Perfluorocarbon Detection For Semiconductor Applications

BY PATRICK SMITH

PFC measurements are important in fabs, but when several compounds are present with overlapping absorbance bands, the task becomes difficult.

Perfluorocarbons (PFCs) are widely used in the semiconductor industry in dry processing applications such as film etching, chemical vapor deposition (CVD) chamber cleaning and as coolants for semiconductor manufacturing tools. Although toxicity levels are not well established, many PFC compounds are considered somewhat toxic. PFCs can also be flammable and have significant global warming potential. Flammable levels are generally high (10s of thousands of PPM), so measurement in hundreds of PPM seems to satisfy most applications. Examples of commonly used PFCs in semiconductor manufacturing:

Name	Use	Flammability	Toxicity
Difluoromethane CH_2F_2	High Aspect Etching	Flammable	Non-Toxic
Fluoromethane CH_3F	Etching	Flammable	Non-Toxic
Hexafluorobutadiene C_4F_6	Dielectric Etching	Flammable	Toxic
Octofluorocyclopentene C_5F_8	Dry Etching	Non-Flammable	Toxic
Trifluoromethane CHF_3	High Aspect Etching	Non-Flammable	Low Toxicity
Perfluorocyclobutane C_4F_8	Deposition, Etching	Non-Flammable	Low Toxicity
Fluorinert $(C_3F_7)_3N$	Heat Transfer Liquid	Non-Flammable	Low Toxicity

Measuring PFCs

Measuring PFC gases in industrial environments is mostly done using pyrolysis[1] or optical sensors. Pyrolyzers offer high sensitivity and optical sensors offer reliability and low maintenance. Both of these types of sensing suffer from lack of specificity and interfering gases can cause false alarms. Heat transfer liquids, isopropyl alcohol, ethanol, and acetone are typical interferents.

Pyrolyzer Interference

Any compound whose deconstructive bonding energy is lower than the thermal energy present in the pyrolyzer will incur decomposition. If the electrochemical sensor reacts to products of the decomposition, the pyrolizer will show response. This occurs with both the target gas and interferents. A typical PCF pyrolyzer measures HF that forms by hydrolysis following the thermal decomposition. Since most compounds containing carbon and fluorine will be pyrolized with this type of device, response will occur from many gases typically present in semiconductor manufacturing. This type of device is really a total PCF detector due to the lack of specificity.

A pyrolyzer system typically requires significant maintenance.

This may not be a problem except that the unit will also respond to inert compounds such as fluorinert. The user may consider this a false alarm.

Pyrolyzer Performance/Expense

Although pyrolyzers are capable of fairly sensitive measurements, since they are not intrinsically safe[2] or explosion proof,[3] many are remotely mounted using a pumped sampling system. This can cause a significant response time delay and increase system costs.

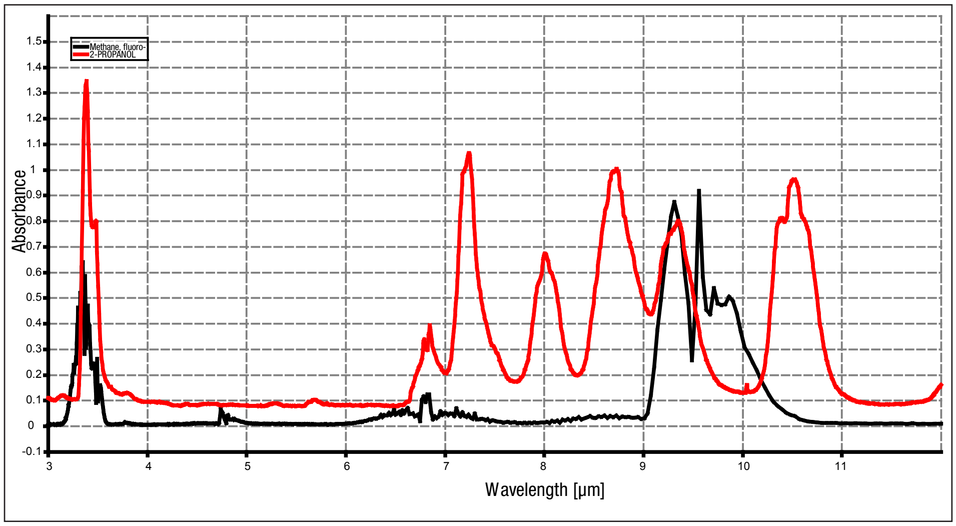

Figure 1. Overlapping absorption bands of fluoromethane and ethanol

Pyrolyzer Maintenance

A pyrolyzer system typically requires significant maintenance. Along with frequent calibrations, heating elements burn out, sampling pumps fail, and the electrochemical sensing element needs to be replaced or refilled with electrolyte. Some pyrolizers are calibrated with a surrogate gas which will test the electrochemical sensor but may not recognize a failed heater.

Optical Sensing

Optical sensing holds many advantages over pyrolysis. Optical sensors are inherently failsafe and simple: no light means lots of gas=ALARM. A well designed optical sensor will have no mechanisms that wears out and a stable optical system. This results in no routine maintenance other than occasional calibration. The biggest hurdle with using an optical sensor in this type of application has been sensing the target gas while ignoring other commonly present gases.

Optical Interference

Infrared optical sensing is well developed and has proven to be very reliable and fairly specific in many areas of the response spectrum. PFCs have significant Infrared absorption lines in the 9-11µm area of the spectrum. Unfortunately, this is a very active part of the spectrum. Many common compounds (including alcohols and acetone) have strong absorption bands in the 9-11µm area. Some even have absorption bands overlapping the PFC absorption bands. This results in a sensor that responds to PFCs but also responds to other gases typically present in semiconductor manufacturing. The problem becomes even more complex when the sensor needs to see some PFCs and not others. For example, the user may not want his CH_2F_2 sensor to respond to his tool coolant. CH_2F_2 and many PFC-based coolants have overlapping optically active bands.

A Better Optical Sensor

Traditionally, spectral absorption is measured in one of three ways:

1. Optical interference filtered sensing element and broadband optical source. This is a very stable reliable method but is limited to single band measurements.

2. Scanning laser diode single line measurement; more selective but still limited to single band measurements. This approach is expensive and requires more maintenance.

3 Spectrophotometer; lots of spectral information but very expensive and not well suited for an industrial installation due to delicate optics.

By monitoring only key optical bands, using proven robust sensing methods, an algorithm can be developed to discern the target PFC from interferents (including other PFCs). An example is shown in Figure 1 illustrating the overlapping absorption bands of fluoromethane and ethanol. With traditional methods, it would be virtually impossible to separate the two by monitoring a single response band. The new algorithm would be able to discriminate between the two and identify the individual components. This new approach enjoys the reliability of 1) and provides multiband spectral information without to resorting to 3). This is the equivalent of a targeted industrial spectrophotometer. The simple limited optical system keeps unit cost low, maintenance low, reliability high and form factor small. In addition, explosion-proof rating allows point-of-sensing mounting that simplifies installation and keeps the sensor response times short. G&I

References

Pyrolysis: The thermochemical decomposition of a compound at elevated temperatures. In this case, the products of decomposition are then measured using an electrochemical sensor. The output from the electrochemical sensor is assumed to be proportional to the concentration of the target compound.

Intrinsically Safe: Electrical device designed so that it is not capable of generating a spark energetic enough to ignite an explosive mixture.

Explosion Proof (Exp): Device designed so that an internal explosion will not ignite an explosive mixture outside the device.

Patrick G. Smith is Vice President and Director of Research and Development for Sensor Electronics, a Minneapolis-based manufacturer of advanced detectors and analyzers of explosive and toxic gases. After graduating from the University of Minnesota with a degree in electrical engineering, Mr. Smith did extensive coursework in chemistry, and then graduate work in computer science and electrical engineering. In his professional career Mr. Smith has worked in optical research, with special focus on ultraviolet and infrared radiation as well as the visible light spectra. He has developed gas-detection systems for applications in the semiconductor, medical, petrochemical, computer and environmental-protection areas. He holds several patents for advanced optical/electronic sensors. He can be reached at 952-938-9486 or psmith@sensorelectronic.com.