REMOVAL OF VOLATILE METALS FROM CORROSIVE GASES BY A NEW PURIFIER

Carrie Wyse, Tadaharu Watanabe, Dan Fraenkel, Robert Torres, and Virginia Houlding
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INTRODUCTION

A new gas purifier has been developed for the removal of volatile metal complexes from corrosive gas, in addition to removing moisture. Performance of the purifier was tested by generating a stream of volatile metals in HCl, challenging the purifier and sampling the outlet of the purifier via hydrolysis. The hydrolysis samples were analyzed for trace metals by ICP-MS. Moisture performance was conducted in both inert and corrosive gases by APIMS and FT-IR.

BACKGROUND

Contamination control in etch processing is one of the key issues in the semiconductor industry. The level of volatile metal species found in HCl gas is typically in the low ppb region even in the cleanest HCl commercially available. These metal species pass through 0.003 μm particle filters to the final product. According to the SIA Roadmap, the estimated allowable level of total metallic impurities in gases is <4 ppt. Thus, trace levels of metal impurities in HCl will be problematic for sensitive processes. However, it is not practical to analyze such low levels of metals in HCl via conventional laboratory methods (e.g. hydrolysis, cold trap method). Consequently, performance testing of the MetalX™ purifier was conducted using relatively high challenges, much greater than would typically be encountered in live gas systems. To make the tests quantitative, HCl gas was deliberately doped with various volatile metal chloride species that are known to be stable.

FINDINGS

A challenge of ppm levels of volatile molybdenum species was generated by flowing HCl through a bed of heated anhydrous MoCl₅. This metal containing gas stream was directed into a MetalX™ purifier and an empty control purifier, each containing a 0.003 μm particle filter, and to the by-pass. ICP-MS analysis of hydrolysis samples show that the volatile molybdenum was removed by the purifier to levels less than the detection limit, 0.004 ppm.

The new purifier was also tested for removal of titanium species in a similar fashion. HCl was bubbled through TiCl₄, which is more volatile than molybdenum chloride. Consequently a challenge of several hundred ppm titanium was generated. Hydrolysis sampling showed that MetalX™ effectively removed hundreds of ppm Ti down to 0.013 ppm in HCl.

In order to rule out any concern that the MetalX™ purifier would emit metals in an HCl gas stream, an experiment was conducted in which hydrolysis samples were collected at the outlet of a MetalX™ purifier, while the purifier was held at elevated temperatures with HCl flow. Hydrolysis results confirm that no metals are emitted from MetalX™ medium, even when heated to 200°C.
MetalX™ efficiency for moisture in corrosive gas was tested in HBr, since HBr is the most corrosive gas that is routinely used in semiconductor processing. The challenge was monitored by FTIR equipped with a MCT-A detector and 10 m pathlength cell. Moisture levels were determined using the water peaks in the region of 3850 cm⁻¹ and a classical least squares algorithm. A challenge of 3 ppm moisture in HBr was generated in a gas mixture of 10% N₂ and 90% HBr using a calibrated moisture generator. When exposed to this challenge, MetalX™ removed the ppm moisture challenge down to less than 100 ppb, the detection limit of the method.

MetalX™ efficiency for moisture in inert gas was also tested using APIMS, since the detection limit is lower. A challenge of 7 ppm moisture in N₂ was removed by MetalX™ to levels less than 1 ppb.

SUMMARY

Conventional corrosive gas purifier technology can merely help avoid the formation of volatile metal complexes by minimizing corrosion facilitated by moisture. Nanochem® MetalX™ can do this very effectively, in addition to providing removal of any trace volatile metal complexes. The results presented demonstrate that MetalX™ effectively removes ppm levels of volatile metal complexes in HCl to levels less than detection limit. MetalX™ also removes moisture down to less than 100 ppb in HBr gas and 1 ppb in N₂. In summary, the MetalX™ corrosive gas purifier offers the unique ability to remove both volatile metal species and moisture.

ACKNOWLEDGMENTS

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REFERENCES

Removal of Volatile Metals from Corrosive Gases by a New Purifier (Nanochem MTX™)

Carrie Wyse, T. Watanabe, D. Fraenkel, R. Torres, V. Houlding

Matheson Tri-Gas

Outline

- Critical contaminants in corrosive systems
- Effects of contaminants on process
- Purifier Technology
- Performance of new purifier
- Benefits of using new purifier
- Summary
Critical Contaminants and Sources

- Moisture
  - Source gas and container
  - Distribution system
  - Cylinder changeouts
- Metals
  - Source gas and container
  - Corrosion (particulates, volatiles)
  - Shedding from mechanical components

Impact of Critical Contaminants

- Moisture
  - Oxygenated species cause haze which affects resistivity (Si epi, Si-Ge epi)
  - Degradation of distribution system due to corrosion
- Metals
  - Highly mobile in semiconductor lattice
    - Can be decreased by removing moisture
    - Particulates can be removed by particle filter
    - Volatiles cannot be removed by particle filter
H$_2$O Levels in Source Gas

Gas Phase Moisture as a Function of HCl Remaining in the Tonner at 70°F, Without Purification

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Metal Specifications for Semiconductor Grade HCl (ppb)

<table>
<thead>
<tr>
<th>Vendor</th>
<th>Fe</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
<th>Total Metals</th>
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<tbody>
<tr>
<td>A</td>
<td>500</td>
<td>100</td>
<td>100</td>
<td>400</td>
<td>&lt;1000</td>
</tr>
<tr>
<td>B</td>
<td>500</td>
<td></td>
<td></td>
<td>400</td>
<td>&lt;1000</td>
</tr>
<tr>
<td>C</td>
<td>500</td>
<td>100</td>
<td>100</td>
<td>100</td>
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</table>

Note: includes particulates and volatiles

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**Piping Composition**

<table>
<thead>
<tr>
<th>Material</th>
<th>C</th>
<th>Co</th>
<th>Cr</th>
<th>Cu</th>
<th>Fe</th>
<th>Ni</th>
<th>Mn</th>
<th>Mo</th>
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<tr>
<td>Monel alloy</td>
<td>0.3</td>
<td>-</td>
<td>0</td>
<td>31.0</td>
<td>2.5</td>
<td>*</td>
<td>2.0</td>
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<tr>
<td>max</td>
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<td>SS 316L alloy</td>
<td>0.03</td>
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<td>68.5</td>
<td>12.0</td>
<td>0</td>
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<tr>
<td>C-22 alloy</td>
<td>0.010</td>
<td>2.5</td>
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<td>3</td>
<td>55.5</td>
<td>0.5</td>
<td>13</td>
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<tr>
<td>max</td>
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</tr>
</tbody>
</table>

* minimum 63% Ni + Co

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**Vapor Pressures of Metal Chlorides**

- FeCl₆
- WCl₆
- TiCl₄
- SnCl₄
- MoCl₅
- Al₂Cl₆
- CrCl₂

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Preliminary Indication of Volatile Metals

<table>
<thead>
<tr>
<th>High Pressure HCl</th>
<th>Fe (ppb)</th>
<th>Mo (ppb)</th>
<th>Ni (ppb)</th>
<th>Cr (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short Term (2 days) (through 0.003 µm filter)</td>
<td>819.4</td>
<td>27.3</td>
<td>226.5</td>
<td>1.09</td>
</tr>
<tr>
<td>Long Term (2 days) (through 0.003 µm filter)</td>
<td>2492.8</td>
<td>74.5</td>
<td>457.0</td>
<td>714.9</td>
</tr>
<tr>
<td>Experiment Control</td>
<td>191</td>
<td>4.6</td>
<td>30.3</td>
<td>45.9</td>
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</tbody>
</table>

Nanochem MTX™ Technology

- Robust inorganic material compatible with high pressure corrosive gases
- Designed to remove volatile metal species
- Engineered for high moisture capacity

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MTX™ Efficiency for Volatile Mo in HCl

MTX™ Efficiency for Volatile Ti in HCl

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Carrie Wyse, Matheson Tri-Gas - Slide 12
MTX™ Efficiency in HBr Service

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MTX™ Efficiency at High Flow

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MTX™ Efficiency in N₂

<table>
<thead>
<tr>
<th>pN₂</th>
<th>2 ppm H₂O</th>
<th>7 ppm H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>@ 2 slpm</td>
<td>@ 2 slpm</td>
<td>@ 1 slpm</td>
</tr>
</tbody>
</table>

H₂O (ppb)

0 1 2 3 4

0 10 20 30 40 50 60 70
time (hour)

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Effect of Moisture Removal on Components

Kal-F valve seat of line valve in HBr service without Nanochem purifier, 1000 cycles
Kal-F valve seat of line valve in HBr service with Nanochem purifier, 1000 cycles

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Effect of Moisture Removal on Particulates Generated in HBr

- Before HBr Exposure
- After HBr Exposure

Particles/cm²

Samples
(u=upstream of purifier; d=downstream of purifier)

Effect of Particulates on Leak Rate of Valves

Across-the-Seat Helium Leak Rates of the Valves

Before HBr Exposure
After HBr Exposure

Samples
(u=upstream of purifier; d=downstream of purifier)
Benefits of MTX™ Purifier on Corrosive Process

- Minimizes Corrosion
- Reduces particulates
- Reduces volatile metals
- Prolongs life of distribution system
- Prevents device failure from oxygenated species, volatile metals, and particulates

MTX™ Summary

<table>
<thead>
<tr>
<th>Impurities Removed</th>
<th>H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Volatile Metal species (e.g. Mo, Ti, Fe)</td>
</tr>
<tr>
<td></td>
<td>Particulates</td>
</tr>
<tr>
<td>Efficiency</td>
<td>&lt;100 ppb H₂O in N₂ (Lambda Scan)</td>
</tr>
<tr>
<td></td>
<td>&lt;1 ppb H₂O in N₂ (APIMS)</td>
</tr>
<tr>
<td></td>
<td>&lt;4 ppb Mo in HCl (Hydrolysis/ICP-MS)</td>
</tr>
<tr>
<td>Capacity</td>
<td>~ 5000 kg HCl</td>
</tr>
</tbody>
</table>
Summary

- Volatile metal species are electronically active contaminants that can cause device failure.

- Volatile metals in corrosive gas distribution systems are not removed by particle filters.

- Nanochem MTX is a corrosive gas purifier which removes volatile metal species, moisture and particulates in one package.