Thermo Scientific™ APIX δQ and APIX Quattro Process Mass Spectrometers

Multi-stream, multi-component UHP Gas Analysis in the Semiconductor Industry

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Introduction

The worldwide semiconductor market is expected to grow to US $551 billion in 2021, which represents a growth-rate of 25.1 percent. In 2020, in the middle of a global pandemic, the market still grew by 6.8 percent.[1] As the industry continues to grow, so too does the demand for ultra-high pure gases and chemicals; silicon wafer production requires a wide range of gases to create the necessary surface features on the wafer. These gases are collectively known as Electronic Specialty Gases (ESG) and need to be delivered to the various stages of the manufacturing process in exactly the required quantity and with strictly defined purity levels. For example, 80,000-100,000 Nm^3/h of Nitrogen with 99.999% purity is required for a 3D NAND fab. Nitrogen, along with other bulk gases such as oxygen, argon, hydrogen, helium, carbon dioxide and bulk ESGs are essential at every process step and tool for semiconductor and display manufacturing.[2]

As manufacturers try to fit more transistors into chips to increase performance and power efficiency, even tiny surface defects can ruin the devices being fabricated. Wafer contamination caused by undetected impurities in the gas supply can cost semiconductor companies production wastage, delay in supply, production line suspension and loss in revenue. In some cases, semiconductor companies have had to scrap large quantities of wafers causing millions of dollars in lost revenue. With shortages of semiconductors damaging automotive makers and tech giants[3], there is increasing pressure to minimize and even eliminate such defects. Strict procedures and quality control measures are put in place to ensure that ultra-high-purity gases are delivered to the manufacturing process.

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Analytical requirements for UHP gas analysis

Historically gas chromatography and various spectroscopic techniques have been used to monitor the purity of ESGs. However the industry's drive to produce ever smaller chips has driven detection limits down to part per trillion (ppt) levels. While no single analyzer can monitor every impurity in every ESG, Atmospheric Pressure Ionization-Mass Spectrometry (API-MS) offers fast, accurate detection limits down to ppt levels for a wide range of impurities in for key bulk UHP gases-nitrogen, hydrogen, argon and helium. In a study to develop a process model to characterize different mechanisms that affect the moisture level at the Point-of-Use (POU) for high purity gases, a Thermo Scientific™ API-MS was used for low and sub ppb moisture measurements, and two Cavity Ring-down Spectroscopy (CRDS) analyzers were used to measure higher concentrations[4].

API-MS principle of operation

Thermo Scientific uses positive ion API-MS for determining trace contaminants in ultra-high purity gases. The sample gas flows into the API ion source at slightly higher than atmospheric pressure. A corona discharge is produced by a needle maintained at a high voltage which is located close to an orifice plate; this results in a stream of electrons which flow from the orifice plate to the needle. The electrons react with the bulk gas, ionizing a large number of bulk gas molecules. Fortunately, the trace contaminant molecules in the bulk gas require less energy to become ionized than do nitrogen, hydrogen, helium or argon. For this reason, when any contaminating molecule appears in the sample stream, there is a very high probability that it will collide with a bulk gas ion. When these collisions occurs, the charge is transferred to the contaminant which then becomes ionized. This charge transfer results in a very high proportion of the contaminant molecules becoming ionized. In fact, the efficiency is about 1,000 times that of other ionization techniques that operate within the vacuum chamber of the mass spectrometer. Figure 1 shows a schematic of the charge transfer process.

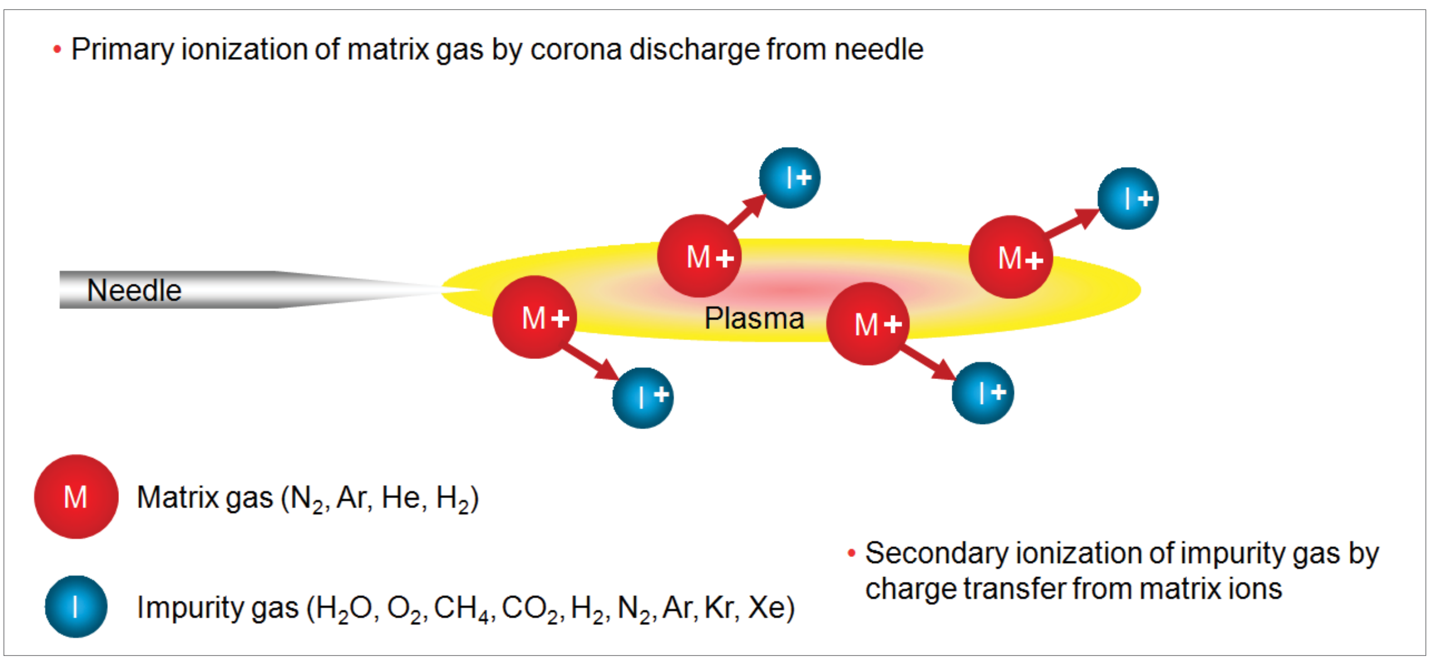

Figure 1. API charge transfer for bulk matrix gas to trace impurities

A proportion of the sample gas, complete with the ionized contaminants, passes through a series of pressure reducing lenses before it enters a quadruple mass spectrometer. A triple-filter unit is used that permits measurements up to 300 Daltons (atomic mass units) allowing the complete contamination spectrum to be measured at the detector. A demountable pulse counting channel electron multiplier detector provides maximum signal and minimum noise for optimum sensitivity to trace impurities. The pulse counting amplifier has a noise level of just 10 counts per 10^6; when combined with the API source the system is able to detect contaminants down to ppt levels.

Benefits of API-MS

Problems in gas delivery systems can quickly lead to potentially damaging impurity levels in the UHP gases. These can only be detected and corrected by fast, sensitive impurity analysis. Figure 2 shows an APIX analysis of methane impurity levels in argon. APIX identifies there is a problem in the gas handling system, with methane levels rising above 40 ppt and excursions over 100 ppt. Following repairs, the methane level drops to single finger ppt levels.

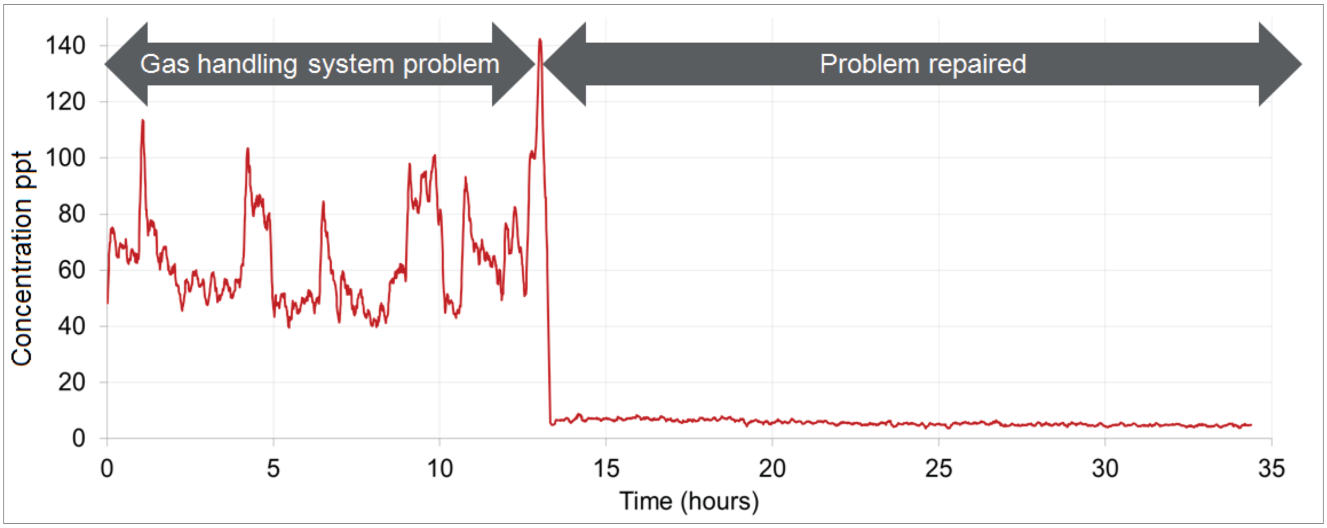

Figure 2. APIX analysis of methane impurity in argon

APIX's ability to provide multi-component analysis is also extremely useful. Figure 3 shows APIX analysis of three impurities in UHP nitrogen over 7 days. Oxygen and carbon dioxide levels are stable, but moisture levels vary by almost 30 ppt, caused by changes in plant temperature. After the 4th day the moisture level is relatively flat—it is the weekend, no-one is going in and out of the area so the temperature is relatively stable.

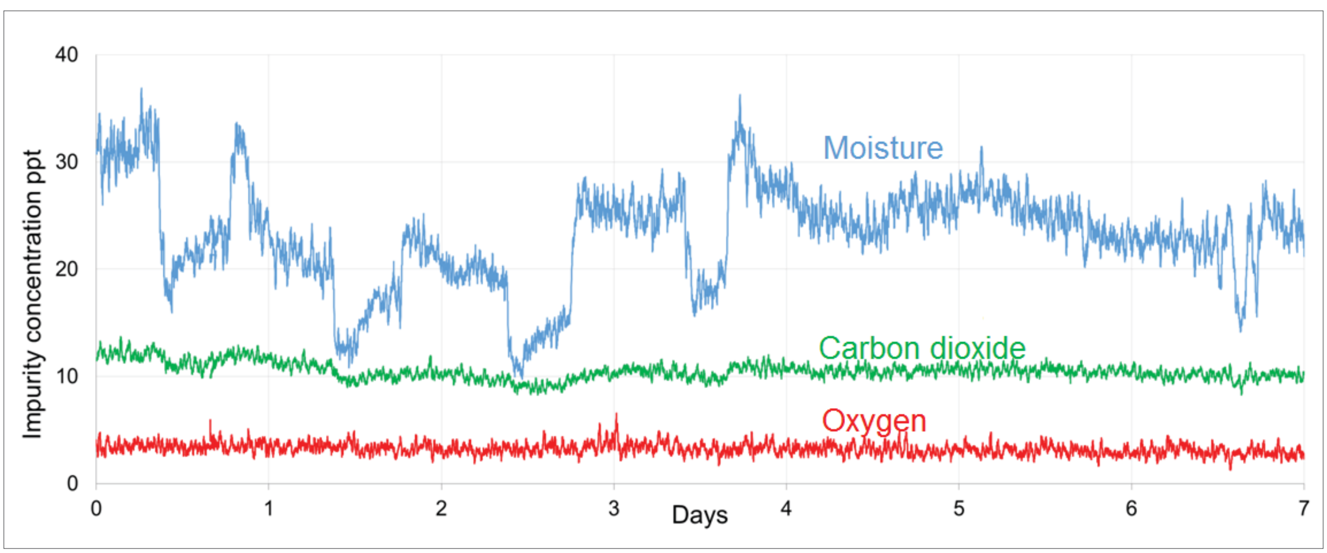

Figure 3. APIX analysis of moisture, carbon dioxide and oxygen in nitrogen

APIX δQ and APIX Quattro

The APIX δQ configuration comprises a single-bay environmental enclosure containing the API-MS analyzer and an gas processor that provides automatic ppb or ppt calibration of the analyzer. The system can be offered with optional dry pumps for a clean room compatible solution. A set of wheels can be provided to allow the unit to be safely pushed from one test point to another. The APIX dQ can be dedicated to the monitoring of one bulk gas or by use of a stream selector can switch between four bulk gases (nitrogen, argon, helium and hydrogen) sequentially. For the continuous analysis of the same four bulk gases without interruption we offer the APIX Quattro. It comprises two single-bay environmental enclosures which contain four API-MS analyzers and a third bay containing the gas processor. Each mass spectrometers is mounted on slides and can be pulled forward for easy maintenance. The top-mounted hood can contain stream switching manifolds for sample gas connections, allowing multiple streams to be connected to each independent bulk gas analyzer. Figure 4 shows APIX δQ and APIX Quattro.

Each mass spectrometer is controlled by an embedded processor that runs a real-time operating system using battery-backed flash memory. The processor acts as a master to a series of internal controllers, interconnected by Ethernet cable. Each of these microcontrollers operates the individual subassemblies such as the gas processor and multi-stream inlet. Each multi-processor analyzer network provides redundant communication channels to permit reliable, stand-alone operation without the need for a PC workstation.

Figure 5 shows a GasWorks screenshot from an APIX Quattro analyzing all four UHP gases (H_2, He, N_2 and Ar) simultaneously.

Figure 4. APIX δQ and APIX Quattro

Analytical performance

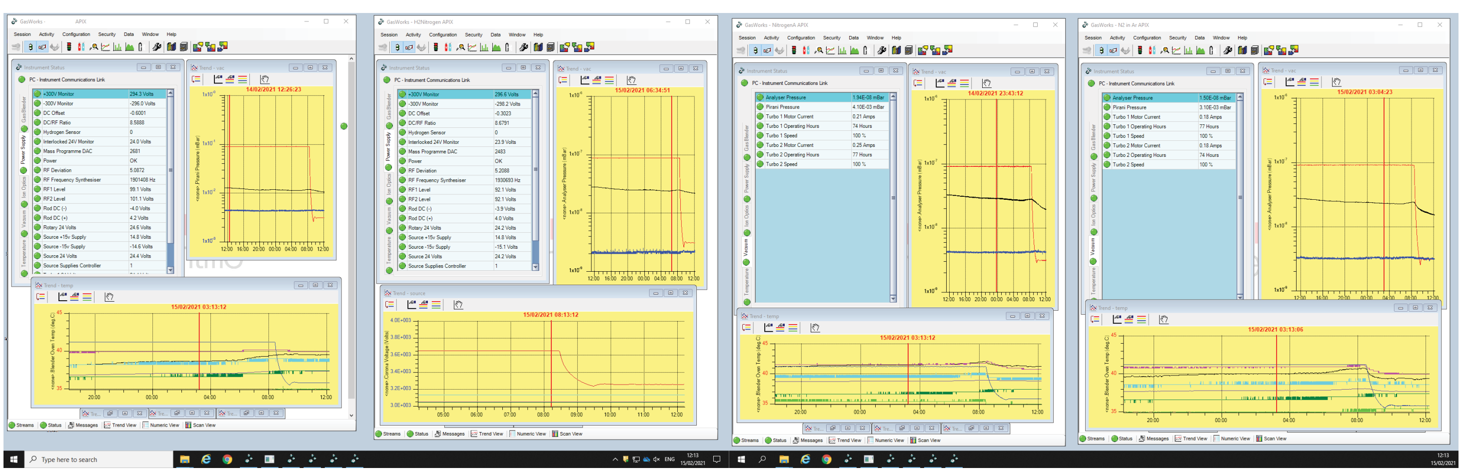

Figure 5. APIX Quattro screenshot showing simultaneous analysis of four UHP gases

Table 1 shows guaranteed APIX δQ Lower Detection Limits based on a two-minute analysis cycle time, measuring all listed impurities in a single bulk gas.

APIX offers a most powerful combination of speed (analysis in seconds), sensitivity (ppt detection levels) and flexibility (analyzes multiple impurities in four UHP gases).

Table 1. Guaranteed lower detection limits for two-minute analysis cycle time to measure all listed impurities in a single bulk gas

Impurity	In UHP Nitrogen (ppt)	In UHP Argon (ppt)	In UHP Helium (ppt)	In UHP Hydrogen (ppt)
Oxygen (O_2)	10	10	10	10
Hydrogen (H_2)	150	100	50	N/A
Methane (CH_4)	10	10	10	10
Moisture (H_2O)	30	30	30	30
Carbon Monoxide (CO)	50	10	10	Not separated from N_2*
Carbon Dioxide (CO_2)	10	10	10	10
Nitrogen (N_2)	X	X	10	150
Argon (Ar)	X	X	10	X
Krypton (Kr)	10	10	10	X
Xenon (Xe)	10	10	10	X

'X' indicates that the component cannot be analyzed. The Upper Detection Limits are 10 ppb for all impurities, and maximum total impurity level must not exceed 100 ppb.

In bulk hydrogen, the measurements of CO and N_2 are combined.

Calibration

As with any process analyzer, the analytical data it provides is only as good as its calibration. Unlike other process gas analyzers however, it is not possible to supply accurate calibration gases with ppb and ppt impurity levels. Since the launch of its API-MS product range Thermo Scientific has worked to solve this problem, so that APIX δQ and APIX Quattro systems are provided with an integrated gas processor. This UHP sample gas conditioning system ensures constant gas flow and pressure to the API source and generates ppb/ppt calibration standards using dilution of ppm standard cylinders (supplied by others). It also uses a temperature stabilized permeation tube to generate moisture calibration standards. The gas processor's operation is fully integrated into the APIX system's operating software.

Figure 6 shows some examples of linearity plots generated by the gas processor, and Table 2 shows an example of the single external calibration standard we recommend to use with the gas processor.

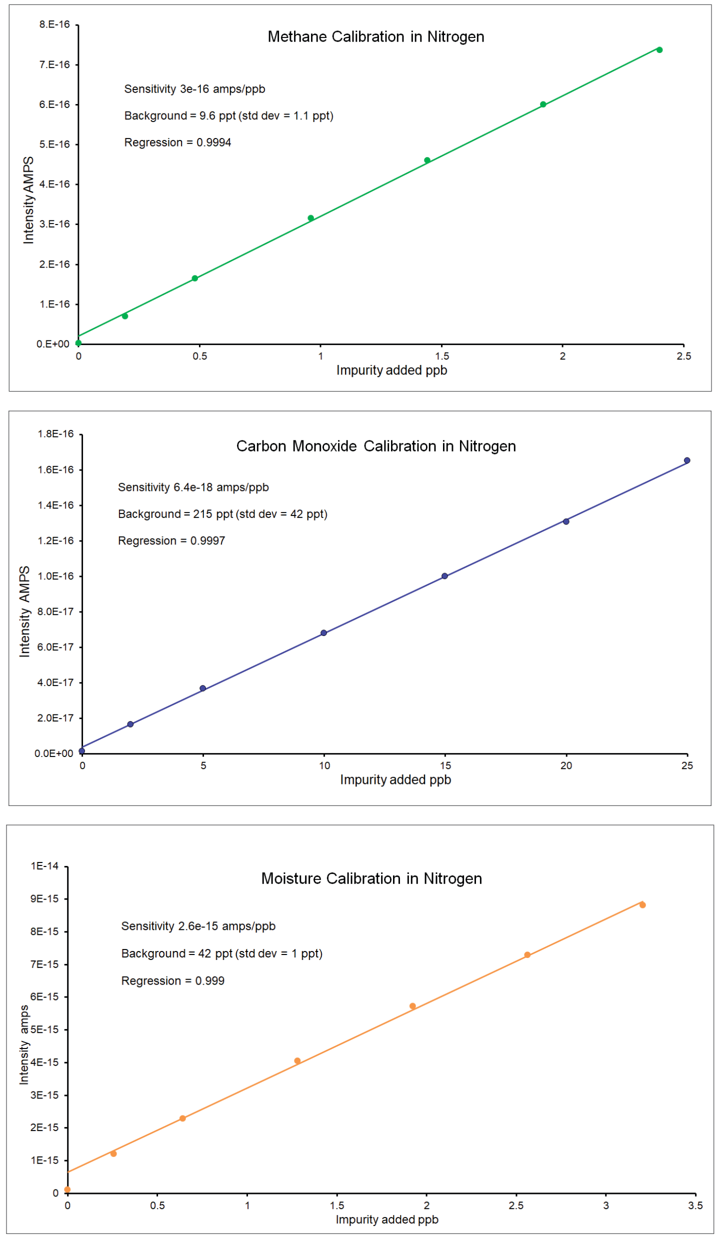

Figure 6. Linearity plots for methane, carbon monoxide and moisture generated by the APIX gas processor.

Table 2. Example of a typical ppm calibration cylinder for use with APIX gas processor

Component	Approx concentration (ppm)
Oxygen	20
Methane	5
Carbon monoxide	50
Carbon dinoxide	5
Nitrogen	20
Argon	10
Hydrogen	50
Xenon (optional)	10
Krypton (optional)	10
Helium	Balance

Modifications for safe operation with hydrogen bulk gas

APIX δQ and APIX Quattro systems configured to monitor bulk Hydrogen are provided with a number of additional safety features. They provide internal protection for the unit and give emergency 'power off' inputs for connection to external monitoring and control systems.

- Vacuum pumps have inert purging to prevent build-up of hydrogen gas.
- The sample inlet manifold always has one inlet dedicated to nitrogen; this is fitted with a normally open valve while the hydrogen sample inlet valve is fitted with a normally closed valve. In the event of a power loss, deliberate or accidental, hydrogen sample is replaced by nitrogen.
- If the vacuum pressure within the MS is too high the hydrogen sample inlet is disabled and nitrogen sample gas replaces it.
- The cabinet has an exhaust at the top of the unit; if a vacuum is not detected in the cabinet exhaust the hydrogen sample inlet is disabled and nitrogen sample gas replaces it. Also, a hydrogen sensor is fitted; if it detects more than 0.1% hydrogen it will trip the power, the hydrogen sample inlet valve will close and the nitrogen inlet valve will open.

Summary

The 2020 edition of the IEEE's International Roadmap For Devices and Systems details a Yield Enhancement (YE) focus area which 'is dedicated to activities ensuring that semiconductor manufacturing is optimized for production of the maximum number of functional units. Identifying, reducing, and avoiding relevant defects and contamination that can adversely affect and reduce overall product output are necessary to accomplish this goal'.[5]

Part per trillion impurity analysis of UHP gases plays a vital role in improving product quality, and Thermo Scientific API-MS systems have been used for over 30 by gas manufacturers and semiconductor companies.

- Fast online measurement (two-minute analysis cycle time) enables immediate response to gas supply upset conditions
- Superior sensitivity with ppt detection capability provides gas analysis suitable for the most stringent quality requirements
- Provides a more complete analysis of impurities, including H_2, CO, CO_2, H_2O, O_2, CH_4, Kr and Xe
- APIX Quattro offers fully integrated multi-analyzer operation providing rapid contamination detection for up to four UHP gases

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