Wet Processing Applications in Integrated Circuit Fabrication

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Part I – Characterization of Acoustic Cavitation in Aqueous Solutions Subjected to Megasonic Sound Field
Introduction

- Megasonic irradiation – Commonly used for particle removal in integrated circuit industry

- Acoustic (frequency, power density) and solution parameters (temperature, surfactants, dissolved gases) – Used for modulating stable and transient cavitation

- Characterization of acoustic cavitation is critical for optimization of experimental conditions to achieve effective cleaning without damage

- In the first part of the presentation, various direct and indirect techniques for characterizing cavitation will be discussed
Megasonic Cleaning

- Megasonic Irradiation
  - Transient Cavitation
    - Bubble Collapse
      - Shock Waves
      - Feature Damage
  - Stable Cavitation
    - Bubble Oscillation
      - Microjets
      - Microstreaming
  - Streaming
    - Particle Removal
Effect of Frequency on Bubble-Size Distribution During Acoustic Cavitation

Bubble-size distribution for 213, 355, 647, 875, 1056 and 1136 kHz. The data for 875, 1056, and 1136 kHz have been scaled down by a factor of 4. The acoustic power at all frequencies = 1.5 ± 0.4 W.

Sonoluminescence (SL) and sonochemiluminescence (SCL) were used to characterize the size distribution of bubbles.

The mean bubble size becomes smaller as acoustic frequency increases.

The distribution itself becomes narrower with increasing frequency.

\[
\left( \frac{DC_S}{\rho_g R_0^2} \right) t = \frac{1}{3} \left( \frac{RT \rho_g R_0}{2M\gamma} + 1 \right)
\]

\(D\): diffusion coefficient
\(C_S\): saturated dissolved gas concentration
\(\rho_g\): gas density in the bubble
\(R_0\): initial bubble radius
\(t\): dissolution time
\(R\): universal gas constant
\(T\): absolute temperature of the liquid
\(M\): molecular weight of dissolved gas
\(\gamma\): surface tension.
Effect of Power on Bubble-Size Distribution During Acoustic Cavitation

Bubble radii (mean of the size distribution) under 1056 kHz sonication as a function of acoustic power

- The mean bubble size increases as a function of acoustic power
- Maximum bubble size is about 4.5 \( \mu m \)
Fluorescence Spectroscopy using Terephthalic Acid (TA) Dosimetry

- Hydroxyl radical trapped using terephthalic acid to form 2-hydroxyterephthalic acid, measured using fluorescence spectroscopy
- 2-hydroxyterephthalic acid is stable up to 6 hours at room temperature

Figure source: S. Kanazawa, T. Furuki, T. Nakaji, S. Akamine and R. Ichiki. I. J. PEST 6, 2 (2012)
Effect of Acoustic Frequency on Hydroxyl Radical Generation in 1:10000 NH₄OH Solutions (pH 10) at 2 W/cm²

- Maximum OH• generation rate is observed to be at 1 MHz
- Decrease in generation rate of OH• with increased frequency
Effect of Solution Temperature on Hydroxyl Radical Generation in 1:10000 NH$_4$OH Solutions (pH 10) at 2 W/cm$^2$

- Decrease in generation rate of hydroxyl radicals with decrease in bulk solution temperature

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Effect of Dissolved Gases on Hydroxyl Radical Generation in NH$_4$OH Solutions at 2 W/cm$^2$

- $OH^*$ generation rate higher in Ar saturated solutions compared to air saturated solutions
- No measureable $OH^*$ conc. in CO$_2$ saturated solutions

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Effect of Dissolved Gases on Sonoluminescence Intensity

- **Ar saturated solutions showed the highest SL intensity, followed by O₂, N₂ and Air saturated solutions.**
- **SL intensity of CO₂ saturated solutions found to be within background levels throughout the applied range of power density.**

Pulse and continuous mode (inset) - SL intensity as a function of power density for DI water saturated with different gases.
Effect of CO$_2$ concentration on Sonoluminescence Intensity

(A) Pulse and continuous mode (inset) - SL intensity as a function of power density for DI water with different levels of dissolved carbon dioxide added by direct bubbling. (B) Pulse and continuous mode (inset) - SL intensity as a function of power density for air saturated DI water from which dissolved air has been partially removed using vacuum.

- **Addition of increasing amounts of CO$_2$ caused decrease in SL intensity**
- **Addition of CO$_2$ removed 5% of dissolved O$_2$**
- **No significant effect on SL intensity was observed when removing up to 5% of dissolved gases**
Characterization of Acoustic Cavitation using a Hydrophone

- Processed data shows peaks at fundamental frequency of 1 MHz and also at harmonics, sub-harmonics and ultraharmonics.
- Integral under the peaks used to characterize the intensity of stable cavitation.

**Diagram:**
- Megasonic Cleaning Tank
- Hydrophone
- Oscilloscope
  - Sample Rate: 50MS/s
- Labview
- FFT
- Matlab
- Pressure – Time Raw Data
- **Graph:**
  - X-axis: Frequency (MHz)
  - Y-axis: Pressure Amplitude (kPa)
  - Peaks at fundamental frequency of 1 MHz and harmonics, sub-harmonics and ultraharmonics.
Quantification of Stable and Transient Cavitation Pressure

Sample 970 kHz Spectrum

- **Direct Field Pressure:** Integral under the fundamental peak above the background.
- **Stable Cavitation Pressure:** Integral under the sub-harmonic, harmonic, and ultra-harmonic peaks above the background.
- **Transient Cavitation Pressure:** Integral under the red line fit to the broadband noise.

**Integral under the broadband signal used for calculation of pressure due to transient cavitation**
Cavitation Pressure as a Function of Acoustic Frequency at Power Density of 2 W/cm²

- Direct field, stable and transient cavitation pressure decrease with increase in frequency
- Transient cavitation absent at 3 MHz, while stable cavitation dominates at 3 MHz

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Transient Cavitation Pressure as a Function of Acoustic Frequency at Power Density of 4 W/cm$^2$

Transient cavitation pressure generally decreases with increase in frequency from 25 through 1000 kHz

M. Zhao, R. Balachandran, P.R. Madigappu, P. Yam, C. Zanelli, R. Sierra and M. Keswani. Proceedings of Ultra Clean Processing of Semiconductor Surfaces (UCPSS)

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Effect of Triton® X-100 on Generation Rate of OH•

Decrease in generation rate of OH• with addition of Triton® X-100 at two different power densities

CMC: 12E-3 – 16E-3% at 25 °C
Effect of Triton® X-100 on Transient Cavitation Pressure in Solutions Subjected to 1 MHz (8 W/cm²)

- Transient cavitation pressure suppressed in the presence of surfactant
- No effect of surfactant concentration on transient cavitation pressure

CMC: 12E-3 – 16E-3% at 25 °C

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1-2 s no meg, 12 s of meg (1 MHz), 1-2 s no meg

The magnitude of current peaks corresponding to transient cavitation intensity is lower in the presence of Triton® X-100
Summary

- Generation rate of $\text{OH}^\bullet$
  - ↓ with acoustic frequency and in the following order of dissolved gases: $\text{Ar}>\text{Air}>\text{CO}_2$
  - ↑ with solution temperature
  - ↓ with addition of Triton® X-100

- Acoustic emission measurements suggest decrease in direct field, stable and transient cavitation pressure with increase in frequency

- Both hydrophone and microelectrode based techniques indicated that transient cavitation decreased in the presence of Triton® X-100

- Hydrophone studies showed that Triton® X-100 concentration (in the range investigated) did not affect transient cavitation pressure
Part II- Contactless Bottom-up Electrodeposition of Cu and Ni for Through Silicon Via Applications
Through Silicon Via (TSV) Technology

TSV – key technology in 3D integrated circuit (IC) Packaging

- **Shortest chip to chip interconnections**
- **Integration of different functional devices into one package**
- **High interconnection density, lower power and good reliability**

Figure source: P. Dixit, J. Miao and R. Preisser. ECS Electrochem. Solid-State Lett. 9(10), G305-G308 (2006)
Challenges in Traditional Process

➢ Filling of high aspect ratio vias (1-200 μm width, up to 20-50 aspect ratio) with Cu at high rates without formation of voids
➢ Keeping Cu overburden to a minimum to reduce CMP cost

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Additive Assisted Bottom-up Cu Filling Process

Conformal deposition achieved by pulse reverse and increased Janus Green B (JGB) concentration

Bottom-up filling can be obtained with JGB concentration of 20 – 50 mg/L

Pulse reverse current is effective in preventing formation of voids and seams

Configuration of Plating Cell

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Additive Assisted Bottom-up Cu Filling Process

<table>
<thead>
<tr>
<th>Basic bath composition</th>
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</thead>
<tbody>
<tr>
<td>CuSO$_4$·5H$_2$O</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Additives</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl$^-$</td>
<td>70 mg/L</td>
</tr>
<tr>
<td>SDDACC</td>
<td>0, 1 mg/L</td>
</tr>
<tr>
<td>SPS</td>
<td>2 mg/L</td>
</tr>
</tbody>
</table>

Effect of SDDACC additive. Electrodeposition with ODT for 25 min. (a) SDDACC: 1 mg/L, SPS: 2 mg/L, and Cl$: 70$ mg/L. (b) SPS: 2 mg/L and Cl$^-$ 70 mg/L.

Cross section of vias. Electrodeposition with ODT for 37 min.

- **Octadecanethiol (ODT) was microcontact-printed on the top surface to inhibit deposition there**
- **Addition of SDDACC suppressed deposition at via opening and led to bottom-up deposition**

Commonly used Additives – ESH and Process Impact

**Leveler: Thiourea**

- Subcutaneous LD$_{50}$ = 1500 mg/kg (mouse)
- Health hazard rating of 2
- Considered a hazardous substance according to OSHA.

**Accelerator**: bis(sodiumsulfopropyl) disulfide

- Oral LD$_{50}$ = 300 mg/kg (mouse)
- Hazardous decomposition products at high temperature

Additives may also reduce the quality and reliability of deposited metal when they get embedded in the metal.

**Accelerator**: 3-Mercapto-1-propanesulfonic Acid Sodium Salt

- Oral LD$_{50}$ = 125 mg/kg (rat)
- Health hazard rating of 3
- Toxic and suspected to cause cancer

**Health hazard rating of 2**

- Considered a hazardous substance according to OSHA.

- Oral LD$_{50}$ = 300 mg/kg (mouse)

- Hazardous decomposition products at high temperature

Additives may also reduce the quality and reliability of deposited metal when they get embedded in the metal.

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Contactless Electrodeposition Process

- Front side of wafer consisting of vias contacts with CuSO₄ – H₂SO₄ with Cu anode immersed in it.
- The backside of wafer contacts SiO₂ etching solution with Pt cathode immersed in it.

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Feasibility Study Conducted on Blanket Wafers

Theoretical rate correlates well with the actual rate

Compact and porosity-free films of electrodeposited Cu and Ni.

Effect of Current Density on Cu Deposition Quality

Experiments were conducted using 0.5 M CuSO$_4$ and 3 M H$_2$SO$_4$ for 2 hours.

Increase of current density from 39 through 207 mA/cm$^2$ significantly reduced the deposition quality.

Effect of Sulfuric Acid Concentration on Cu Deposition

- Addition of $\text{H}_2\text{SO}_4$ is to improve conductivity
- Change of $\text{H}_2\text{SO}_4$ concentration from 3 M to 0.2 M slightly improved deposition quality
- Excessive amount of $\text{H}^+$ causes $\text{H}_2$ liberation and leads to non-uniformity

$3\text{ M }\text{H}_2\text{SO}_4$

39 mA/cm$^2$

$0.2\text{ M }\text{H}_2\text{SO}_4$

108 mA/cm$^2$
Effect of Copper Sulfate Concentration on Cu Deposition

- Experiments were conducted at 108 mA/cm²
- Increase of CuSO₄ concentration from 0.5 to 1 M greatly improved the uniformity
- Further increase of CuSO₄ concentration from 1 to 1.5 M did not cause much difference

Effect of Deposition Solution Composition and Current Density on Ni Deposition

- Uniformity of Ni layer was compromised when the current density increased from 108 to 152 mA/cm²
- Addition of Cl⁻ to the deposition solution significantly increased microroughness on Ni surface

NiSO₄ + H₃BO₃
NiSO₄ + H₃BO₃
NiSO₄ + H₃BO₃ + NiCl₂
Better uniformity was observed at lower current density and w/o Cl⁻.

Cl⁻ causes localized corrosion and generates irregularity, subsequent electrolyte diffusion deteriorates the non-uniformity.
Ni films were orientated in (220) plane w/o Cl\(^-\) and in (200) plane when Cl\(^-\) being added

Increase in current density decreased the relative intensity of (220)/(200) peaks, and slightly increased the average grain size

Addition of Cl\(^-\) to the deposition solution significantly increased the average grain size
Solutions with higher total F (49% HF) attained current densities as high as 220 mA/cm² at room temperature (20°C), while a 3% HF solution exhibited only about 115 mA/cm².

Etching of silicon dioxide important in regenerating the silicon surface for achieving higher deposition rates.
Oxidation and etching reactions more important than metal ion diffusion for achieving higher overall current density for deposition

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NaF solution may be used as an alternative etching solution (instead of HF) in this process.

Below pH = 6, there is a rapid increase in current density, which reaches maximum at pH = 3 in the investigated pH range of 3-10.
Summary and Future Work

➤ **Summary**

➤ Feasibility of contactless process demonstrated with high deposition rates and excellent uniformity w/o additives for blanket films

➤ **Future work**

➤ Conduct studies on patterned wafers with vias of different sizes, aspect ratios and profiles

➤ Establish correlations between morphological, crystallographic, microstructural, chemical, and mechanical properties of the electrodeposited metal and process parameters

➤ Develop a process simulation model for transport and deposition of metals

➤ Extend the use of technique to metals beyond copper and nickel
Acknowledgements

• **Applied Materials, Inc. and SRC-ERC for financially supporting this project**
• **PCT Systems for support with the megasonic systems**