Contamination Control in Carbon Monoxide Processes

Carrie Wyse, Tadaharu Watanabe, Joe Vininski,
Rob Torres, Mark Raynor, and Virginia Houlding

Matheson Tri-Gas Inc., Advanced Technology Center
1861 Lefthand Circle, Longmont, CO 80501

Overview

Contamination in carbon monoxide processes can be minimized using two enabling technologies. Use of an iron- and nickel-free cylinder package reduces iron and nickel contamination in CO gas to sub-ppb levels as shown by hydrolysis sampling, and reduces contamination on silicon wafers dry etched with CO by three orders of magnitude, as shown by TXRF. Point-of-use purification removes moisture to less than 1 ppb, as shown by APIMS in addition to removing iron and nickel carbonyls generated in-situ.

Introduction

Carbon monoxide is used in the semiconductor industry for several purposes. CO is a key component of the gas mixture used for selective etching of oxide films deposited over silicon nitride, in which it forms an oxygen rich polymer layer at the oxide/nitride interface. This reduces the etch rate of the silicon nitride and improves the selectivity of the process. CO is also used for silicon dioxide contact and via etch.

As with all process gases, the purity of the CO gas directly impacts the overall process yield and quality. For plasma etch processes, the selectivity and etch rate must be maintained at particular levels by precisely controlling process parameters and gas mixture concentrations. Thus purity control in each gas component results in more precise process control. This leads to improved control of the dimensions and shape of the etched pattern and ensures uniform etch selectivity. Furthermore, metal contamination is particularly detrimental, because metal ions can be deposited onto the etch surface by the process and can then diffuse during subsequent steps. This directly impacts the electrical characteristics of the device, such as resistivity.

It is well established that iron pentacarbonyl and nickel tetracarbonyl can form via gas-solid reactions under high pressure CO[1], such as in a compressed gas cylinder.

$$Fe\ (s) + 5\ CO\ (g) \rightleftarrows Fe(CO)_5\ (l)$$

$$Ni\ (s) + 4\ CO\ (g) \rightleftarrows Ni(CO)_4\ (l)$$

Not only are iron pentacarbonyl and nickel tetracarbonyl readily formed under these conditions, they are both relatively volatile complexes. Thus, these metal-containing impurities can be transmitted in the gas phase throughout the process lines, thereby contaminating the device.

In addition to metal carbonyls, carbon monoxide is known to contain low-level moisture. This paper describes two developments by Matheson Tri-Gas for enhanced contamination control of CO processes: improved cylinder package and a point-of-use purifier designed to remove both metal carbonyls and moisture.

Experimentation

Ultraline Cylinder Package - Hydrolysis studies

Matheson Tri-Gas has developed an iron- and nickel-free cylinder package for carbon monoxide. This Ultraline package is specifically designed to eliminate steel and nickel wetted parts, thus minimizing contamination due to iron and nickel carbonyls.

The unique Ultraline cylinder has been proven to provide higher purity CO based on metals analysis of the gas.[2] Three different packages were tested for metal contamination using a hydrolysis sampling method. One package consisted of a standard 4130 carbon steel cylinder outfitted with a brass packed valve, which is representative of packages commonly used in the gas industry. The second was a 6061 aluminum cylinder outfitted with a 316 stainless steel diameter index safety system (DISS) diaphragm valve. The third was the new iron- and nickel-free Ultraline package developed by Matheson Tri-Gas, consisting of an aluminum cylinder, brass valve, and a pressure relief device containing a copper rupture disk in place of the standard nickel disk.

Hydrolysis samples were collected from each test cylinder using a method in which 3.5 kg of CO was sampled through 18-MΩ water at 1 liter/min. Analysis of the hydrolysis samples was performed by GFAA for iron and ICP-MS for other elements. Although the hydrolysis sampling method has not been demonstrated to be quantitative for metal carbonyl sampling, it is assumed that the amount of metals captured by hydrolysis is proportional to their concentration. Therefore, the method is useful for comparison purposes. The average metals from two cylinders of each type are reported in Table 1 below.

Table 1. Average elemental impurity concentrations in CO from various cylinder packages, measured by GFAA and ICP-MS after hydrolysis sampling (ppb).

Element	Carbon steel package	Ultraline package with SS valve	Ultraline package with brass valve
	4130 carbon steel cylinder C37700 brass valve	6061 aluminum cylinder 316L SS valve	6061 aluminum cylinder C37700 brass valve
Fe	869	48.8	0.622
Ni	0.112	0.989	0.185
Al	0.003	0.032	0.367
Cu	0.019	0.012	0.057
Zn	0.020	0.060	0.146

The CO in the Ultraline package contained significantly less iron impurity than either of the other two packages. This package yielded approximately 1400 times less iron than the carbon steel package, and 78 times less iron than the Ultraline DISS package. This trend of iron contamination measured in the CO directly corresponds to the relative iron levels found in each package: the carbon steel package containing the most iron; followed by the Ultraline DISS package, and the Ultraline package, which has the least amount of iron.

The nickel contamination measured in the CO from the Ultraline DISS package was six times greater than that found in the other two packages. This difference can be explained by the fact that the Ultraline DISS package had a stainless steel valve, which is 12% nickel, whereas the other two packages had brass valves.

The zinc levels were approximately two times greater in the Ultraline package than the Ultraline DISS, and seven times that in the carbon steel package. Although zinc is a component of brass, there is no correlation between the brass content of the package and the zinc levels found in the CO. Copper levels from all packages were sub-ppb, and there is no correlation of copper contamination and package materials. Aluminum contamination was also at sub-ppb levels for all packages, but was slightly higher in the Ultraline CO. However, no direct reactions between CO and solid aluminum, zinc, or copper were found in the literature. The presence of these particular impurities in the hydrolysis samples is not likely to be a result of reaction between the CO and the components, but rather a result of particulate shedding.

The Ultraline cylinder package developed for CO reduces iron contamination by three orders of magnitude and nickel contamination by a factor of 5. This significant reduction in iron and nickel impurities achieved in the CO is supported by wafer studies, which verify that the silicon wafers processed with Ultraline CO have lower iron and nickel contamination, and show no increase in the other metal impurities.

Ultraline Cylinder Package - Wafer studies

Further investigation showed that the dramatic improvement in CO purity from the Ultraline package does indeed produce higher quality silicon.[3] This was proven in a study in which CO was used as an additive gas to plasma-etch clean silicon. The etch process consisted of a fluorocarbon etchant and additive CO. Three control wafers were left unetched, three wafers were etched with CO from a steel cylinder outfitted with a 316L stainless steel valve and nickel rupture disk, and three wafers were etched using CO from the Ultraline package. The silicon wafers were then analyzed for surface metals contamination via total reflectance X-ray fluorescence (TXRF). This experiment demonstrates a dramatic reduction in the metal contamination of silicon wafers when processed with CO packaged in the Ultraline package, as shown in the TXRF results reported in Table 2.

Table 2. Average elemental impurity concentrations on silicon wafers after etch processing with CO from different cylinder packages, measured by TXRF (10^{10} atoms/cm^2).

Element	Control	Carbon steel package	Ultraline package
	Unetched dielectric film	4130 carbon steel cylinder 316L SS valve Ni rupture disk	6061 aluminum cylinder C37700 brass valve Cu rupture disk
Fe	2.32	12500	29.3
Ni	1.09	382	75.2
Cr	0.36	12.4	0.94
Cu	1.43	3.61	1.73

Point-of-Use Purifier

Even when the highest available grade gas is used in a particular process, impurities can still contaminate a system downstream of the cylinder. For example, moisture can enter a distribution system during cylinder change-out or inadequate purge procedures, and metal carbonyls can be generated in-situ by reaction between CO matrix gas and iron and nickel containing components (stainless steel, Ni gaskets, MFC's, etc.). The predominant material of choice for gas distribution tubing is normally 316L stainless steel, which contains 65% Fe and12% Ni. Therefore, the gas may exit the cylinder with sub-ppb levels of volatile metal complexes and moisture, but the concentration of these contaminants will certainly increase as the gas progresses toward the tool. Thus Point-of-Use (POU) purification is essential to maintain the integrity and consistency of an ultra-pure process by removing the metal and moisture contaminants within the process gas stream.

1) Removal of iron pentacarbonyl

The MetalX™ purifier recently developed by Matheson Tri-Gas removes both moisture and iron pentacarbonyl from CO.[4] It is expected that MetalX™ will also remove $Ni(CO)_4$ since its chemical and physical characteristics are similar to that of $Fe(CO)_5$ with respect to the purifier medium. FT-IR experiments were conducted to test the purifier for the removal of iron pentacarbonyl in CO. Due to the instability of $Fe(CO)_5$, calibration standards are not trustworthy, so it was not feasible to generate quantitiative calibration curves for $Fe(CO)_5$ in matrix gases for this study. However, using spectroscopic data[5] 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 $Fe(CO)_5$ for this study.

A moderate challenge of iron pentacarbonyl was generated in CO gas by flowing carbon monoxide over frozen $Fe(CO)_5$ at a flow rate of 350 sccm. Iron pentacarbonyl levels were monitored using the peak height of the most intense absorption band at 2013 cm^{-1}. Using a semiquantitative absorption coefficient, the concentration of $Fe(CO)_5$ generated under these conditions was calculated to be 4 ppm. (Note that there is overlap between the $Fe(CO)_5$ absorption band at 2013 cm^{-1} and the CO absorption. Thus, the background spectrum of the CO gas was subtracted from each sample spectra, revealing the $Fe(CO)_5$ absorbance.) The challenge gas stream was then directed into the MetalX™ purifier and by-pass, followed by the FT-IR. The spectrometer was equipped with a 10 m pathlength cell and a liquid nitrogen cooled MCT-A detector. No $Fe(CO)_5$ was detected at the outlet of the purifier during the 4 ppm challenge as seen in Figure 1.

Capacity studies in nitrogen were also conducted, using a high challenge of iron pentacarbonyl generated by bubbling 30 sccm N_2 through the neat liquid at 0°C mixed with 450 sccm N_2. Although the IR signal was saturated at the by-pass, due to the high concentration of $Fe(CO)_5$, quantitative analysis of the scrubber solution indicated that there was ~700 ppm $Fe(CO)_5$ in the challenge. When the MetalX™ purifier was challenged with this high level of iron pentacarbonyl, no $Fe(CO)_5$ was detected at the purifier outlet, until breakthrough at a capacity of 2.2 L/L.

2) Removal of Moisture

In addition to the removal of iron pentacarbonyl, a cylinder of CO containing ppb levels of moisture was flowed through the MetalX™ purifier. Studies showed that the moisture was removed to levels below the detection limit of the FT-IR, 50 ppb.

Additionally, moisture performance of the MetalX™ purifier was quantitatively tested in N_2 using APIMS and a calibrated moisture generator. It is assumed that the moisture performance in N_2 is similar to that in CO matrix gas, because both N_2 and CO have little chemical interaction with the purifier medium. The results, found in Figure 2, show that when the purifier was challenged with 2 ppm H_2O at a flow rate of 2 slpm for over 20 hours, the efficiency was less than the detection limit, 1 ppb. When the challenge was increased to 7 ppm H_2O at a flow rate of 1 slpm, the efficiency was still less than 1 ppb. Capacity tests show that the purifier has a moisture capacity of 17 L/L, using FT-IR.

Summary

Two developments for contamination control of ultrapure semiconductor processes involving carbon monoxide have been discussed. Target impurities in carbon monoxide processing are moisture and both $Fe(CO)_5$ and $Ni(CO)_4$. Iron and nickel carbonyls are generated in CO cylinders and distribution systems by reaction of CO with any iron or nickel containing components in the system. First, the Ultraline cylinder package is specifically designed to minimize metal carbonyl impurities in CO by using an iron and nickel free container. Hydrolysis studies verify that this unique package reduces nickel and iron contamination in CO by one and three orders of magnitude respectively, compared to the conventional package. This is confirmed by wafer studies, in which silicon wafers were dry etched using a fluorocarbon process with additive CO from different packages. TXRF analysis of the wafers processed with the Ultraline CO showed a reduction in metal contamination by three orders of magnitude. Second, the point-of-use purifier MetalX™ effectively removes metal carbonyls and moisture from CO. FT-IR studies demonstrate the MetalX™ has an iron pentacarbonyl capacity of 2.2 L/L, and a moisture with an efficiency of less than 1ppb (APIMS) with a capacity of 17 L/L. Therefore, the use of the iron and nickel free CO package, in addition to the POU purifier, will significantly enhance carbon monoxide process control and yield.

Acknowledgments

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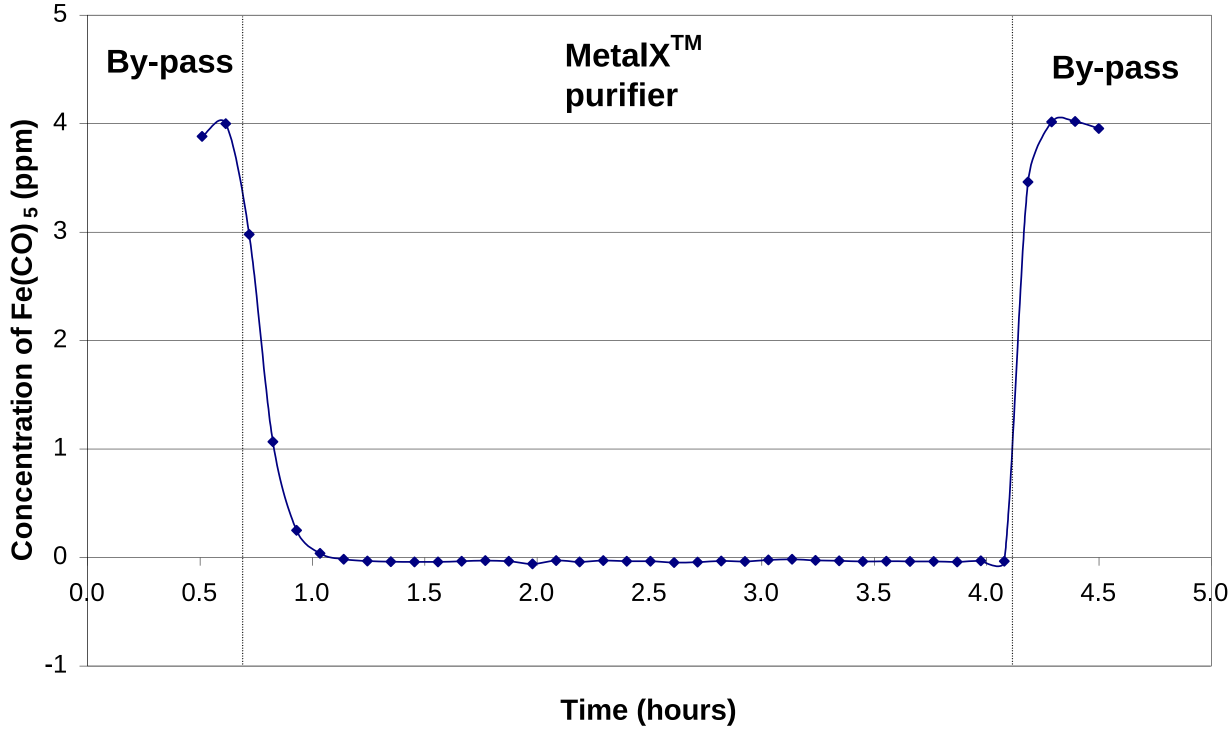

Figure 1. Removal of iron pentacarbonyl by MetalX™ purifier in CO gas, measured by FT-IR, based on a calibration using peak heights and the absorption coefficient for the 2013 cm^{-1} absorption band.

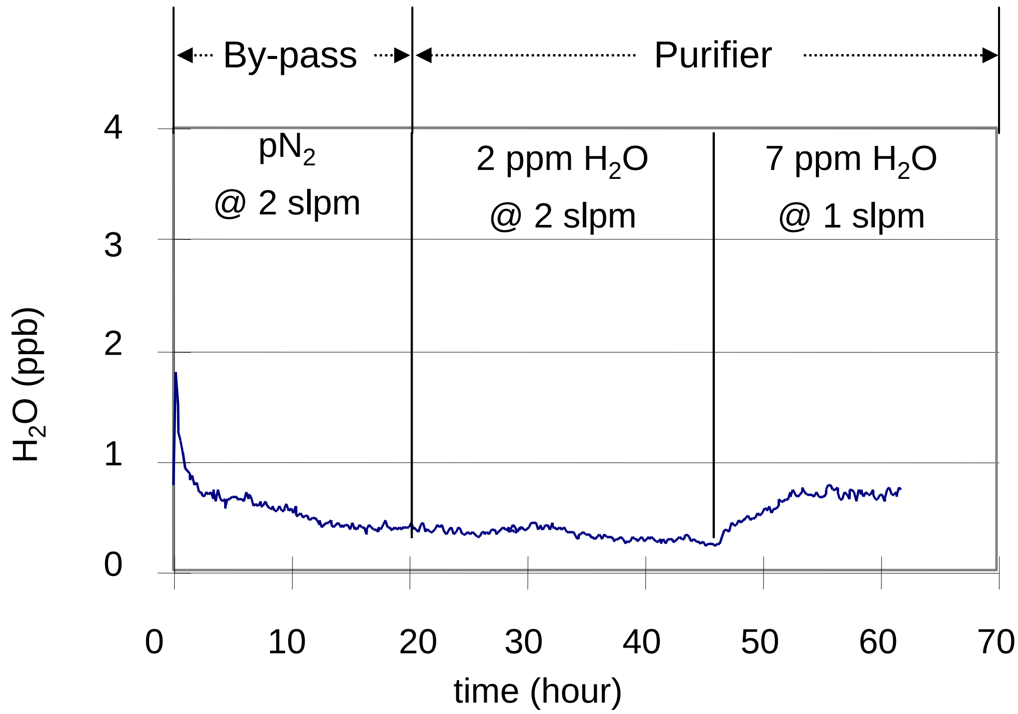

Figure 2. Purifier efficiency for moisture at different challenge levels and flow rates, measured by APIMS.