Removal of metal carbonyl and moisture impurities through

POU purification of CO gas

OVERVIEW An elaborate testing methodology is used to study the impurity removal characteristics of point-of-use carbon monoxide gas purifiers. Test results demonstrate efficient removal of impurities, such as harmful metal carbonyls and moisture, from carbon monoxide gas. In addition to reviewing those results, this article discusses how a unique purification technology would benefit certain wafer-processing applications such as plasma etch.

Carbon monoxide (CO) finds various applications within and outside the realm of semiconductor manufacturing. Its application as a selectivity enhancer in plasma etch processes has gained widespread acceptance within the semiconductor industry. This application has picked up greater momentum with the advent of very large aspect-ratio features and increased the need for more selective etch processes. CO is also used in the synthesis of carbon nanotubes [1, 2]. Various processes have been reported for the manufacture of nanotubes, and CO is used as the primary feedstock gas in a majority of those processes.

CO is widely used as an additive with fluorocarbon gases to enhance the selectivity of high aspect-ratio oxide etch processes. A prominent theory is that the CO "scavenges" reactive atomic fluorine to decrease the etch rate of silicon-rich underlayers (silicon nitride, polysilicon), thus increasing selectivity [3]. The polymerization tendency of the CF_x species is also enhanced with the addition of CO, which aids in decreasing the etch rate of the underlayer via the formation of a protective polymer film on the underlayer. In addition, CO provides atomic carbon, resulting in increased carbon concentration in the polymer and rendering it more etch-resistant. This can minimize sidewall undercutting during high aspect-ratio etch processes, enabling greater dimensional control.

CO has been known to contain relatively large amounts of metal carbonyl and moisture impurities. Even 99.998% pure (research-grade) CO is reported to have up to 1 part-per-million (ppm) of moisture and up to 0.5ppm each of nickel and iron carbonyl [4]. Of greater concern is the fact that CO reacts with many metals, most notably nickel and iron, to form volatile metal carbonyl complexes. Such metals are common constituents of delivery systems and delivery line components, leading to an increased risk of metal carbonyl formation downstream of the gas source. Formation is accelerated at higher pressures and also occurs more readily with the presence of moisture impurity [5]. The relatively high volatility of metal carbonyls increases the risk of these impurities entering the process chamber. Gas manufacturers have taken several measures to alter the materials used in the storage and delivery of CO [6]. Additionally, there have been other measures taken to reduce the exposure of CO to nickel and iron during gas production. However, complete elimination of metals that react with CO to form metal carbonyls is unlikely because they are inevitably present, to some extent, in gas lines, delivery systems, and components. Thus, the concentration of metal carbonyls at the point of introduction to the process chamber is likely to be higher than at the gas source.

Table 1. Initial cleanliness test results and low metal-carbonyl challenge efficiency testing

Impurity concentration downstream of purifier (ppbv) (Average removal efficiency, %)				
Impurity	**Pall A080**	**Pall A082**	**Pall A081**	**Purifier B**
Initial cleanliness test results				
$Ni(CO)_4$	Below DL to 0.85	0.84–1.23	Below DL to 1.03	9.36 initially, fell to 0.87
$Fe(CO)_5$	Below DL	Below DL	Below DL	Below DL
Low metal-carbonyl challenge efficiency testing				
$Ni(CO)_4$	0.46–0.94 (99.939)	0.98–1.32 (99.915)	1.29–2.53 (99.837)	0.70–1.05 (99.932)
$Fe(CO)_5$	Below DL (>99.978)	Below DL (>99.978)	Below DL (>99.978)	Below DL (>99.978)

Point-of-use (POU) gas purification technology has been widely accepted as a viable solution for ensuring gas purity at the point of introduction into the process chamber and for enhancing process and device yield, uniformity, and predictability. Effective POU purification of CO assures that levels of metal carbonyls and moisture impurities do not exceed part-per-billion (ppb) levels when the gas enters the process chamber.

Metal carbonyls have been known to affect device quality and wafer yield. Once they enter the process chamber, they are deposited onto the wafer surface, resulting in altered electrical parameters. They could be a potential source of shorts or altered contact resistance after via and trench etch processes. Thermal anneal steps following metal carbonyl deposition drive these impurities into the bulk material, thus changing bulk-silicon electrical properties. Removal of these metal carbonyls by subsequent wafer cleans is also difficult because they are deposited during a plasma processing step.

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Table 2. High metal-carbonyl challenge efficiency testing

Impurity	Flow rate (slpm)	Impurity concentration downstream of purifier (ppbv) (Average removal efficiency, %)			
		Pall A080	Pall A082	Pall A081	Purifier B
$Ni(CO)_4$	0.25	8.16–8.64 (99.991)	1.64–2.02 (99.998)	2.97–3.14 (99.997)	1.42–2.44 (99.998)
	0.5	2.98–3.48 (99.997)	3.26–4.38 (99.996)	2.17–2.19 (99.998)	Breakthrough
	1.0	2.84–2.96 (99.997)	0.70–2.5 (99.998)	1.50–1.59 (99.998)	Breakthrough
$Fe(CO)_5$	0.25	7.71–10.31 (99.986)	0.57–1.22 (99.999)	1.20–1.63 (99.999)	0.37–1.14 (99.999)
	0.5	2.13–2.83 (99.998)	1.78–2.62 (99.998)	0.90–0.91 (99.999)	0.97–1.08 (99.999)
	1.0	1.53–1.63 (99.998)	1.29–1.29 (99.999)	0.55–0.62 (99.999)	Breakthrough

In addition to accelerating the generation of harmful metal carbonyls, moisture impurity in CO may also lead to unpredictable changes in the etch rate and subsequent corrosion in the underlying metal for dual-damascene via etch processes [7].

A purification material developed by Pall removes metal carbonyls, moisture, O_2, and CO_2 from CO gas by the following four mechanisms: direct chemisorption; dissociation of the impurity followed by dissolution or reaction with the purification material; chemisorption of dissociation reaction products; and chemisorption and/or physisorption on the substrate. Test data presented here reveals a strong affinity of the purification media toward metal carbonyl and moisture impurities in CO gas. The purifier is integrated with a built-in particle filter capable of removing ≥3nm particles with 9-log efficiency.

A study assessed three key characteristics of CO POU purifiers: efficacy of the purifier to remove molecular impurities such as metal carbonyls and moisture from CO gas; the capacity to remove metal carbonyl impurities; and the captured metal-carbonyl desorption behavior of the purifier upon undergoing substantial utilization.

Experiment and results

Three Pall 1.125-in. C-Seal top-mount purifiers were tested for metal-carbonyl removal performance using a gas chromatograph equipped with an electron capture detector (GC-ECD). A successful commercially available POU CO purifier produced by another manufacturer (referred to as Purifier B) was tested simultaneously for comparison purposes. Nickel and iron carbonyl were the only metal carbonyl species monitored, as significant quantities of these two species are present in ultrahigh-purity (UHP) CO gas due to the high reactivity of nickel and iron with CO.

The testing apparatus consisted of cylinder sources of purified and metal carbonyl impurity-laden CO, a customized gas sampling system, and precision mass flow controllers (MFC) that were calibrated in CO prior to testing. Lower detection limits (LDL) of 0.7ppbv for $Ni(CO)_4$ and 0.3ppbv for $Fe(CO)_5$ were established for the instrumentation prior to testing. However, background levels in the instrument while measuring the zero CO source (APCI BIP-grade gas with additional in-line purification) for both metal carbonyls fluctuated during the testing (e.g., $Ni(CO)_4$ varied from a low of 0.72 to a high of 12.24ppbv with the typical being between 1 and 5ppbv). The calibration curves and detection limits were obtained in accordance with SEMI spec C10-0299, "Guide for Determination of Method Detection Limits."

Metal-carbonyl cleanliness testing

The initial metal-carbonyl cleanliness testing was performed to investigate whether the POU purifier generates any nickel and/or iron carbonyls upon initial installation. It further establishes the out-of-package cleanliness of the sample and the instrumentation background levels.

The test was conducted at room temperature with a flow rate of 1 standard liter/minute (slpm) of UHP CO. It should be noted that the POU CO purifiers are rated for service at flow rates up to 3slpm. A total of three C-Seal purifiers and one commercially available POU CO purifier were tested and the downstream (of the POU purifiers) metal carbonyl levels were monitored for 1 hr. The results from the testing are outlined in **Table 1.** The manifold system with all its components (except the purifier samples) was "conditioned" prior to testing to ensure that no more than trace levels of metal carbonyls were present (i.e., to ensure no contribution from the system). SEMI Standard F30-0298, "Start-up and Verification of Purifier Performance Testing for Trace Gas Impurities and Particles at an Installation Site," was followed as closely as possible throughout this testing.

Metal-carbonyl removal efficiency testing

The metal-carbonyl removal efficiency testing was conducted to determine the efficacy of the purifiers in removing nickel carbonyl, iron carbonyl, and moisture from an impurity-laden CO gas stream. SEMI Standard F68-1101, "Test Method for Determining Purifier Efficiency," was followed as closely as possible throughout this testing.

The metal carbonyl removal efficiency testing was conducted at both a low and a high metal-carbonyl challenge concentration. This was done to verify that the purifier behaved similarly at both low and high impurity challenge concentrations.

The low-challenge testing was performed at 1.0slpm with an inlet pressure of 5psig of CO. The challenge source was a CO calibrant gas-cylinder SG 9169903ABL; independent Fourier transform infrared (FTIR) spectroscopy analysis revealed the concentrations of $Ni(CO)_4$ and $Fe(CO)_5$ to be 1.56ppmv and 1.37ppmv, respectively. The downstream results were monitored for a total of 2 hr and are shown in Table 1.

The high-challenge testing was performed at varying flow rates of 0.25, 0.5, and 1.0slpm, starting with the lowest flow rate. The flow rate was increased to the next level after 30 min of testing at each

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Table 3. Metal-carbonyl removal capacity results

Impurity (100ppmv)	Capacity (hr) at 1slpm				
	Pall A080	Pall A082	Pall A081	Average for Pall	Purifier B
$Ni(CO)_4$	34.5	35.5	31.1	33.7	0.24
$Fe(CO)_5$	35.3	44.3	39.1	39.6	0.56

flow rate. The challenge source was CO calibrant gas-cylinder SG 9928932AAL; independent FTIR analysis revealed that the concentrations of $Ni(CO)_4$ and $Fe(CO)_5$ were 96.9ppmv each. An inlet pressure of 5psig was maintained throughout the test (see **Table 2**). It should be noted that the remark "breakthrough" refers to the fact that breakthrough or exhaustion of the purification function of the POU purifier took place, indicating insufficient capacity.

Metal-carbonyl removal capacity testing

An accelerated life test was conducted to determine the POU CO purifier's capacity to remove nickel and iron carbonyls from an impurity-laden CO gas stream. The testing was performed at 1.0slpm with an inlet pressure of 5psig of CO. A high metal-carbonyl challenge concentration source, CO calibrant gas-cylinder SG9928932AAL, with 96.9ppmv each of $Ni(CO)_4$ and $Fe(CO)_5$ was used for this testing. Concentrations were determined independently by FTIR analysis. SEMI Standard F67-1101, "Test Method for Determining Inert gas Purifier Capacity," was followed as closely as possible throughout the testing.

For the purposes of this testing, breakthrough was defined as the time when the concentration of $Ni(CO)_4$ equaled or exceeded 30ppbv, while capacity was the total time the 96.9ppm of each metal carbonyl contaminant was removed to the point of breakthrough. **Table 3** displays the results of this testing. No breakthrough for

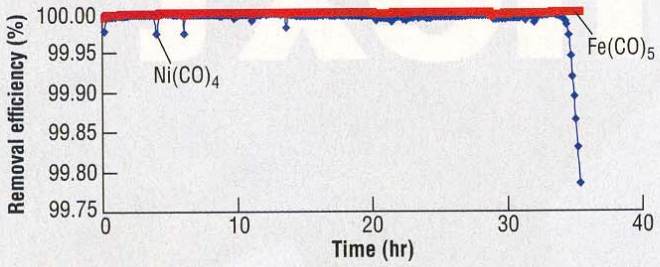

Figure 1. Typical capacity curve, using Pall A080 sample with 1slpm CO flow. Challenge concentrations were 96.9ppmv for both $Ni(CO)_4$ and $Fe(CO)_5$.

$Fe(CO)_5$ was observed during the testing of the samples; capacities reported reflect the amount of $Fe(CO)_5$ removed when the capacity testing was terminated.

A typical capacity curve (Pall A080 sample capacity curve shown) is displayed in **Fig. 1.** The figure depicts removal efficiency instead of the more typical effluent concentration. A graph like this takes into account both the inlet challenge level and the effluent concentration. A removal efficiency of 99.98% indicates an effluent concentration of 10.0ppbv with a challenge of 100ppmv. Similar capacity curves were obtained for the other purifier samples.

Metal-carbonyl desorption testing

Because a portion of the Pall purification material is known to physisorb metal carbonyls, a desorption test was conducted on a C-Seal purifier sample to verify that the metal contaminants were chemically bound during removal [5]. By subjecting the sample to a metal carbonyl challenge that utilized a substantial amount of its capacity and then switching to zero CO gas for an extended duration, it is possible to see if there was any previously adsorbed $Ni(CO)_4$ or $Fe(CO)_5$ released from the purifier. Any release would indicate that

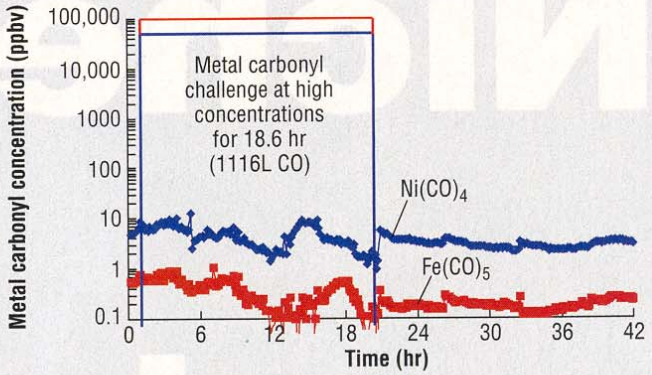

Figure 2. Desorption test results on Pall A083 sample with 1slpm CO flow. Challenge concentrations were 63.4 and 109.2 for $Ni(CO)_4$ and $Fe(CO)_5$, respectively.

the adsorption bonding was weak and reversible (i.e., that the mechanism for removal was physisorption and not chemisorption).

For the purposes of this test, a new CO purifier sample labeled A083 was challenged with $Ni(CO)_4$ and $Fe(CO)_5$ impurity-laden CO gas for a total time of 18.6 hr at a flow rate of 1slpm and inlet pressure of 5psig. The $Ni(CO)_4$ and $Fe(CO)_5$ concentrations in this CO calibrant gas cylinder (SG9928936AAL) were determined to be 45.9ppmv and 90.2ppmv, respectively, as determined by independent FTIR analysis. Following this, the $Ni(CO)_4$ and $Fe(CO)_5$ desorption behavior of the purifier was monitored by flowing purified UHP CO gas through the sample at 1slpm for 20 hr. The effluent CO gas was monitored throughout this testing on the GC-ECD and the results are depicted in **Fig. 2**.

Moisture-removal efficiency and capacity testing

Two additional POU CO purifier samples (a Pall C-Seal purifier and a Purifier B, both new samples) were tested for moisture removal efficiency and capacity using Meeco Inc.'s Tracer moisture analyzer. Literature for this instrument claims a moisture LDL of 1.0ppbv in inert gas with an accuracy of ±4.0ppbv. Although detection of moisture in CO is possible with this analyzer, the manufacturer does not establish a LDL for this. Both samples achieved downstream (of purifier) moisture readings below 1.0ppbv while being challenged with approximately 100ppmv of moisture in CO at a flow rate of 1.25slpm; however, the Pall sample demonstrated a capacity of 66.3 hr while that of Purifier B was 6.8 hr. SEMI Standard F67-1101, "Test Method for Determining Inert gas Purifier Capacity," was followed as closely as possible throughout the testing.

Discussion

The initial metal-carbonyl cleanliness test results indicate good startup performance of the CO purifiers. The $Ni(CO)_4$ concentration remained at or near the LDL of the analytical instrument.

The removal efficiency testing revealed that the C-Seal purifier demonstrated good metal-carbonyl removal efficiency, both at high- and low-challenge concentrations. Furthermore, during the high-challenge testing different flow rates did not significantly affect the removal efficiency of these purifiers. When used to purify UHP CO gas, which typically has nickel and iron carbonyl content of 0.5ppmv each, it is expected that metal carbonyl levels ≤1.0ppbv will be achieved; however, available instrumentation is limited in its ability to perform measurements at these concentrations.

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The metal-carbonyl removal capacity testing revealed an average capacity of 33.7 hr for $Ni(CO)_4$ and 39.6 hr for $Fe(CO)_5$ for the C-Seal purifiers. In comparison, Purifier B exhibited a capacity of 0.24 and 0.56 hr for $Ni(CO)_4$ and $Fe(CO)_5$, respectively.

The desorption testing showed that no adsorbed metal carbonyls were released, even with a substantial purge, indicating that the primary removal mechanism of the Pall purification material is chemisorption.

The results of the moisture efficiency and capacity testing clearly show that both the purifiers can effectively achieve trace levels of moisture, although the C-Seal purifier had significantly higher removal capacity. Additional testing using atmospheric-pressure ionization mass spectrometry in inert gas has shown that Pall's purification material can efficiently remove O_2, H_2O, and CO_2 contaminants with good capacity [9]. Similar results are expected in CO gas service.

Conclusion

The performance parameters evaluated and the test methodology used in this study serve as a basis for understanding the capabilities of POU CO purifiers. It is evident from the testing that both CO purifiers were effective in removing low concentrations of metal carbonyls to trace levels; however, only the C-Seal purifier demonstrated a very large capacity. Even in gas service that is expected to be ultrapure, POU CO purifiers assure consistent delivery of CO gas with trace levels of carbonyls and moisture that may result from preventive maintenance or system upsets. Such consistent gas quality leads to more predictable and higher-quality processes. ■

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