Application Note #9

PPM-Level Gas Analysis: The Closed Ion Source (CIS) Advantage

Introduction

Quadrupole Mass Spectrometers are used in a large variety of analytical applications, from basic research to on-line process monitoring and control. Ease of use, a compact design, excellent dynamic range and very stable operation are some of the main features that make the instruments so popular.

The most common use of quadrupole mass spectrometers in vacuum applications is as residual gas analyzers (RGA). Most commercially available RGA's are very small and can be attached to virtually any vacuum chamber. The prototypical RGA has an **open ion source (OIS)** and the entire analyzer operates at the pressure of the vacuum system. The maximum operating pressure is 10^{-4} Torr.

More recently, quadrupole mass spectrometers have been increasingly used as process monitors. By far, their most common application is for the detection of low-level contaminants in process gases. Modern day contamination requirements often fall in the PPM and sub-PPM levels, and will continue to decrease as processes become more sophisticated and the components being manufactured require additional refinement.

Although traditional quadrupole mass spectrometers designed for residual gas analysis have adequate dynamic range to detect PPM-level contaminants in principle, interferences from process gases, and background interferences from the sensor itself can make the detection of PPM levels of certain contaminants difficult in practice. The partial pressure detection limit of a mass spectrometer depends both upon the sensitivity of the sensor and upon the background signals that are present in its mass spectra. In applications requiring the measurement of pressures between 10^{-4} and 10^{-2} Torr, the problem of background contributions to the spectra can be significantly reduced by replacing the RGA with a **closed ion source (CIS)** sampling system.

The following sections of this document describe the performance specifications of open and closed ion source quadrupole mass spectrometers. The main objective of this information is to introduce the basic concepts required to choose the best gas analyzer for any practical application, and to discuss some of the basic operating principles that must be kept in mind to assure the optimum performance of the instrument selected.

Residual Gas Analyzers (P<10^{-4} Torr)

The prototypical RGA has an open ion source (OIS) and is attached directly to the vacuum chamber so that the entire analyzer is at the same pressure as the rest of the vacuum system. The maximum operating pressure is 10^{-4} Torr.

In **high vacuum applications** such as research chambers, surface science setups, accelerators, aerospace chambers, scanning microscopes, outgassing chambers, etc., RGA's are effectively used to monitor the quality of the vacuum and can easily detect even the most minute impurities in the low pressure gas environment. Trace impurities can be measured down to 10^{-14} Torr levels, and sub-PPM detectability is possible in the absence of background interferences. During system troubleshooting, RGA's are also used as sensitive, in-situ, helium leak detectors.

In the **semiconductor industry**, RGA's are best used in evaporators, sputterers, etchers or any other high vacuum systems that are routinely pumped down to better than 10^{-6} Torr. The main use is to check the integrity of the vacuum system and the quality of the vacuum before the wafers are committed to the process. Air leaks, virtual leaks and many other contaminants at very low levels can ruin wafers and must be detected before the process is started. As the semiconductor processes become more sophisticated, they also become less tolerant to contaminants. Residual gas analysis in a process chamber helps eliminate uncontrollable variables and thus increase up-time and production yield and reduce cost of ownership.

RGA's are not limited to the analysis of gases at pressures below 10^{-4} Torr. Higher gas pressures can be sampled with the help of a differentially pumped **pressure reducing gas inlet system (PRGIS),** consisting of a restriction and a vacuum pump package. Common restrictions are pinholes and capillaries, which can provide pressure reductions of more than 6 decades of pressure. Vacuum pump packages typically consist of a turbomolecular pump backed by a foreline pump.

The Open Ion Source (OIS) (P < 10^{-4} Torr)

The standard ion source used in most commercially available RGA's is the **open ion source (OIS)**. This source is considered the *"do it all"* source for RGA's. It has been around, in its cylindrical, axially symmetrical version since the early 1950's. A schematic of the OIS design used in the SRS RGA Probe is shown in the following figure.
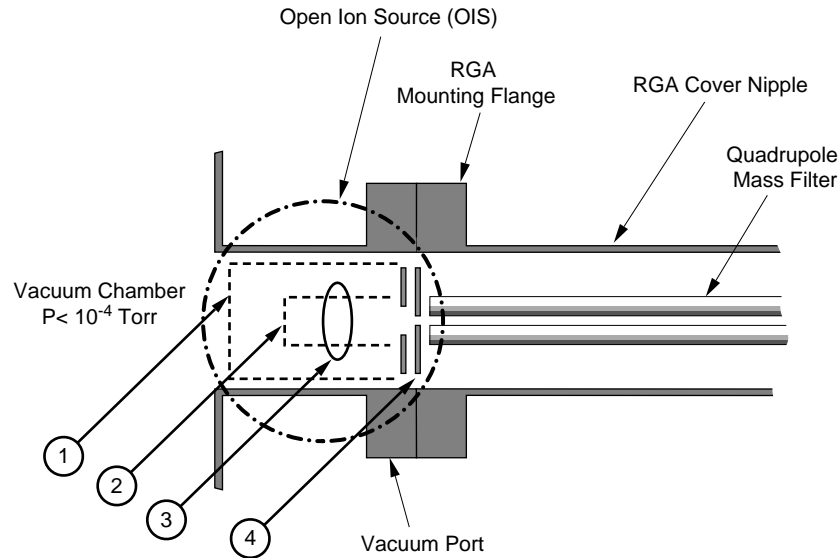
Open Ion Source (OIS)

RGA
Mounting Flange

RGA Cover Nipple

Quadrupole
Mass Filter

Vacuum Chamber
P< 10^{-4} Torr

1
2
3
4

Vacuum Port

Figure 1 SRS Open Ion Source (OIS) schematic.

1. Repeller, 2. Anode Grid, 3. Filament, 4. Focus plate

The OIS penetrates into the process chamber. The filament wire and the anode wire cage are "open" to the surrounding vacuum chamber. All molecules that are moving around in the vacuum chamber can easily move through the ion source. The pressure in the ionizer is the same as in the rest of the surrounding vacuum and also the same as in the quadrupole mass analyzer and ion detector. The OIS is "*open*" to all the gaseous molecules in the vacuum chamber and can be used to monitor and detect changing gas levels as long as the overall pressure remains under 10^{-4} Torr. Higher pressures result in a decrease in sensitivity due to space charge repulsion between ions.

Performance limitations of the OIS

Overall, most commercially available OIS RGA's do a very good job at measuring residual gas levels without affecting the gas composition of their vacuum environment. However, some potential limitations must be kept in mind, particularly when the sensor is used routinely to monitor minute trace impurities (i.e. PPM and sub-PPM levels) or UHV environments (10^{-9} Torr or less).

The following is a list of the different ways in which an OIS RGA can contribute to its background signals, decreasing the detection capabilities of the sensor:

Outgassing

The OIS is a **hot-cathode** ion source. The filament wire (i.e. the cathode) must be heated to high temperatures (i.e.>1300° C) in order to establish an electron emission current. In the high vacuum, most of the energy required to heat the filament is dissipated to the surroundings through radiative processes. As a result, the entire ionizer and the adjacent walls "*run hot*". The elevated temperatures

result in increased **outgassing** from the OIS itself, and from the adjacent chamber walls. In the most benign cases outgassing simply modifies the composition of the gas mixture being measured. However, under some circumstances outgassing can be a serious problem and even ruin experiments and samples.

The gases emitted by the outgassing process obscure **the minimum detectable partial pressures (MDPP 's)** of many important gases including: H_2, H_2O, N_2, CO and CO_2. **Degassing** the ionizer can help minimize some of the background signals; however, this is usually only a temporary solution (During a degas the ion source is ramped up to a temperature significantly above its normal operating value, and bombarded with high energy electrons, in order to accelerate the outgassing process.)

Some RGA manufacturers offer UHV versions of their OIS with anodes (and sometimes entire ionizer assemblies) made out of **platinum clad molybdenum** wire. This highly inert material exhibits decreased adsorption for many gases and provides reduced outgassing and ESD.

Water outgassing is a frequent interference, and especially important because it is a serious source of contamination in many high vacuum processes. Overnight **bakeouts** at >200°C are the best option to minimize water outgassing from an OIS RGA.

H_2 outgassing from the OIS electrodes is only a concern for users operating in the UHV regime. H_2 is dissolved in most varieties of SS300 and readily outgasses from the hot OIS electrodes contributing to the background signals for the gas.

Electron Stimulated Desorption (ESD)

Even after an RGA has been thoroughly baked out, peaks are frequently observed at 12, 16, 19 and 35 amu, which are formed by ESD from surfaces within the OIS rather than by electron-impact ionization of gaseous species. ESD affects the RGA performance in a way similar to regular outgassing.

Several steps can be taken to minimize the effect:

- Degassing with high electron energies.
- Gold plating the ionizer decreases the adsorption of many gases and hence reduces the ESD effect. Using platinum clad molybdenum ionizers is another alternative.
- Reducing the extent of the electron beam.
- Reducing the surface area of the OIS (For example, use wire mesh instead of solid perforated metal.)
- Avoid contaminating the ionizer.

Background interferences

The quadrupole mass filter assembly has a large surface area in comparison to the ionizer and even though it does not get as hot as the ionizer during operation it still outgasses. The fact that the OIS is exposed to the same vacuum environment as the rest of the sensor makes the ionizer sensitive to the impurities outgassed by the rest of the quadrupole assembly. A serious problem for a lot of RGA users (particularly in the UHV range) is H_2O outgassing from unbaked RGA's.

However, lots of other species are also present that can affect the background readings. For example, high Ar backgrounds can be expected if the sensor was recently exposed to large levels of the gas because it tends to get adsorbed on all surfaces and desorbs slowly.

The ionizer is also sensitive to impurities generated at the hot filament. Gas molecules can suffer thermal cracking and chemical reactions at the filament surface and the products of the reaction can easily find their way into the ionization region. The impurities generated in this fashion are usually an important source of contamination of the ionizer's surfaces and have a serious effect on the RGA's long term stability. For example, CO and CO_2 are emitted by most hot filaments (Carbon impurities in the filament wire react with Oxygen) and easily find their way into the ionizer and vacuum system.

Partial Pressure Reduction (PPR) systems (10^{-4} Torr < P < 10Torr)

RGA's are not limited to the analysis of gases at pressures below 10^{-4} Torr. Higher gas pressures can be sampled with the help of a differentially-pumped **pressure reducing gas inlet system (PRGIS),** consisting of a restriction and a **vacuum pump package**. Common restrictions are pinholes and capillaries, which can provide pressure reductions of more than 6 decades of pressure. Vacuum pump packages typically consist of a turbomolecular pump backed by a foreline pump. The combined RGA, gas inlet system and pumping station constitute what is usually referred to as a **Partial Pressure Reduction (PPR) System**. These systems are commonplace in gas phase processes and are available from most RGA manufacturers.

The PPR system, manufactured by Stanford Research Systems, and depicted in figure 2, is a perfect example of the typical pressure reduction setup used to step process pressures down to levels acceptable to the OIS RGA. The PRGIS actually contains two inlet paths to the RGA: a **high conductivity path** for monitoring base vacuum and a **low conductivity** (i.e. pressure reducing) path for monitoring gases at operating pressure.
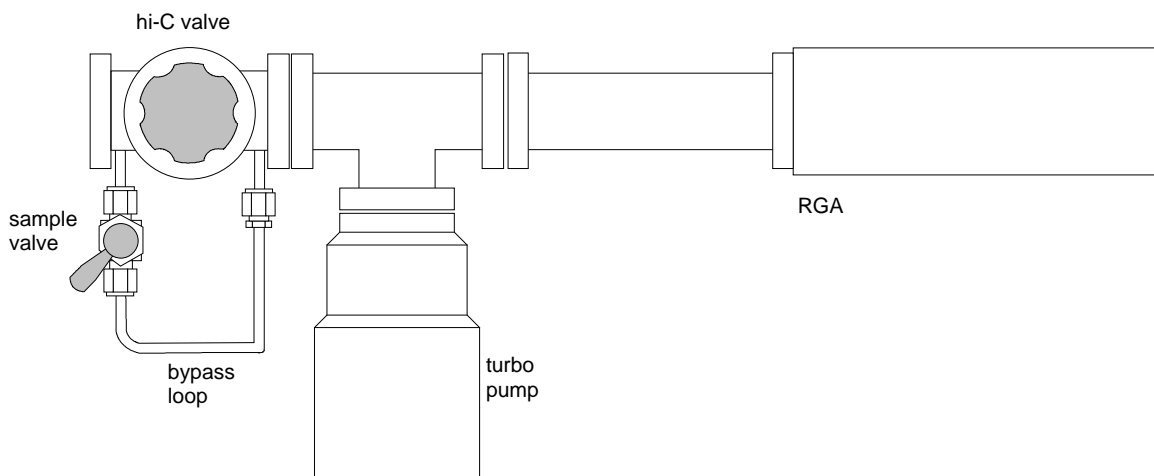

Figure 2 SRS PPR Inlet system components.

The **high conductivity (Hi-C)** path is used when the vacuum system is at pressures below 10^{-4} Torr. At high vacuum, typical applications are leak testing and monitoring the ultimate vacuum of the chamber. For example, in a sputtering chamber, the first stage of the process is always a pump-down to $<10^{-6}$ Torr. At this point the RGA may be used to check the quality of the background for leaks and contaminants. Once the quality of the vacuum is satisfactory the sputtering chamber is backfilled with argon at a few mTorr and sputtering is started.

The **low conductivity (Lo-C)** path is used when the process chamber is at pressures above 10^{-4} Torr. This path contains a micro-hole orifice which reduces the pressure several decades to a level suitable for the RGA (typically around 10^{-5} Torr). Apertures are available for operating pressures as large as 10 Torr. For example, during a sputtering process the RGA may be used to monitor water vapor and hydrocarbon levels to assure they do not exceed certain critical levels that degrade the quality of the sputtered films.

A pair of pumps draws the gas through the aperture to the RGA and establish the pressure drop. The pumps are compact, completely oil-free and require minimal maintenance.

For pressures higher than 10 Torr the gas flow rates into the sample inlet side become extremely small and the time response is too slow for any practical measurements. In those cases, a **bypass pumped sampling system**, with a much larger gass flow rate and faster response, is a much better choice than a single-stage PRGIS. A commercially available example of a bypass pumped system is the QMS Gas Analyzer manufactured by Stanford Research Systems.

MDPP limitations of a PPR system with an OIS RGA

An OIS RGA connected to a pressure reducing gas inlet system does an excellent job sampling gases at pressures $>10^{-4}$ Torr. However, even though most of the commercially available RGA's have adequate sensitivity and dynamic range to detect PPM level contaminants in principle, interferences from process gases and background interferences from the sensor itself can make the detection of PPM levels of impurities difficult in practice.

The two basic sources of interference that are observed in PPR systems are:

Background interference

> The background gases present in the analyzer chamber can obscure the MDPP's of many important gases (particularly: H_2, H_2O, N_2, CO, and CO_2). Background gases are due to outgassing, electron stimulated desorption, and the finite compression ratio of the pumping system.

> In order to best illustrate the limitation in MDPP levels, lets consider, as an example, the analysis of water in a 10^{-2} Torr Ar sputtering process. During process monitoring, the mass spectrometer typically runs at about 10^{-5} Torr,

corresponding to a three decade reduction factor across the low conductance path of the PRGIS. The pressure drop, brings a 1 PPM of water in the process chamber to a partial pressure in the mass spectrometer of about 10^{-11} Torr (well within the detection limit of a typical RGA). However, with the mass spectrometer isolated form the process gases, the residual pressure in the PPR chamber is, at best, in the order of 10^{-9} Torr with most of that being water. This water level is one hundred times larger than the 10^{-11} Torr corresponding to 1 PPM of water in the process chamber, meaning that the water vapor concentration cannot be reliably measured to better than 100 PPM under these "*very common*" operating conditions. The MDPP limit could be improved to 20 PPM increasing the operating pressure in the RGA chamber to $5 \cdot 10^{-5}$ Torr during analysis. However, even a 20 PPM MDPP limit for water is not low enough in many cases.

The same limitations must be kept in mind for all other potential interfering gases. In order for any species to be detectable at the PPM level (i.e. 10^{-8} Torr in a 10mTorr process) the residual mass spectrum for the PPR must show pressure readings of less than 10^{-11} Torr at the mass values corresponding to the peaks of that species. Such levels are not easily achieved repeatedly in any vacuum system unless very special precautions are taken to eliminate all sources of contamination. The problem is particularly serious for masses under 50 amu where there is always a variety of background peaks in the residual mass spectrum. Even though the RGA is intrinsically capable of performing sub-PPM measurements, it is usually not easy to find places in the residual mass spectrum of the RGA where the background is readily in the PPM levels.

The MDPP limit for air is usually limited by the compression ratio of the pumping station. In the SRS PPR the N_2 levels usually go down to $<10^{-9}$ Torr, with oxygen levels approximately 5 times lower. This corresponds to MDPP levels of better than 20 PPM for 28 amu and 4 PPM for 32 amu. However, the MDPP levels at 28 amu are also affected by the CO contribution from the OIS filament.

Other sources of background interference are contamination from pump oil backstreaming into the RGA chamber in systems that use conventional, oil-based, roughing pumps.

Hydrogen is usually impossible to detect at PPM levels because it outgasses readily from the analyzer. A gold coated or platinum clad OIS can help in this case.

Process Gas Interference

The other limitation to PPM detection levels in a typical RGA based PPR system is caused by interference from the same process gases that are being analyzed.

The best way to illustrate this point is to go back to the example of water analysis in the 10 mTorr Ar sputtering process. We saw that detecting water at better than 20 PPM levels is very difficult unless the PPR chamber is very carefully baked out and protected from water contamination. However, as we will see, this is only

part of the problem, there is also a serious interference at m/e 18 from the same Ar used in the sputtering system. The isotope ^{36}Ar is present at 0.34%. In the electron ionization process, doubly charged argon is formed leading to peaks at m/e 20 (^{40}Ar^{++}) and m/e 18 (^{36}Ar^{++}). For 70 eV electron impact energy, a typical level of ^{36}Ar^{++} is 350 PPM. So if you want to detect PPM levels of water in an Ar based sputtering system , you must solve two problems:

1.   Background contribution of water outgassing from the sensor
2.   Interference at m/e 18 from ^{36}Ar^{++}.

A thorough bakeout can reduces the background water contribution to the low tens-of-PPM levels, but eliminating the ^{36}Ar^{++} interference requires the use of several tricks that are used by most RGA users. As usual, some of those tricks work better than others.

Some users simply choose to monitor the m/e 17 peak due to the [OH]$^{+}$ water fragment. For 70 eV ionizing electrons, this peak is four times smaller than the main one at 18 amu. This results in a significant reduction in sensitivity for water detection and also adds the problem of abundance sensitivity while trying to measure the mass 17 intensity next to a large ^{36}Ar^{++} peak at 18 amu.

A better option (and the one recommended for RGA's with programmable ionizer voltages) is to operate the ionizer with the electron impact energy reduced to <40eV. This ionization energy is below the appearance potential (43.5eV) of Ar^{++}. For example, the peaks at masses 18, 19 and 20 due to Ar^{++} disappear while operating an RGA with 35 eV electrons, and this is achieved with minimal reduction in the sensitivity of detection of Ar^{+} at 36, 38 and 40 amu. Reduction of the electron energy usually imposes an extra load of work on the filament and will reduce its lifetime. However, the reduced interference effects offset the extra costs of filament replacement. As we will see later, the more compact design of closed ion sources makes it very natural for them to operate with 35 eV electrons, without sacrificing the filament's lifetime.

The Closed Ion Source (CIS) (10^{-4}Torr < P < 10^{-2}Torr)

In applications requiring the measurement of pressures between 10^{-4} and 10^{-2} Torr, the problem of background and process gas interferences to the mass spectra can be significantly reduced by replacing the traditional OIS PPR configuration described above with a **closed ion source (CIS) sampling system**. A cross section of a generic CIS setup is shown in the following figure.
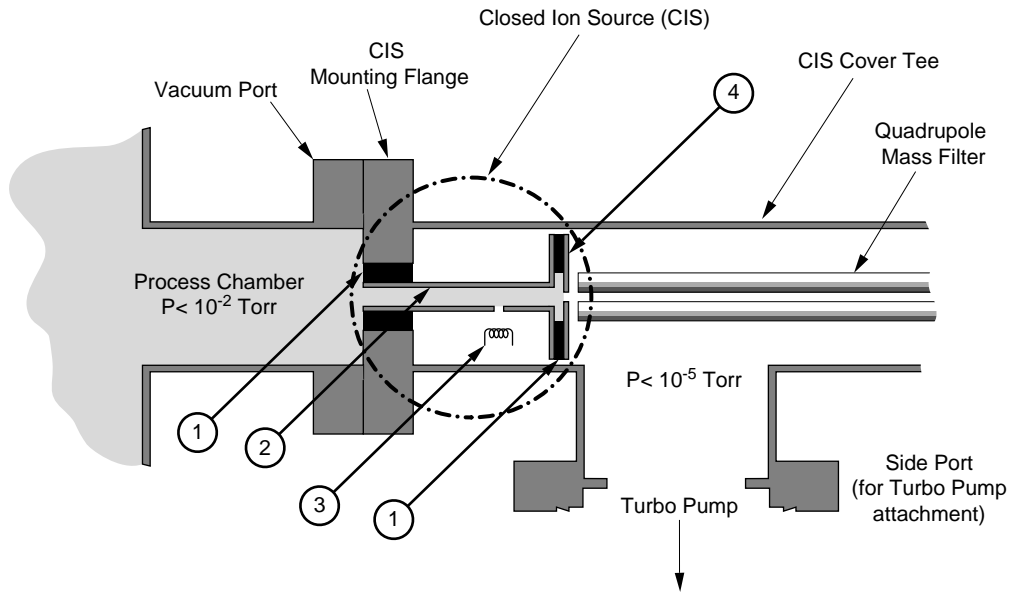
Figure 3 Cross section of a generic closed ion source (CIS)
1. Insulator and seal, 2. Ionization Tube(Anode), 3. Filament, 4. Exit Plate

The CIS Ionizer sits on top of the quadrupole mass filter replacing the more traditional OIS used in conventional RGA's. It consists of a short, gas-tight tube with two very small openings for the entrance of electrons and the exit of ions. Electrons enter the ionizing region through an entrance slit of small dimensions. The ions are formed close to, and attracted by, a single extraction plate and exit the ionizer through a circular aperture of small diameter. Alumina rings seal the tube from the rest of the quadrupole mass assembly and provide electrical insulation for the biased electrodes. Ions are produced by electron impact directly at the process pressure. A pumping system, similar to the one used in PPR systems, keeps the filament and the rest of the quadrupole assembly at pressures below 10^{-5} Torr through differential pumping. The design is very simple and was successfully used for many years in gas chromatography/mass spectrometry instruments before it was applied in general to quadrupole gas analyzers.

Advantages of the CIS

An understanding of the performance differences between the CIS setup and the more traditional RGA based PPR system is indispensable when trying to choose the sensor setup that is best suited for a particular process application. A CIS system usually offers several advantages over the OIS PPR. Process engineers should carefully weigh those differences before choosing an analyzer configuration for their application.

Direct sampling

The CIS Anode can be viewed as a high conductance tube connected directly to the process chamber**.** The pressure in the ionization area is virtually the same as

that in the process chamber. The CIS Ionizer produces ions by electron impact directly at process pressure, while the rest of the mass analyzer and the filament are kept under high vacuum. The electrons emitted by the filament in the high vacuum region enter the high pressure ion formation region through the emission aperture on the side of the anode tube. Once formed, the ions are extracted for mass analysis through the ion extraction orifice centered on the exit plate. Direct sampling provides good sensitivity due to the large ion densities available and also fast response times. The "*memory effects*", typically associated to pressure reduction and conductance orifices, are significantly reduced.

Improved Signal-to-background ratios

Because the sampling pressure in the CIS is typically two decades higher than that of the rest of the sensor's vacuum system, the signal-to-background ratio is significantly increased relative to the OIS PPR systems. *This is particularly important when measuring common residual gases, such as water*. In order to best illustrate this point we go back to the example of a 10^{-2} Torr Ar sputtering process. The sampling orifice in the OIS PPR inlet system reduced the Ar partial pressure from 10^{-2} down to 10^{-5} Torr at the OIS. Water vapor levels were measured in a background of at least 10^{-9} Torr of residual water. This corresponded to a 100 PPM MDPP limit for water. Things are much better in the CIS system. In this case, the Ar gas is ionized directly at 10^{-2} Torr (i.e. three orders of magnitude higher than in the OIS PPR!) but in the same background (10^{-9} Torr) of residual water. This residual level now corresponds to a 100 PPB MDPP level for water in the CIS system. *This is quite an improvement over the OIS PPR performance!*

The combination of direct sampling and differential pumping provides the potential for PPM and sub-PPM detection limits for even the most pervasive residual gases.

For other common interferences, such as organic contaminants or reaction by-products of the filament, the gas tight design of the source reduces the visibility of the ionization region to those gases providing a very clean residual gas spectrum, free of many of the spectral overlaps that are common in OIS PPR setups.

Interference from contaminants generated by ESD is also reduced in the CIS because a much smaller electron beam penetrates the ionizing volume. In addition, the inside walls of most commercially available CIS's are made out of highly inert materials such as gold, platinum clad and pure molybdenum which adsorb less impurities than stainless steel.

Reduced Ionizer Contamination

In an OIS PPR system, sample molecules that have suffered thermal cracking or chemical reaction at the filament, are free to drift into the ionization region. This is a very significant source of surface contaminants for electron impact ionizers. In contrast, the gas tight design of the CIS reduces the visibility of the source to those contaminant gases, providing reduced contamination and better long term

stability. Most CIS manufacturers utilize exclusively Tungsten filaments in their systems. W resists many corrosive gases (such as WF_6) and reactive gases (such as Silane) minimizing reactions at the filament that contribute to the background, also resulting in extended filament lifetime.

Versatility

CIS based systems are extremely versatile. The low detection limit together with the wide dynamic range provided by the quadrupole mass filter fitted with an electron multiplier, makes the CIS a versatile system for: on-line process monitoring and control, verification of process gas purity at the point of use, high vacuum residual gas analysis, and process equipment leak checking.

Different modes of operation can easily be achieved by simply changing some of the sensor's operating parameters. A CIS Gas Analyzer, even though not as sensitive as an RGA, can tackle most residual gas analysis and leak checking tests. The sensitivity of the CIS is reduced over the OIS because of the very small holes for electron entrance and ion exit. However, in most cases this reduction in sensitivity is easily made up by running the electron multiplier at higher gain levels than the RGA. The electron emission current is usually raised while using the sensor for residual gas analysis to increase sensitivity, and reduced during process monitoring to avoid space charge saturation effects in the ionizing volume. The tight design of the CIS also makes it possible to operate the ionizer at lower electron ionization energies than are possible with OIS's. As a result, most of the commercially available CIS systems offer two modes of operation with electron ionization energies of 70 and 35 eV. The 70eV setting is mostly used for leak testing and routine residual gas analysis. The spectra collected are virtually identical to those obtained with standard RGA's. The 35eV setting is used during process monitoring to eliminate process gas interference peaks. A good example is the elimination of the doubly ionized $^{36}Ar^{++}$ peak that interferes with water detection at 18 amu in sputtering processes. Different electron ionization energies are often used to selectively ionize species in a gas mixture.

High Pressure Sampling with a CIS Analyzer (10^{-2}Torr < P < 10Torr)

CIS Analyzers can usually sample gases *directly* up to about 10^{-2} Torr pressure levels. The upper pressure limit is set by the reduction in mean free path for ion-neutral collisions, which takes place at higher pressures, and results in significant scattering of ions and reduced sensitivity. *However, operation is not limited to the analysis of gases at pressures below 10^{-2} Torr.* Higher gas pressures can be sampled with the help of a differentially pumped **pressure reducing gas inlet system (PRGIS)** just as it is done with conventional RGA's. A pressure reducing gas inlet system matched to the conductance of the CIS analyzer will allow the sensor to sample gas pressures as large as 10 Torr. As in the case of the PPR systems, the penalty paid is reduced sampling speed at the sample inlet and possible memory effects at the ionizer. However, these problems can

be usually eliminated by the addition of bypass pumping in the ionizing region as the process pressures start to get large.

Conclusions

Strict modern-day contamination control requirements for gas phase processes are constantly pushing the limits of performance of quadrupole gas analyzers. The technology is rapidly evolving and adapting to lower contamination level specifications. A good understanding of the different factors affecting the detection limits of the different gas analysis systems currently available, is an essential tool while selecting a sensor for a specific application. As it is usually the case, most choices involve compromises, and a good understanding of the basic tradeoffs will minimize mistakes and maximize productivity. A well-matched gas analyzer rapidly becomes an integral part of the processing system, and its information eliminates most of the guesswork that is part of all troubleshooting procedures.

The main purpose of this application note was to introduce the basic concepts required to choose the best gas analyzer for any practical application, and also to present some of the basic operating principles that must be kept in mind to assure the optimum performance of the instrument selected.

All gas phase processing setups can benefit from the addition of a quadrupole gas analyzer. Miniaturization, smart software interface, and improved detection limits are some of the features to look for in future instruments. As sensors become more affordable, they will rapidly become commonplace in all industries requiring the strict control of contamination levels in process gasses.