An Advanced Cleaning Technique that is Environmentally Benign

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Drive Toward New Generation Cleans

- **Cost Reduction**
  - Reduction or elimination of solvents
  - Reduction in excessive use of water
  - Integrated clean processing

- **Technology**
  - Compatibility with new IC materials
  - Limitations of water-related wetting
    - surface tension
    - corrosion promotion

- **Environmental**
  - Use environmentally benign chemicals
  - Recycle chemical reagents
Next Generation Clean Requirements

- Smaller, higher aspect ratios
- Unique etch chemistries
- New materials: dielectrics
- Polymer with imbedded metals
- High percent of overetch
- New materials: metals
Clean Challenges

- Water surface tension and viscosity
  - High surface tension and high viscosity of water
    - Prevents drying of high aspect ratio vias
    - Prevents wetting if extremely small vias
Clean Challenges

- Compatibility with new IC materials
  - High organic percent low-κ materials will be a challenge to clean
    - Augmentation of the dielectric constant
    - Undercutting of the hard mask

![Diagram showing compatibility with new IC materials with low-κ materials and photoresist oxide hard mask.](image)
Emerging Dry Clean Technologies

- **Particle Removal**
  - Laser cleaning
  - Cryogenic snowballs- CO$_2$ or Ar/N$_2$
  - Charged liquid clusters

- **Post-Etch Residue Removal**
  - Supercritical Fluids- CO$_2$ based
  - Low Pressure Gas- SO$_3$ based
  - High Pressure Fluid- NH$_3$ based
    - Densified Fluid Cleaning (DFC)
Emerging High Pressure Clean Technologies

Challenges:
• High aspect ratio
• Small CD
• New materials

Technologies under development
- H$_2$O/CO$_2$
- HiP alcohols
- SCH$_2$O

Technologies at funded companies
- SCCO$_2$
- NH$_3$
- Vapor SO$_3$

Low Pressure
Advantages of High Pressure Technology

- Able to penetrate high aspect ratios
- Able to remove residue from small vias
  - Low surface tension
  - Low viscosity
High Pressure Cleaning

- Platform and Chamber
- Chemical Re-circulation and Purification
- High Pressure Toxic Gases
  Production Worthy
  Cost Effective
  Environmental
- Process and Applications
- Safety Requirements
- GaSonics International
Densified Fluid Cleaning - DFC

- Densified Fluid Cleaning
  - A non-aqueous cleaning technology
  - Using anhydrous liquid ammonia
  - At elevated pressure and low temperature
- DFC is applied to post-etch residue removal
  - Applications
    - via/trench
    - metal cleans
    - deep trenches
    - low-κ materials
Reactor Safety - Design Considerations

- Reactor Material Yield: 4000 psig
- Reactor Design Pressure: 1000 psig
- Reactor Proof Pressure: 750 psig
- Burst Disk Rating: 750 psig
- Hardwired Interlock: 650 psig
- Saturation @ Max Temp: 480 psig
- Operating Pressure: 350 psig
Fugitive Emissions Control

- Reactor Scavenger Emissions Detector
- Gas Box Scavenger Emissions Detector
- Exhaust
- Reactor Door Emissions Detector
- PS - Pressure Switch
- AT - Analytical Transmitter
- Gas Box Leak Exhaust
Purification Process Flow

Pure NH₃  750 psig, 90º C

Impure NH₃  5 psig  25º C

- DFC Tool
- Filter 1
- Filter 2
- Moisture Removal
- Gaseous and Metal Impurity Removal
- Heat Pump
- Compressor
- Surge Tank
- Particles

Impurity sampling points
Prototype Purifier at GaSonics
Purifier Results for Metal Contamination

- post-dfc
- post-filter1
- feed tank
- post-filter2
- membrane

ppb

Na
Mn
Fe
Purifier Results for Metal Contamination

ppb

post-dfc post-filter1 feed tank post-filter2 membrane

P K Ca

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Purifier Results for Metal Contamination

ppb

post-dfc  post-filter1  feed tank  post-filter2  membrane

Li  Cr  Mo

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Metal Contamination Removal Efficiency

Removal Efficiency %

- Sb: 87.2%
- Zn: 87.2%
- Fe: 87.2%
- Cr: 87.2%
- Ca: 87.2%
- Na: 87.2%
- Li: 87.2%
- Ti: 87.2%
- Mo: 87.2%
- K: 81.3%
- Mn: 72.3%
- P: 72.3%
Ammonia Recovery vs. Product Purity

100 ppm feed impurities

Impurity Concentration in Recovered Product (ppm)

Ammonia Recovery (%)
Purifier Results for Gaseous Contamination

Ammonia Recovered at 97%

- N2: post-filter 100%, feed tank 99%
- O2: post-filter 85%, feed tank 100%
- H2: post-filter 100%, feed tank 100%
- CO2: post-filter 100%, feed tank 100%
- CH4: post-filter 100%, feed tank 100%
- CO: post-filter 100%, feed tank 100%
DFC Process Sequence

- **Hot ammonia introduced into reactor**
  - Controlled pressurization (10-15 psig/sec)
  - Hot vapor condenses on surface
  - Wafer platen held at 20°C

- **Pre-process nitrogen purge**
  - Eliminate oxygen
  - Eliminate water vapor

- **Reactor de-pressurized**
  - Controlled de-pressurization (15-20 psig/sec)
  - Ammonia evaporates completely
  - Residual ammonia is purged with UHP N₂
  - Ammonia is recycled and purified

- **Wafer at steady state**
  - Multi-step processing
  - Maximum 300 psig (20.4 atm) 80°C, NH₃ flow continuous
  - Platen rotation & megasonics enhance cleaning action
Via to Low-$\kappa$/Copper: Post-Etch

Presented at ECS Fall 1999 Clean Symposium

Structure:

- Oxide Cap
- Low-$\kappa$ Flare
- Si3N4
- Cu

Acknowledgements go to Sematech for providing samples

Sidewall Polymer and Metal Residue

GaSonics INTERNATIONAL
Via to Low-κ/Copper: Post-DFC

Presented at ECS Fall 1999 Clean Symposium

After DFC process only: Residue-free
Effects on Thin Films: Low-κ FTIR

Allied Signal HOSP™

Presented at ECS Fall 1999 Clean Symposium

GaSonics INTERNATIONAL
Via to TEOS/Al: Post-Plasma and DFC

After Microwave Plasma + DFC: Residue-free

Structure:

- TiN
- TEOS Oxide
- Al
## Effect on Thin Films Exposed to DFC

<table>
<thead>
<tr>
<th>Film</th>
<th>Thickness Change</th>
<th>Index of Refraction</th>
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<tbody>
<tr>
<td></td>
<td>After 5 minute exposure to DFC</td>
<td></td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.01 %</td>
<td>0.02 %</td>
</tr>
<tr>
<td>TEOS</td>
<td>0.05 %</td>
<td>0.03 %</td>
</tr>
<tr>
<td>SOG</td>
<td>&lt; 0.7 %</td>
<td>0.1 to 0.2 %</td>
</tr>
<tr>
<td>Flare™</td>
<td>&lt; 0.01 %</td>
<td>&lt; 0.01 %</td>
</tr>
<tr>
<td>HOSP™</td>
<td>0.03%</td>
<td>&lt; 0.01 %</td>
</tr>
<tr>
<td>Poly-Si</td>
<td>None</td>
<td>None</td>
</tr>
</tbody>
</table>
Process Development Characterization

Design of Experiment 1

- Varied
  - Meg Power
  - Pressure
  - Cycles
  - Rotation

- Recipe Optimized

Response:
PR removed (Å)
Clean Mechanisms

- Removal of Residue and Particles
  - Physical
    - Breaking apart matrix- liquid gas phase changes
    - Washing away particles- fluid shearing flow
    - Megasonic action- cavitation or pressure pulses
    - Thermophoresis- temperature gradient
  - Chemical
    - Swelling residue and photoresist
    - Dissolving residue
    - Solvating metals
Clean Mechanism

- Residue removal physically
  - Gas rapidly evolving from liquid
  - Breaks apart residue matrix to particles
Clean Mechanism

- Residue removal mechanism similar to thermophoresis observed with snow and aerosols
  - heat transfer by shearing gas flow as $\text{NH}_3$ evaporates
  - dislodges particles and is removed in downstream flow
Clean Mechanism

- Residue removal by megasonics
  - Cavitation or pressure pulses from acoustical streaming
  - Dislodges particles by high pressure imploding bubbles or pressure gradient
Conclusions

- DFC is a non-aqueous, non-damaging, low temperature wafer cleaning technology
- A two step all dry process is used to remove post-etch residues
  - Microwave plasma + DFC
- DFC does not affect materials used in integrated circuit device manufacturing
  - Oxides
  - Low-κ
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