New Sensor for Measuring Trace Impurities in Ultra Pure Hydrogen

Dr. Peter R. Bossard[*], Dr. Jacques Mettes[*], Luis Breziner[*] and
Prof. Emeritus Fred Gornick[**]

[*]Power & Energy, Ivyland, PA, US. [**] University of Maryland.

1. Abstract

Parts per trillion analysis of ultrapure hydrogen is currently done by Atmospheric Pressure Ionization Mass Spectrometry, APIMS, which requires sophisticated laboratory instrumentation and a specialized operator. In Hydrogen Elimination Mass Spectroscopy, HEMS, the concentration of impurities is enriched using a chemically pumped palladium membrane to remove the vast majority of the matrix hydrogen and analyzing the remainder with an RGA operating in static mode. To illustrate the method, a one part per billion contaminant species in an accumulated 1 standard liter of ultrapure hydrogen sample that ends up in the closed 1 liter RGA chamber represents a partial pressure of 7.6E-7 Torr. Experimental data is presented demonstrating linearity of accumulation, calibration, the chemistry in the RGA chamber and a ppt level sensitivity for impurities. Associated manipulations and data interpretation are simple enough for the creation of an online sensor device highly desirable for gas quality monitoring in semiconductor manufacturing or in hydrogen filling stations for cars in the future. As a first, in-house HEMS application, very low level contamination mechanisms downstream of the dense palladium alloy membrane of hydrogen purifiers (P&E’s commercial products) were identified and remedied.

2. Introduction

Ultra Pure Hydrogen Applications Impurities below parts per billion levels are required for applications of ultra pure hydrogen in semiconductor manufacturing such as LEDs, photo-voltaics, LCD and Power electronics, reference 1. Impurities below parts per million levels are required for energy application such as Hydrogen Vehicles, Fuel Gas Processing and Auxiliary Power generation.

State of the Art The choice of analytical techniques for pure hydrogen at the lowest levels is APIMS, reference 2. Though APIMS can be configured as an online tool, it is basically a laboratory type of instrument, ref. A slipstream of analyte is passed through atmospheric pressure corona discharge leaving a fraction of the carrier gas as ions. These ions will undergo a high number of collisions at this pressure among which are collisions with impurity species with a lower ionization potential than the carrier gas species. Ion-molecule charge transfer causes these impurities to end up ionized with a typically 10^5 times enhancement factor. Other analytical techniques for ppm levels are GC, GC-MS and FTIR.

Meinders in reference 3 shows mass spectrometry on a sample undergoing a sweep gas based palladium membrane hydrogen matrix removal. Operating on continuously flowing gas flows, a 0.3 ppm total contamination detection limit is obtained with 2-3 orders lower levels for single impurities limited by residual contributions (filaments, pump back-diffusion).

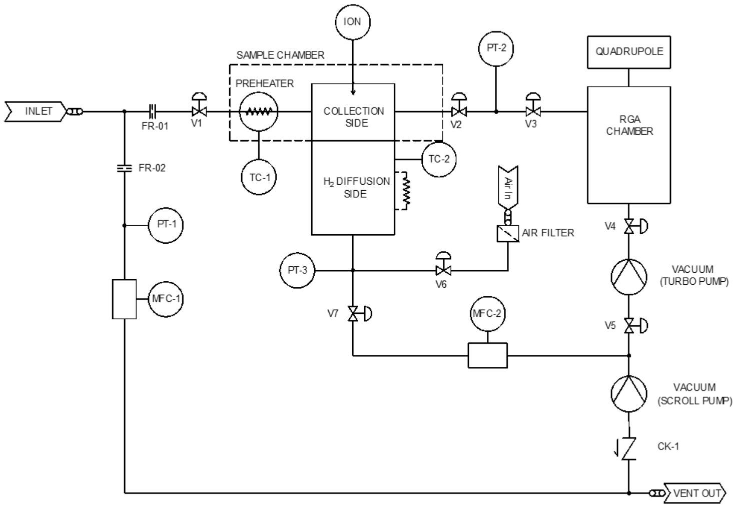

Figure 1 HEMS schematic

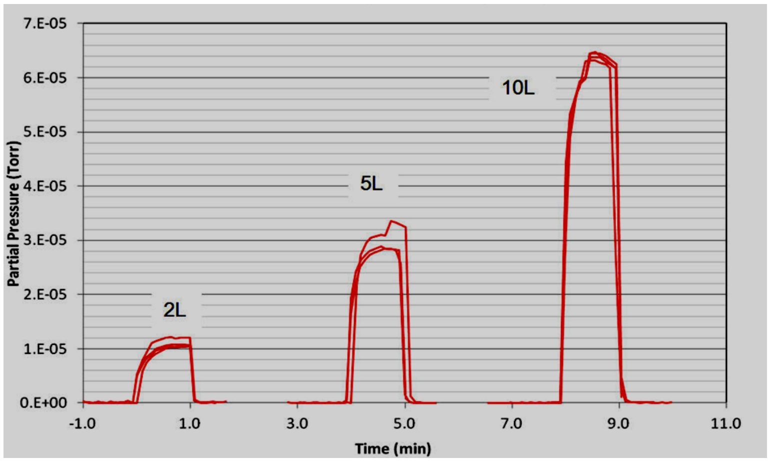

Figure 2 shows a number of one minute periods of RGA signal on mass 16 CH_4 for different volumes of sampled analyte.

3. HEMS

Principle of Operation

An analyte slipstream, teed off from a larger bypass stream, is dead ended into a sample chamber containing a palladium alloy membrane see figure 1. The matrix hydrogen gas passes through the membrane leaving impurities accumulating into the chamber. The downstream side of the membrane is held at pre-vacuum pressure while the amount of sampled matrix gas is controlled with a mass flow controller.

Impurity back diffusion, out of the chamber, is prevented by a high velocity section in the incoming slipstream. Repeatability and the efficiency of trapping the accumulating impurities is shown hereunder in figure 2.

After accumulation, the analyte slipstream is isolated by closing a valve and the matrix hydrogen removal continues until reaching a pressure of 1E-1 Torr in the sample chamber after around 2 minutes. Then, the pre-vacuum is replaced by atmospheric pressure air which causes chemical pumping by oxidizing hydrogen exiting the membrane irreversibly into H2O. When the sample chamber pressure drops to 4E-6 Torr after about 6 minutes, a valve is opened connecting to an RGA chamber that is priory evacuated with a turbo pump to below 1E-8 Torr. Just before opening this connection, the RGA's turbo pump is isolated from the RGA chamber causing it to operate in the static mode. RGA signals are recorded as a function of time for a number of selected masses typically 2, 16, 18, 28, 44. Given that non-hydrogen species are no longer pumped, their partial pressure will gradually change due to outgassing, hydrogen release and the associated chemistry of the various chamber walls and the RGA ionizer's filament, see figure 3. Given the low pressures involved, these phenomena happen at a slow enough timeframe to be followed as intensity changes in the sequence of RGA spectra. Specifically, they can be measured and studied independently on ultrapure "zero" gas samples as is presented hereunder. This allows to disentangle the above mentioned slower chemistry kind of changes from the rapid redistribution of species when connecting the sample chamber to the RGA volume, which has a more step function profile and is the relevant part for the analysis.

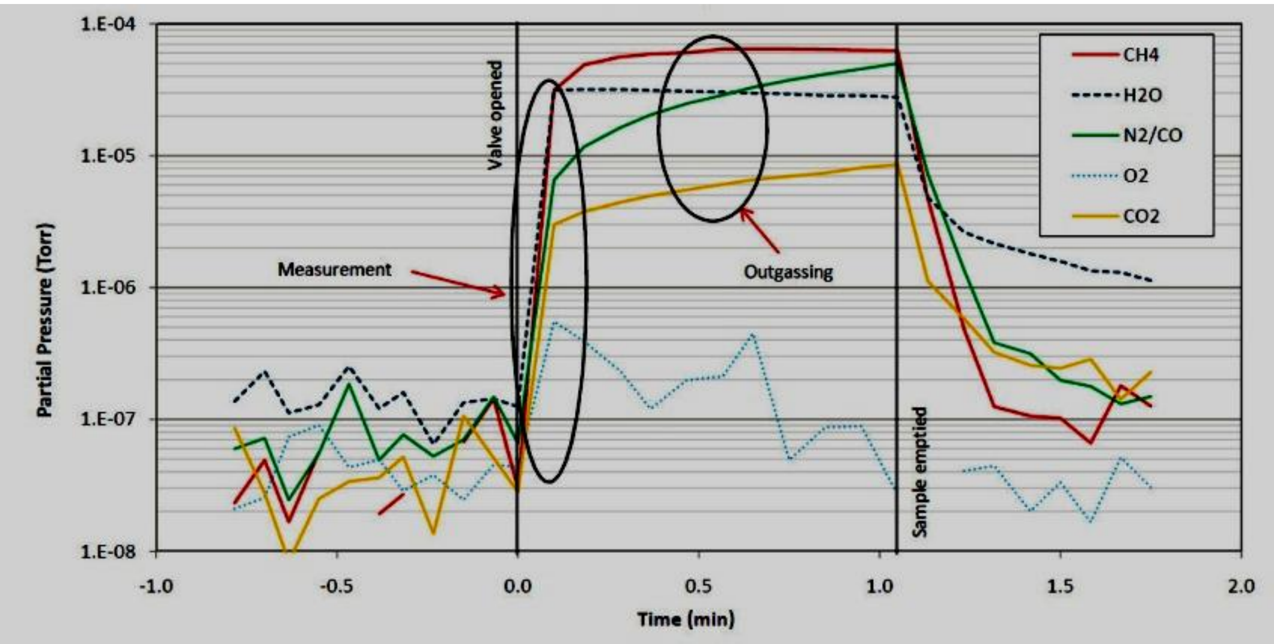

Figure 3, Typical partial pressure verses time for contamination collected in the HEMS.

Zero Gas

A reference zero gas is created inside an isolated sample chamber by routing sample hydrogen to the opposite (plumbing not shown in figure 1) side of the palladium alloy membrane. Prior to entering the zero gas, the sample chamber is evacuated pumping it with the turbo pump to about 1E-8 Torr. This zero gas is ultra pure as it passed through the dense membrane which blocks all non-hydrogen components. It should be noted that the membrane can be rigorously checked for leaks using the RGA. The zero gas pressure and the time it is left in the chamber are chosen identical to those used during sample gas analysis. Subsequent pre-vacuum pumping, chemical pumping and the RGA analysis are performed in an identical manner as for regular sample analysis.

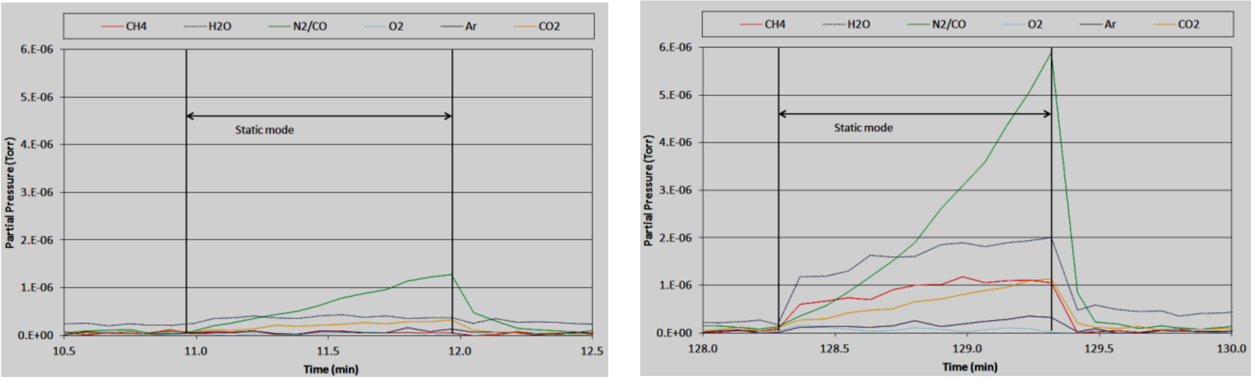

Figure 4 Ultrapure "zero" gas reactions and outgassing. On the left, 5 seconds holding time, 5 minutes on the right

HEMS use in hydrogen purifier development

The table on the right shows HEMS results used to validate the output of a purifier running at 500 slpm system before it is shipped to a customer. Figure 5 shows the cleanup of impurities after a new purifier unit is put in service during a factory product validation. Occasional initial contamination when running new purifiers at flowrates below specification is shown on the left hand side of figure 5. Mechanisms for this contamination could be linked to the low carbon steel's carbon content and oxidation downstream of the palladium alloy membranes. The effectiveness of a range of possible remedies involving a variety of design, material choice and treatments options could be measured with HEMS leading to solutions that otherwise would be hard to engineer.

Impurity	**Value (ppb)**	**Customer Spec. (ppb)**
CH_4	0.329	< 1.0
H_2O	0.015	< 1.0
N_2 , CO	0.047	< 1.0
O_2	0.002	< 1.0
CO_2	0.022	< 1.0

The instrument The experimental setup is shown in figure 6, while a commercial unit will be available in begin 2113.

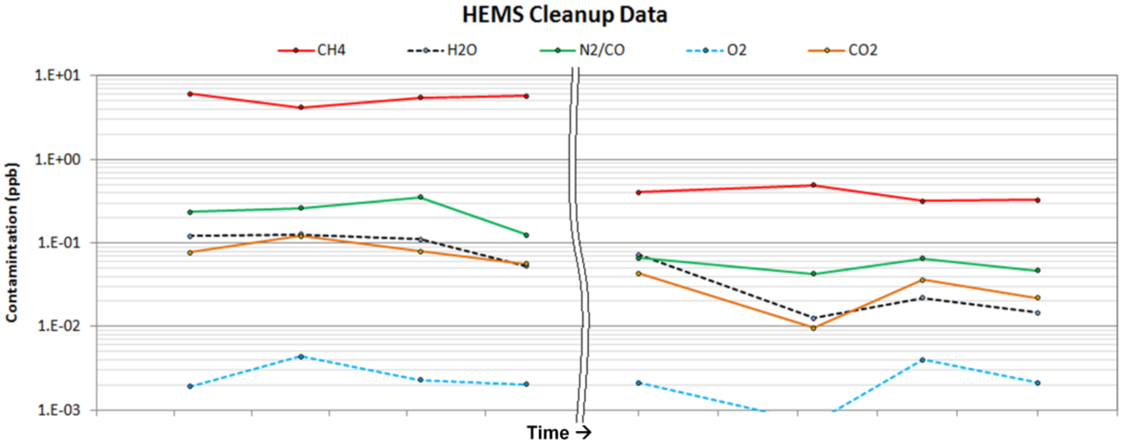

Figure 5 Dry-down and conditioning curves during purifier validation .

Figure 6 Experimental HEMS setup

4. Discussion The presented HEMS technology combines very high impurity enrichment with the use of a mass spectrometer operating it in the static mode. Test results show linear accumulation over the range investigated and good repeatability of the analysis. The unique ability to generate a highly reliable “zero” gas and to follow it through the analytical procedure provide information how an analyte sample is impacted interacting with heated walls and the hot RGA filament. This information allows one to compensate for such effects during HEMS analysis.

In state of the art APIMS analyzers the sample gas is passed through atmospheric pressure plasma created by a corona discharge and the resulting concentrations of species are reported. Similarly, the presented novel HEMS technology exposes its sample gas to an arguably less harsh environment consisting of 300 – 400 ˚C, catalytically active walls when at atmospheric kind of pressures and the hot filament of the mass spectrometer’s ionizer when at mid- to pre-vacuum pressures. This practice turns out to be acceptable in the case of ultra pure gases where there are only a handful of known impurities with very limited interaction between them while relatively low accuracies are acceptable at the involved ppb and ppt levels. Specific impurities such as H2S require a case by case study to check for expected interaction with the wetted parts of the analyzer. In as far the HEMS measurements rely on partial pressure and flowrate measurements, end result concentration values can be derived directly given known volumes of the involved chamber. This is particularly important at sub ppb levels where precise traceable standards are difficult to obtain.

5. **Conclusions/Outlook** Possibilities and limitations are presented of the novel HEMS technology that combines very high impurity enrichment with the use of a mass spectrometer operating it in the static mode. Measurement results of the linearity and repeatability of the impurity enrichment process were shown as well as data regarding the impact of outgassing and interference of the wetted analyzer parts and the use of an RGA in the static mode. HEMS detection limits exceed demands from the most stringent semiconductor manufacturing applications and its ease of use and calibration make it a potentially economical alternative to APIMS.

6. References

1 J. Newey, Compound Semiconductor. 12 (2001) 51-54
2 H. Funke et al, J. of Crystal Growth, 248 (2003) 72-76.
3 H. Meinders, Mass Spectrometric Determination of Impurities in Hydrogen, Analytical Chemistry, vol. 45, No. 14, 1973, pp 2354-2358.

(10/05/2012 JJA)