

Analytical Methodology for Evaluating Purifiers Containing a Novel Purification Medium for Hydrogen Chloride Gas

BISWANATH ROY, PH.D., RYAN RIETH, PH.D., AND ROB NINE

An extensive qualification process using proper test equipment and methodology demonstrates actual product benefits.

Abstract

Moisture removal from hydrogen chloride (HCl) gas is often accomplished with adsorptive purification technology. When selecting an appropriate process gas purifier, consideration must be given not only to moisture removal capability, but to attributes such as metal and particle contribution. Evaluation of these attributes requires a comprehensive approach. This article will present and discuss a set of analytical methods used to evaluate purifiers containing a novel purification medium for HCl gas.

Introduction

Hydrogen chloride gas is used in semiconductor device fabrication for etching and process chamber cleaning, both of which are very sensitive to contamination. Ultrapure HCl gas is critical in these types of applications, and can be ensured if the appropriate purification medium is used. An example of a specific process where the use of ultrapure HCl is necessary is pre-epitaxial deposition etching. In this process, the prevention of oxide formation is needed to achieve better wafer surface morphology and improved film quality. A suitable purification medium will remove moisture to trace levels, providing consistent, ultrapure gas, and minimizing process variability.

Pall Corporation recently introduced the AresKleen™ HCLP purification material, which can remove moisture contamination from HCl gas to <15 parts per billion (ppb)

without contributing volatile metals or particles to the process stream. This novel material consists of a proprietary metal halide supported on an inorganic substrate. A packed bed of the material is encapsulated within a 316L stainless steel housing to form the Gaskleen® gas purifier assembly. This flow-through corrosive gas purifier assembly also incorporates a ≥3 nanometer (nm) stain-

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less steel particle filter, thereby providing purification and filtration within a single assembly.

Determining performance of a purifier in HCl gas is a complex task requiring various analytical tools to measure different performance attributes. These tools include a cavity ring-down spectrometer (CRDS) for determining moisture removal in HCl service, an atmospheric pressure ionization mass spectrometer (APIMS) for establishing baseline moisture removal efficiency in inert gas, an inductively coupled plasma mass spectrometer (ICP-MS) for evaluating metal contribution, and a condensation nucleus counter (CNC) for measuring particle contribution.

Moisture Removal

A key performance characteristic used in the selection of a gas purifier is removal of molecular impurities. AresKleen HCLP purification material has been shown to remove moisture to <15 ppb in HCl gas service using a Tiger Optics LaserTrace* CRDS. The purification material has demonstrated <1 ppb moisture removal in inert gas service using a Hitachi dual chamber APIMS (model UG-510P). Each instrument was chosen based on its ability to achieve different detection limits for moisture in specific process gases.

Cavity Ring-Down Spectroscopy (CRDS)

Cavity ring-down spectroscopy is an extremely sensitive spectroscopic technique that is used to detect very low levels of chemical contamination in process gases. The technique involves measuring the absolute optical attenuation of a beam of

light by targeted impurity molecules that absorb light of predetermined energy. Specifically, the instrument measures the time it takes for the light intensity to fade or *ring-down* [1]. The ring-down time is generally fast and on the order of microseconds [2]. The CRDS, also known as cavity ring-down laser absorption spectroscopy (CRLAS), is used widely in industry to analyze gases, particularly corrosive gases. It can be used to determine impurity concentration down to the single-digit ppb level in HCl gas [3].

During the operation of the instrument, a beam of light originating from a continuous wave diode laser is directed by a highly reflective mirror and travels into an absorption cell, or *cavity* (see Figure 1). Two highly reflective mirrors face each other from opposite ends of the cavity. The laser light enters through the first mirror and a photodiode, which is located after the second mirror, outside the cavity, measures the energy of light leaking out of the cavity. Once this

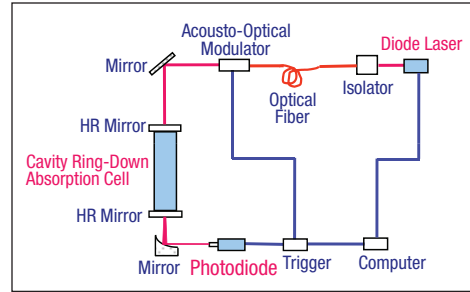


Figure 1. Internal components of a Tiger Optics LaserTrace CRDS**

energy attains a predetermined level, the light source is shut off. In the cavity, the light reflects repeatedly between the mirrors, essentially creating a total optical path of many kilometers [2]. The photodiode detects the change in the intensity of the light, which rings down in an exponential fashion as it travels between mirrors. Once ring-down of the light is complete, the time constant of the exponential decay, called *ring-down time*, is used to calculate the impurity concentration in the gas flowing through the cavity.

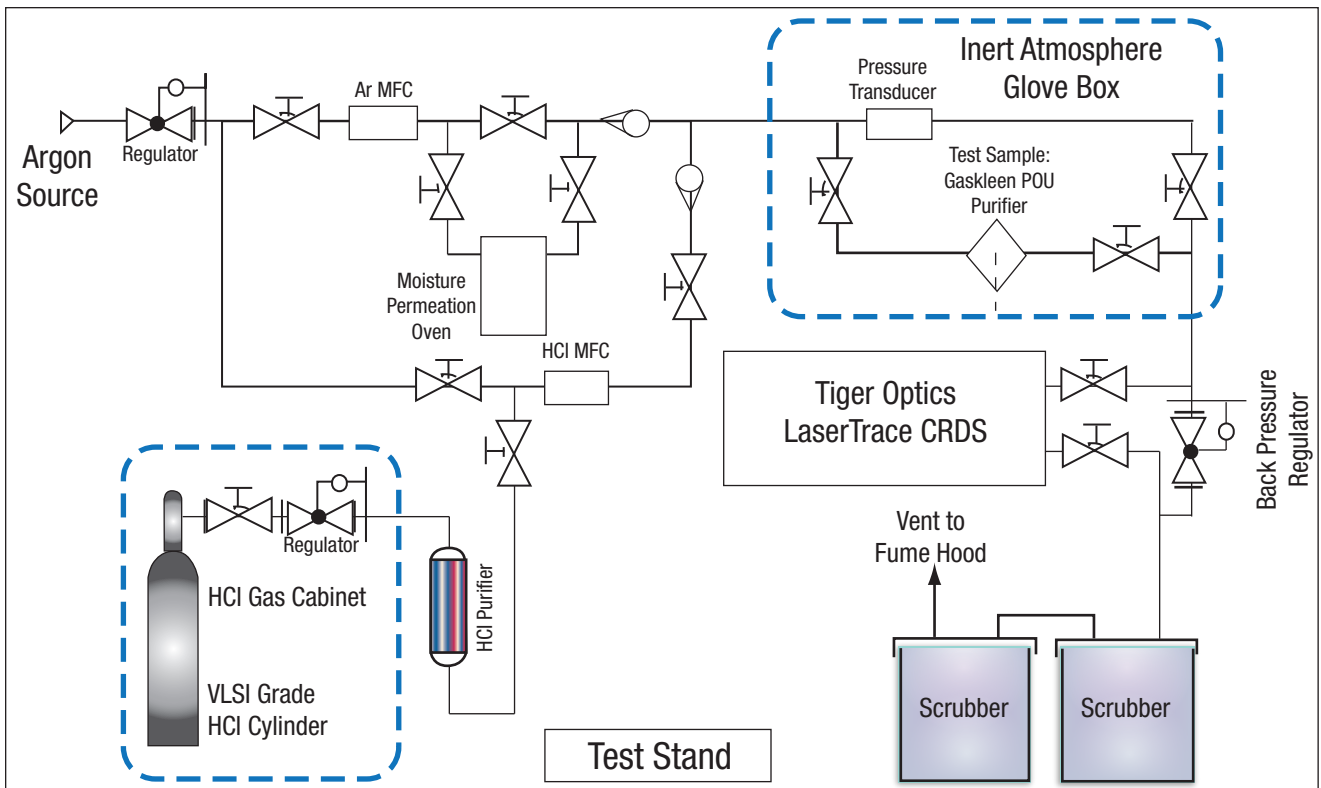


Figure 2. General connectivity of components for analysis of the moisture removal capability of Gaskleen purifiers

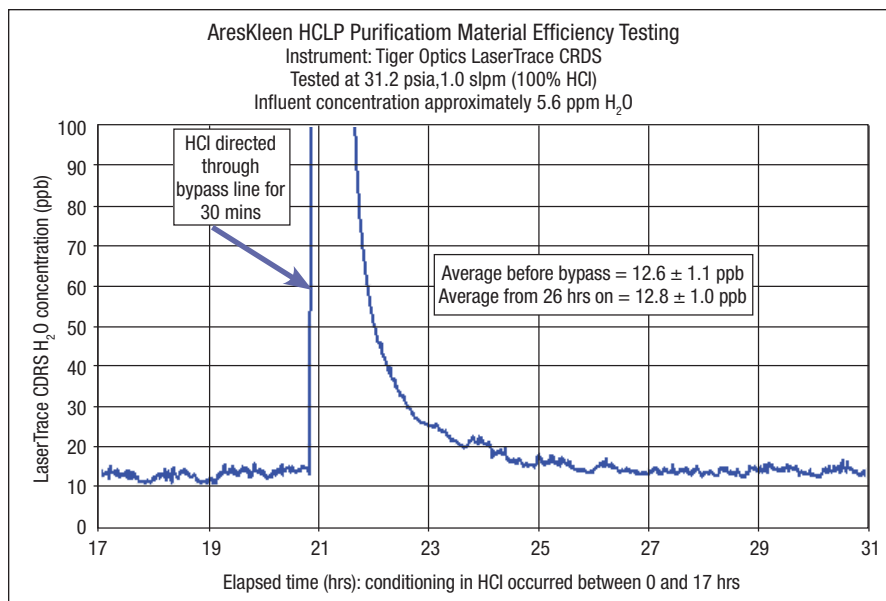


Figure 3. Typical moisture removal levels achieved using Gaskleen purifiers in HCl gas service (as monitored by CRDS)

To evaluate the effectiveness of AresKleen HCLP material in removing moisture from HCl gas streams, a Tiger Optics LaserTrace CRDS was employed to monitor the quality of the effluent gas downstream of Pall's Gaskleen purifiers, which contain this material. Purifiers designed for different flow ratings were challenged with 99.997% HCl gas (<1 parts per million [ppm] of moisture), [4] and the downstream gas was analyzed for moisture concentration. The data demonstrated that a moisture level of <15 ppb in HCl gas can be attained under laboratory conditions.

For the experiment, [5] the Gaskleen purifier was installed [6] in a stainless steel gas delivery manifold in an inert atmosphere. The manifold was equipped with ultrahigh purity components (such as mass flow controllers [MFCs], pressure regulators, and diaphragm valves) to minimize potential impurity contributions from the system to the gas stream (see Figure 2). During installation of the purifier, purified argon gas from a liquid source was directed to it at a flow rate of ~1 slpm (standard liter per minute). After passing through the purifier, the gas traveled through the CRDS before being vented through a series of aqueous scrubbers.

Once in line, argon flow was continued through the purifier to establish an initial level of cleanliness for the system. After a

consistently low moisture level (~5 ppb) was indicated by the CRDS, the gas flow was switched to 100% HCl at a flow rate of 1 slpm. After initial conditioning of the purifier was complete, a new baseline level of moisture was reached, representing the extent to which the moisture was being removed from the HCl gas stream. To determine the quality of HCl gas upstream of the purifier, the sample was bypassed for approximately 30 minutes while the moisture level from the process gas continued to be tracked by the CRDS. As shown in Figure 3, after >22 hours (h), returning the purifier to the gas flow path reestablished the previously observed low levels of moisture, demonstrating the effectiveness of the purifier even when it was challenged with high-concentration influent.

Atmospheric Pressure Ionization Mass Spectrometry (APIMS)

Atmospheric pressure ionization mass spectrometry is an ultrasensitive, state-of-the-art technology that is used to measure extremely low (parts per trillion [ppt]) levels of trace contaminants within a gas stream. It has been applied to inert gases (e.g., argon, helium, and nitrogen), as well as hydrogen, silane, and oxygen.

The Hitachi APIMS Model UG-510P has been used to study moisture removal

performance of the AresKleen material in inert gases. By measuring the moisture concentration in the gas, APIMS can be used to estimate the ability of the material to remove moisture to trace levels. CRDS can be used to measure moisture concentration in HCl gas, but APIMS has an LDL (lower detection limit) that is lower than that of CRDS (~20 ppt vs. single-digit ppb), which allows for collection of more sensitive removal capability data.

In the dual chamber APIMS, the carrier gas is first ionized in the primary ionization chamber by a corona discharge under atmospheric pressure. Using focusing lenses (i.e., charged plates), ionized gas molecules are directed through an aperture into a drift chamber. The sample gas is introduced into the drift chamber, via a second gas port, where collisions between carrier gas ions and test gas molecules occur. These collisions result in a charge transfer from the molecules with a higher ionization potential to those with a lower ionization potential. Argon and nitrogen, which are primarily used as carrier gases, have significantly higher ionization potentials than oxygen, moisture, carbon dioxide, and the other impurities present in the test gas. The drift chamber is maintained near atmospheric pressure, which creates a shorter mean free path for the gas molecules compared to that created under vacuum conditions. A shorter mean free path raises the probability of collisions between the ions and the gas molecules. As a consequence, virtually complete ionization of the impurity molecules in the drift chamber is achieved.

The ionized sample molecules are then focused with lenses and slits to the quadrupole mass filter as the pressure is reduced from atmospheric to 10^{-6} torr. The quadrupole mass analyzer consists primarily of four parallel stainless steel rods, to which a combination of RF and DC voltages are applied. The combination of these voltages allows ions of a specific mass/charge ratio to be transmitted by the analyzer. The positive ions that exit the mass analyzer reach the detector and bombard its surface, eventually producing measurable electrical signals. These signals are measured as current signals for each mass number and are converted by the instrument into concentration data [7].

In the experiment, [5] a purifier sample containing AresKleen HCLP material was installed, following the same basic procedure used for CRDS analysis. After installation, argon flow to the purifier at ~1 slpm was sustained for roughly 16h, ensuring that an initial baseline moisture concentration level of <1 ppb was established. Using a moisture permeation source and argon carrier gas, a relatively high moisture challenge was generated and then introduced to the purifier. Even after approximately 125h of exposure to argon gas, with >50 ppm moisture flowing at ~0.9 slpm, the sample continued to supply effluent gas containing <1 ppb of moisture, a value that is indicative of optimal purifier performance (see Figure 4).

Loading / Lifetime Calculation

In addition to excellent contaminant removal performance, an ideal purifier should provide high contaminant loading. High loading results in long service life, which has the benefit of reducing the frequency of changeouts and costly downtime.

One way to ensure long service life is to use a purification material with superior bed-packing characteristics. Such a material provides uniform flow distribution throughout the entire bed of material. This results in a shorter reaction zone, promoting maximum utilization of the material. Inferior or improperly packed beds may form a flow channel, causing the gas to bypass the majority of the reaction sites, greatly reducing service life.

Compact beds generally demonstrate steady downstream contaminant levels with a sharp breakthrough curve, which is a consequence of the short reaction zone. A short reaction zone is not only an outcome of a well-packed bed, but of a high proclivity for adsorption of the contaminant as well. A sharp breakthrough curve, as shown in Figure 5, indicates that both conditions are satisfied and confirms that the purification material is efficiently utilized. Curves such as this, which are generated using data corresponding to testing based on varied process conditions, allow for accurate estimations of service life.

Metal Contribution

Metal contamination in HCl gas can lead to shorts in semiconductor devices and can react

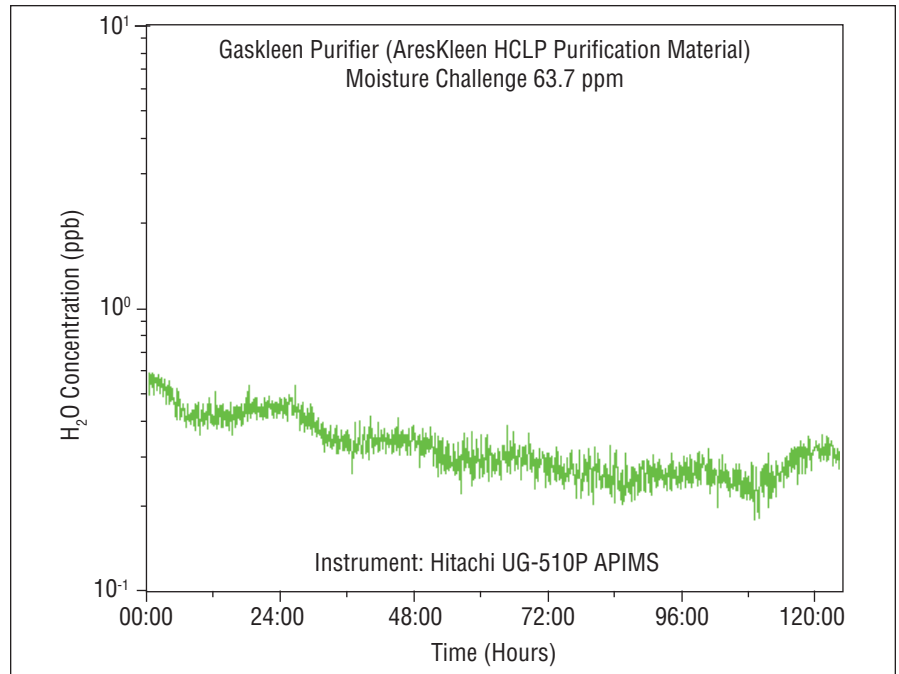


Figure 4. APIMS data demonstrating the moisture removal capability of Gaskleen purifiers in inert gas service

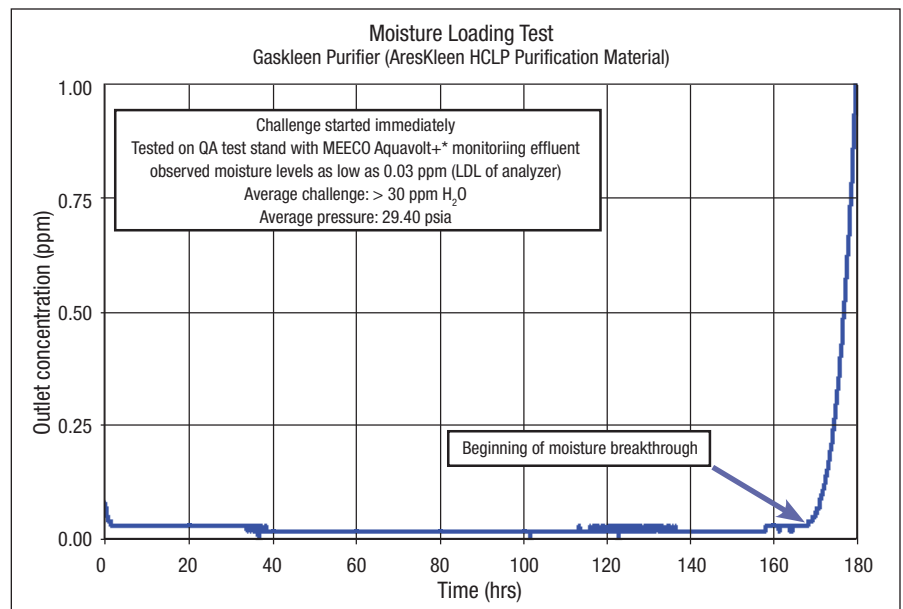


Figure 5. Typical moisture loading breakthrough curve (from data obtained during performance testing of a Gaskleen purifier)

with moisture to form metal oxide defects on the wafer surface. Consequently, it is important to ensure that purifiers will not contribute metal contaminants to the process stream. The Agilent ICP-MS (model 7500cs) was used to confirm that Gaskleen purifiers do not add volatile metal impurities to the gas stream at trace levels (i.e., at the LDL for the instrumentation and methodology used).

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Inductively coupled plasma mass spectrometry is a category of mass spectrometry that can detect a wide range of metals and several nonmetals in concentrations of sub-ppb levels [8]. The technique consists of combining an inductively coupled plasma (ICP)

to produce ions with a mass spectrometer (MS) to separate and detect ions.

A liquid test sample is introduced by a peristaltic pump to a nebulizer, where an aerosol of analyte molecules in the sample matrix is formed. The plasma is produced by introducing argon (Ar) gas through a series of concentric quartz tubes that are wrapped with a radio frequency (RF) coil at the downstream end. The RF energy needed to produce plasma is supplied using a torch located in the center of the coil. As the incoming Ar comes into contact with the torch, the stream is partially ionized (Ar^+), and the plasma is generated as highly energized Ar molecules collide. As the sample aerosol enters the argon plasma, which has a temperature of 6,000 – 10,000 K, it instantaneously decomposes and creates analyte atoms that are concurrently ionized. The ions produced from the sample aerosol are extracted from the plasma into the mass spectrometer, which is maintained at a high vacuum level ($\sim 10^{-6}$ torr). Using a series of positively charged lenses, the ions are directed to a quadrupole mass analyzer, where—as in APIMS—ions are analyzed based on their mass/charge ratio.

Testing was performed to determine whether volatile metal contaminants are contributed to the process gas stream upon flow through a Gaskleen purifier, which contains AresKleen HCLP material. As in the CRDS procedure, inert gas was initially directed through a purifier at ~ 1 slpm until baseline moisture levels were achieved. HCl gas flow was then directed to the purifier at a flow rate of 0.5 slpm. After a short conditioning of the purifier, 100 L of HCl gas was passed through the purifier and bubbled into 0.5 L of deionized (DI) water, where it was hydrolyzed (dissolved), thereby creating an acidic solution of approximately 24% w/w HCl. After hydrolysis of the effluent gas, analysis for trace metals in HCl gas was conducted using an Agilent 7500cs ICP-MS.

Samples were analyzed by the ICP-MS to accurately determine the concentration of metallic contaminants trapped in the acidic solution, and results were compared with matrix-matched standards. Solution samples for analysis were diluted using DI water to prevent harm to the detectors in the ICP-MS. The resulting data were corrected to account for the dilution factors used.

| Metal | Without Purifier (ppb) | With Purifier (ppb) | LDL (ppb) |
|-------|------------------------|---------------------|-----------|
| Be | < LDL | < LDL | 2 |
| B | < LDL | < LDL | 3 |
| Na | < LDL | < LDL | 2 |
| Mg | < LDL | < LDL | 2 |
| Al | < LDL | < LDL | 4 |
| K† | 5 | 5 | 2 |
| Ca | < LDL | < LDL | 4 |
| Ti | < LDL | < LDL | 2 |
| V† | 4 | < LDL | 4 |
| Cr | < LDL | < LDL | 1 |
| Mn | < LDL | < LDL | 2 |
| Fe† | 7 | < LDL | 2 |
| Co | < LDL | < LDL | 1 |
| Ni | < LDL | < LDL | 1 |
| Cu | < LDL | < LDL | 2 |
| Zn | < LDL | < LDL | 8 |
| Mo | < LDL | < LDL | 2 |
| Ag | < LDL | < LDL | 9 |
| Cd | < LDL | < LDL | 2 |
| Ba | < LDL | < LDL | 3 |
| Tl | < LDL | < LDL | 2 |
| Pb | < LDL | < LDL | 9 |

Table 1. ICP-MS data indicating no detectable metal contribution at trace levels to purified HCl gas. (LDL = lower detection limit; † = metal levels within experimental error [with and without the purifier])

Sample solutions from both purified and unpurified HCl gas streams were collected and analyzed. By comparing results from each group, it was possible to determine if there had been any metal contribution from the purifier after exposure to HCl gas. For this analysis, typical method detection limits of < 10 ppb (weight of metal in weight of HCl) were used. The data demonstrated that no detectable trace-level metal content was contributed to the gas stream by the purifier (see Table 1).

Particle Contribution

All components within the HCl distribution system, including the particle filter, are

potential sources of particle contribution. Since Gaskleen purifier assemblies come packaged with integral particle filters, it was important to demonstrate that these filters do not contribute particles to the gas stream. To accomplish this, a particle counter was used to monitor the number of particles ≥ 3 nm present in the effluent gas stream in the absence of any external challenge.

Condensation Nucleus Counter (CNC)

The condensation nucleus counter acts very much like an optical counter that is capable of detecting particles as small as 3 nm in diameter with high efficiency [9]. Particles entering the CNC as components of an incoming gas stream first encounter a chamber saturated with n-butyl alcohol vapor. Flow through this chamber, known as a saturation block, results in the addition of volatile alcohol to the stream. As the alcohol-laden gas proceeds to a chilled vertical condenser, the alcohol nucleates onto particles having a diameter of ≥ 3 nm. The resulting droplets are then directed to an optical detector that individually records the arrival of each particle. This event is characterized by the scattering of cross-flowing pulses of light that originate from a laser diode. The scattered light travels through a collecting lens that gathers and focuses it onto a photodetector. At the photodetector, the light is converted into a measurable electrical signal [10].

Testing was conducted on a Gaskleen purifier assembly using a CNC (TSI Model 3025). Analysis of a background filter was performed first to determine the particle level in the system. Initially, the filter was installed in a clean dry air line having several control components upstream of the filter, namely a bulk particle filter, a pressure regulator, and an MFC. Appropriately sized isokinetic samplers were used to ensure proper gas sampling, and the flow was adjusted to the recommended rate for the purifier. The filter was then exposed to four consecutive cycles of steady flow (5 or 10 minutes per cycle), followed by a 10-minute cycle of pulsed flow. The same procedure used for analysis of the background filter was repeated for the purifier assembly. As expected, the results showed that the Gaskleen purifier contributed < 1 particle/ft³ of air (above background level) at rated flow.

Summary

Many considerations must be taken into account when selecting an appropriate purifier for HCl gas. The product should remove moisture to low ppb levels, should not contribute volatile metals or particles to the process stream, and should have a long service life. A purifier with an integral filter provides the additional benefits of particle removal and fewer components in the distribution system.

Product performance testing should be conducted using the actual process gas, whenever practical. Because of its aggressive nature, testing in HCl gas may yield different results from testing in an inert gas. Proper analytical equipment and test methodology are critical to verify that the product claims are met.

Pall Corporation's Gaskleen purifiers containing AresKleen HCLP material have gone through an extensive qualification process. Moisture testing with a CRDS has demonstrated removal of moisture to <15 ppb in HCl gas; APIMS testing has established trace-level moisture removal to <1 ppb in inert gas; ICP-MS results have confirmed that the material contributes no trace-level metals; and results from CNC testing have shown that there is no particle contribution above background levels. Using a well-engineered HCl purifier can ensure that a consistent and superior grade of gas is being delivered to process tools. The resulting benefits are minimized process variability and limited defects, improved wafer surface morphology, and enhanced film quality. In addition, the correct purifier can reduce the likelihood of downstream distribution system corrosion, which can lead to process contamination and necessitate premature replacement of components.



*LaserTrace is a trademark of Tiger Optics, LLC; Aquavolt is a trademark of MEECO, Inc.

**Figure used with permission from Tiger Optics, LLC.

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BISWANATH ROY HOLDS A PH.D. IN MATERIALS SCIENCE AND ENGINEERING AND HAS BEEN INVOLVED WITH THE SEMICONDUCTOR INDUSTRY FOR 10 YEARS. AS STAFF SCIENTIST IN PALL CORPORATION'S GLOBAL SCIENTIFIC AND LABORATORY SERVICES GROUP, HE IS INVOLVED WITH THE PURIFICATION AND FILTRATION OF GASES FOR MICROELECTRONICS APPLICATIONS AND WITH DEVELOPING CUSTOMER SOLUTIONS. DR. ROY HAS AUTHORED AND CO-AUTHORED NUMEROUS PRESENTATIONS AND HAS PUBLISHED IN ESTEEMED JOURNALS. HE HOLDS A PATENT AND HAS RECEIVED AWARDS FOR HIS WORK. DR. ROY IS ACTIVELY INVOLVED WITH THE ITRS YIELD ENHANCEMENT WORKING GROUP ON GASES AND SERVES ON THE SEMI FILTERS AND PURIFIERS TASK FORCE AND PHOTOVOLTAIC GASES AND CHEMICALS PURITY TASK FORCE. HE CAN BE CONTACTED AT BISWANATH_ROY@PALL.COM.

RYAN RIETH IS A RESEARCH/MATERIALS SCIENTIST AT PALL CORPORATION IN CORTLAND, NY. HE CONTRIBUTES TO THE DEVELOPMENT, EVALUATION, AND SPECIFICATION OF NOVEL PURIFICATION MATERIALS DESIGNED FOR MICROELECTRONICS APPLICATIONS. BEFORE JOINING PALL, DR. RIETH ATTENDED THE UNIVERSITY OF ROCHESTER, WHERE HE RECEIVED HIS PH.D. IN INORGANIC CHEMISTRY (2007) FOR STUDIES RELATED TO TRANSITION METAL-PROMOTED STRONG BOND ACTIVATION. HE CAN BE REACHED AT RYAN_RIETH@PALL.COM.

ROB NINE IS SENIOR MARKETING MANAGER IN PALL CORPORATION'S MICROELECTRONICS GROUP AND HAS 17 YEARS EXPERIENCE IN THE GAS FILTRATION AND PURIFICATION MARKET. MR. NINE HOLDS A B.S. DEGREE IN ELECTRICAL ENGINEERING FROM CLARKSON UNIVERSITY. HE CAN BE REACHED AT (516) 801-9104 OR ROB_NINE@PALL.COM.