NANOCHEM® Metal-X™
Corrosive Gas Purification

Advanced Technology Center & Frontier Purification Technology
Contents

• Delivery Issues of Ultra-Pure HCl
• Problem: Moisture Causes Corrosion & Metals
• Solution: NANOCHEM® MetalX™
• NANOCHEM® MetalX™ Applications
  – Source, Distribution & Point-of-Use
• Case Studies
  – HCl & HBr Examples
• Summary
Delivery Issues of Ultra-Pure HCl

• **Moisture**
  – Causes corrosion resulting in emission of
    • metal oxide and metal chloride particles
    • volatile metal chlorides

• **High Pressure/High Flow**
  – Can result in condensation, aerosol formation causing
    • incorrect mass flow control
    • liquid transport of moisture which accelerates corrosion
    • liquid transport of non-volatile metal compounds, particulates

• **Volatile Metal Compounds**
  – Are present in HCl source
  – Are generated by corrosion
  – Cannot be removed by particle filter
Problem Identification:

Moisture Causes Corrosion & Creates Volatile Metals
Moisture Increase in HCl BSGS

Gas Phase Moisture in HCl Ton Unit at 70 °F, Without Purifier

- Moisture Level not constant through life of cylinder!
- This effect observed for other liquefied gases.
- Average Moisture level introduced into purifier is **Not** specification concentration!
- Higher than expected moisture levels cause unexpected corrosion!
- MTG recommends using only 70% of a cylinder or tonner
H₂O Causes Corrosion - MetalX™ Eliminates It! (Ex. 1)

Purifier Inlet in HBr service

Purifier Outlet in HBr service
H$_2$O Causes Corrosion - MetalX™ Eliminates It! (Ex. 3)

Top: Diaphragm of line valve used in HBr for 3 years without purification
Bottom: Diaphragm of line valve used in HBr for 3 years with purification
Particle Counts of Valves Showing Benefits of MTX™ Purifier

Without MTX Purifier

With MTX Purifier

Particles per Cubic ft.

Average of 3 Valves

Average of 3 Valves

Before Corrosive Gas Exposure

After Corrosive Gas Exposure

Measured with Laser particle counter (0.16 μm detection): sampling rate 14 slpm in N₂
Volatile Metals Generated in HCl

High Pressure HCl was stored in manifold (20 foot length of 1/4” EP 316L SS tubing and SS particle filter) for 6 days, and then passed through a 0.003 μm teflon particle filter. The table shows metal levels in HCl from volatile metal chlorides.

<table>
<thead>
<tr>
<th>Metal</th>
<th>(ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>8,510</td>
</tr>
<tr>
<td>Cr</td>
<td>2,766</td>
</tr>
<tr>
<td>Mo</td>
<td>234</td>
</tr>
<tr>
<td>Ti</td>
<td>23</td>
</tr>
<tr>
<td>Mn</td>
<td>404</td>
</tr>
</tbody>
</table>
Solution:

NANOCHEM® MetalX™ Purification
NANOCHEM® MTX™ Applications

- Reduce metals in etching, epi & chamber clean processes
  - HCl, HBr, (BCl₃), (SiCl₄), Br₂, Cl₂
  - Epi Si CVD, Metal Etch, III-V semiconductor MOCVD
  - SiC-coated graphite susceptors
- Reduce metals in Epi Si CVD source gas
  - (DCS), (TCS)
- Fiber Optics
  - Cl₂, (SiCl₄), (GeCl₄)
- Component protection for corrosive gases
  - High pressure regulators: HCl, HBr

( ): Consult NANOCHEM® Purification Systems
NANOCHEM® MTX™
Volatile Metal (Ti) Removal from HCl

Control = empty purifier w/ 0.003 μm particle filter only

MetalX™ Removes Volatile Ti to D/L!!

Measured with hydrolysis, HCl 1 slpm using L-60 at atm. pressure
NANOCHEM® MTX™

Volatile Metal (Mo) Removal from HCl

<table>
<thead>
<tr>
<th></th>
<th>By-pass</th>
<th>MTX</th>
<th>Control</th>
</tr>
</thead>
<tbody>
<tr>
<td>ppm Mo in HCl</td>
<td>8.707</td>
<td>7.875</td>
<td>&lt;0.004</td>
</tr>
</tbody>
</table>

MetalX™ Removes Volatile Mo to D/L!!

(0.003 um Particle Filter Only)

Control = empty purifier w/ 0.003 μm particle filter

Measured with hydrolysis, 1 slpm HCl using L-60 at atm. pressure
**MetalX™: Source Gas Installation**

- Corrosive gas
  - Remove moisture from corrosive gas
  - Install before the high pressure regulator to protect the entire system

**Benefits:**
Remove $H_2O$ & Metals at Source, Prevent Corrosion of Components & Piping
Leak Rates of Valves Showing Benefits of MTX™ Purifier

Helium Leak Rates of Line Valves

Before Corrosive Gas Exposure

After Corrosive Gas Exposure

Without MTX Purifier

With MTX Purifier

Valve Samples

Helium Leak Rate cc/sec

1.0E-09 1.0E-08 1.0E-07 1.0E-06 1.0E-05 1.0E-04 1.0E-03

1.0E-03 1.0E-04 1.0E-05 1.0E-06 1.0E-07 1.0E-08 1.0E-09

1 2 3 4 5 6
NANOCHEM® MTX™
Proven for High Pressure, High Flow (BSGS HCl)

Benefits:
- Remove Metals & H₂O at Source, Prevent Corrosion of Components & Piping
- Use Stainless Steel Instead of Hastelloy. Proven LP Installations (> 3 yrs!)

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Moisture from Ton Unit Through Purifier at Full Cylinder Pressure (613 PSIG)

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Moisture Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>20</td>
<td>5 SLPM Through Purifier</td>
</tr>
<tr>
<td>40</td>
<td>100 SLPM Through Purifier</td>
</tr>
<tr>
<td>60</td>
<td>900 SLPM Through Purifier</td>
</tr>
<tr>
<td>80</td>
<td>900 SLPM Bypass Purifier</td>
</tr>
<tr>
<td>100</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>

Test with FTIR in HCl matrix using L-2000

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Matheson: ask. . . The Gas Professionals™
Maximize the Benefits of MetalX™ with NANOCHEM® Purge Gas Purifiers

- Ensure integrity of the manifold and pipework
- Ensures that cylinder changes do not contaminate the process lines
- NANOCHEM OMX-Plus comes with end point detection

**Benefits:** Remove H₂O & Other Oₓ Species, For Quick Dry Down & Prevent Line Contamination

Diagram:
- Distribution Line
- Process Tool
- N₂ Purifier
- Process Gas Cylinder
- Purge Gas Cylinder
- Gas Cabinet

**Diagram Label:**
- Distribution Line
- Process Tool
- N₂ Purifier
- Process Gas Cylinder
- Purge Gas Cylinder
- Gas Cabinet

**Image:**
- NANOCHEM® L-Series

**Logo:**
- Matheson
- ask. . .The Gas Professionals™
NANOCHEM® OMX/OMX-Plus™ for N₂ & H₂ Purification

Highest Performance (O₂ Removal)

Very low leakage of impurities, even at very high impurity concentrations

![Graph showing oxygen outlet concentration vs. time]

**Even with 200 ppm O₂ inlet, purifier outlet is < 1 ppb!!**

NOTE: OMX Resin can withstand up to ~2-5% O₂

O₂ Conc. > 5-10% will result in localized breakdown of resin matrix
MetalX™: Distribution Installation

- Install in the VMB or GIB
- POU solution for higher gas flows or when space is limited at the tool
- More economical than POU for multiple tool system

Benefits: Remove H₂O & Metals at VMB For Multiple Tools

Gas Cabinet

Distribution Line

LP MTX Purifier

Process Tool

Process Tool

NANOCHEM® Bloc-Series
MetalX™: Point-of-Use Installation

- Ensure gas purity at the process tool
- Install on the gas stick before MFC or before the chamber
- Includes particle filter, sized to be drop-in filter (only) replacement
- Size purifier according to flow rate

Benefits: Remove H₂O & Metals at Chamber Entrance – Ideal Final Polish

NANOCHEM® PuriFilter®
The “Need” for Point-of-Use Purification

<< Metals and Moisture Created In-Situ >>

Although a gas distribution system may be dried to ppb levels, introduction of HCl or HBr will cause the formation of water and metal chlorides!

- Ultra dry Steel will still produce H$_2$O and metal chlorides upon introduction of HCl.

\[
\text{Fe}_2\text{O}_3 + 6\text{HCl} \rightarrow 2\text{FeCl}_3 + 3\text{H}_2\text{O} \quad \Delta H = -145 \text{ kJ}
\]

- Iron Chloride produced
- Water produced

- H$_2$O now present in package can catalyze further corrosion
Case Study 1
(MetalX™ in HCl)

Corroded HCl Lines, Installed Point-of-Use MetalX Purifier…
Too Little, Too Late?
Corrosion from Delivery Lines, VMB, and/or Gas Cabinet, without MTX™ PURIFIER

0.003µm HCl particle filter in service for ~3 years, removed from epi tool inlet.

Corrosion byproducts at particle filter inlet VCR

Non-volatile particles trapped inside the particle filter

MATHESON
Corrosion from Delivery System, without MTX™ PURIFIER

Corrosion byproducts at particle filter inlet from gas line considered to be clean until this investigation took place.

Conclusions:
Replacement of this particle filter with a MTX purifier did NOT significantly effect the diffusion length values.

This was thought to be due to additional corrosion downstream of the purifier that re-contaminated the gas stream prior to entering the epi-tool.

SPV measurements of wafers manufactured from this line exhibited sporadic and unacceptable diffusion lengths.
Case Study 2
(MetalX™ in HBr)

Major Tool Maker Request to Reduce Fe on Wafer

Success with Point-of-Use PuriFilter™ MetalX™ Purifier!!
Objective:
- Determine if Nanochem MTX™ purifier reduces Fe and Cr contamination when used with HBr.

Method:
- Purifier was properly conditioned prior to use in HBr
- The purifier was placed as the last metal component in the gas supply line followed only by Teflon tubing
- A process run was completed with the MTX™ purifier and silicon wafer under HBr etch conditions
- A control experiment was performed with the same process, but using a standard metal gas line and no MTX™ purifier
- Fe and Cr contamination were measured on the wafer by Vapor Phase Decomposition and ICP/MS
Metal Reduction On Wafer Using
NANOCHEM® MetalX™ (in HBr)

HBr Gas Cabinet

Gas Box

MTX Purifier

C-22™
>300’

Teflon Tube

Reactor

Metal Reduction On Wafer Using
NANOCHEM® MetalX™ (in HBr)
Metal Reduction On Wafer Using NANOCHEM® MetalX™ (in HBr)

Reduced Fe on Wafer Below Customer Target!!
Metal Reduction On Wafer Using NANOCHEM® MetalX™ (in HBr)

Conclusion from Study

- Target metal contamination levels could not be achieved by using highly corrosion resistant delivery system such as Hastelloy® C-22 lines and Nickel lined cylinders.
- MTX™ purifier shows decrease of iron on the wafer by more than one order of magnitude and allows the iron level to decrease below target levels.
- Chromium reduction was not conclusive since the challenge level of Cr metal was below detection limit.

MTX™ Purifier was the single factor that allowed for removal of metals to below the target levels!

Metal Reduction On Wafer Using NANOCHEM® MetalX™ (in HBr)
Case Study 3
(MetalX™ in HCl)

SiGe Wafer Manufacturer

Success with Point-of-Use PuriFilter™ MetalX™ Purifier!!
Metal Reduction On Wafer Using NANOCHEM® MetalX™ (in HCl)

- **Objective:**
  - Determine if Nanochem MTX™ was a contributing factor in metals contamination on Si-Ge low temp epi layer.

- **Method:**
  - Purifier was properly conditioned prior to use in HCl
  - The purifier was used at the point of use as near to tool as possible.
  - A process run was completed with the MTX™ purifier in line and MTX purifier bypassed.
  - Al, Ca, Cr, Cu, Ge, Fe, Mg, Ni, K Na, and Zn were measured on the wafers for the two different runs by Vapor Phase Decomposition and ICP/MS
VPD-ICPMS Results of Wafers Grown with and without MTX purification

MTX provided lower metals on the wafer in 7/8 cases.
Only Ge levels were higher for this SiGe Process.
Conclusion from Study

- Study showed that MTX reduced metals on the wafer for 7/8 metals. The only metal that exhibited elevated levels compared to the bypass was Ge. For a SiGe process it is possible that the Ge levels are introduced from the chamber.

- Study revealed that MTX was not responsible for metals problem on the wafer.

- MTX™ purifier showed best results for Fe and Ni.

- Cr, Cu, and Mg results were not conclusive since the levels observed were below the detection limit of the method.

MTX™ Purifier was demonstrated to be a critical factor in reducing and eliminating metals contamination on the wafer.
NANOCHEM® MetalX™: Summary

• Moisture increases with HCl use, and Matheson Tri-Gas recommends limiting the use of HCl cylinders/tonners

• Moisture causes corrosion, shortens the life of components and generates killer metal impurities

• NANOCHEM MetalX purifiers eliminate corrosion by removing moisture AND volatile metals

• MetalX purification is recommended at the source (H₂O) AND at the VMB or point-of-use (residual H₂O and metals)

• Case studies were presented where Metal-X may have been too late to benefit, but beneficial if used early in the process.

• MetalX gives utmost protection against corrosion and improves process performance and yield