CVD COATINGS TO CONTROL METAL-ION AND PARTICULATE CONTAMINATION

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SilcoTek® Company Information

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SilcoTek Key Facts

• **Year founded:** 2009

• **Mission:** To create game-changing coatings.

• **Purpose:** SilcoTek exists to change the game for our customers; to solve their toughest material problems, help them beat the competition, and take their innovations to the next level.
Brief History

1987
Restek® invents SilcoSteel® to make stainless steel GC capillary columns inert like glass columns.

1990-2008
New coatings are created for a variety of applications as demand grows for “Restek Performance Coatings” beyond just chromatography (Restek’s core business).

2009
14 Restek Performance Coatings Employees spin-off to form SilcoTek®, an independent company dedicated solely to coatings.

2013
SilcoTek builds a 36,000 ft² state-of-the-art coating facility, tripling previous coating capacity.

2019
SilcoTek builds an addition to their current building to accommodate growth and double the size of their facility.
What SilcoTek Does For You

• Surface enhancement/ engineering via CVD technology
  – Silicon- (a-Si) and silicon oxide-based coatings
  – Surface functionalization and modification
  – Characterization and testing
  – Custom solution development
  – Technical support

ISO 9001:2015 Certified

>100 Patents and Patent Applications
The CVD Process

Under 500°C
The CVD Process

- Commercialized process
- 3-D deposition allows coating of all surfaces
  - High aspect ratio
  - Complex geometries
- Bonded to substrate material
- Wide range of substrate materials
  - Stainless steel, glass, ceramics, aluminum, superalloys.
- Scalable process
  - Small fittings to large chambers.
- Thin coating: ~100 nm up to nearly 2 µm
  - Does not impact drawing dimensions or tolerances.
Contamination Challenges

• Purity is increasingly important.
• Pushing physical limits:
  – Devices become smaller.
  – Metal ion contamination is more important.
• Etch (and cleaning) chemistries
  – Number of removal steps increasing.
  – Gas chemistries are more aggressive.
• Corrosion limits productivity
Solutions for Semiconductor Contamination

**Silcolloy®** is a multi-layered amorphous silicon coating with no added functionalization and will not flake or generate particulate, even in highly sensitive environments like semiconductor manufacturing.

**Dursan®** is a functionalized layer of amorphous silicon, oxygen, and carbon offering corrosion resistance, low carry-over, and low organic sticking.

**Dursox®** is a thin but durable silicon oxide (SiO) high purity barrier coating that prevents semiconductor tool corrosion and erosion.
Solutions for Semiconductor Contamination

- Thermally stable
  - Wide operating temperature range.
- Reasonable cost
  - Superalloys are much more expensive.
- Environmentally known
  - Silicon is a primary material.
- Amorphous
  - Conformal over edges.
  - Allows for mechanical flexing.
- Low outgassing
  - Vacuum compatible.
  - Barrier to substrate effects (moisture or outgassing).
The Silcolloy® Coating Process

- The Silcolloy® coating process results in a non-metallic, chemically protective, corrosion resistant, multi-layered barrier of amorphous silicon.
- Gas delivery and exhaust are prime application areas where a barrier coating will provide corrosion resistance and prevent metal interactions with carrier gases.

<table>
<thead>
<tr>
<th>Coating Structure:</th>
<th>Hydrogenated amorphous silicon (a-Si:H)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Temperature:</td>
<td>1410°C</td>
</tr>
</tbody>
</table>
| Substrate: | Compatibility: Stainless steel, Exotic alloys, Ceramics
Size: Up to 78” (198 cm)
Geometry: Any shape, including complex geometries |
| Typical Thickness: | 180 – 800 nm |
| Hydrophobicity (contact angle): | $\geq$ 40° |
| Allowable pH Exposure: | 0 - 8 |
Coating Composition

![Graph showing coating composition analysis](chart.png)
Coating Composition

Focused Ion Beam (FIB)
Field-Emission Secondary Electron Microscopy (FESEM)

X-Ray Photoelectron Spectroscopy (XPS)
Coating Composition

<table>
<thead>
<tr>
<th>Element</th>
<th>Coating Contents</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>&lt; 20 ppm</td>
</tr>
<tr>
<td>Chromium</td>
<td>0 ppm</td>
</tr>
<tr>
<td>Iron</td>
<td>&lt; 100 ppm</td>
</tr>
<tr>
<td>Nickel</td>
<td>&lt; 10 ppm</td>
</tr>
<tr>
<td>SilcoTek Silicon CVD Coating</td>
<td>99.98 % purity</td>
</tr>
</tbody>
</table>

- Contains no metal unlike similar barrier coatings such as yttria
Amorphous and Hydrogenated

- Amorphous coatings are potentially less prone to particle generation through mechanical stress than crystalline coatings such as yttria.
Improved Vacuum Pumpdown

- Evacuation test on fixed volume chamber.
- Corrected for background outgassing.
SilcoTek® coatings provide a continuous, pinhole-free barrier to corrosion that improves equipment performance and yield.
Corrosion Testing

• Measure Mass Loss During Immersion
• Calculate Corrosion Rate in mils per year (MPY)

\[
\text{Corrosion Rate} = \frac{\text{Weight loss (g)} \times K\text{-factor}}{\text{Density} \left(\frac{g}{cm^3}\right) \times \text{Area (A)} \times \text{Time (hr)}}
\]
HCl Corrosion Testing

- Test Conditions
  - 6 M HCl
  - Room temperature solution
  - 24 hours of exposure

30x more material lost on uncoated coupon
Elevated Temperature HCl Corrosion Testing

- Test Conditions
  - 6 M HCl
  - 50° C solution
  - 7 hours of exposure

30x more material lost on uncoated coupon
HBr Corrosion Testing

- Test Conditions
  - 6 M HBr (gas dissolved in DI Water)
  - Room temperature solution
  - 72 hours of exposure

7x more material lost on uncoated coupon
Data Extrapolation

• How long will the coating last in service?
  – Typical maintenance Cycle – 3,000 RF Hours
  – Improvement of coated vs. uncoated is ~7.21x (using exposure of 6 M HBr for 72 hours at room temperature)
  – Possible Lifetime Extension – 23,000+ RF Hours
Plasma Exposure

- 50 W SF$_6$ remote plasma exposure (3 minute exposure).
- Stainless steel appears to begin to pit.
- Some etching of silicon.
The Dursan® Coating Process

- The Dursan® coating process deposits a chemically protective barrier of amorphous silicon, oxygen and carbon that is further functionalized.
- Reducing wall interactions with organic precursor gases or applications where hydrophobicity are critical are both areas where barrier coatings excel.

<table>
<thead>
<tr>
<th>Coating Structure:</th>
<th>Functionalized silica-like coating (a-SiO$_x$:CH$_y$)</th>
</tr>
</thead>
</table>
| Maximum Temperature: | 500°C (inert atmosphere)  
                       450°C (oxidative) |
| Substrate:         | Compatibility: Stainless steel, exotic allows, ceramics  
                    Size: Up to 78" (198 cm)  
                    Geometry: Any shape, including complex geometries |
| Typical Thickness: | 400 – 1600 nm |
| Hydrophobicity (contact angle): | < 81° |
| Allowable pH Exposure: | 0 - 14 |
Dursan® Hydrophobicity Properties

Rough: 120 grit; 58 rms (µin.)
Smooth: mirror-like #8; 10 rms (µin.)
Dursan shows a 170x improvement over uncoated stainless steel.
The Dursox® Coating Process

- The Dursox® coating process results in a chemically protective barrier of thin but durable silicon oxide (SiO).
- Protecting the chamber from silicon etch/clean chemistries is a challenge and can be addressed with barrier coatings.

<table>
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<tr>
<th>Coating Structure:</th>
<th>Silica-like coating (a-SiO$_x$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Temperature:</td>
<td>1250°C</td>
</tr>
</tbody>
</table>
| Substrate: | Compatibility: Stainless steel, exotic allows, ceramics  
Size: Up to 78” (198 cm)  
Geometry: Any shape, including complex geometries |
| Typical Thickness: | 400 – 1600 nm |
| Hydrophobicity (contact angle): | < 60° |
| Allowable pH Exposure: | 0 - 14 |
Dursox® Properties

Water on Dursox, 46 degree contact angle.
Coating Composition

Dursox®
SIMS Elemental Data
Conclusions

• Amorphous, hydrogenated silicon can be used as a barrier coating for gas delivery in both etch and deposition environments.

• CVD deposition of a-Si:H offers unique benefits including non-line-of-sight deposition on existing components and good adhesion to a wide variety of commonly used materials.

• Additional benefits from a-Si:H deposition may be seen in low outgassing of surfaces in vacuum and low particulate creation from gas-surface interactions.
Future Directions

- Develop method for characterizing gas corrosion.
- Develop method of characterizing lifetime in direct plasma environment.