Meeting Selectivity Needs with Unique Corrosion Inhibitors in Cleaning and Surface Finishing Practices

John Moore, Technical Director
DAETEC, LLC

LEVITRONIX Ultrapure Fluid Handling and Wafer Cleaning Conference
February 2008
Agenda

- **Inhibitor Types**
- Inhibition by Chemisorption
- Ex. Performance (Cu, Al, Sn)
- In-Tool Processing
- Applications
- PQA Program
- Summary
Inhibition Types

- Chemisorption (e.g. triazoles, silicates, etc.) react with the substrate to form a protective layer, thickness can be monolayer or continues to coat to excess.
- Coating (e.g. organic protective film) barrier to reactive species.
- Other - solution additives exist to tie-up reactive species or produce a “reducing” environment.
Factors Affecting Corrosion

- Chemistry
- Conductivity
- Heat
- Agitation
- Other - current density, dissimilar metals

- Aluminum Oxidation
  \[ \text{Al}_{(s)} \rightarrow \text{Al}^{3+} + 3\text{e}^- \]
  \[ E = 1.66\text{v} \]
- Strong bases & acids
Inhibitor Activity

Most inhibitors have max and min activity regions dependent upon the media (I.e. acid/base)

Certain inhibitors may operate well in corrosive media while others may exhibit synergism

Optimization is needed
Agenda

- Inhibitor Types
- Inhibition by Chemisorption
- Ex. Performance (Cu, Al, Sn)
- In-Tool Processing
- Applications
- PQA Program
- Summary
Chemisorption Inhibitors

- Triazoles - good for Cu, prone to residue
- Borates, phosphates, iodics, silicates, carboxylics, nitrites, sulfites, amines, specialties & organometallics, surfactants
- Blends may achieve synergism
- Buffering/leveling for maximum activity
Inhibition by Chemisorption
Ex. Cu-Triazole, network formation
Inhibition by Chemisorption
Cu/Triazole - XPS Surface Analysis

Convert reactive Cu(2) to inert Cu(1)

Convert C from oxidized to phobic
Inhibition by Chemisorption
Cu/Triazole - Ellipsometry

Inhibitor must be thin layer to meet device dimension needs

- Triazole 1
- Triazole 2
- Triazole Mix

BTA
TTA
Mix
Inhibition by Chemisorption

Hg-Probe I-V Plots of Triazoles on Cu

Triazoles, 0.5% Aqueous Solns RT 30sec Exposure

Current (uAmps)

Voltage (volts)

BTA
TTA
Mix

DAETEC
Accelerating Products to Market
Slide #11
Agenda

- Inhibitor Types
- Inhibition by Chemisorption
- Ex. Performance (Cu, Al, Sn)
- In-Tool Processing
- Applications
- PQA Program
- Summary
Example Performance

- Determined on metal film
- Extended period of time
- Dilute concentrations for “in-tool” mixing
- Elevated temperature - representative for etch residue & resist removal applications
- Benefit measured relative to baseline (i.e. no inhibitor)
Copper Inhibitor Systems in H2SO4
0.1% w/w Inhibitor

Etch Rate (A/min)

- Reference: 3
- A001: 1.5 (2-Fold Benefit)
- A002: 0.7 (5-Fold Benefit)
- A003: 2 (0.7-Fold Benefit)

DAETEC Method Gravimetry

Accelerating Products to Market
Slide #14
Copper Protection in H2SO4
Ave Benefit vs Concentration

Inhibitor (% w/w)

Benefit Measured for All Cu Inhibitors A001 - 003

DAET'EC
Accelerating Products to Market
Aluminum Etch Rate vs Temperature
0.26N TMAH (pH = 14)

Alkyl-silicate
Aluminum Etch Rate in Aqueous TMAH

MIF Inhibitor, pH = 14 Media

Etch Rate (A/min)

- Control
- Inhibitor

Temperature (°C)

- 20
- 60
- 100

Alkyl-silicate
Tin Metal Protection In Stripper Media
Choice of Solvent & Inhibitor

Full factorial of 4 inhibitors & Solvents
Best Systems appear to be I-1 & I-2
with possible synergism for I-2 & LMW ketone

Etching not detected

Inhibitors I1 - I4

Accelerating Products to Market
Agenda

- Inhibitor Types
- Inhibition by Chemisorption
- Ex. Performance (Cu, Al, Sn)
- **In-Tool Processing**
- Applications
- PQA Program
- Summary
Review - Current Cleaning/Finishing

Immersion
Removal by chemical interaction of the bulk fluid

Batch Spray
Removal by Momentum-energy Transfer

Single Wafer
Combination of spray principles and fluid control during drying
In-Tool Liquid Controls

- Inhibitor designed for metal protection & rapid processing from cleans to rinsing
- Able to work in a range of chemical media for in-tool mixing
- Deliver reduced surface tension for improved wetting & rinsing
- No or low foam
Reduced Surface Tension
Processing Aids

- Greater penetration to small areas
- Reduced redeposition
- Improved mixing during rinse cycle
- Low-foaming conditions
Inhibitor Pkg for Spray Tools
Surface Tension vs Concentration

Concentration as Inhibitor Pkg
Applicable for Cu (acid/base media)

Concentration (% w/w)
Screen for Foaming

Effects of Foaming of Surfactant Draves Foam Height vs Conc

RM = Ross-Miles Test

RM 3sec

RM 15sec

RM study conducted with aggressive mixing - 10sec shake
Agenda

- Inhibitor Types
- Inhibition by Chemisorption
- Ex. Performance (Cu, Al, Sn)
- In-Tool Processing
- Applications
- PQA Program
- Summary
Inhibitor Processing

- Pkg design for spray tools, immersion, etc.
- Dilute forms (i.e. most are \( \leq 1\% \))
- Simple in-tool mixing and delivery
- Fast reaction - on contact
- Thin coating (i.e. monolayer)
- Low ST and non-foaming
- Easy water rinse
## Formulation for Processing

<table>
<thead>
<tr>
<th>PR</th>
<th>Solvent</th>
<th>Active Agent</th>
<th>Tool</th>
<th>Process Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Novolac, FPD</td>
<td>BDG, DMSO</td>
<td>Monoethanolamine (MEA)</td>
<td>Conveyor/spray</td>
<td>Corrosion, foam, compatibility</td>
</tr>
<tr>
<td>Acrylic, bumping</td>
<td>DMSO</td>
<td>Tetramethylammonium hydroxide (TMAH)</td>
<td>Immersion</td>
<td>Corrosion, dissolution</td>
</tr>
<tr>
<td>PHost, Cu/Low-K</td>
<td>Sulfuric</td>
<td>Peroxide</td>
<td>Single Wafer</td>
<td>Corrosion</td>
</tr>
<tr>
<td></td>
<td>Glycol + water</td>
<td>MEA</td>
<td>Single Wafer</td>
<td>Corrosion, rinsing</td>
</tr>
</tbody>
</table>
## Common Inhibitors

<table>
<thead>
<tr>
<th>Metal</th>
<th>Stripper pH</th>
<th>Inhibitors*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Alkali, acid</td>
<td>Silicate, citrate, phosphate, triazole, succinate, borate, catechol (EHS options)</td>
</tr>
<tr>
<td>Pb, Ag, Cu</td>
<td>Alkali, acid</td>
<td>Thiocyanate, triazole, EDTA, imidazole</td>
</tr>
<tr>
<td>Cu, Ti, Ta</td>
<td>Alkali, acid</td>
<td>Triazole, phosphate, citrate, resorcinol</td>
</tr>
</tbody>
</table>

Solubility dependence on pH, organic content, salt level, and material form.
Applications - Strippers

Bumping Chemistries w/No Inhibitor → w/Inhibitor

FPD Chemistries w/No Inhibitor → w/Inhibitor

Al-based devices gross damage

Accelerating Products to Market
Accelerating Products to Market

Solder (SnPb, SnAgCu)

Dry Film PR
Cured >250 °C

UBM (Ti/Al/NiV)

Passivation (PI, BCB, PBO)

Chip Substrate

Pad (Al or Cu)

Suppliers
DuPont Riston
RHEM-Shipley
Eternal
Asahi (Sunfort)
Hitachi

Mylar
Resist
Polypro
Strippers for FCT Bumping

Formula:
- Alkali
- Solvent
- Co-solvent
- Inhibitor

Inhibitors: phosphates, succinates, imidazoles
FPD Process Strip & Rinse

Conveyor Tool: heat, pressure, time control

Dirty Tank → Strip → Stripper → Clean Tank → Rinse (House DI Water) → Dry (Hot N₂ Dry) → Clean

Accelerating Products to Market
### Demo on Alloy Blanket

<table>
<thead>
<tr>
<th>Stripper</th>
<th>H₂O 0%</th>
<th>H₂O 10%</th>
<th>H₂O 25%</th>
<th>H₂O 50%</th>
<th>H₂O 75%</th>
<th>H₂O 90%</th>
<th>H₂O 95%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PR Strip A</td>
<td>NC</td>
<td>NC</td>
<td>5min</td>
<td>5min</td>
<td>3min</td>
<td>2min</td>
<td>2min</td>
</tr>
<tr>
<td>PR Strip B</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>4min</td>
<td>3min</td>
<td>2min</td>
</tr>
<tr>
<td>PR Strip C Inhib.</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
<td>NC</td>
</tr>
</tbody>
</table>
Metal Etch Rate Measurement

- PR Strip A
- PR Strip B
- PR Strip C + Inhibitor

Etch Rate Study
50C, 30min
Tested at H2O mix Ratio

Corrosion (A/min)

H2O Mixing (%)

0 50 90

DAETEC
Accelerating Products to Market
Slide #35
Panel Device After Process

A-series: baseline (no inhibitor), B-series: stripper + inhibitor
Cu/Low-K Residue Cleans

Cu Etch Rate in Dilute H2SO4

- **Reference**: Representative data for comparison.
- **A1**: Lower etch rate compared to reference.
- **A3**: Lowest etch rate among the three.

**Concentration (%)**

- **Etch Rate (A/min)**
  - **0.2**
  - **0.4**
  - **0.6**
  - **0.8**
  - **1.0**

**Daetec Method #G001**
Agenda

- Inhibitor Types
- Inhibition by Chemisorption
- Ex. Performance (Cu, Al, Sn)
- In-Tool Processing
- Applications
- PQA Program
- Summary
Chemical Industry

- $2trn global enterprise
- 70,000 different products
- Several hundred large producers @ @ >$1bn, thousands of small
- Triad locale: EU, N. America, Japan
- Not including pharma
- Many materials not included (i.e. final forms: metals, polymers, detergents)
Accelerating Products to Market

PQA Supplier

- Pre-screened
- Flex Pkg
- Low-cost Conc.
- COA docs
- Toll blending

Raw Material Suppliers

DAETEC Accelerating Products to Market Slide #40
Pre-Qualified Agents (PQA)

- Tested for performance - key benefits expected;
- Tested for media compatibility - limitations on pH, solubility, etc.;
- Tested for process integration - suggested use rates, properties per the industry, example formulary;
- Available in concentrate - low cost;
- Single source, ISO certified, flexible pkg.
Pre-Qualified Agents (PQA)

- **Formulators** - reduces test requirements, accelerates new product development;
- **Tool Companies** - facilitates in-tool mixing, accelerates process development and new tool designs;
- **End Users (Fabs)** - allows feasibility and R&D on integration challenges for next generation devices.
PQA Product Listing

- GaAs-safe solvents & amines
- Cu-safe amines
- Inhibitors for Cu, Al, and other metals
- Alkali agents, high TMAH content
- Surfactants for low ST and emulsification
- Viscosity modifiers (gels)

- Polymers - Coatings, HT applications
- Polymers - Coatings, aqueous wash applications & HT
- Polymers - Adhesives for wafer thinning
- Carrier solvents for coatings - high dep & low TTV
Agenda

- Inhibitor Types
- Inhibition by Chemisorption
- Ex. Performance (Cu, Al, Sn)
- In-Tool Processing
- Applications
- PQA Program
- Summary
Various inhibitors exist, chemisorption types may be preferred;

Inhibitor pkg must be optimized for the media, sometimes aggressive chemistry, to ensure maximum activity, low residue, easy rinsing, etc.

Pre-Qualified Agents available to accelerate product development;

DAETEC offers development and technical support in a variety of business models
Contact for More Information

- Pre-Qualified Agents for new product development:
  DAETEC (805) 484-5546
  info@daetec.com  www.DAETEC.com

Applications include: etch residue, hard baked, & thick resist removal, high temp protective coatings, aqueous washable coatings, polymers for 3D-Pkg and wafer thinning.