

New Technology

Advances in purifier technology:

Removal of volatile metal complexes and moisture from HCl and CO etch gases

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

Contamination control in etch processing is one of the key issues in the semiconductor industry. Even the highest-purity etch gases are known to contain volatile metal species in addition to trace moisture and particles. Volatile metal species pass through 0.003 μm particle filters to the wafer surface. Thus, it is essential to remove these impurities from sensitive processes such as front-end etch that require stringent control of metals.

Ultra-high-purity gases are in demand in the semiconductor industry, as minimizing contamination is becoming critical to quality and yield. As device dimensions get smaller, trace impurities become more significant. Front-end processes, such as wafer clean, silicon epi and front-end etch, are particularly susceptible to metals contamination, as trace metals in these areas have a maximum effect on electrical performance of the device. Thus, the removal of trace metal impurities is of great interest.

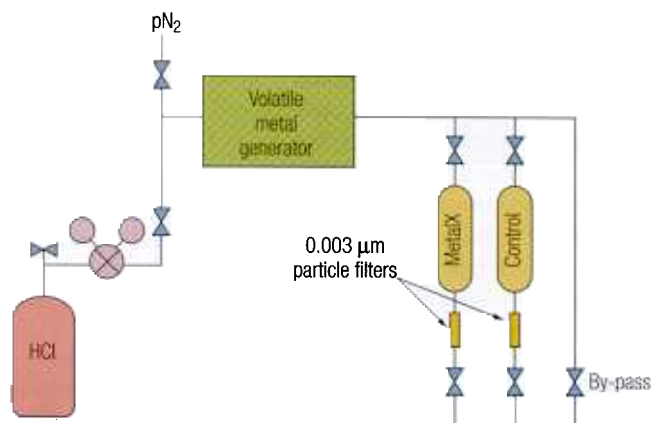
Even when the highest-available grade of gas is used in a particular process, impurities can be introduced to a system by processes such as cylinder changes, inadequate purge procedures and by reaction between the process gas and components in the distribution system. Thus, Point-of-use (POU) purification is essential to ensure the integrity of an ultra-pure gas distribution system.

Typically, corrosive gas delivery systems are outfitted with moisture purifiers and

particle filters. This helps minimize corrosion and degradation of expensive components, and removes particles shed due to mechanical devices (e.g. valves). However, moisture purifiers do not eliminate the problem of molecular metal contaminants, which pass through particle filters.

Corrosive gases, such as HCl and HBr, are known to contain trace levels of volatile metal complexes and can generate them *in-situ* via reaction with

Figure 1: Apparatus for testing removal of volatile metal species in corrosive gas



process hardware. Removal of moisture merely decreases the contaminants generated by corrosion, but it does not eliminate volatile metal complexes that are present in the source gas or created in the process stream.

Similarly, carbon monoxide, which is widely used in selective front-end etch, inherently contains volatile metal complexes due to reaction of the gas with available steel surfaces, including cylinders, piping and gas-delivery components. Pure CO reacts even at moderate pressure with iron and nickel in stainless steel, forming volatile metal carbonyls ($\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$). Control of carbonyl impurities in CO is thus a critical step in control of metals during etch.

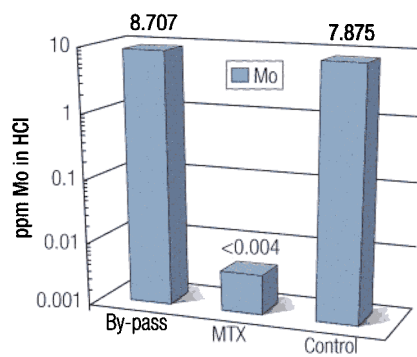
Removal of volatile metals from HCl

The level of volatile metal species found in HCl gas is typically in the low ppb region even in the cleanest HCl commercially available.^{1,2} According to the SIA Roadmap, the estimated allowable level of total metallic impurities in gases is <4 ppt.³ 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 new Nanochem 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.

MetalX was first tested for the removal of volatile molybdenum chloride. A challenge gas stream was generated by

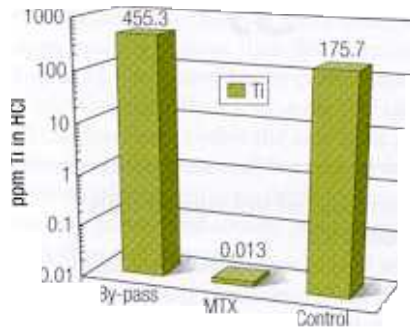
Figure 2: Removal of volatile molybdenum species in HCl by MetalX



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Figure 3: Removal of volatile titanium species in HCl by MetalX



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 $0.003 \mu\text{m}$ particle filter, and to the by-pass. Hydrolysis samples were collected at each port (see Figure 1).

The hydrolysis samples were analyzed by ICP-MS for trace metals. These experiments demonstrate that the MetalX purifier effectively removed ppm levels of volatile molybdenum to the detection limit of <4 ppb in HCl matrix, as seen in Figure 2. Because purifier efficiency is directly related to the challenge, it is reasonable to expect the purifier to effectively remove low levels of volatile metals with ppt efficiency.

The purifier was also tested for removal of TiCl_4 in a similar fashion. TiCl_4 is more volatile than molybdenum chloride, and 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, as seen in Figure 3.

To rule out any concern that the MetalX would emit metals in an HCl gas stream, an experiment was conducted in which hydrolysis samples were collected at the outlet of a 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 degrees Celsius.

Removal of volatile $\text{Fe}(\text{CO})_5$ from CO

The new purifier was also tested for the removal of $\text{Fe}(\text{CO})_5$ using a moderate challenge in CO and a high challenge in N_2 . Iron pentacarbonyl levels were mon-

itored by FTIR, using the peak height of the most intense absorption bands at 2013 and 644 cm^{-1} . Due to the instability of $\text{Fe}(\text{CO})_5$, calibration standards are not trustworthy, so it was not feasible to generate quantitative calibration curves for $\text{Fe}(\text{CO})_5$ in matrix gases for this study. However, using spectroscopic data from reference 4 and assuming both Beer's Law and the absence of a matrix effect, it was possible to obtain semi-quantitative estimates of the level of $\text{Fe}(\text{CO})_5$ for this study.

A moderate challenge of $\text{Fe}(\text{CO})_5$ was generated in CO gas by flowing carbon monoxide over frozen $\text{Fe}(\text{CO})_5$

held at -72 degrees C. Using a semi-quantitative absorption coefficient, the concentration of $\text{Fe}(\text{CO})_5$ generated in N_2 under these conditions was calculated to be 4 ppm. (Note that there is overlap between the $\text{Fe}(\text{CO})_5$ absorption band at 2013 cm^{-1} and the P branch of CO. Thus, the background spectrum of the CO gas was subtracted from each sample spectra, revealing the $\text{Fe}(\text{CO})_5$ absorbance.)

This challenge gas stream was then directed into the purifier and by-pass, followed by the FTIR, as seen in Figure 4. This challenge was completely removed; no $\text{Fe}(\text{CO})_5$ was detected at the outlet of

Figure 4: $\text{Fe}(\text{CO})_5$ test apparatus

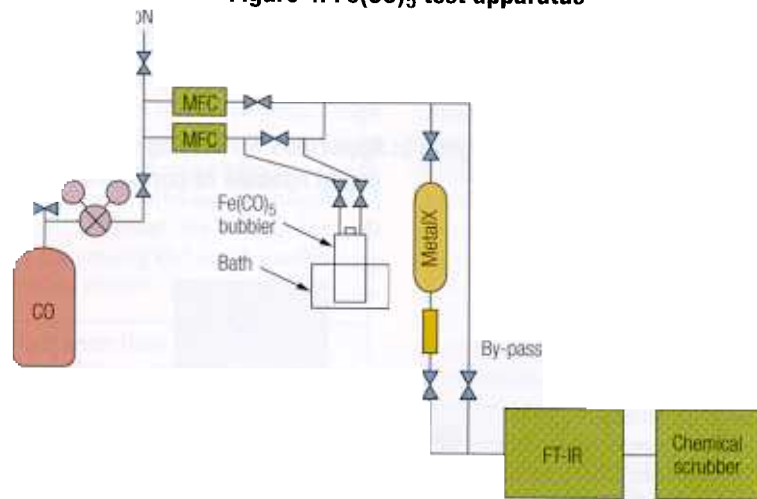
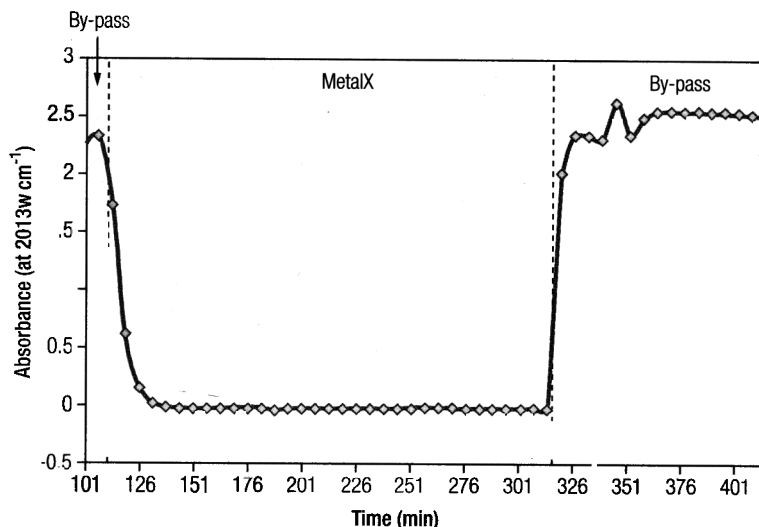


Figure 5: Removal of $\text{Fe}(\text{CO})_5$ by MetalX in CO gas



the purifier, as seen in Figure 5. It was also found that the ppb level moisture impurity from the CO cylinder was removed.

A high challenge of Fe(CO)₅ was generated by bubbling N₂ through Fe(CO)₅ liquid at 0 degrees C. This saturated the IR signal due to the high concentration of Fe(CO)₅. Quantitative analysis of the scrubber solution indicated the challenge stream contained Fe(CO)₅ on the order of 700 ppm. This gas stream was directed into the purifier and by-pass, followed by the FTIR. When the purifier was challenged with several hundred ppm Fe(CO)₅, no Fe(CO)₅ was detected at the outlet.

Removal of H₂O from HBr

MetalX efficiency for moisture in corrosive gas was tested in HBr, because 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 percent N₂ and 90 percent 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.

Summary


In the case of corrosive gases, conventional purifier technology can merely help avoid the formation of volatile metal complexes by minimizing corrosion facilitated by moisture. In the case of carbon monoxide, current purifier technology can simply remove moisture as an impurity in itself, but cannot solve the problem of volatile metal carbonyls. We have proven that MetalX can solve both problems. ■

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