFOS carefully managed in Semiconductor Manufacturing

- Small quantities of PFOS in “critical” applications
- PFOS *stringently managed* in photolithography process to minimize emissions and exposure
- End result: *de minimis* emissions and exposure

*While PFOS may present a *hazard*, semiconductor critical uses do not present an environmental or health *risk**

*Data Source: ESIA-SEMI 2002 PFOS Mass Balance*
Back Up
Generic Semiconductor PFOS Mass Balance Flow Diagram

- Cleans
- Photo
- Develop
- Trash (solid)
- Incineration
- Wastewater
- Dry Strip
- Wet Strip

Flow Diagram:

- Resist Chemical
- Developer Chemical
- Trash (solid)
- In Some Countries
- Incineration
- Air

PFOS Destroyed

Processing Steps
PFOS Waste Sinks
### Semiconductor Industry

**PFOS Use in Perspective – EU Case**

<table>
<thead>
<tr>
<th>Industry Sector</th>
<th>2002 EU Use [kg/year]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photographic Industry</td>
<td>1000</td>
</tr>
<tr>
<td>Semiconductor Related Photolithography</td>
<td>470*</td>
</tr>
<tr>
<td>Hydraulic Fluids (Aviation)</td>
<td>730</td>
</tr>
<tr>
<td>Metal Plating</td>
<td>10000</td>
</tr>
</tbody>
</table>

*BEFORE elimination of non critical uses

Data source: RPA/BRE RRS August 2004

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Semiconductor uses of PFOS in EU have gone down significantly as non-critical uses have been eliminated.
Photoacid Generator Example

PAGs give a 2:1 resist polymer chain destruction for each photon of light - CHEMICAL AMPLIFICATION
Photoacid Diffusion Control

Path of catalyst
Resist morphology
Feature Foot

Short Diffusion
Well resolved features
Smaller scale roughness
(exemplary of PFOS PAG)

Long Diffusion
Poorly resolved features
Larger scale roughness
(exemplary of non-PFOS PAG)

Feature roughness can cause failure in critical applications
Metal substrates can reflect photons back from the surface – into areas of the resist not to be exposed.

ARCs absorb the photons and prevent them from reflecting back – the composition and capabilities of the ARC must be matched to the resist and the light source.