

技術紹介

半導体製造工場で使用されるフッ素系地球温暖化ガス用 除害装置の排ガス分析システム (AGAS)

Abatement Gas Analysis System (AGAS) for Destruction or Removal Efficiency Testing of Fluorinated Greenhouse Gas Abatement Equipment in Electronics Manufacturing

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1. Introduction

In December 2010, the USA Environmental Protection Agency (EPA) issued a final rule (40 CFR part 98) for mandatory reporting of fluorinated greenhouse gas (F-GHG) emissions by the semiconductor industry¹⁾. This rule requires either the use of a default destruction or removal efficiency (DRE) of 60% for abatement units or that actual DRE measurements are made using a designated EPA protocol (EPA 430-R-10-003)²⁾. In response, Matheson has designed and built a portable and fully contained abatement gas analysis system (AGAS) for DRE testing of abatement units at customer sites. This paper discusses the AGAS and how DRE measurements are made. Data on the system performance are also presented.

2. Experimental

The AGAS (Fig. 1) is SEMI-S2 certified and has dedicated sampling manifolds and two Fourier transform infrared (FTIR) spectrometers to simultaneously sample and monitor the concentration of F-GHGs from the abatement inlet and outlet in real time following the EPA Protocol and SEMATECH guidelines^{2,3)}. The FTIRs are fitted with appropriate long and short pathlength cells depending on the concentration range to be measured.



Fig. 1: Photograph of Matheson's AGAS for making DRE measurements from abatement units

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Gas samples are withdrawn from the abatement inlet/s and outlet as shown in Fig. 2 into the AGAS. Each sampling line has a bellows pump to withdraw the sample from the duct as well as a particle filter, a dehumidification unit, a hydrogen fluoride trap and a mass flow controller to pretreat and deliver the sample to the respective FTIR⁴⁾. In addition, a quadrupole mass spectrometer (QMS) is also incorporated for total volume flow measurements downstream of the abatement unit.

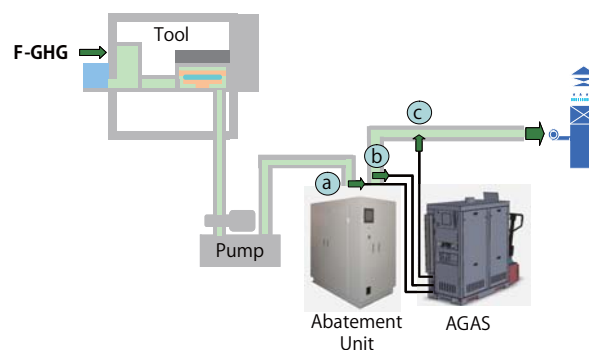


Fig. 2: Sampling at abatement inlet (a) & outlet (b).

3. Results and Discussion

3.1 Dilution Factor

Since the tool foreline pump and abatement unit introduce purge and combustion gases respectively into the effluent system, it is important to initially determine the dilution factor (DF) across the abatement unit. This is done by measuring the total volumetric gas flow (TVF) entering and exiting the abatement system. TVF upstream of the abatement unit is determined by introducing three flows of F-GHG process gas (S_f) from the tool and measuring the F-GHG concentration (C_{ef}) at the abatement inlet (Fig. 3).

Similarly, the TVF downstream of the abatement unit is determined by flowing three flows (S_f) of Kr tracer gas back into the abatement inlet at sampling point (a) in Fig. 2 from the AGAS and measuring

the Kr concentration (C_{ef}) at the abatement outlet (point b in Fig. 2) using the QMS. A similar temporal concentration plot to that in Fig. 3(b) is obtained. The TVF is calculated using the expression:

$$TVF = S_f / C_{ef} \times 10^{-6}$$

The dilution factor across the abatement unit is calculated using:

$$DF = TVF_{out} / TVF_{in}$$

The EPA protocol requires that certain criteria are met to prove that data are statistically sound. Firstly, a minimum of 40 FTIR data points (or 60 QMS data points) must be collected and used in calculations. Secondly, all measurements must have a relative error of <5% and thirdly, calibration curves must have at least 5 points and a correlation coefficient of 0.98 or more. The AGAS system has on-board gas standards and a dilution manifold for instrument calibration to meet these criteria.

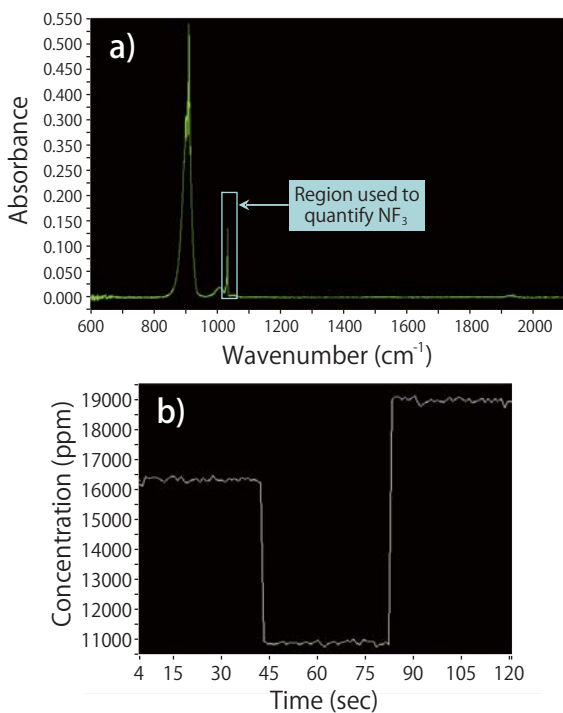


Fig. 3: (a) IR spectrum (from short path FTIR) showing region used for NF₃ quantification. (b) Temporal NF₃ concentration measured at abatement inlet as three NF₃ flows were introduced from the tool (plasma off).

3.2 Abatement System DRE

DRE testing of abatement units may be performed in two ways according to the EPA Protocol. In EPA Method 1, the process tool plasma (RF) is off during data collection and process gas is introduced from the process tool at three flow rates resulting in steady state conditions at each flow rate. Concentration

measurements are made at the abatement inlet and outlet in the same way as for TVF and together with the DF are used to calculate the DRE according to:

$$DRE_1 = (1 - (C_{out} \times DF) / C_{in}) \times 100$$

As shown in Fig. 4 the combustion products from the abatement step significantly complicate the IR spectrum in the abatement effluent and must be accounted for in the F-GHG quantification. Fig. 5(a) shows the expanded spectral region from Fig. 4 used to quantify NF₃ in an abatement effluent during DRE testing by Method 1.

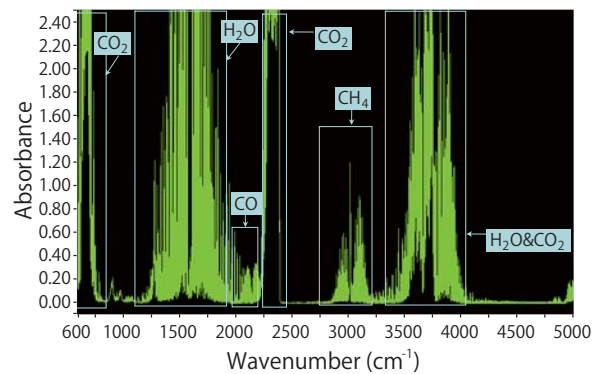


Fig. 4: IR spectrum of abatement effluent showing presence of large amounts of H₂O, CO₂, and CH₄.

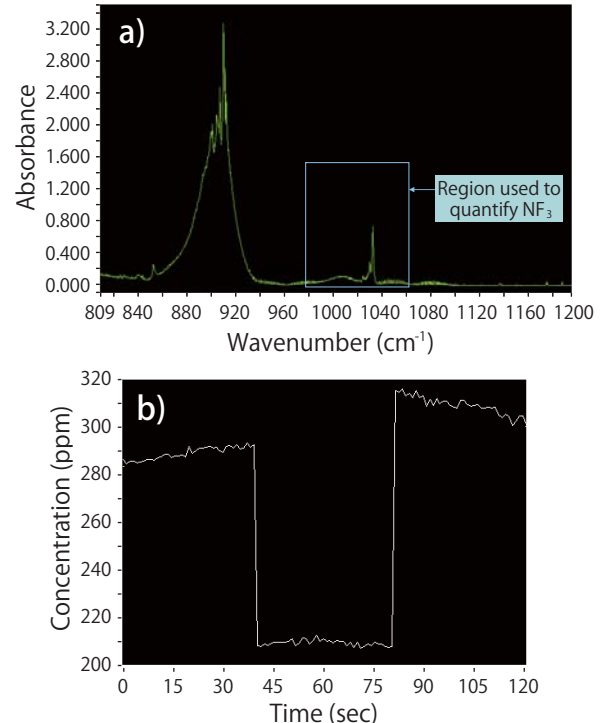


Fig. 5: (a) Expanded IR spectrum (from long path FTIR) of the abatement unit effluent, showing detectable NF₃ and region used for NF₃ quantification (b) Temporal concentration of NF₃ measured downstream of an abatement unit as three flows of NF₃ were introduced from the process tool (plasma off).

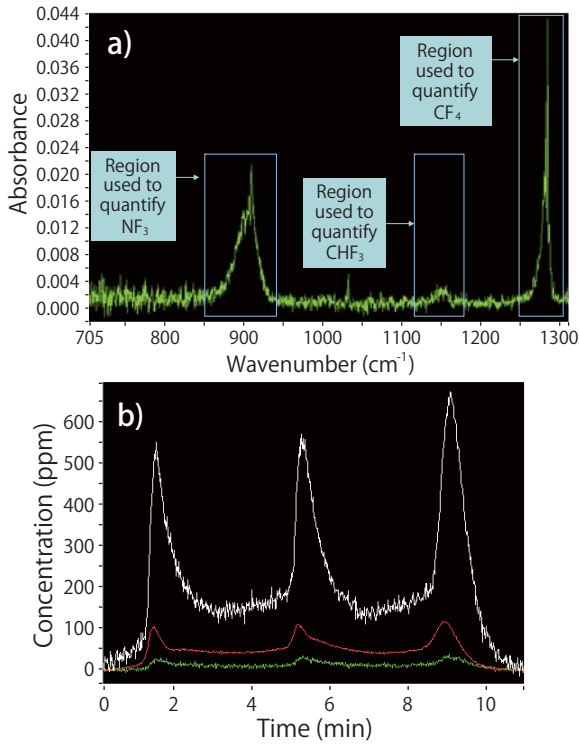


Fig. 6: (a) Representative IR spectrum (from short path FTIR) of process tool effluent measured upstream of an abatement unit during a chamber clean process. Regions used to quantify NF_3 , CHF_3 , and CF_4 are highlighted. (b) Temporal concentration (ppm) profiles of NF_3 (white), CF_4 (red), and CHF_3 (green) measured upstream of an abatement unit during three sequential chamber clean processes (Method 2) with plasma on.

The temporal concentration of NF_3 measured in the abatement effluent as three steady state flows were introduced from the process tool with the RF plasma off is shown in Fig. 5 (b). Although Method 1 has the advantage of steady state conditions and simpler calculations, it does not reflect real abatement performance under process conditions because when the process tool is off by-product gas/gases will not be generated or measured.

EPA Method 2 involves collecting data during actual process conditions and is therefore preferred over Method 1. It requires no modification to the process tool for either process or by-product DRE measurements and again concentration measurements are made at the abatement inlet and outlet. However, with Method 2, as concentrations are non-steady state, the total volume of process gas entering (V_{in}) and exiting (V_{out}) the abatement system must be estimated by integrating the FTIR signal over time using the following expressions.

$$\text{DRE}_2 = (1 - V_{out} / V_{in}) \times 100$$

$$V_i = \int_0^T V_i(t) dt = \sum_{j=1}^N F_j C_j \Delta t = F \sum_{j=1}^N C_{ij} \Delta t$$

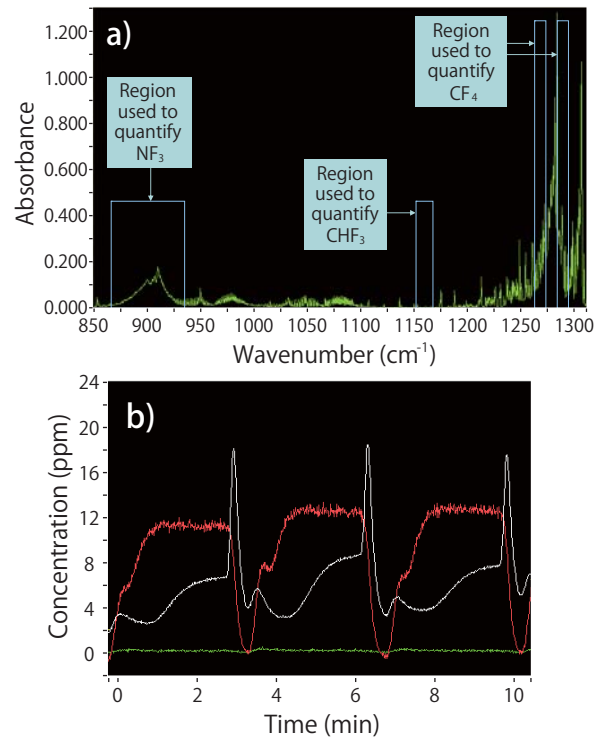


Fig. 7: (a) Representative IR spectrum (from long path FTIR) of an abatement unit effluent measured during a chamber clean process. Regions used to quantify NF_3 , CHF_3 , and CF_4 are highlighted. (b) Temporal concentration (ppm) profiles of NF_3 (white), CF_4 (red), and CHF_3 (green) measured downstream of the abatement unit during three sequential chamber clean processes with plasma on.

Where i denotes either the outlet or inlet F-GHG gas, F denotes the corresponding inlet or outlet flow, Δt denotes the integration interval, C_{ij} denotes the concentration of F-GHG either entering or exiting the abatement system and the sum is taken over the period T of production processing. When monitoring real processes, not only the process gas/gases but also any reaction products formed must be measured, so data processing is more complicated in EPA

Method 2 and spectral regions must be carefully selected for accurate quantification. Fig. 6(a) and Fig. 7(a) show representative IR spectra of a process tool effluent measured upstream and downstream of an abatement unit during a NF_3 chamber clean process respectively. The spectra show regions used to identify and quantify NF_3 as well as CHF_3 , and CF_4 .

Temporal concentration (ppm) profiles of NF_3 , CHF_3 , and CF_4 measured at the abatement inlet during three sequential NF_3 chamber clean processes are shown in Fig. 6(b). Corresponding data for the three components measured downstream of the abatement unit are shown in Fig. 7(b). The results show the analytical potential of the AGAS for real time multi-species detection and for making DRE measurements.

4. Conclusion

Recent US legislation now requires that large semiconductor facilities count their F-GHG emissions. To achieve this either the DRE of point of use abatement units must be measured or a default DRE value of 60% must be used. Matheson's AGAS is a compact, portable and fully integrated unit that is being used for DRE testing at customer sites. It contains one QMS and two FTIR instruments that are used to measure F-GHG or Kr tracer concentrations at the abatement unit inlet and outlet.

The data presented in this paper show the capability of the AGAS for simultaneous real-time multispecies analysis of the two sample streams. The unit has sample pretreatment capability (particle filtration, dehumidification and HF removal traps)

as well as on-board gas standards and a dilution manifold for instrument calibration. These features enable rapid DRE testing according to the EPA Protocol and therefore minimize tool downtime.

References

- 1) EPA 40 CFR Part 98, Part II, "Mandatory Reporting of Greenhouse Gases: Additional Sources of Fluorinated GHGs: Final Rule" December 1, 2010.
- 2) EPA 430-R-10-003, "Protocol for Measuring Destruction or Removal Efficiency (DRE) of Fluorinated Greenhouse Gas Abatement Equipment in Electronics Manufacturing", March 2010.
- 3) International SEMATECH (2006). Guideline for the Characterization of Semiconductor Process Equipment, International SEMATECH Technology Transfer # 06124825A-ENG, December 22, 2006.
- 4) PFC Emission Analysis, Taiyo Nippon Sanso Technical Report, 27, 58 (2008).