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S C I E N T I F I C

FTIR gas analysis

Measuring destruction efficiency of greenhouse gases released by semiconductor fabrication tools

Background

Modern materials processing activities involve the use of cold plasmas employing fluorinated gases as reactive species. Some of these gases have been demonstrated to exhibit deleterious environmental consequences resulting in their being labelled as greenhouse gases or GHGs. Among the list of GHGs undergoing intense review are those of fluorinated gases, such as NF_3, CF_4, SF_6, CH_2F_2, etc. Many of these gases are either reactants or are generated as by-products of semiconductor wafer fabrication processes, such as etching and chemical vapor deposition. Therefore, semiconductor fabrication plants (SemiFabs) employ abatement tools to destroy and dilute these fluorinated gases before they reach a stack scrubber. This process assures that they will meet EPA regulations which require yearly facility-dependent GHG emission audits. European and Asian semiconductor manufacturers must meet similar regulations as well.

Problem

To ensure that the abatement process occurs efficiently, SemiFabs are required to audit selected abatement devices (one per each wafer processing tool employed) such that each device gets periodically reviewed for efficiency in destroying these GHGs before they are released to the scrubber. Since there are hundreds of abatement devices within a single SemiFab, the monitoring process must be accurate, fast (one or two hours), and able to monitor multiple fluorinated species simultaneously. Most SemiFabs utilize a series of devices to perform the

necessary measurements required to calculate an overall destruction efficiency for each fluorinated species. Among the measurements required are the dilution factor (the overall ratio of the flowrate into the abatement device to that of the flowrate out of the abatement device). In most cases, this requires the use of a krypton gas tracer and a mass spectrometer (for measurement of flowrate out) in addition to an FTIR to measure a separate infrared-active gas tracer (for measurement of flowrate in). Also required is another more sensitive FTIR to measure the residual fluorinated gases which survived destructive processes within the abatement device. The result is a very bulky and cumbersome system to measure input and output flows and concentrations. What is needed is a much simpler and fully integrated measurement system capable of performing ALL these tasks.

Solution

Thermo Fisher Scientific has developed a new methodology for measuring abatement destruction efficiencies with a much simpler system. The system uses the Thermo Scientific™ MAX-iR™ FTIR Gas Analyzer with DTGS detector in conjunction with the Thermo Scientific™ Automated Sample Console (ASC-10™). The MAX-iR analyzer can monitor the entire IR spectral range (500-5000 cm^{-1}) without the need for liquid nitrogen. The ASC-10 allows for the precise measurement of post-abatement flow by determining the dilution of a tracer infrared gas or gases; this obviates the need for a spacious and costly mass spectrometer and krypton gas utilized in the previous system.

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A necessary pre-requisite to determining abatement efficiencies is accurate measurement of pre-abatement device gas(es) input. This was a challenge for conventional methods since the input gas concentration was so high that a second FTIR with a short pathlength gas cell was required to maintain infrared absorptions in a linear regime without saturating the detector. Unfortunately, this FTIR was too insensitive to measure the post-abatement (low gas concentration) side, thus requiring another FTIR with a much longer pathlength. In the new configuration, the ASC-10 is employed to maintain a precise dilution on the pre-abatement levels while allowing post-abatement effluents to be measured directly. In this way, the overall system is reduced from 2 FTIRs and a mass spectrometer to 1 FTIR and 1 ASC-10—a much simpler, less bulky, and equally capable system configuration.

How the process works

A. A 100% tracer gas cylinder is attached to the ASC-10 and a precise flow through its mass flow controller (MFC) is initiated. This known gas sample is injected just after the abatement device (point C on figure 1) and a sampling probe (typically a curved piece of stainless-steel tubing which is directed toward the center of the abatement exhaust) located upstream at least 3 or 4 feet away from the injection point (point D on figure 1) to allow for turbulent mixing of the tracer gas with the diluting stream from the abatement device. This positional placement of tracer gas admission and collection accessories (curved tubing probes) will prevent laminar flow and stratification of the tracer gas, which could result in an incorrect reading of the actual ambient concentration in the flow. By measuring the resulting concentration and ratioing this value to 100% (i.e., 1,000,000 ppm) a scaling factor is derived permitting calculation of the total volumetric flow out (TVF_{out}) from the abatement device.

B. Much in the same way, we can measure the total volumetric flow into the abatement device (TVF_{in}) by using a precise flow from the upstream tool, e.g., etch station, which is set up by the tool operator in the clean room. Again, 100% tracer gas is used at the tool (point A on figure 1) and the collection (or sampling) probe is now located after the roughing pump but before the abatement device (point B on figure 1). The same principle of measured dilution provides the data needed to calculate TVF_{in}.

C. Once these flows are measured, there are enough data to calculate the dilution factor (DF), which is the ratio TVF_{out}/TVF_{in}. In the absence of any additional gas destruction within the abatement unit, this would constitute the natural reduction in concentration of the GHG directly through dilution within the gas effluent stream.

D. To determine the overall destruction efficiency, defined as DF multiplied by an abatement-unit-specific gas destruction factor, the overall concentration of each GHG must be measured before and after the abatement oven. As mentioned previously, the pre- to post-abatement gas concentrations can vary by hundreds (or even thousands) of ppm, so dilution is used to bring the pre-abatement level into a measurable range. This is done in a unique way by leveraging the functionality of the ASC-10. The high pre-abatement concentration is measured directly with a normally very weak infrared band in the GHG. Then the ASC-10 is set up to inject a diluting nitrogen stream providing a 90% dilution, or a 1/10th concentration level of the direct stream. The exact dilution can be fixed by observing the GHG concentration and throttling the probe flow when the 1:10 concentration is reached. With this dilution, the FTIR calibration method can then be set up to retrieve gas concentrations using other, perhaps stronger and/or less interfered with non-saturating absorption bands (signals); the SAME bands used to estimate concentrations for the post-abatement effluents.

To recap, we have a probe sampling exactly 1/10th the pre-abatement concentration (at point B in figure 1) and a probe directly sampling the post-abatement concentration (at point D in figure 1). By switching between these two probes, the pre- and post-abatement GHG concentrations can be sequentially measured using data acquired from a single FTIR instrument and processed using a single calibration method. By measuring the concentration pre-abatement (C_i) and the concentration post-abatement (C_o) and using the calculated dilution factor (DF), the abatement device specific destruction efficiency (DRE) is calculated as:

$$DRE(\%) = \left[1 - \frac{(Co * DF)}{Ci}\right] * 100$$

This procedure is much faster (1–1.5 hours) and much simpler (one system instead of three) for performing the abatement analysis process.
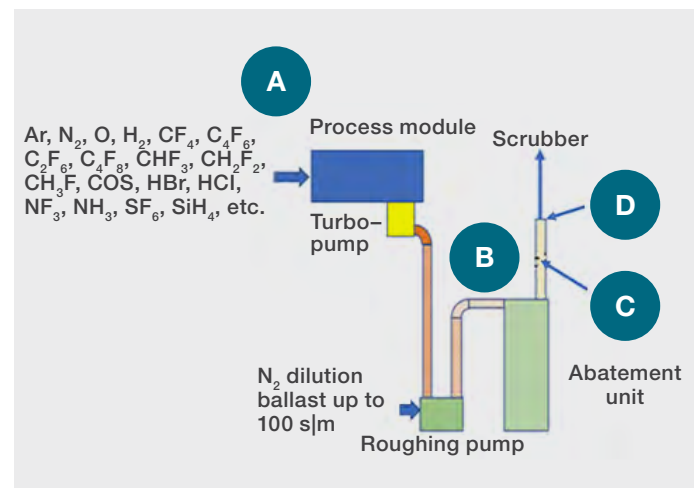

Ar, N_2, O, H_2, CF_4, C_4F_6, C_2F_6, C_4F_8, CHF_3, CH_2F_2, CH_3F, COS, HBr, HCl, NF_3, NH_3, SF_6, SiH_4, etc.

Figure 1: Layout of abatement system.

Results

As an example of the results obtained from the abatement measurements, the resulting spectra for perfluorocyclobutane (C_4F_8) is shown below as measured by the MAX-iR/ASC-10 system. The spectrum marked "C_4F_8 in" is the sampling of the pre-abatement level of C_4F_8 coming from the etch tool. As

mentioned previously, this is a 1:10 dilution of the concentration such that the spectrum remains on scale. The feature at 960 cm^{-1} is used as the quantification region for this species. The observed average was C_i = 854.5 ppm for the input concentration (after scaling up by 10x). Using this same feature on the post-abatement side marked as "C_4F_8 out", where there is large water and CO_2 spectra (due to the dilution by air), an average value of C_o = 7.92 ppm is measured. Using CF_4 as a tracer gas in steps (a) and (b), a dilution factor of DF = 9.75 was determined. So, putting these numbers into the previous equation, a destruction efficiency of 91% was calculated. Likewise, in the same manner, all GHGs of interest can be spectrally measured and destruction efficiencies calculated. The DRE values exhibited a wide variance during our testing, from a high of >98% for C_4F_6 to a low of 17% for CF_4.

C_4F_8 Spectrum in


C_4F_8 Spectrum out
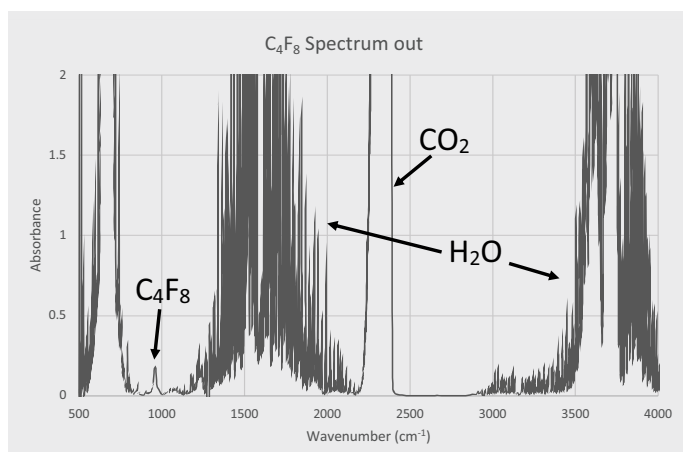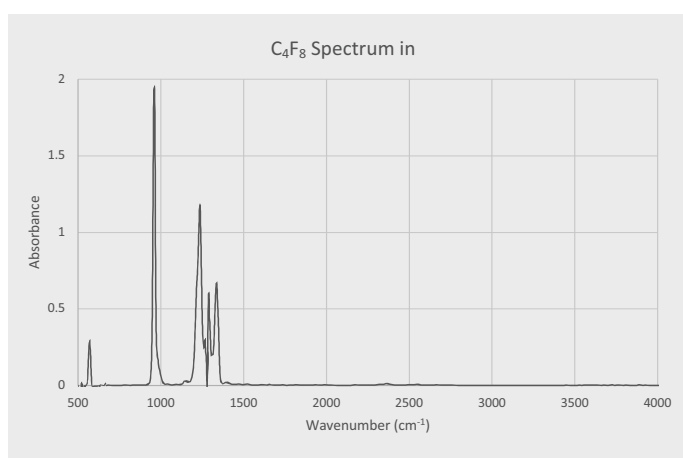
Plasma by-products

One other set of data which arose from these studies is the determination of by-products during a plasma operation with a standard etch mix. In this case, a plasma off/plasma on cycle with a mix of C_4F_6, O_2 and Ar was observed and the spectrum of C_4F_6 with the plasma off was recorded to get a clear picture of what happened. To no surprise, it was analyzed as ~700 ppm C_4F_6. Spectra were then recorded during the plasma cycle, which revealed a complex mix of reactant and new product species. Both pure reactant (Plasma Off) and reaction mixture (Plasma On) spectra are shown below. To facilitate deconvolution and identification of etch-process generated product species a Thermo Scientific™ MAX-Acquisition™ Automation Software feature, which allows the entire Plasma Off C_4F_6 spectrum to be inserted as a component of the plasma on analysis, is applied to quantitatively subtract any C_4F_6 from the Plasma On spectrum, revealing what is generated in the plasma.

C_4F_6 Spectrum Plasma Off

C_4F_6 Spectrum Plasma On
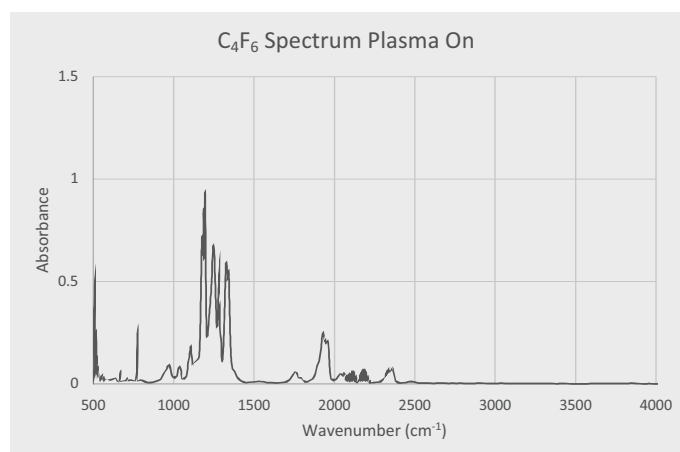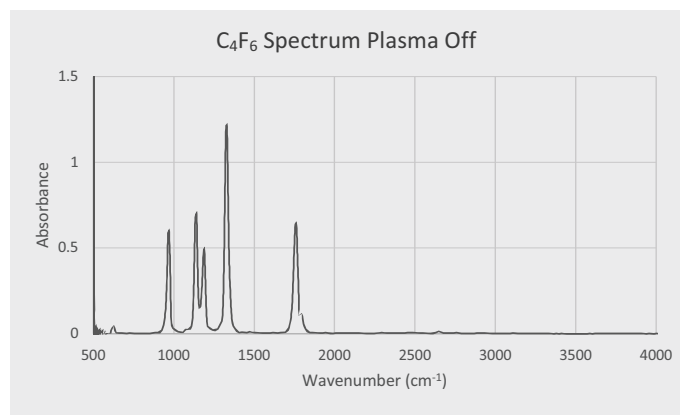
In the resulting product species-only spectrum there are some obvious compounds, namely CO and CO_2. In addition, even though it is a collection of small features, there is a definite presence of HF in the spectral region from 3800 – 4000 cm^{-1}. Other species found were: COF_2, CF_4, SiF_4 and C_2F_6.

After removing the spectral contributions from all the identified species, there remained two features (around 1170 cm^{-1} and 1345 cm^{-1}) which could not be identified in our method (the "method" being the list of likely gases that the software was to detect and quantify). An expanded search was undertaken using the Peak Matching Tool to select the unidentified regions and perform a global search versus the NIST/EPA gas phase data base. The result is shown on the next page. The agreement is quite good and reveals that the missing component is tetrafluoro ethylene (C_2F_4), which is a chemically relevant etch process product.

Plasma On - Plasma Off
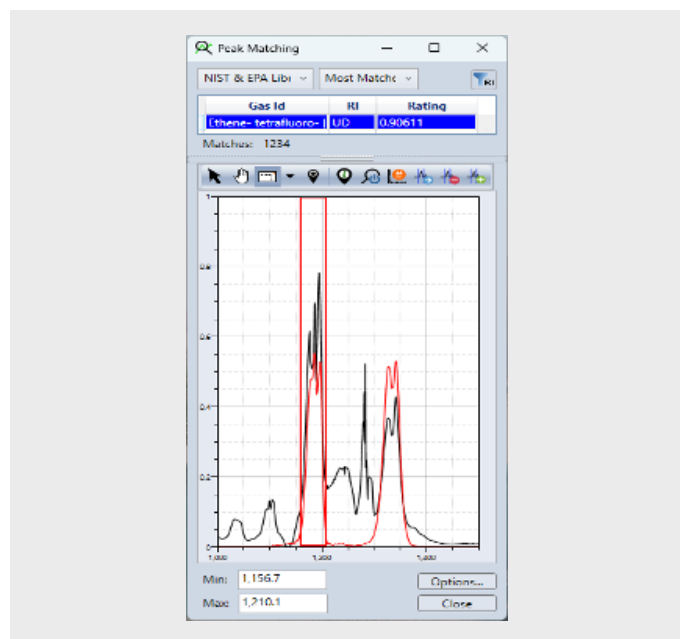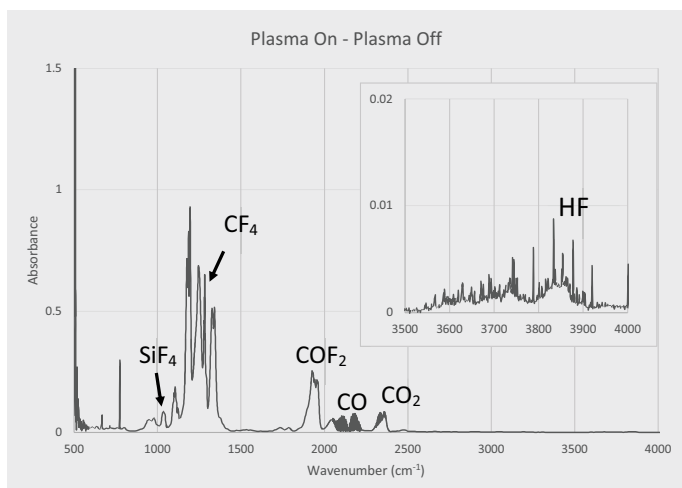
Summary of conclusions

- It was demonstrated that a simpler, less bulky, single FTIR-based system can perform measurements of destruction efficiencies of fluorocarbon GHGs in SemiFab abatement devices to achieve performance comparable to multi-FTIR/mass spectrometric systems, thus creating a faster, less costly, and easier tool to use for the customer.

- This same system also has the capability of directly monitoring the process gasses in the etch tool and reactive by-products during the plasma etch sequence.

- Further added value is offered by the MAX Acquisition Automation software by detecting and characterizing unknown features within the analyzed spectrum to provide a fuller analysis of the etch process.

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