

Comprehensive Performance Testing and Characterization of Various Point-Of-Use (POU) Inert Gas Purification Technologies Used in Microelectronics Fabrication Processes

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Abstract

A comprehensive test plan was devised and executed to test the various performance aspects of different POU inert gas purification technologies. A Pall Gaskleen® II gas purifier of the Pall AresKleen™ family of products, along with various other purification technologies, were evaluated in order to obtain data indicative of POU purifier performance in various microelectronics gas applications. The study yielded useful information regarding both molecular and particulate impurities, and demonstrated the potential impacts of inert gas purification on applications such as plasma etch, chemical vapor deposition, sputter, atomic layer deposition, and epitaxy processes.

1. Introduction

The continued scaling of linewidths and deposited film thicknesses has augmented the need for gas purification. With films approaching two or three atoms in thickness, any impurity atoms (both molecular and particulate) in such films will have greater impact on film properties and ultimately on the device characteristics. 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.

Inert gases are widely used in semiconductor fabrication processes as carrier gases, purge gases, and chuck cooling gases. The purity levels maintained by gas manufacturers are sometimes not adequate to meet today's stringent process requirements. This is aggravated by disparities in gas purity between the cylinder (or gas cabinet) and the point where gas is introduced to the process chamber, a problem emanating from out-gassing and particle shedding in the gas lines, and various impurities from mass flow controllers (MFCs) and regulators.

Pall's AresKleen purification material is based on a purification technology using an activated carbon substrate. The purifier works on removing impurities by four mechanisms: direct chemisorption; dissociation of the impurity followed by dissolution or reaction with the purification material; chemisorption of reaction products; and chemisorption and/or physisorption on the substrate. Test data has revealed a strong affinity of the purification media toward impurities like oxygen, moisture, carbon dioxide, and carbon monoxide in various inert gases. Furthermore, the purifier is integrated with a built-in particle filter capable of removing 3nm particles with 9-log efficiency.

While the benefits of gas purification are enormous, the gas purifiers themselves must not contribute further molecular and particulate impurities in a process. Moreover, the efficacy of the various purification technologies to remove molecular and particulate impurities has to be defined. Two other purifier characteristics should be examined—that is, the capacity to remove molecular impurities and service lifetimes. The assessment of these key characteristics was the objective of this study.

“The pressure drop characteristics of a purifier have significant implications for low-vapor pressure gases”

2. Experiment and Results

The performance of a Pall Gaskleen II purifier (Part No. GLP2INPVMM4) of the AresKleen family of products was evaluated alongside three other purifiers (Purifier A,

Purifier	Test Flow Rate (SLPM)	Particles ($\geq 3\text{nm}$)/ft ³
Pall Gaskleen II	3.0	< 1
Purifier A	1.0	< 1
Purifier B	5.0	34
Purifier C	5.0	2

Table 1: Impurities in Bottled N₂ Supply

B, and C) representative of various other POU purification technologies. The Gaskleen II Purifier is a combination of purification and filtration technologies. It has dimensions of 3.31" in length by 1.36" in diameter. The competitive purifiers A, B, and C were selected based on their similar performance claims. In addition, they were all slightly larger than the Pall purifier in one way or another. The test conditions were chosen based on the individual recommended usage of the four purifiers in order to generate meaningful comparative data.

The tests performed on the purifiers were as follows (listed in chronological order):

1. Initial "out-of-bag" particle cleanliness (particle shedding test)
2. Purifier flow characteristics test (pressure drop)
3. Particle removal efficiency test
4. Molecular impurity removal efficiency test
5. Stepped oxygen challenge test
6. Oxygen removal capacity test
7. Orientation sensitivity test

2.1 Initial "Out-Of-Bag" Particle Cleanliness (Particle Shedding Test)

The four purifiers were first taken out of the package and tested with a sequential steady and pulsed flow of argon to detect the levels of particles ($\geq 3\text{nm}$ in size) shedding from the purifier upon installation. This would be indicative of the level of particles that the purifier would dis-

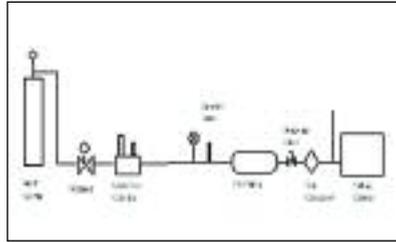


Fig 1: Test stand for initial cleanliness test

charge during initial installation in a process gas line. All testing was conducted according to SEMI Standard F43-0699, "Test Method for Determination of Particle Contribution by Point-of-Use Purifiers." The test flow rates and results are shown in Table 1. The flow rates were chosen based on the recommended operating flow rate for the respective purifiers. The test-stand schematic for the initial cleanliness test is shown in Figure 1.

The pre-purifier (Pall Maxi-Gaskleen[®]) was used to ensure complete removal of all particles and molecular impurities in the incoming argon gas. The argon gas used was 99.999% pure and all regulators and MFCs were ultra-high purity (UHP) components. The initial cleanliness test consisted of three cycles of 5 minutes steady and 10 minutes pulsed Argon flow for a total of 45 minutes test time per purifier. The total particle counts seen during this test period are outlined in Table 1. Prior to testing every purifier, the background particle cleanliness level was confirmed without a test purifier installed. This was to ensure that no particles entered the test purifier during the cleanliness test.

2.2 Purifier Flow Characteristics Test (Pressure Drop)

The purifier flow characteristics were determined by measuring pressure drop across the purifiers at various flow rates. All testing was performed according to SEMI Standard F59-0302, "Test Method for Determining of Filter or Gas System

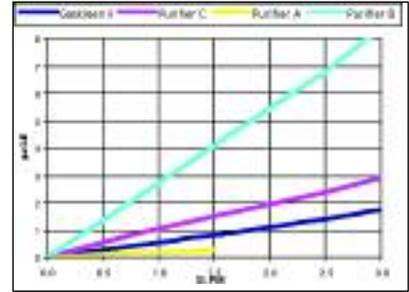


Fig 2: Pressure drop comparison at 15psig inlet pressure and 70°F

Flow Pressure Drop Curves." The results associated with this testing are outlined in Figure 2.

All the purifiers were tested up to their maximum flow rating, as shown in Table 1. As seen in Figure 2, pressure drop could vary significantly between purifiers. For example, at a flow rate of 2.5 SLPM, the pressure drop between the Gaskleen II purifier and Purifier B differs by as much as 5.3 psid. Such variations are generally caused by differences in the filtration technologies employed.

2.3 Particle Removal Efficiency Test

The particle removal efficiency test was performed last after the purifiers were fully spent under a controlled exposure in an argon stream with a 100ppm oxygen concentration. All testing was performed according to SEMI Standard F38-0699, "Test Method for Efficiency Qualification of Point-of-Use Gas Filters." The upstream particles were generated using a TSI Six Jet Atomizer and a 0.04% NaCl solution to generate the challenge aerosol with an upstream level of 2.8E9 particles/ft³ in a filtered nitrogen stream. The test flow rates and results are outlined in Table 2.

The test was run for 90 minutes at steady nitrogen flow; baseline particles were measured prior to the test to ensure that no particles came from the purifiers. All baseline counts indicated < 1 particle/ft³.

Purifier	Flow Rate SLPM	Upstream Particles >3nm/ft ³	Downstream Particles >3nm/ft ³	Reduction
Gaskleen II	3	2.83E9	< 1	> 2.83E9
Purifier A	1	2.83E9	71	3.98E7
Purifier B	5	2.83E9	< 1	> 2.83E9
Purifier C	5	2.83E9	1	2.83E9

Table 2: Particle removal efficiency test results

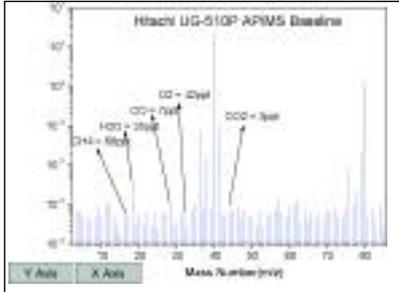


Figure 3: APIMS background measurement

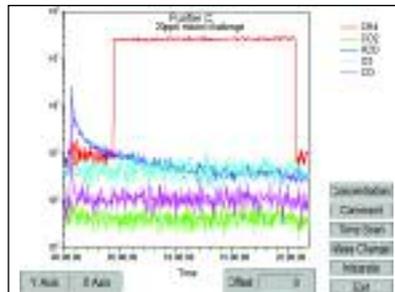


Figure 6: APIMS spectra for Purifier C

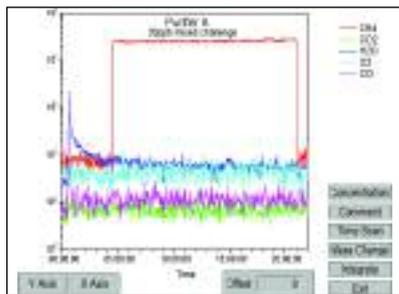


Figure 4: APIMS spectra for Purifier A

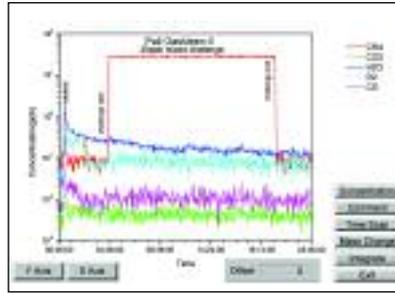


Figure 7: APIMS spectra for Gaskleen II Purifier

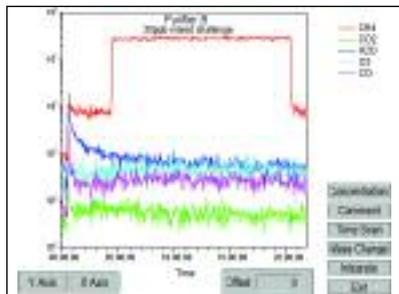


Figure 5: APIMS spectra for Purifier B

Inlet pressure during the entirety of the testing was 30psi.

2.4 Molecular Impurity Removal Efficiency Test

The molecular impurity removal efficiency test was performed with the aid of a Hitachi UG510P, an

ultra low-level detection Atmospheric Pressure Ionization Mass Spectrometer (APIMS). A typical background measurement on this APIMS system is shown in Figure 3. As displayed, lower detection limits of 25ppt and 42ppt for moisture and oxygen respectively are routinely achievable.

The purpose of this test was to quantify the performance of the purifiers with respect to molecular impurity removal from an inert gas stream. An intentional and controlled mixed impurity challenge was prepared for the purpose of this testing. This consisted of a calibrated cylinder with 1ppm each of CH₄, CO₂, CO, and O₂ in argon that was diluted 50-fold with purified zero argon gas to yield a concentration of

20ppb for each of the impurities. Moisture was present in this calibrated cylinder, measuring 1ppm according to the APIMS. During the challenge period, this impurity mixture in argon was introduced through the samples in order to characterize the impurity removal efficiencies of the various purifiers. Figures 4 through 7 show APIMS concentration spectra associated with this testing. It should be noted that the CO curves in all the spectra are in fact CO/N₂, due to the APIMS's inability to distinguish between CO and N₂.

Each graph shows four steps; for the first 20 minutes, the APIMS background concentration was monitored to establish the purity of the zero argon gas. Then, the sample purifier was installed and purged using zero argon gas while the effluent cleanliness was monitored for four hours according to SEMI Standard F30-0298, "Start-up and Verification of Purifier Performance Testing for Trace Gas Impurities and Particles at an Installation Site." After this, the challenge mixture was introduced and maintained for 16 hours and the effluent was monitored. For the remainder of the time, the mixed challenge was removed and the zero argon gas through the sample purifier was monitored. The flow rate was maintained at 1 SLPM throughout the testing.

2.5 Stepped Oxygen Challenge Test

The purpose of this test was to evaluate the behavior of the purifiers when various elevated levels of oxygen impurity were directed through the purifier. All testing was performed per SEMI Standard F68-1101, "Test Method for Determining Purifier Efficiency." The test was conducted at oxygen concentrations of 1ppm, 5ppm, and 10ppm in argon prepared by dilution of a calibrated cylinder consisting of 500ppm O₂ in argon. Trace amounts

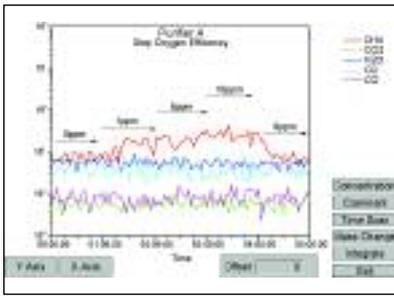


Fig 8: Stepped oxygen challenge results for Purifier A

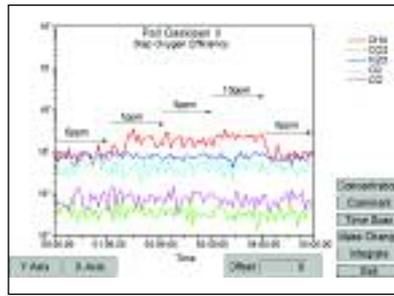


Fig 11: Stepped oxygen challenge results for Gaskleen II

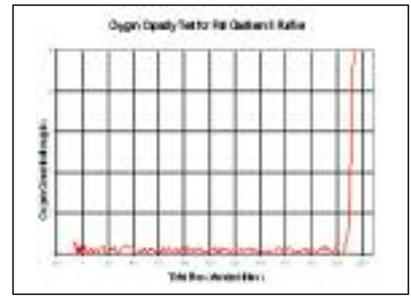


Fig 12: Oxygen capacity curve for Gaskleen II

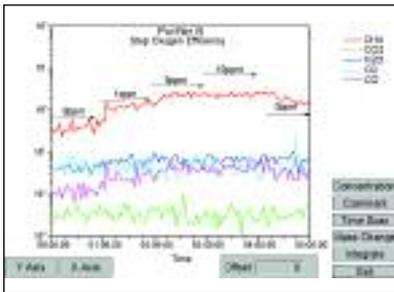


Fig 9: Stepped oxygen challenge results for Purifier B

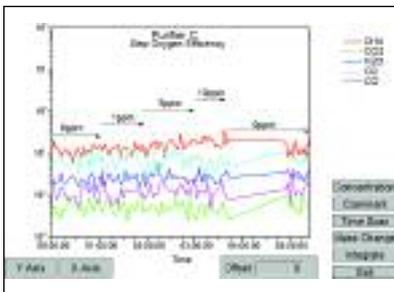


Fig 10: Stepped oxygen challenge results for Purifier C

of CH₄ and H₂O were found to be present in the cylinder source. The CH₄, CO₂, CO, O₂, and H₂O levels in the effluent were monitored using the APIMS. Results from this test are outlined in Figures 8 through 11. Once again, it should be noted that the CO curves in all the spectra represent CO/N₂, due to the inability of the APIMS to distinguish between CO and N₂.

After a one-hour period of zero argon gas purge, increasing oxygen concentrations were introduced for one hour each. This was followed by another zero argon gas purge for one

hour. The flow rate was maintained at 1 SLPM throughout the testing.

2.6 Oxygen removal capacity test

The purpose of this test was to determine the capacity or life of the purifiers when challenged with oxygen. While various factors (such as flow rate and impurity concentration) can affect the capacity of a purifier, a fixed set of conditions were used for this test. The test was performed using a measured oxygen concentration of approximately 100ppm in helium at a flow rate of 1 SLPM. The analytical instrument used for the analysis was a UTI Instruments closed-source High Pressure Quadrupole Mass Spectrometer (HP-QMS). The O₂ detection limit of this instrument is 0.2ppb. A typical oxygen capacity curve (Gaskleen II capacity curve shown here) is displayed in Figure 12. Similar capacity curves were obtained for the other purifier samples. On each sample, an UHP diaphragm valve was installed upstream of the purifier to allow for a contaminate-free transfer between the APIMS and the HP-QMS (i.e., samples were pressurized with a zero argon gas purge prior to removal). All testing was performed per SEMI Standard F67-1101, "Test Method for Determining Inert Gas Purifier Capacity."

Oxygen removal capacity is defined as the total volume (in standard liters) of oxygen impurity (in helium) flowed through the purifier

until the concentration of oxygen in the effluent reached the 10ppb level. The oxygen capacity test results for the various purifiers are outlined in Table 3. Table 3 also outlines the oxygen capacity estimates calculated and derived from the various purifier product claims.

For Purifier A, the calculation of the claimed capacity was performed using conditions of 100ppm O₂ challenge and a flow rate of 1.0 SLPM. For Purifier B, these conditions were 10ppm O₂ challenge and a flow rate of 1.0 SLPM; the information available for this purifier indicated that the capacity would not change with increases in challenge concentration. For Purifier C, conditions used were 2ppm of challenge and a flow rate of 1.0 SLPM; no information was available for this purifier with regard to the impact of challenging at 100ppm versus 2ppm.

With the exception of the Gaskleen II purifier, the claimed oxygen capacities varied significantly from the observed oxygen capacities for the various purifiers tested.

2.7 Orientation sensitivity test

The undesirable characteristic of variation in oxygen removal capacity of a purifier as a function of purifier orientation was studied. This was accomplished by recording the oxygen capacity of the various purifiers when installed in the vertical position versus when installed in the horizontal position (all other test conditions were the same—pres-

Purifier Sample	O ₂ Capacity (Std. L O ₂)	Claimed O ₂ Capacity (Std. L O ₂)	Measured to Claim Ratio
Gaskleen II	0.2147	0.2167	99.1 %
Purifier A	0.6237	0.8639	72.2 %
Purifier B	0.2803	0.4800	58.4 %
Purifier C	0.3237	0.6832	47.4 %

Table 3: Oxygen removal capacity test results

sure, flow rate, and O₂ challenge concentration). A second group of sample purifiers was obtained for this testing. As displayed in Table 4, few of the purifiers exhibited sensitivity to orientation, indicating discrepancies in purification material bed packing characteristics.

With the exception of the Gaskleen II purifier and the purifier B, the oxygen removal capacities varied markedly with orientation of the purifier.

Discussion

The initial particle cleanliness test results indicate that Purifier B discharges a significant amount of particles $\geq 3\text{nm}$ in size upon installation. Such particle emissions could have

Purifier Sample	O ₂ Capacity (Std. L)
Gaskleen II	Sample 1 - Vertical orientation: 0.2147 Sample 2 - Horizontal orientation: 0.2110 Capacity Reduction: 1.7%
Purifier A	Sample 1 - Vertical orientation: 0.6237 Sample 2 - Horizontal orientation: 0.1410 Capacity Reduction: 77.3%
Purifier B	Sample 1 - Vertical orientation: 0.2803 Sample 2 - Horizontal orientation: 0.2730 Capacity Reduction: 2.6%
Purifier C	Sample 1 - Vertical orientation: 0.3237 Sample 2 - Horizontal orientation: 0.1090 Capacity Reduction: 66.3%

Table 4: O₂ capacity dependence on purifier orientation

negative effects on the process if they continue to occur for prolonged times. The other purifiers performed well within their respective product claims.

Pressure drop in POU purifiers is primarily a result of the filter(s) used in the assembly. The pressure drop characteristics of a purifier have significant implications for low-vapor pressure gases. Low-vapor pressure gases are more prone to adiabatic expansion cooling due to the Joule-Thompson effect in purifiers with higher pressure drops. This effect can lead to condensation of the parent gas within the filter, which in turn can create further pressure drop problems. The pressure drop of a purifier also determines the flow characteristics of a gas, an increasingly important factor for low-vapor pressure gases. Such effects could potentially contribute to process variation. Hence, a lower pressure drop across a purifier is desirable. As seen in Figure 2, Purifier B has a significantly higher pressure drop than all the other purifiers tested. Expectedly, this disparity increases with higher flow rates. The Gaskleen II, Purifier A, and Purifier C exhibit low pressure drops with minimal differences in pressure drop among them.

The particle removal efficiency test revealed that with the exception of Purifier A, all the other inert gas purifiers exhibited $\geq 2.83\text{E}9$ particle reduction, which converts to a Log Reduction Value (LRV) of 9.45. A particle reduction of $1\text{E}9$ or a LRV of 9 is considered the industry standard.

The molecular impurity removal efficiency test revealed the inability of any of the purifiers to remove methane. In addition, the undesirable generation of methane by Purifier B was observed when monitoring the effluent of this puri-

fier. This is evident when closely observing Figure 5. The methane concentration increases by an order of magnitude from approximately 0.09ppb to 1ppb upon introduction of Purifier B to the zero argon gas stream. With the exception of methane, all impurities challenged were removed down to a 0.1ppb level or lower with the purifiers tested. All purifiers also displayed good moisture dry-down characteristics.

The stepped oxygen challenge test showed that with the exception of Purifier B, all other purifiers displayed steady and constant removal of oxygen impurity despite higher oxygen impurity challenge concentrations. Such a characteristic is desirable as it indicates that the purifier impurity removal efficiency performance is independent of the impurity load. This was evaluated only for oxygen impurity. In addition, CO, CO₂, and water levels also stayed constant with an increasing oxygen impurity challenge concentration. Methane displayed a slightly different behavior than the other impurities. For all purifiers except Purifier B, the methane level increased slightly with each increase in the O₂ challenge; this was attributed to the trace amount of CH₄ present in the high O₂ cylinder. Although Purifier B also exhibited a relationship between the O₂ challenge concentration and CH₄ levels, it was at a significantly higher CH₄ concentration, suggesting that the reaction that causes O₂ to be removed also leads to the generation of CH₄ for this purification material. This is not desirable as methane could have detrimental effects to some processes even if generated at trace levels.

The oxygen removal capacity of the purifiers was determined by testing and comparing the oxygen removal capacity claims of the respective purifiers. Such comparisons revealed significant disparities between actual capacities, as determined by testing, and capacities reported in product claim information. The Gaskleen II exhibited an

oxygen removal capacity within 1% of the product claims. All other purifiers exhibited a difference of 28% to 53% between the determined and claimed oxygen removal capacity. While the Gaskleen II had the lowest total capacity for O₂, it was the only purifier to show complete agreement with the capacity claim. Furthermore, the Gaskleen II Purifier was the smallest purifier of the samples tested—others were either longer or had a larger diameter. Increasing either of these dimensions creates more available volume for purification material, but does not necessarily lead to easy replacement of existing filters within fixed space requirements.

Sensitivity of the purifiers to orientation was also tested as part of this study. Specifically, the oxygen removal capacity of the purifiers was analyzed as a function of purifier orientation. The oxygen removal capacity of Purifiers A and C depended significantly on the purifier orientation during testing. This would also be indicative of orientation dependence during service. Sample 2 of Purifier A, which was installed and tested in the horizontal orientation, displayed an oxygen removal capacity 23% of that of Purifier A's sample 1, which was tested in the vertical orientation. Sample 2 of Purifier C (installed and tested in the horizontal orientation) exhibited an oxygen removal capacity 34% of that of sample 1 of Purifier C, which was tested in the vertical orientation. With the Gaskleen II and Purifier B, oxygen removal capacity did not show significant dependence on purifier orientation. Dependence on orientation is a problem since it is widely assumed that POU purifiers can be installed in any orientation without affecting the performance. Orientation sensitivity leads to reduced capacity due to early breakthrough and safety concerns when the purifier is removed from service, since active material may still be present.

4. Conclusion

It is evident that there are a significant number of performance differences among POU gas purifier manufacturers and technologies. There are also numerous other performance characteristics, such as flow rate and temperature effects, by-product generation, and oxygenated and corrosive gas aspects that need to be investigated. Such testing was out of the scope of the current study but will be conducted in the future.

In addition, there has been a trend towards replacement of nickel gaskets with stainless steel gaskets for the face seal fitting. This trend has intensified ever since nickel carbonyl contamination generated by nickel and carbon monoxide was reported. But many purification technologies depend on nickel or nickel oxide based purification media. This requires special attention by the semiconductor industry in light of the trend towards elimination of nickel-based materials from the gas piping. The performance parameters evaluated and the test methodology used in this extensive study serves as a basis for understanding the capabilities of various POU purifiers available in the market today. Among other performance specifications, a POU gas purifier also has to function effectively as a POU gas filter. Meeting each and all aspects of performance is no easy task for a single POU purifier. Careful consideration and judicious selection of the overall POU purifier performance is needed for its successful application.

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6. References

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