REMOVAL OF VOLATILE METALS FROM CORROSIVE GASES BY A NEW PURIFER

Carrie Wyse, Tadaharu Watanabe, Dan Fraenkel,
Robert Torres, and Virginia Houlding
Matheson Tri-Gas, Inc., Longmont, CO

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.[i,ii] 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.[iii] 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 $MoCl_5$. 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 $TiCl_4$, 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% N_2 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 N_2 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 N_2. In summary, the MetalX™ corrosive gas purifier offers the unique ability to remove both volatile metal species and moisture.

ACKNOWLEDGMENTS

The authors acknowledge *Analysis Now!* For providing trace metals analysis, and Ehrich Diede of Diede Precision Welding, Inc., for welding and assembly of manifolds.

REFERENCES

[i] N. Anderson, et al., "Modeling Contaminants Generation from Tubing during Start-up and Following Moisture Upsets in HCl Distribution Systems", ISSM Symposium, San Francisco, October 1997.
[ii] N. Verma, et al., "Modeling purity in Bulk Reactive Gas Distribution Systems", Proceedings Institute of Environmental Sciences, 351-359, 1997.
[iii] Semiconductor Technology Workshop Group Reports, Semiconductor Industry Associated, San Jose, CA, November 1992.

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

semi

Outline

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

semi

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

semi

Carrie Wyse, Matheson Tri-Gas - Slide 3

Impact of Critical Contaminants

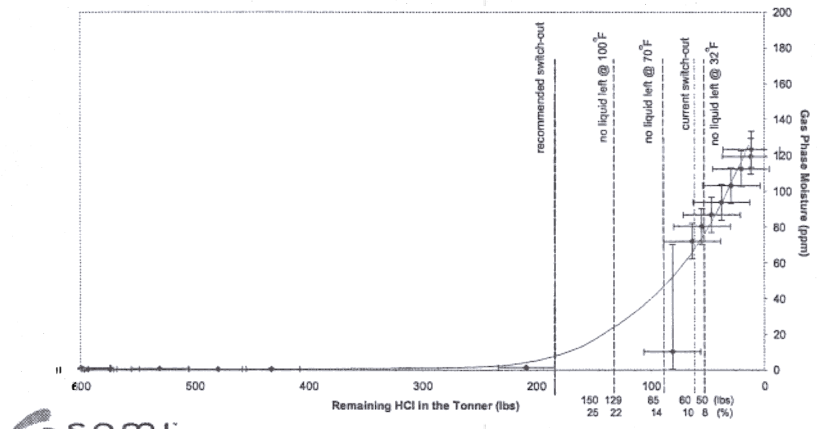
- Moisture
  - oxygenated species cause haze which affects resistivity (Si epi, Si-Ge epi)
  - degradation of distribution system due to corrosion
- Metals
  - highly mobile in semiconductor lattice
    - can be decreased by removing moisture
    - particulates can be removed by particle filter
    - volatiles cannot be removed by particle filter

semi

Carrie Wyse, Matheson Tri-Gas - Slide 4

H_2O Levels in Source Gas

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



Carrie Wyse, Matheson Tri-Gas - Slide 5

Metal Specifications for Semiconductor Grade HCl

(ppb)

Vendor	Fe	Ni	Cu	Cr	Total Metals
A	500	100	100	400	<1000
B	500	-	-	-	<1000
C	500	100	100	100	-

Note: includes particluates and volatiles

Carrie Wyse, Matheson Tri-Gas - Slide 6

Piping Composition

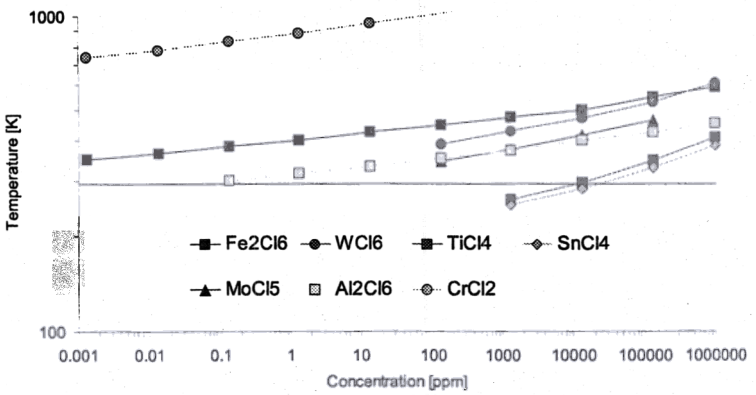
Material	C	Co	Cr	Cu	Fe	Ni	Mn	Mo
Monel alloy	0.3 max	*	0	31.0	2.5	*	2.0	0
SS 316L alloy	0.03 max	0	17.0	0	68.5	12.0	0	2.5
C-22 alloy	0.010 max	2.5	22	0	3	55.5	0.5	13

* minimum 63% Ni + Co

semi

Carrie Wyse, Matheson Tri-Gas - Slide 7

Vapor Pressures of Metal Chlorides



semi

Carrie Wyse, Matheson Tri-Gas - Slide 8

Preliminary Indication of Volatile Metals

High Pressure HCl	Fe (ppb)	Mo (ppb)	Ni (ppb)	Cr (ppb)
Short Term (2 days) (through 0.003 µm filter)	819.4	27.3	226.5	1.09
Long Term (2 days) (through 0.003 µm filter)	2492.8	74.5	457.0	714.9
Experiment Control	191	4.6	30.3	45.9

semi

Carrie Wyse, Matheson Tri-Gas - Slide 9

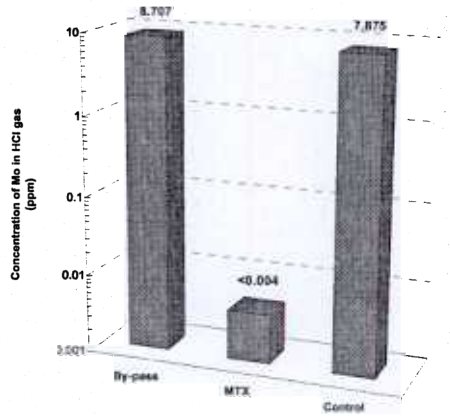
Nanochem MTX™ Technology

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

semi

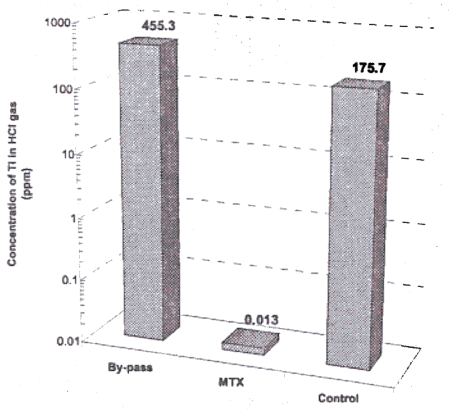
Carrie Wyse, Matheson Tri-Gas - Slide 10

MTX™ Efficiency for Volatile Mo in HCl



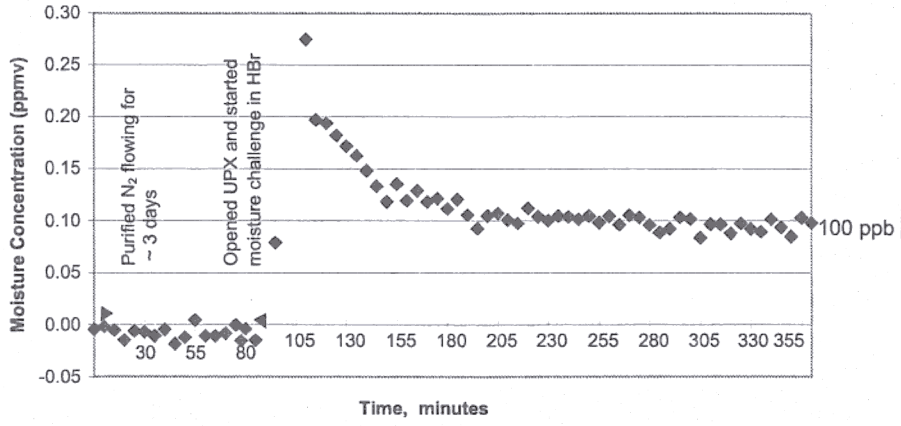
Carrie Wyse, Matheson Tri-Gas - Slide 11

MTX™ Efficiency for Volatile Ti in HCl



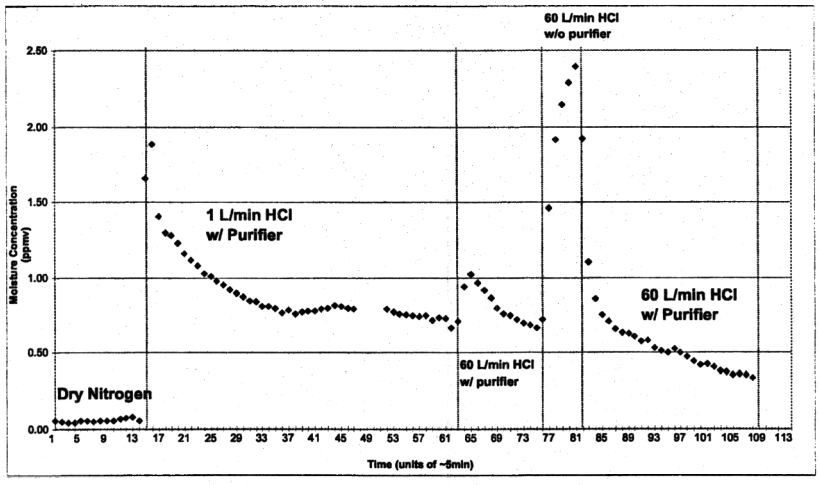
Carrie Wyse, Matheson Tri-Gas - Slide 12

MTX™ Efficiency in HBr Service



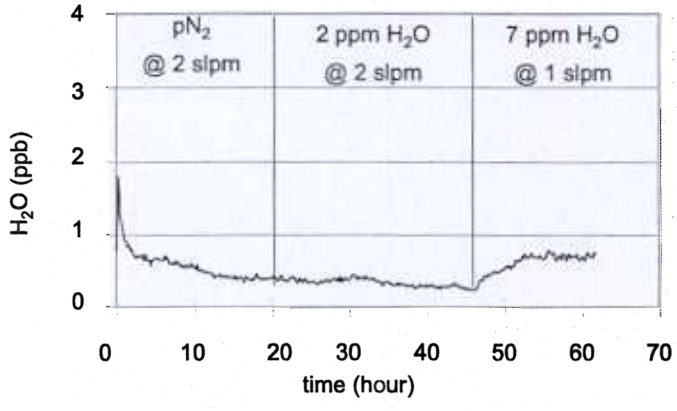
Carrie Wyse, Matheson Tri-Gas - Slide 13

MTX™ Efficiency at High Flow



Carrie Wyse, Matheson Tri-Gas - Slide 14

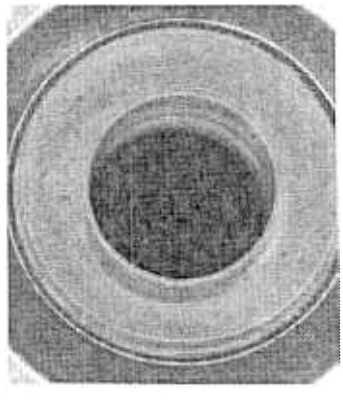
MTX™ Efficiency in N_2



Carrie Wyse, Matheson Tri-Gas - Slide 15

Effect of Moisture Removal on Components

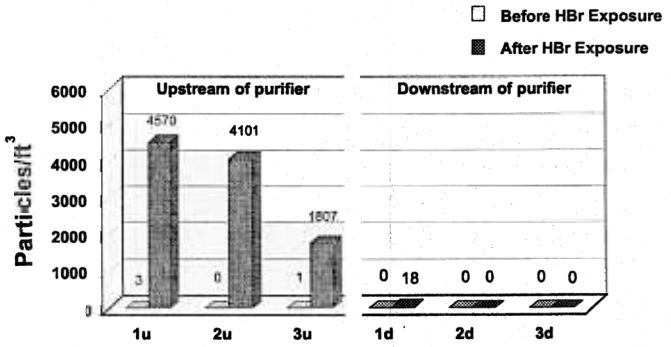
Kel-F valve seat of line valve in HBr service without Nanochem purifier, 1000 cycles



Kel-F valve seat of line valve in HBr service with Nanochem purifier, 1000 cycles

Carrie Wyse, Matheson Tri-Gas - Slide 16

Effect of Moisture Removal on Particluates Generated in HBr

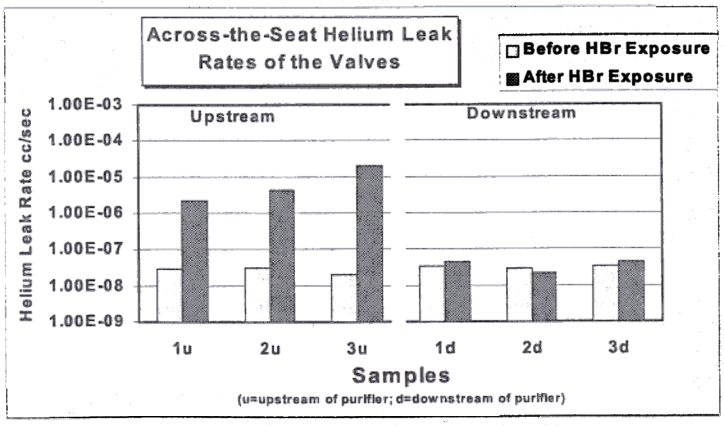


(u=upstream of purifier; d=downstream of purifier)

semi

Carrie Wyse, Matheson Tri-Gas - Slide 17

Effect of Particluates on Leak Rate of Valves



semi

Carrie Wyse, Matheson Tri-Gas - Slide 18

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

semi

Carrie Wyse, Matheson Tri-Gas - Slide 19

MTX™ Summary

Impurities Removed	H_2O Volatile Metal species (e.g. Mo, Ti, Fe) Particulates
Efficiency	<100 ppb H_2O in N_2 (Lambda Scan) <1 ppb H_2O in N_2 (APIMS) <4 ppb Mo in HCl (Hydrolysis/ICP-MS)
Capacity	~ 5000 kg HCl

semi

Carrie Wyse, Matheson Tri-Gas - Slide 20

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.**

semi

Carrie Wyse, Matheson Tri-Gas - Slide 21