Monitoring of volatile vacuum species using remote optical emission spectroscopy

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Outline of the talk

- Explanation of the Remote Plasma Emission (RPEM) method
- Gas detection and quantification by RPEM
- Examples of data from ALD, Etching and solvent analysis
- Conclusions
RPGA vs RGA

OPTIX – remote plasma gas analysis (RPGA)
Optical method

Remote plasma

Quadrupole Residual Gas Analyzers (RGAs)

Low ppm detection
OPTIX Remote Plasma Gas Analysis RPGA

Vacuum process 0.5 to $10^{-6}$ mbar or with a rotary pump to support atmospheric sensing

Wide pressure range remote plasma generator

High intensity plasma

Spectrum analysis gives species composition

Wide range spectrometer 200-850nm
OPTIX operates in the typical plasma processing pressure range

Easy to use and wide operating range

Plasma has some non-linearity

Plasma light intensity too low

1E-6 mbar – 0.5 mbar

RGA

RGA with differential pump

Operating Pressure (mBar)
OPTIX vacuum based applications

- Evaporation
- Sputtering
- CVD / PECVD
- MF/RF Plasma surface treatment

Pressure (mbar): 1E-6, 1E-5, 1E-4, 1E-3, 1E-2, 1E-1
OPTIX Plasma Generation

Unlike RGA’s OPTIX detector is separated from the chemicals by an optical window – more rugged – detector cannot contaminate

- Purpose designed and patented plasma generation source
- Very wide range of operation - Plasma present from 0.5 to $10^{-6}$ mbar
- Fast current feedback control
- Constant current = constant excitation source
- DC mode as standard for 95% of applications, Pulsed DC for highly contaminating atmospheres
- Atmospheric sampling via simple mechanical pump – no turbo required
Software Spectrum View - spectrum displays the constituent species of the plasma

The various gas peaks are automatically identified.
Software Gas Tracking View
Quantification of gas levels using RPGA

- The sensor results as displayed in the raw spectrum are **qualitative** due to the interaction of different gases within the vacuum.
- Even quantities of a gas are equally likely to be collide with free electrons.
- Gencoa have developed a mathematical treatment to accurately calculate gas partial pressure.
Quantification - Pressure limitations

- Higher currents give a superior signal to noise ratio but at the expense of upper operating pressure limit.
- Maximum linear operating range can be achieved with a lower current setpoint – OPTIX can select the current via the user interface.
Quantification of gas partial pressures – Plasma Power correction

- The power delivered to the plasma generator will modify the emission intensities and hence distort the gas partial pressure measurement.

- A correction factor based on the measured power can be applied to the emission to remove this effect.
Quantification - Power correction

- The effect of the correction can be clearly seen when compared with a differentially pumped RGA
Quantification of gas levels using RPGA

- Introduction of a >> larger quantity of an additional gas will reduce the likelihood of electron impact on species of a << smaller quantity
- This will have an effect of suppressing the emission of these species
- The OPTIX has a correction algorithm for the gas interaction effect to allow accurate quantification of the gas partial pressures
Quantification – Gas interaction

Experimental setup

- The most significant challenge for quantification of the sensor readings is the interactivity of gases.
- Without correction the readings are **relative** not absolute.
- i.e. increasing partial pressure of one gas will lead to a reduction in the readings of other gases.
- An experimental setup was constructed to investigate this effect and to demonstrate the correction method.

Gas input – Ar, N₂, O₂

- Diff. pumped side
- High pressure side
Quantification – Gas interaction

- Ar, N₂, and O₂ were mixed in varying quantities
- Total pressure variation was from 1E-5 to 2E-2 mbar on the high pressure side
- Differentially pumped side was kept below 1E-4 mbar

![Graph showing pressure over time for 28 amu (N₂), 32 amu (O₂), and 40 amu (Ar)]

![Graph showing total pressure for OPTIX side over time]
Gas interaction effects can be clearly seen on the OPTIX readings resulting in different partial pressure measurements compared to the RGA.
Quantification – Accurate gas partial pressure measurements after the gas effect correction algorithm is used

- An algorithm can be used to correct for the interaction effects
- Partial pressures can then be derived
Remote Plasma Gas Analysis
Highly Sensitive Optical Method

Which species can be observed?

• Atomic emissions and molecular emissions

• Larger molecules are observed as fragments – due to disassociation in the sensor’s plasma

Isopropanol (CH₃CHOHCH₃)
Caveats and considerations when using Remote Plasma Gas Analysis - Disassociation

- “Fingerprints” of the original molecule

Graph showing emissions from different molecules and energy transitions:
- Isopropanol (CH₃CHOHCH₃)
- Acetone (CH₃COCH₃)

Energy levels and transitions:
- $A^2\Pi - X^2\Pi$ for CO₂⁺
- $B^1\Sigma - A^1\Pi$ for CO
ALD monitoring experimental setup

University of Liverpool

Dr. Richard Potter and Ben Peek

ALD reactor
Optix
Rotary pump
Precursor detection

**NH₃**

NH (328 nm)

NH (336 nm) overlapping with smaller N₂ peak at 337 nm)

Suppression of residual nitrogen
Atomic layer deposition precursor monitoring

$\text{NH}_3$

Injection
Precursor detection

NH₃

NH (328 nm)

NH₃ only

NH₃ with Ar
Precursor detection

\[ \text{H}_3\text{C}-\text{Al}-\text{CH}_3 \]

TMA

- \text{OH (283 nm)}
- \text{OH (310 nm)}
- \text{CH (431 nm)}
- \text{H (656 nm)}

Wavelength (nm)
Atomic layer deposition precursor monitoring

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{Al} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{TMA}
\end{align*}
\]

Injection

TMA Ar chamber injection (1 sec int, 900uA DC), with heating
Deposition cycle monitoring

Synchronisation of the CCD capture with the ALD pulse
Deposition cycle monitoring

Synchronisation of the CCD capture with the ALD pulse

- A series of CCD spectrum captures is synchronised with each precursor injection
Deposition cycle monitoring

Synchronisation of the CCD capture with the ALD pulse

- The H maxima of each precursor pulse was recorded
Application Example Atomic layer deposition precursor monitoring
Deposition of NbN via PEALD

ALD user, Japan

- Detection of TrisNb via CH, N and H

- Detection of NH\textsubscript{3} via N and H
OPTIX Atomic layer deposition precursor monitoring

NbN deposition step

Species concentration (% of sensor full scale)

Time (s)

- NH₃ + Ar
- Plasma on
- TrisNb
- MFC bleed and purge
- Cycle repeats

- N₂⁺ (391.5nm)
- H (656.3nm)
- Ar (750.2nm)
- CH (387.2nm)
ALD Monitoring – Full process for 2.7 hours

Deposition of NbN via PEALD
Atomic layer deposition precursor monitoring

Deposition of NbN via PEALD

- Sensor is robust of the full 2+ day deposition cycle and displays variations in the process over a longer period.

![Graph showing species concentration over time](image-url)
Application Example - Characterising a reactive ion etch process

Detection of reactive ion etching effluent in the process backing line

Processing chamber

Etch head

CF4

Ar

Optix

Pressure 4E-2 mbar

N2 purge

Roughing pump
CF$_4$ detection (no Ar background)
CF4 detection (Ar background)

- 40 sccms
- 20 sccms
- 10 sccms
- 5 sccms
Acetone has a higher CO reading due to the presence of a CO bond.
Remote PEM combined with spectroscopy can perform “RGA-like” functions

Can use this method directly at higher process pressures – no need to differentially pump unless atmospheric sensing

The detector is separated from the vacuum environment hence not affected by hostile chemistry present in the vacuum

OPTIX is hence less sensitive to contamination than RGA’s, can be used for ’dirty’ hydrocarbon environments as well as etch, CVD and ALD type processes.

This sensing technique is highly robust – plasma generator will not contaminate or stop functioning