

TECHNICAL NOTE

The Use of Quadrupole Mass Spectrometry to Detect Sub-PPM Level Contaminants in Gas-Phase Samples and Processes

Quadrupole mass spectrometers are commonly used in vacuum industries for residual gas analysis (RGA). In its traditional role as an RGA, the mass spectrometer is used to test the quality of vacuum in process chambers and to leak check vacuum chambers. Recent trends show mass spectrometers being used as process monitors, as well as residual gas analyzers. For instance, in sputtering processes mass spectrometers are used as *in-situ* monitors for the purity of process gasses and for contaminants from the targets and wafers. Many process gas suppliers are also using mass spectrometers to certify the purity of their products and to ensure that delivery systems are not adding contaminants to the process.

As the processes become more sophisticated, they also become less tolerant of contaminants. Thus there is now a need in many processes to ensure that contaminants (e.g., water and oxygen in semiconductor sputtering processes) do not exceed low ppm levels. Although traditional mass spectrometers designed for residual gas analysis have adequate sensitivity to detect ppm-level contaminants in principle, interferences from process gasses, and background interferences from the sensor itself can make detection of ppm levels difficult in practice.

MEASURING PPM-LEVELS WITH AN OPEN SOURCE CONFIGURATION

Figure 1 shows a mass spectrum of Krypton in air obtained with an INFICON mass spectrometer fitted with an open ion source and a Faraday cup detector. The air sampling system

utilizes a two stage pressure reduction inlet connected to a vacuum chamber pumped by a turbo pump/forepump combination. The equilibrium pressure in the chamber is approximately 1×10^{-4} Torr.

The major stable isotope of Krypton (m/e 84) is present in air at a concentration of approximately 650 ppb. The spectrum in Figure 1 shows the presence of Kr, even at these sub-ppm levels. Clearly, this most simple of quadrupole MS sensors has the sensitivity to detect ppb level contaminants.

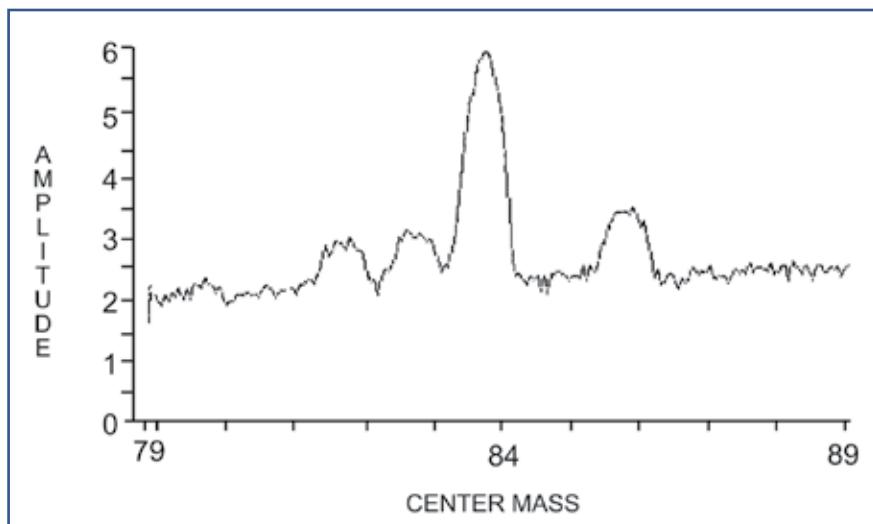


Figure 1: Spectrum of Kr in Air

So why do we need closed ion sources, electron multipliers and elaborate pumping systems? The answer is interferences and backgrounds.

PPM MEASUREMENTS IN Ar SPUTTERING PROCESSES

Unfortunately, there is not a large market for detecting Kr in air. A more meaningful application is the detection of water and oxygen in an Ar sputtering system. It is well known that even sub-ppm levels of water or oxygen contaminants can cause failures in metal interconnects.

A typical sputtering process operates at around 1×10^{-2} Torr Ar pressure. At 1ppm, water would have a partial pressure of 1×10^{-8} Torr. During the process, the mass spectrometer typically runs at about 1×10^{-5} Torr; the pressure reduction of 1000x being accomplished by an orifice between the process and the mass spectrometer pumping system. This pressure drop brings the 1ppm of water in the chamber to a partial pressure in the mass spectrometer of about 1×10^{-11} Torr, well within the detection limit of a typical RGA. However, with the mass spectrometer isolated from the process chamber, the base pressure in the mass spectrometer reaches around 1×10^{-9} Torr with much of the residual gas being water. The result is that the background water pressure in the mass spectrometer is about two orders of magnitude higher than a 1ppm water level sampled from the process chamber.

There is also an interference at m/e 18 (the base-peak for water) from the Ar used in sputtering systems. 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 ($^{40}\text{Ar}^{++}$) and m/e 18 ($^{36}\text{Ar}^{++}$). A typical level of $^{36}\text{Ar}^{++}$ is 340ppm, although this is dependent on the electron energy used in the ionizer.

So if you want to detect ppm levels of water in an Ar sputtering process, you must solve two problems:

- Relative background contribution of water from the mass spectrometer;
- Interference at m/e 18 from $^{36}\text{Ar}^{++}$.

The problem of background contribution is solved by the closed ion source (CIS) configuration (Figure 2). In this system, the ion formation region is kept at a pressure between the process pressure and the mass spectrometer pressure. Thus, the pressure drop from the process chamber to the ionization region is on the order of 10x rather than 1000x. A further pressure drop of 100x between the ion source and the analyzer keeps the analyzer chamber at a suitable operating pressure. A 1ppm level of water in the process chamber is only reduced from 1×10^{-8} Torr to 1×10^{-9} Torr in the ionization region. This level is on the same order of magnitude as the background level of water in the mass spectrometer.

To eliminate interferences from $^{36}\text{Ar}^{++}$, some manufacturers simply choose to monitor the m/e 17 peak due to the $[\text{OH}]^+$ fragment from water. In the INFICON Transpector CPM system, the electron energy of the ionizer is reduced to 40eV. This is well below the appearance potential (43.5eV) of Ar^{++} . Figure 3 shows a comparison of the 70eV (3a) and 40eV (3b) Ar spectra in the region of m/e 20. Unlike Ar^{++} , the ionization of water is nearly as efficient at 40eV as it is at 70eV. If one chooses to monitor m/e 17 at 70eV the sensitivity is decreased by about a factor of four (i.e., the m/e 17 ion is about 27% of the m/e 18 ion).

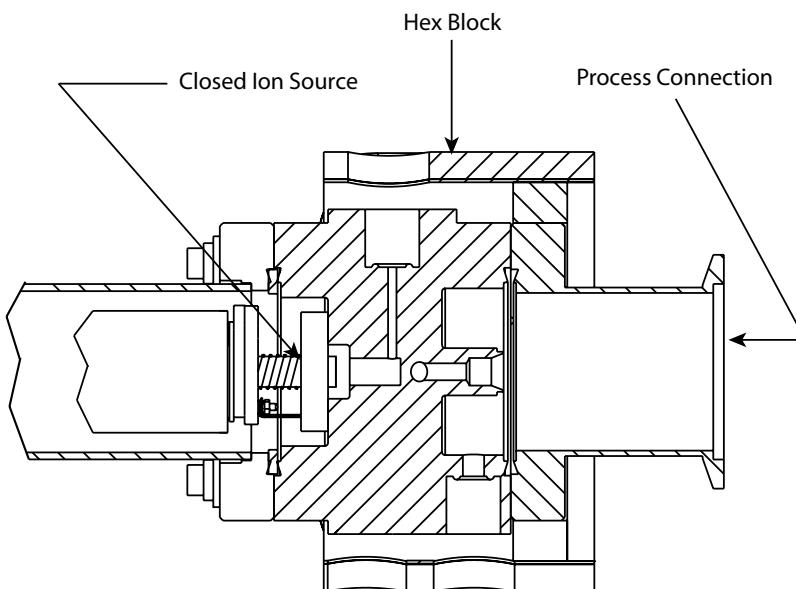
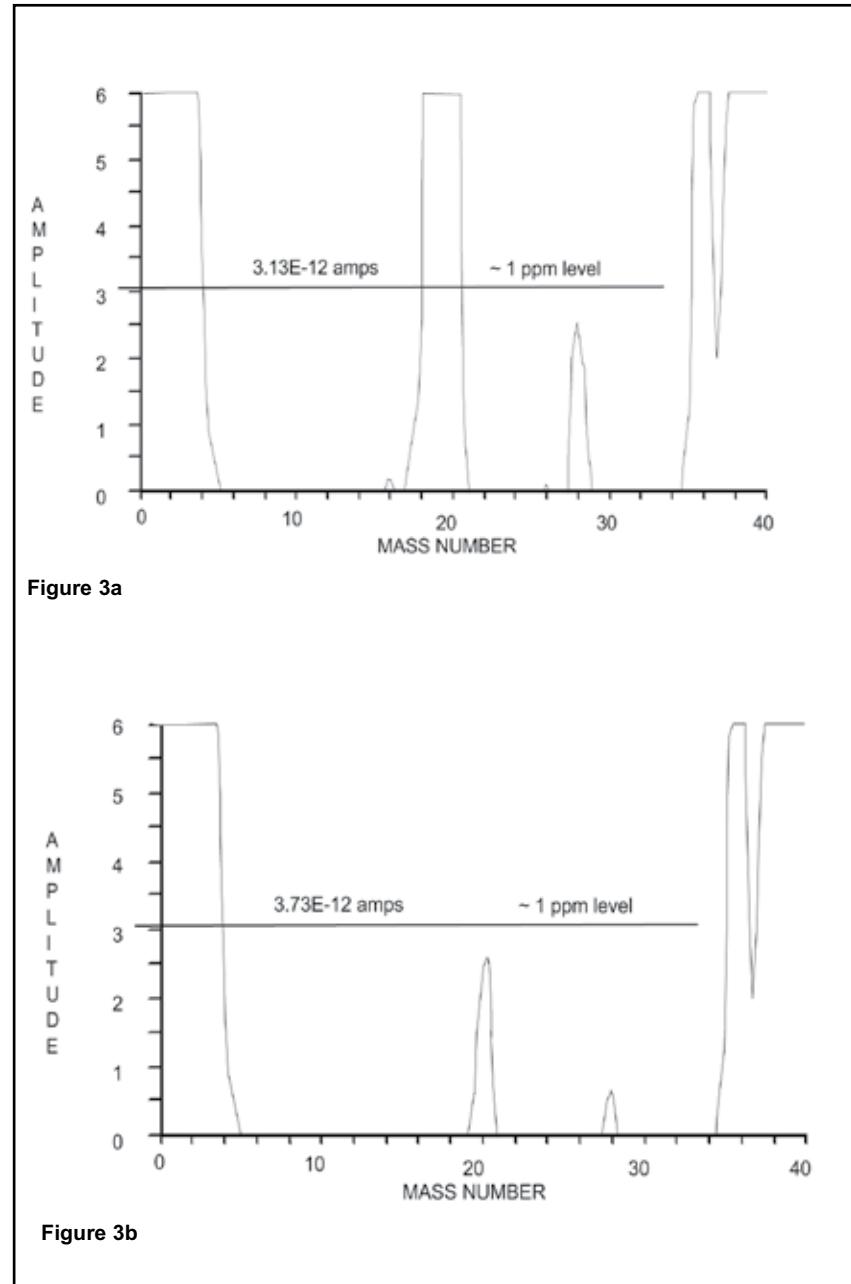


Figure 2: CIS Source Configuration

Furthermore, depending on the abundance sensitivity of the sensor, there can be a significant contribution to the intensity at m/e 17 from the large Ar⁺⁺ produced by 70eV ionization. The combination of a closed ion source and a 40eV ionization energy allows sub-ppm detection of water as well as oxygen and nitrogen, during argon sputtering processes (see figure 4 for an example). It should be pointed out that the mass spectra obtained at 40eV ionization energy can be quite different from standard reference spectra used in routine residual gas analysis. This would normally make the CPM less well-suited to residual gas analysis. However, INFICON has designed the Transpector CPM system to run in two modes of operation; one in which the electron energy is 40eV and one in which it is the normal 70eV. A simple software switch allows the user to choose between residual gas analysis and sputter process monitoring.



(3a) and (3b) - Comparison of 70eV and 40eV Spectra at m/e 20

PPM MEASUREMENT IN HIGH PRESSURE GAS ANALYSIS APPLICATIONS

The problems associated with trace analysis of gasses at atmospheric or higher pressures are similar in principle to those in vacuum systems. However, the practical solutions to the problems can be quite different. The major concerns are again background levels in the mass spectrometer system, and interferences (spectral overlap). If the application is to find trace water levels in Ar supply tanks, then the problems and solutions are the same as above. However, if one is interested in finding trace organic gasses (e.g., benzene, dichloromethane) in air samples, then the background from the mass spectrometer vacuum manifold is not normally an issue. If an atmospheric sampling system (a simple capillary inlet) is connected to the mass spectrometer such that the pressure in the chamber is 1×10^{-4} Torr, a 1 ppm level gas would have a partial pressure of 1×10^{-10} Torr. This pressure is well above the minimum detectable partial pressure for an open ion source sensor with a Faraday cup detector. It is easy to see that with the added sensitivity of an electron multiplier, the detection limits can be pushed to ppb levels with direct sampling inlets.

1	1E+05	3	1E+12	5	1E-12
040 Argon		000		000	
2	1E+00	4	1E+11	6	1E-12
028 Nitrogen		000		000	

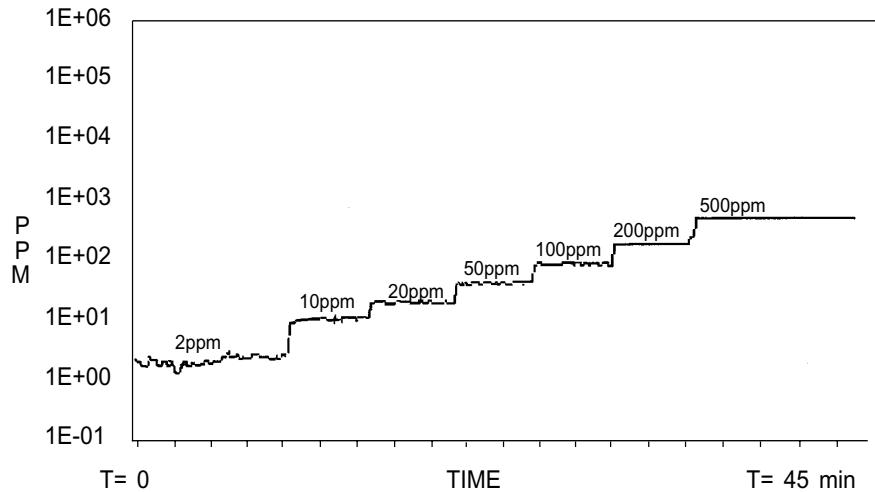


Figure 4: Stepwise trend

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