CMP Waste Treatment with a Forced-Flow Electrophoresis Device

(Subtask A-4-1)

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Outline

• Motivation
• Description of Forced-Flow Electrophoresis
• Results
• Additional Research
• Potential Transfer of Technology
• Concluding Remarks
In 2002 CMP will constitute approximately 30% of UPW usage. UPW consumption continues to exceed Roadmap goals.


\[ \text{Total UPW} = \text{UPW usage} \times \text{UPW cost} \] (in \( \text{gallons/year} \))

\[
\begin{align*}
\text{Year} & \quad \text{Total UPW} \quad (10^9 \text{gallons/year}) \\
1994 & \quad 10 \\
1996 & \quad 15 \\
1998 & \quad 20 \\
2000 & \quad 25 \\
2002 & \quad 30 \\
2004 & \quad 35 \\
2006 & \quad 40 \\
\end{align*}
\]
Current Trend†

• One CMP tool requires:
  - 7,000 gallons of UPW per day
  - 12,000 gallons feed water per day

• As device linewidths shrink, additional CMP will be required

ITRS Goals‡

• Net feed water consumption drop from 13 gal/in² (of silicon) to 2 gal/in² by 2008

• Obtain environmental sustainability through waste management

† Corlett, G. Advancing Applications in Contamination Control 2000, 3(11), 9.
ITRS Technology Barrier: Waste Production vs. Environmental Regulations

Single fabrication plant produces 200 GPM of CMP effluent.†

† Maag, Benoit, “Copper CMP Effluent Flow in a Semiconductor Facility”, NSF/SRC ERC for Environmentally Benign Semiconductor Manufacturing TeleSeminar, April 6, 2000
ITRS Technology Barrier: Waste Production vs. Environmental Regulations (cont.)

Waste Characteristics†

- 50-5000 ppm total suspended solids
- 0.1-50 ppm soluble copper

Environmental Regulations†

Waste must be reduced to the following levels prior to discharge to waste treatment system:

- < 5 ppm total suspended solids
- 0.1-2 ppm soluble copper
- Regulations vary according to location.
  - San Jose Code Limitations:‡ Cu = 2.7 ppm
  - Austin Code Limitations:‡ Cu = 1.9 ppm

‡ Corlett, G. Advancing Applications in Contamination Control December 1998, pg. 19.
Forced-Flow Electrophoresis (FFE)

Research Objectives

• Liquid/solid separation
  o good performance at high concentrations; retard filter cake buildup
  o create possibilities for water recycle/reuse

• Copper removal from waste stream

ESH Impact

• Recovery and recycle of water

• Help achieve ITRS goals for environmental sustainability through waste management

• Compliance with environmental regulations for waste streams
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FFE: Cross-Flow Filtration with Electric Field

- An electric field $E$ enhances cross-flow filtration process by electrophoretically driving particles away from filter surface, while driving electrodialysis of ionic solutes (e.g. Cu)

- Thus: (1) filter cake is suppressed and filter effectiveness maintained; and (2) the permeate is either enriched with, or depleted of, ionic solutes (including Cu), depending on the type of membrane used (e.g. cation exchange or anion exchange)

$V_f$ - direction of flow of permeate water
$V_p$ - direction of electrophoretic migration of particles
Expanded FFE Cell Assembly

A  End plate with Platinum Electrode
B  Dialyzing Membrane
C  Input Spacer for 1st Cell
D  Micro Filter (Whatman, 20 µm)
E  Output Spacer for 1st Cell
F  Dialyzing Membrane
G  Input Spacer for 2nd Cell
H  Micro Filter (Whatman, 20 µm)
I  Output Spacer for 2nd Cell
J  Dialyzing Membrane
K  Input Spacer for 3rd Cell
Device Components and Operating Conditions

- Electrodes: platinum
- Membranes: regenerated cellulose
  (weak cation exchange properties)
- Filters: Whatman®, 20 µm porosity
- Influent flow rate: 80 ml/min
- Permeate and retentate flow rate: 40 ml/min
- Effective volume: 180 ml
Entire FFE Apparatus

Marriotte Supply Bottle

Influent Suspension

FFE Device

Permeate

Retentate

Water Manometer

Water Manometer
FFE Apparatus

- FFE method developed by: Bier, M. et al., 1959
- Additional research on FFE: Henry, et al., 1977
  Wakeman, et al., 1987
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## CMP Waste Characteristics

<table>
<thead>
<tr>
<th>Waste Stream</th>
<th>Turbidity (NTU)</th>
<th>Conductivity (µS/cm)</th>
<th>pH</th>
<th>Cu$^{++}$ Conc. (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model Oxide</td>
<td>450$^\dagger$</td>
<td>230</td>
<td>10.5</td>
<td>—</td>
</tr>
<tr>
<td>Texas Instruments</td>
<td>1550</td>
<td>160</td>
<td>9.0</td>
<td>—</td>
</tr>
<tr>
<td>Model Copper</td>
<td>410$^\ddagger$</td>
<td>570</td>
<td>5.0</td>
<td>20</td>
</tr>
</tbody>
</table>

$^\dagger$ 1000 ppm Klebosol® colloidal silica; mean particle size, 80 nm

$^\ddagger$ 900 ppm Klebosol® colloidal silica; mean particle size, 80 nm
Electrophoretic Filtration of Particles for Model Oxide CMP Waste

Influent Suspension Characteristics:
- $[\text{SiO}_2] = 1000$ ppm
- Conductivity = 230 $\mu$S/cm
- Turbidity = 450 NTU
- pH = 10.5
Electrodialysis Mechanism

- Anions: silica, sulfate
- Cations: copper, sodium

M Membrane (negative charge)
F Fluid partition (filter)

Permeate

Anode
Retentate

NSF/SRC Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
Electrodialysis of Ionic Solutes for Model Oxide CMP Waste

Influent Suspension
Characteristics:
[SiO₂] = 1000 ppm
Turbidity = 450 NTU
Conductivity = 230 µS/cm
pH = 10.5

Conductivity of Influent Suspension

Conductivity of Retentate

Conductivity of Permeate

Ion Mass Balance

E (V/cm)
FFE of Industrial Oxide CMP Waste from Texas Instruments Inc.

Influent Suspension Characteristics:
- Turbidity = 1550 NTU
- Conductivity = 160 µS/cm
- pH = 9.0
Electrophoretic Filtration of Particles for Model Copper CMP Waste

Influent Suspension Characteristics:
- $[\text{SiO}_2] = 900$ ppm
- $[\text{Cu}] = 20$ ppm
- $[\text{Citric Acid}] = 66$ ppm
- $[\text{BTA}] = 37$ ppm
- Conductivity = 570 $\mu$S/cm
- Turbidity = 410 NTU
- pH = 5.0
Electrodialysis of Ionic Solutes for Model Copper CMP Waste

Influent Suspension Characteristics:

- \([\text{SiO}_2]\) = 900 ppm
- \([\text{Cu}]\) = 20 ppm
- \([\text{Citric Acid}]\) = 66 ppm
- \([\text{BTA}]\) = 37 ppm
- Turbidity = 410 NTU
- Conductivity = 570 µS/cm
- pH = 5.0

Ion Mass Balance

- Permeate
- Retentate

Conductivity of Influent Suspension

Conductivity/
Electrodialysis of Copper for Model Copper CMP Waste

Influent Suspension Characteristics:
- \([\text{SiO}_2]\) = 900 ppm
- \([\text{Cu}]\) = 20 ppm
- \([\text{Citric Acid}]\) = 66 ppm
- \([\text{BTA}]\) = 37 ppm
- Turbidity = 410 NTU
- Conductivity = 570 \(\mu\text{S/cm}\)
- \(\text{pH} = 5.0\)
Energy Consumption: Forced-Flow Electrophoretic Filtration vs. Mechanical Filtration

<table>
<thead>
<tr>
<th>Filtration Technique</th>
<th>Energy Consumption/Permeate Flow Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultrafiltration (with 45% pump efficiency)</td>
<td>5 kJ/gallon of permeate</td>
</tr>
<tr>
<td>FFE Industrial Oxide CMP Waste Conductivity = 160 µS/cm</td>
<td>3 kJ/gallon of permeate</td>
</tr>
<tr>
<td>FFE Model Copper CMP Waste Conductivity = 570 µS/cm</td>
<td>20 kJ/gallon of permeate</td>
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Effects of Various Additives on FFE Process: Electrodialysis of Copper

Influent Suspension Characteristics:
Conductivity = 570 µS/cm
pH = 5.0
Effects of Various Additives on FFE Process
Electrodialysis of Copper (cont.)

Influent Suspension Characteristics:
Conductivity = 570 µS/cm
pH = 5.0

Copper Concentration in Influent Suspension vs. E (V/cm)

- Copper
- Copper and Silica
- Copper, Silica and Citric Acid
- Copper, Silica, Citric Acid, and BTA

Copper Concentration in Permeate/
Copper Concentration in Influent Suspension
Effects of Various Additives on FFE Process
Electrophoretic Filtration of Particles (cont.)

Influent Suspension Characteristics:
Conductivity = 570 $\mu$S/cm
pH = 5.0
Effects of Various Additives on FFE Process
Electrophoretic Filtration of Particles (cont.)

Influent Suspension Characteristics:
- Conductivity = 570 µS/cm
- pH = 5.0

![Graph showing the relationship between turbidity of permeate and turbidity of influent suspension with various additives at different electric field strengths (E V/cm)].

- **Silica**
- **Silica, Copper**
- **Silica, Copper, Citric Acid**
- **Silica, Copper, Citric Acid, BTA**
Effect of Various Additives on Electrophoretic Mobility of Particles and Copper

Capillary Electrophoresis

- Additives effect electrophoretic mobilities of particles or copper?
- Additives effect distribution of particle mobilities?

![Diagram of Capillary Electrophoresis]

Absorbance

Silica

Marker

Time (minutes)
FFE with Strong Cation Exchange Membranes

Influent Suspension Characteristics:
- \([\text{SiO}_2]\) = 900 ppm
- \([\text{Cu}]\) = 20 ppm
- [Citric Acid] = 66 ppm
- [BTA] = 37 ppm
- Turbidity = 410 NTU
- Conductivity = 570 \(\mu\)S/cm
- pH = 5.0
FFE with Strong Cation Exchange Membranes (cont.)

Influent Suspension Characteristics:
- $[\text{SiO}_2] = 900$ ppm
- $[\text{Cu}] = 20$ ppm
- $[\text{Citric Acid}] = 66$ ppm
- $[\text{BTA}] = 37$ ppm
- Turbidity = 410 NTU
- Conductivity = 570 $\mu$S/cm
- $\text{pH} = 5.0$

Copper Concentration in Permeate/Copper Concentration in Influent Suspension

E (V/cm)

Regenerated Cellulose Membrane

“Strong” Cation Exchange Membrane
FFE with Strong Cation Exchange Membranes (cont.)

Influent Suspension Characteristics:
- $[\text{SiO}_2] = 900 \text{ ppm}$
- $[\text{Cu}] = 20 \text{ ppm}$
- $[\text{Citric Acid}] = 66 \text{ ppm}$
- $[\text{BTA}] = 37 \text{ ppm}$
- Turbidity = 410 NTU
- Conductivity = 570 $\mu$S/cm
- pH = 5.0
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Potential Industrial Applications

1. Use as filtration device on each individual CMP tool.

- Forced-flow electrophoresis device (FFE) could act as a CMP tool “kidney” that could be switched on and off according to demands of CMP tool.
- Permeate stream, reduced of particle and copper contamination, could be recycled back into the CMP process.
Potential Transfer of Technology (cont.)

2. Use immediately before standard ultra-filtration (UF) and ion-exchange (IX) processes to pre-treat CMP waste.

- Forced-flow electrophoresis pre-treatment will yield less consumables (e.g. UF cartridges, ion-exchange resin, etc.)
Industry Interaction

The following companies have provided assistance:

- **Semiconductor Research Corporation**
- **Texas Instruments**, Jeff Joiner and John DeGenova
- **Ionics**, Ted Prato and Russ MacDonald
- **Pall Corporation**, Joe O’Sullivan
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Concluding Remarks

- Have demonstrated simultaneous removal of particles (ca. 90 to 99%) and ions (including >85% of Cu) from CMP permeate streams.

- Energy requirements are not significantly different from those of standard ultrafiltration.

- FFE may have the potential to serve as a CMP waste management device and could help the semiconductor industry comply with the environmental regulations for the waste streams.