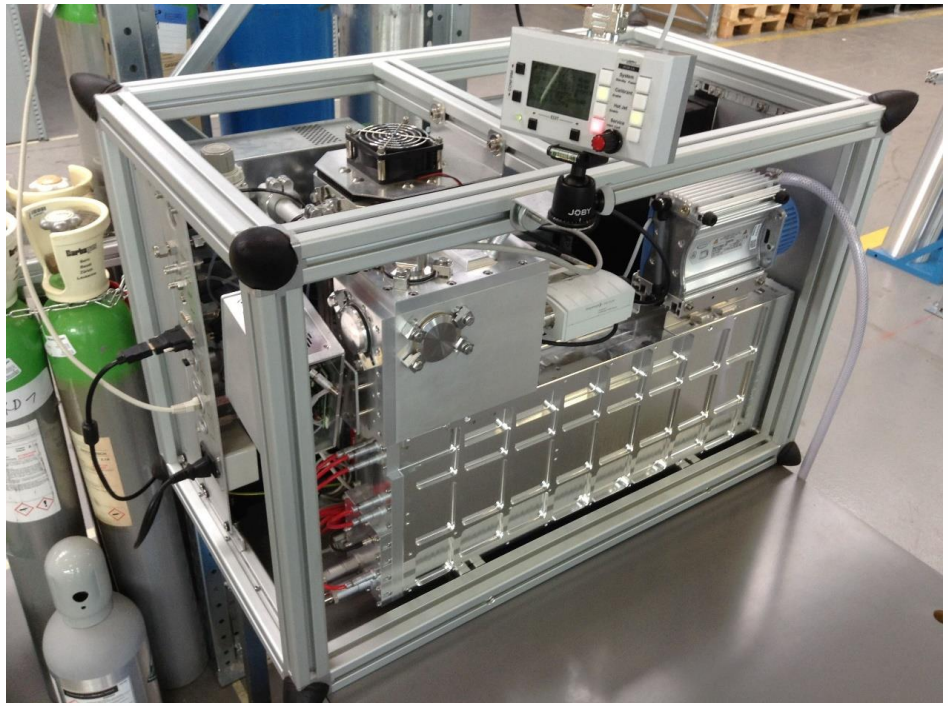
pgaTOF

Fast, Sensitive TOFMS for Process Gas Analysis

09/24/2020

pgaTOF Models



pgaTOF Models

Property	pgaTOF S	pgaTOF R	pgaTOF 2R
Analyzer	CTOF	HTOF	LTOF
Mass Resolving Power R =	800 Th/Th	4000 Th/Th	8000 Th/Th
Mass Range	1000 Th	1000 Th	1000 Th
Mass accuracy	< 2 mTh		
Dynamic Range			
Max. Spectra Rate	1000 Hz	1000 Hz	1000 Hz
Size W x D x H	47 x 47 x 100 cm	cm	48 x 62 x 148 cm
Mass m =	90 kg	85 kg	160 kg
Power Consumption P =	490 W	320 W	550 W
Line Power	110 VAC – 250 VAC / 50 – 60 Hz / 1 phase		
Power Connector			
Exhaust Connector			
Comments			

GC-TOF Technical Specifications

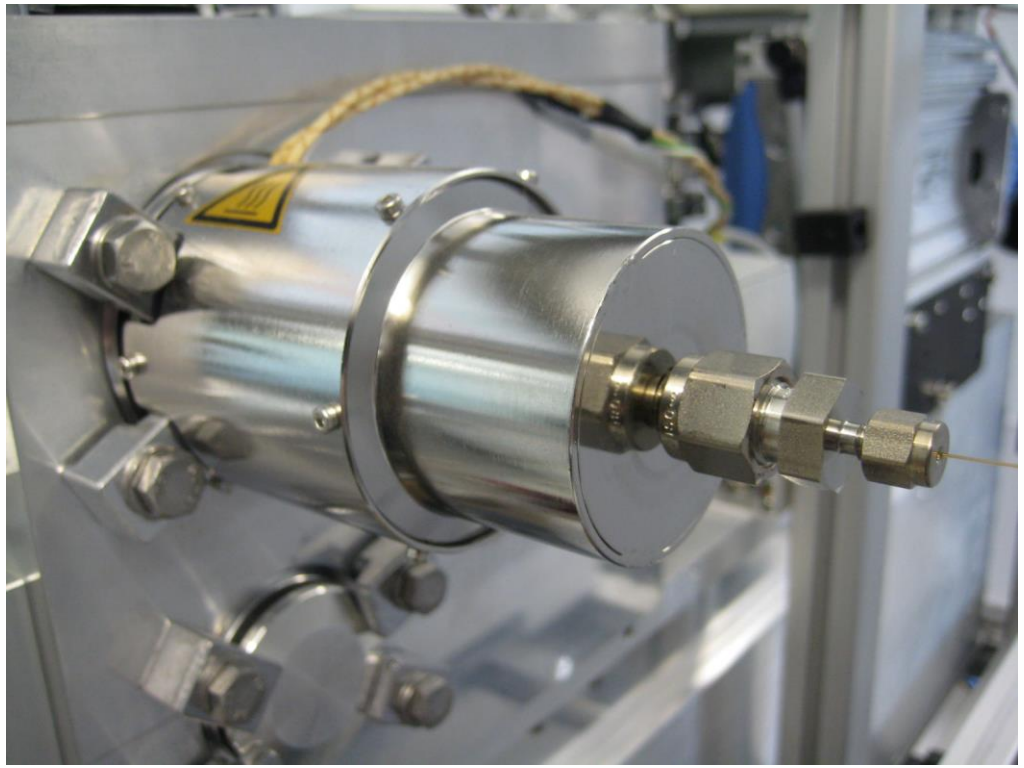
Property	
Resolving power	700 (M/ΔM)
Mass range	1 – 1000 Th
Mass accuracy	< 2 mTh
Dynamic range	$2x10^5$ (10 ms) $1x10^6$ (1 s)
TOF extraction frequency	100 kHz
Spectra download rate	400 Hz
Linearity	< 2%
Ionization	EI, Soft EI, CI

Sensitivity	
LOD (3σ) BTX (100 µl, 50 ppb)	< 200 ppt
LOD (3σ) OFN (1pg on column)	5 fg
signal/LOD OFN (1pg on column)	> 50

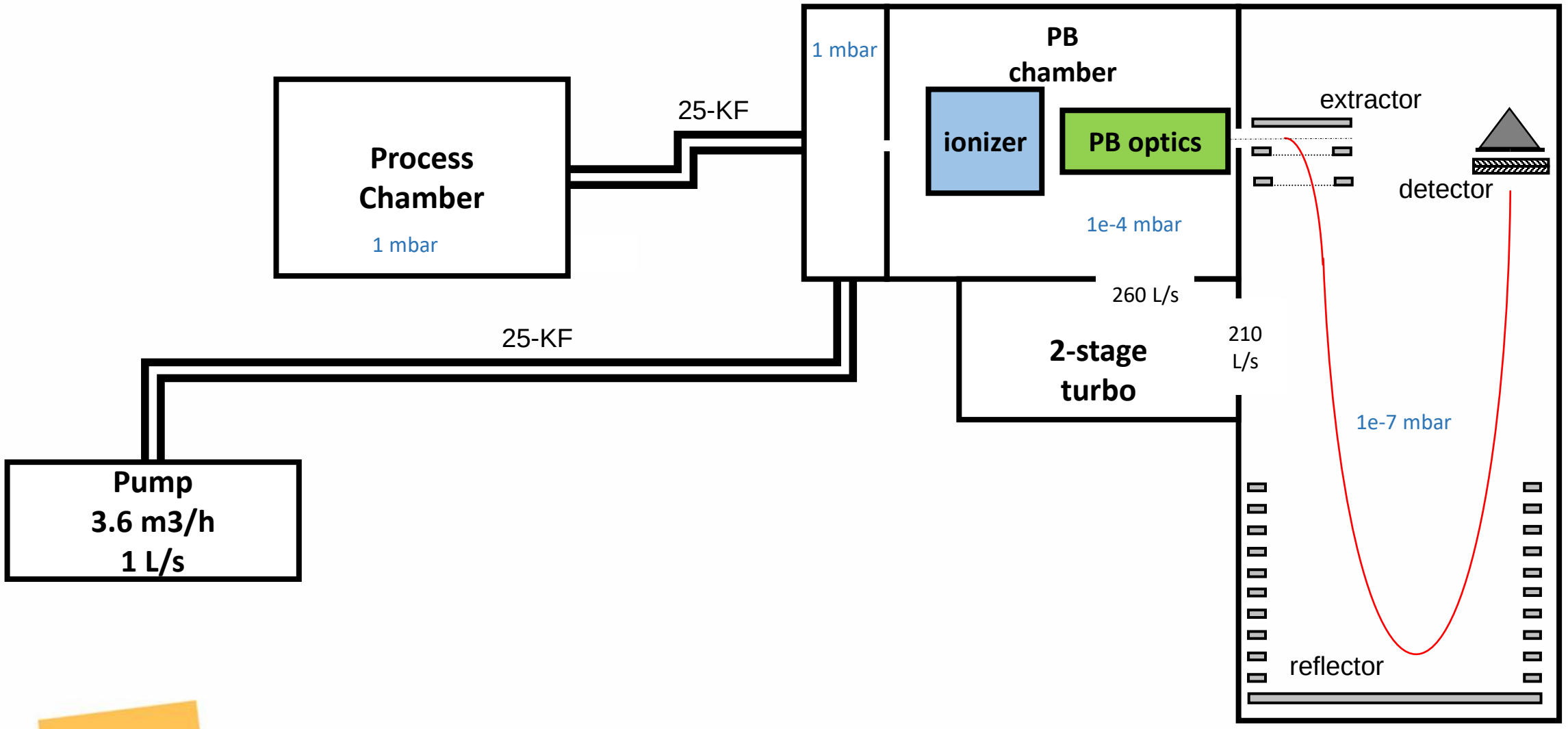
pgaTOF sample gas inlet

Not heated

Heated



Vacuum Scheme



MS components

DAQ

- 1.6 GS/s 14-bit ADC with up to 1000 ions/(peak*extraction)
- NDiS167 PC

Vacuum

- Diaphragm fore pump
- Split-flow turbo pump with large pumping speed

Giraff Controller

- A versatile controller that controls:
  - 3 x heaters
  - 2 x valves: vent valve and shipping valve
  - 1 x fore pump, 1 x turbo pump
  - 6 x pressure gauges
- Data of all these devices is written into the data files

Software

Thuner

- Instrument auto-optimization

TofDaq Library

- TOF specific functions to be called from any software

TofDaq Recorder

- Controls data acquisition (TofDaq library functions)
- HDF5 format (read by Matlab, Igor, IDL, etc)
- Real time data display

GCsquare

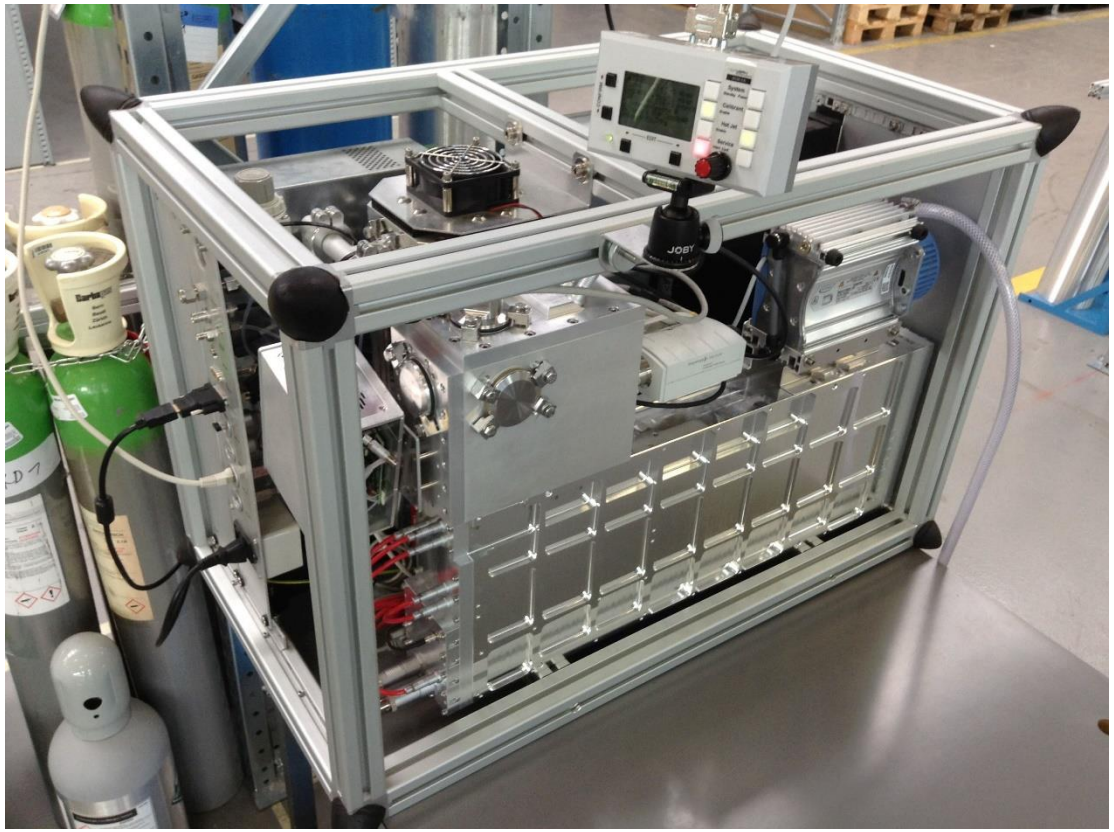
- Sets up and runs GC methods
- Records, displays, and saves GC-TOF data
- Records time-monitoring GC-TOF measurements.

Etch and Atomic Layer Deposition (ALD) Process Gas Analysis by pgaTOF

09/24/2020

Instrumentation

pgaTOF



- Orthogonal extraction TOF
- Electron Ionization (EI) Ion Source
- Mass Resolving Power: up to 5000
- Mass Range: 1-5000 Th
- TOF extraction frequency: typically 40 kHz

- Control electronics, pumps, and PC included in frame
- Operate in any position
- Size: 85 x 57 x 48 cm
- Mass: approx. 90 kg
- Large pumping speed
- Power consumption: 320 W

Summary

pgaTOF

Two sets of experiments were conducted:

- In the first one, a pgaTOF was used to perform the following experiments:
  1. an Atomic Layer Deposition (ALD) reactor was used to perform Al_2O_3 thin film deposition and
  2. the same reactor was used to perform Si etching runs using XeF_2 (spontaneous or thermal etching)
  3. both input gases and reaction products were measured.
- In the second, data, using the same instrument, were collected during Si etch using CF_4 and CF_4/O_2 in two types of reactors.
  1. the first was in a remote plasma configuration; i.e. mainly neutral radicals are present
  2. the second was in a reactive ion etching configuration; i.e. neutral and ionic radicals and electrons are present

Limits, Capabilities, and unique selling points

pgaTOF

- We have demonstrated that significant process insight can be gained from the collected data. Process gases and reaction products mass spectra can be unambiguously assigned, and their time variation measured with a time resolution of few seconds. Their time variations and intensities scale well with the expected surface chemistries.

- Conclusions for both etch and deposition processes are that a pgaTOF instrument should permit:

    1. determination of the exact species at play even when complex chemistries are present,

    2. despite using a non-invasive pgaTOF configuration, time variation in the few seconds range can be easily monitored,

    3. the instrument's sensitivity/dynamic range, mass resolution, acquisition rate and the measured signal levels should easily permit monitoring onset of process chemistry changes; a must for:

    4. accurate end point detection determination,

        (1) flux calibration,

        (2) reactor state of health, etc.

Other Relevant Applications

pgaTOF

- Process Chamber State of Health (preventive maintenance, cleaning, Calibration)
- Process Gas Purity (precursors stability, storage tank outgasing, delivery hardware QC, etc.)
- Plasma Source Design (internal leaks, outgassing, etc.)

  (Multipole and new technology required for the 300 mm to 450 mm Process Transfer)
- Plasma Source Qualification (interaction with process gases, stability, etc.)

Basic Si Etch Chemistry

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Spontaneous Etching

- Si Etching with XeF_2

  XeF_2 -> XeF + F -> Xe + F_2; 2 Si + 2 F_2 -> SiF_4

Plasma Etching

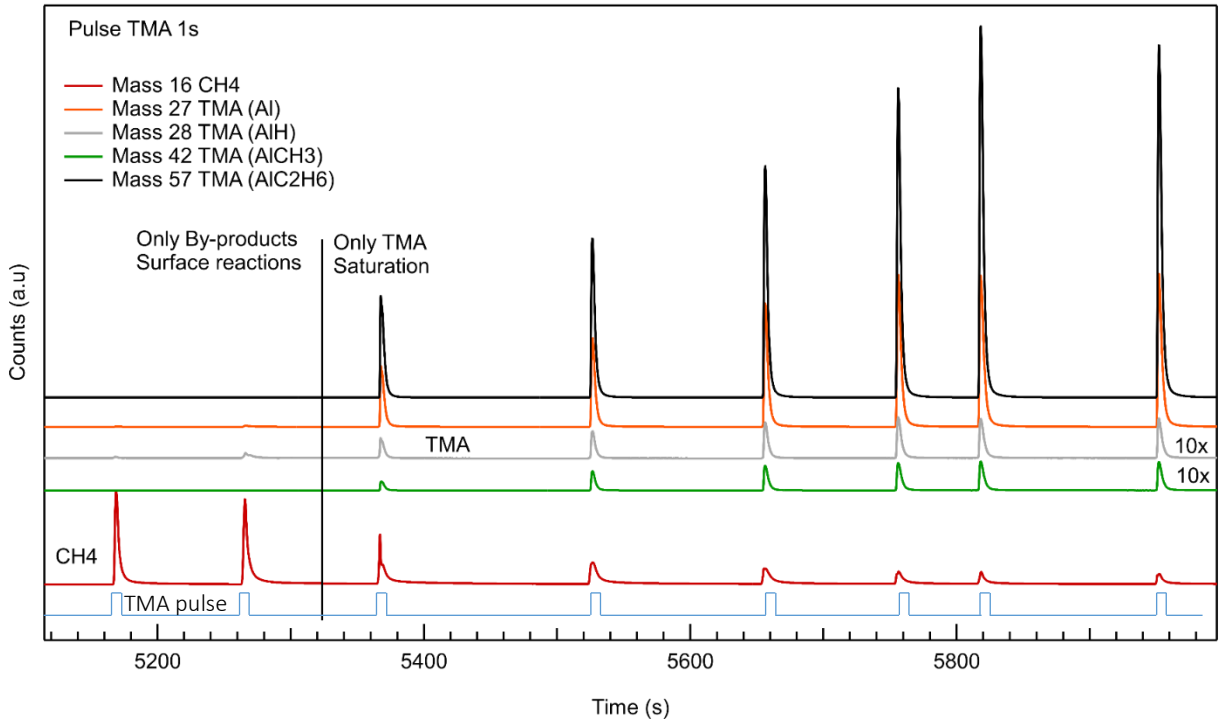
- Si Etching with CF_4 and CF_4/O_2

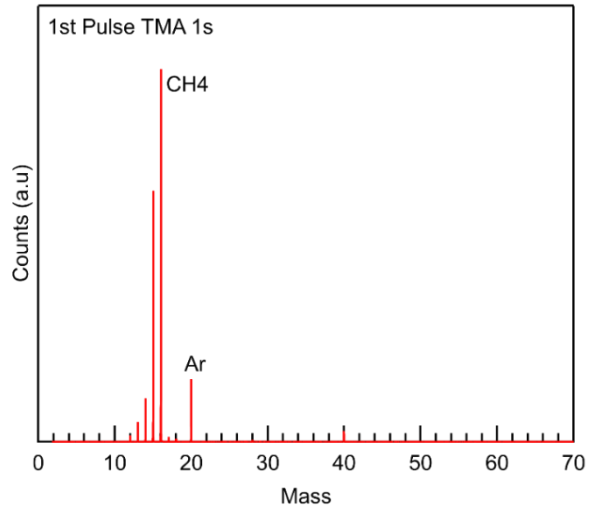
  Si + CF_4 -> SiF_4 + C; Si + CF_4 + O_2 -> SiF_4 + CO_2

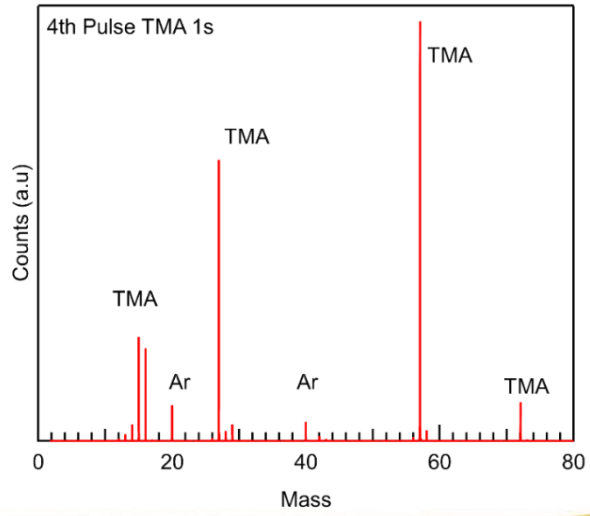
- **Note:** In a CF_4 plasma**,** non-volatile carbon compounds accumulate on the sample surface and hinder surface chemistry. Adding O_2 to the etch gas results in reaction of these non-volatile compounds and formation of CO_2, greatly increasing the etch rate

Mass Spectra of consecutive Pulses of TMA for saturation and self-limiting studies (similar results are found for H2O experiments)

- For every new precursor/process tested, saturation of the precursor inside the chamber needs to be guaranteed
- This shows the amount of precursor needed to ensure the reaction with all of the available surface groups in the chamber







1st Pulse TMA: Only By-products (CH_4)- All TMA pulsed into the chamber is consumed by surface OH groups- no TMA fingerprint detected

3th Pulse TMA: CH_4 still produced but with unreacted TMA- All surface OH groups reacted with TMA and the unreacted TMA is detected

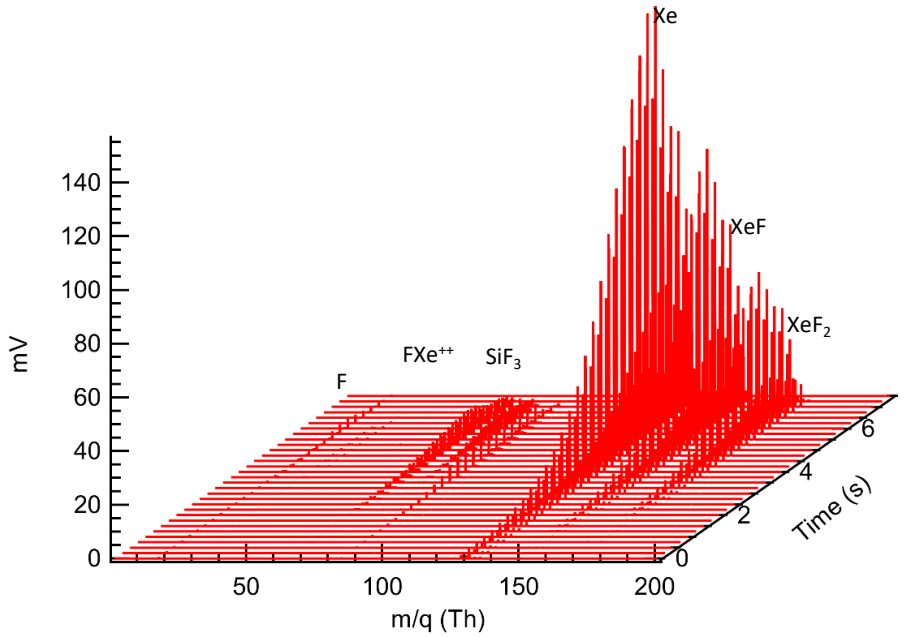
After 4th Pulse TMA: Only TMA is detected because all of the OH groups have reacted.- Saturation is achieved and Self-limiting behavior of the process is evidenced

~3 s of TMA are needed to react with all of the -OH groups in the surface of the chamber.

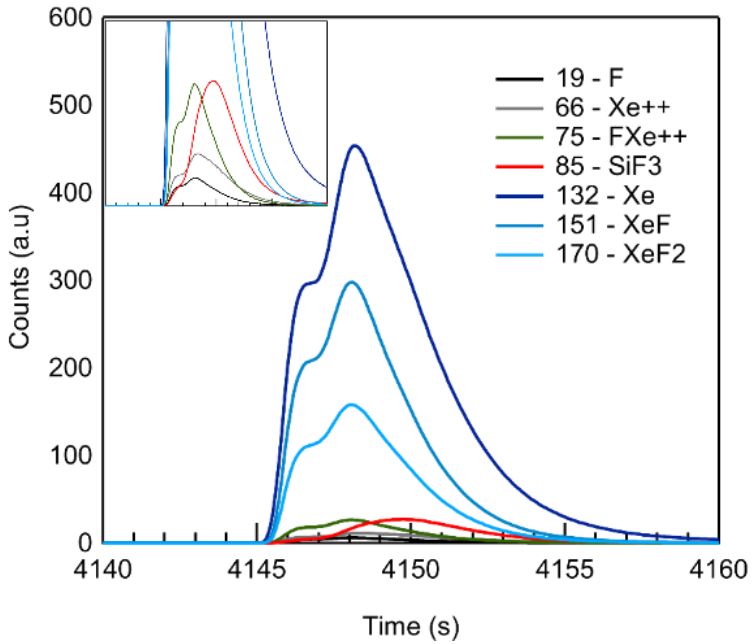
Spontaneous Etching: silicon etching with XeF_2

Detection of the immediate appearance and the time needed to purge out the by-products (SiF_3) and the unreacted XeF_2 unreacted precursor

Mass Spectra of a Silicon Etch process with XeF_2



Time-traces of selected analytes



- Analysis of all masses in real time
- Detection of all by-products and gas precursors in every cycle in the deposition process
- Monitoring the evolution of the deposition process
- Detection of anomalies during the etching process by setting a benchmark spectra at the beginning of each process.

Mass Spectra of a Silicon Etching process with XeF_2

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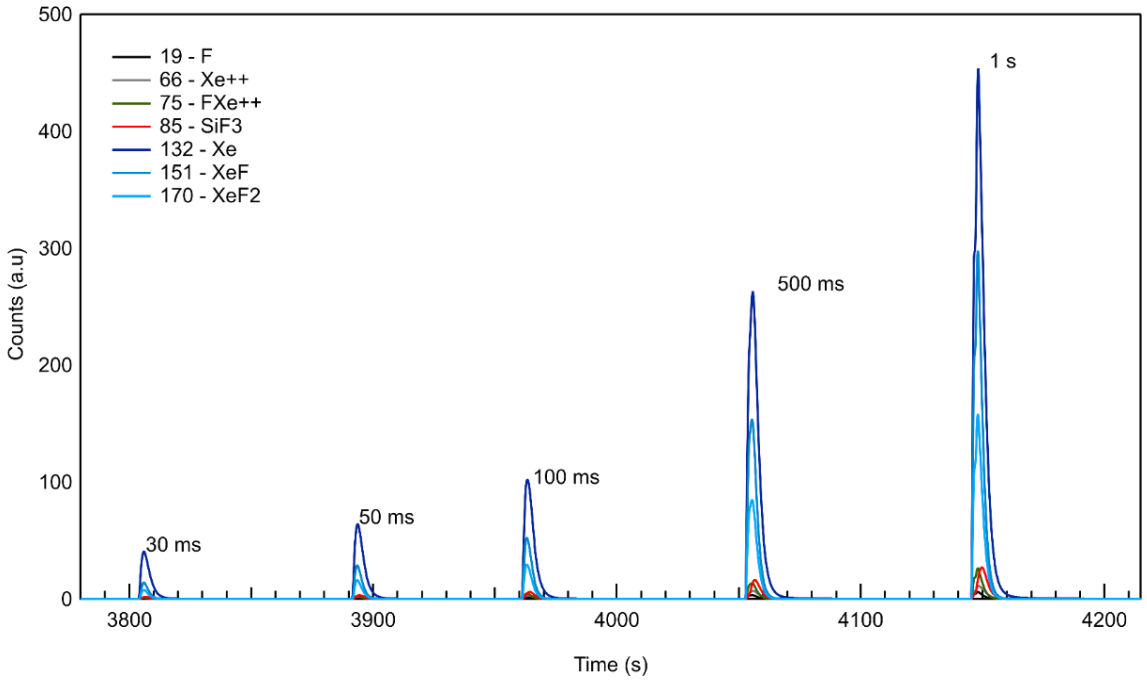
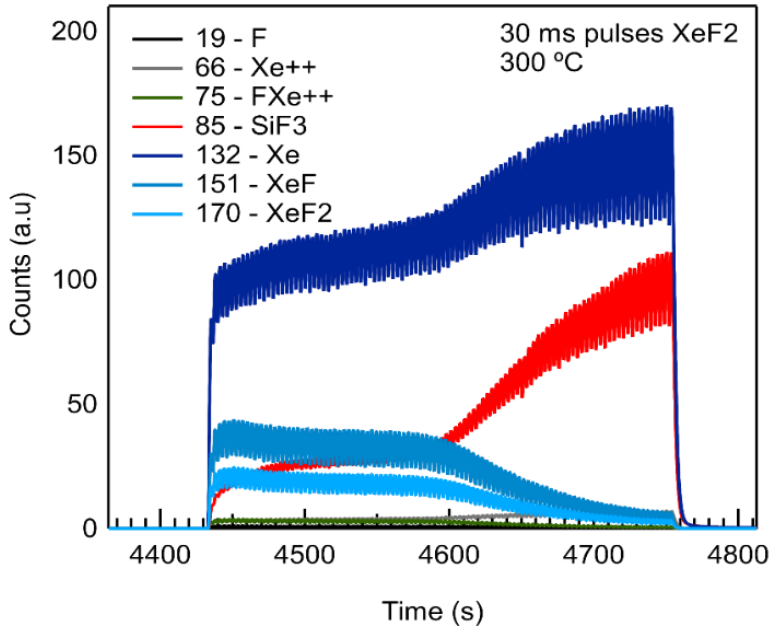
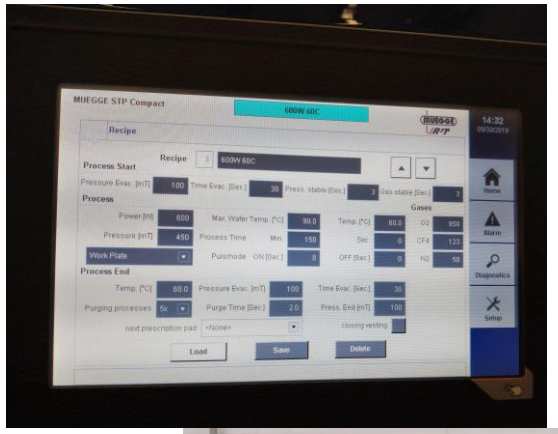
Detection of relative concentration of by-products and unreacted precursors as a function of pulsing times



Monitoring the evolution of a process for process quality control



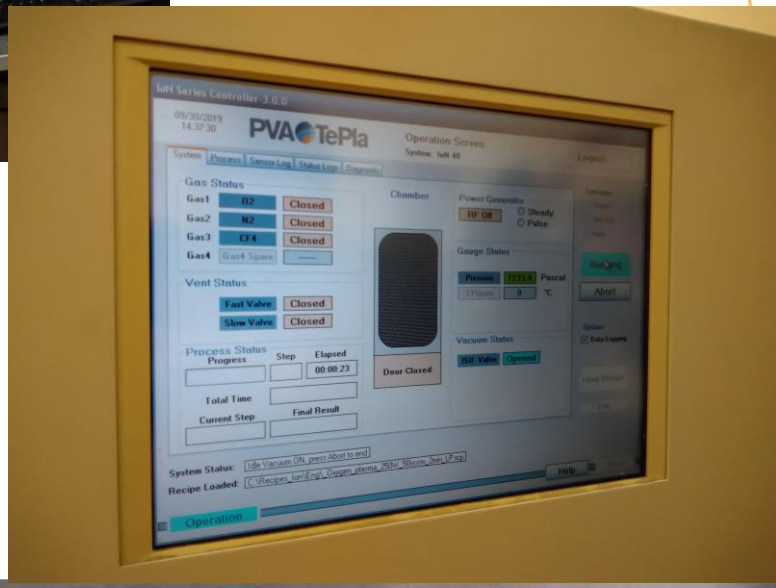
Remote Plasma Chamber



- Microwave Plasma
- Frequency: 2.4 GHz
- Pressure in chamber: 0.4 - 2.4 mbar = 0.3 - 1.8 Torr
- Gases: CF_4, O_2, N_2 and mixtures
- Plasma power: up to 1 kW CW
- Substrate can be heated up to 100 °C
- Plasma-Substrate distance: 30 cm

RIE Chamber (Reactive Ion Etching)

- RF Plasma
- Frequency: 13.56 MHz
- Pressure in chamber: 0.2 - 3 mbar = 0.12 – 2 Torr
- Gases: CF_4, O_2 and mixtures
- Plasma is direct, all substrate is inside the plasma
- Plasma power: Up to 600 W



Experimental conditions used for TOF

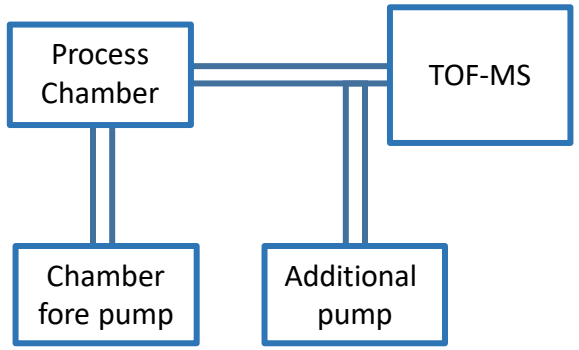
pgaTOF

pgaTOF Set Up

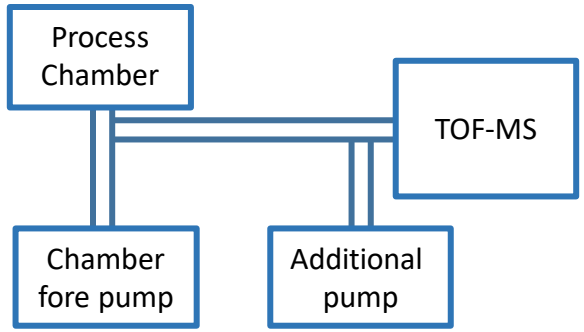
- Ion Source: Open Ion Chamber configuration
- Ion source temperature: 280 °C
- Ionization energy: 70 eV
- Mass range: 1-580 Th
- Spectral rate: 10 Hz
- Emission current: 0.1 mA
- Intense Ion Signals (e.g. CF_3+ ions – 69 Th) were blocked from entering the analyzer using Notch filter technology
- Sample flow into the pgaTOF ionizer was adjusted to 1-4 sccm

Connection of pgaTOF to etching chambers

- Remote Plasma Chamber

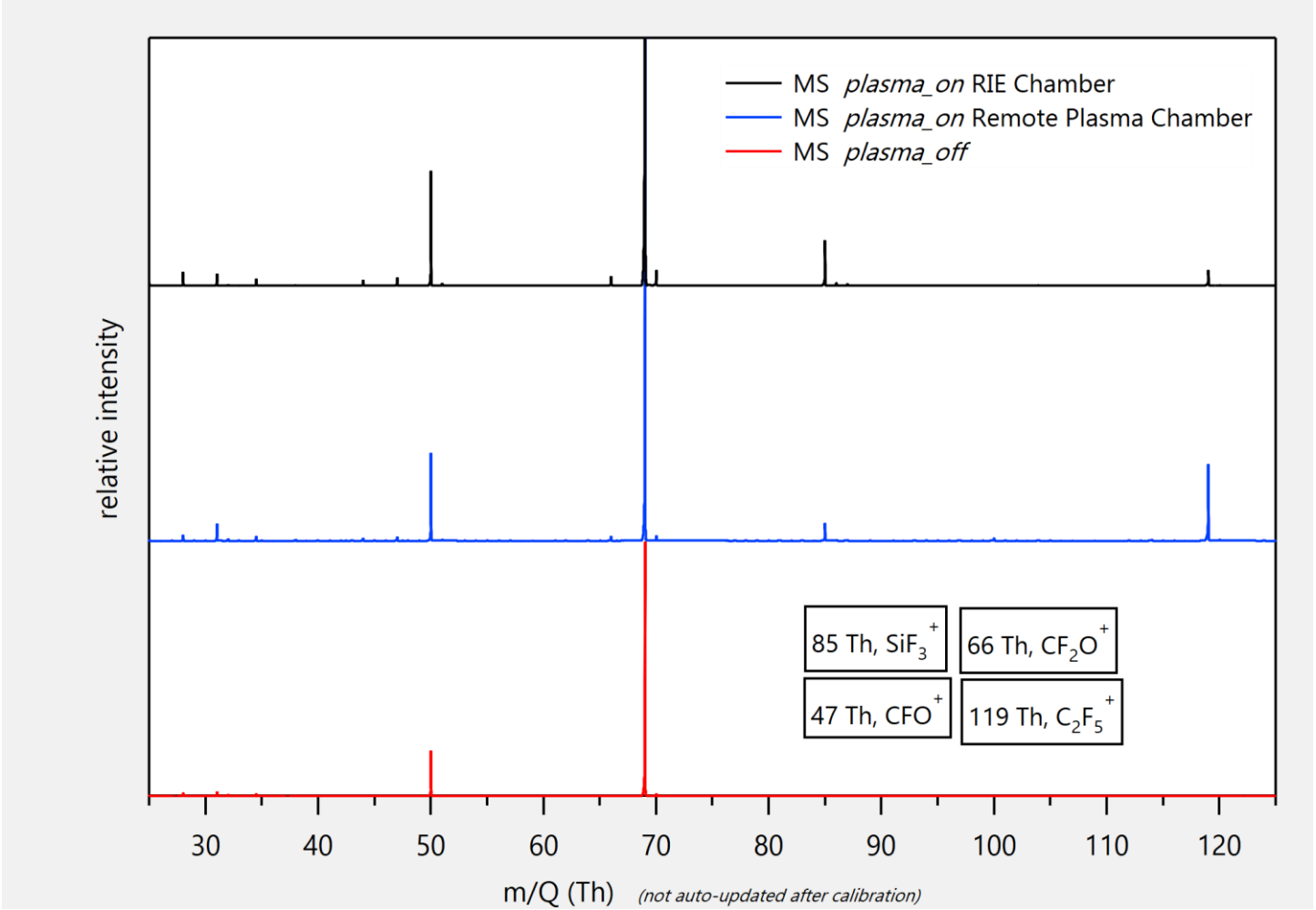


- Direct Plasma Chamber



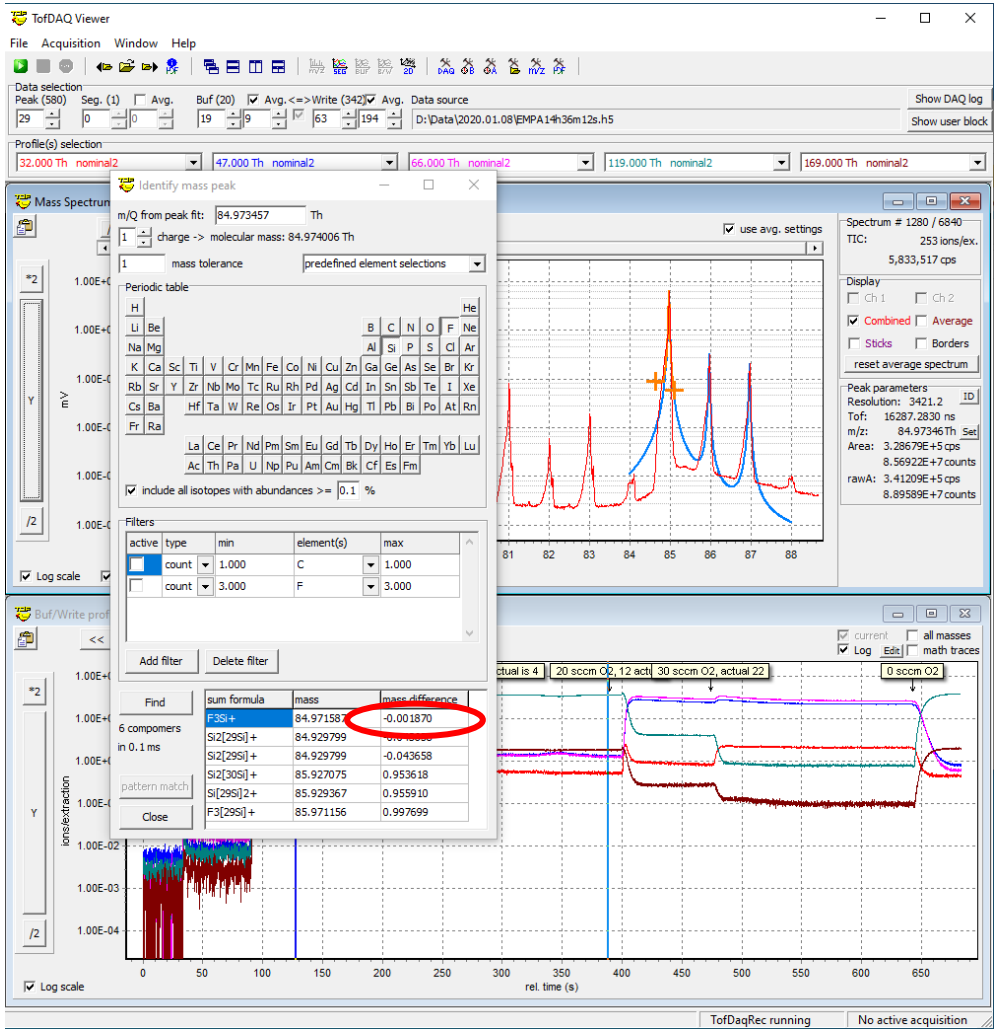
Results: mass spectra

- Plasma OFF/Plasma ON in the two chambers
- Plasma species ($C_2F_5^+$) and etching products (SiF_3^+) appear in the presence of plasma
- Plasma diagnostics: CFO^+ and CF_2O^+ indicate presence of O_2 in the chamber.



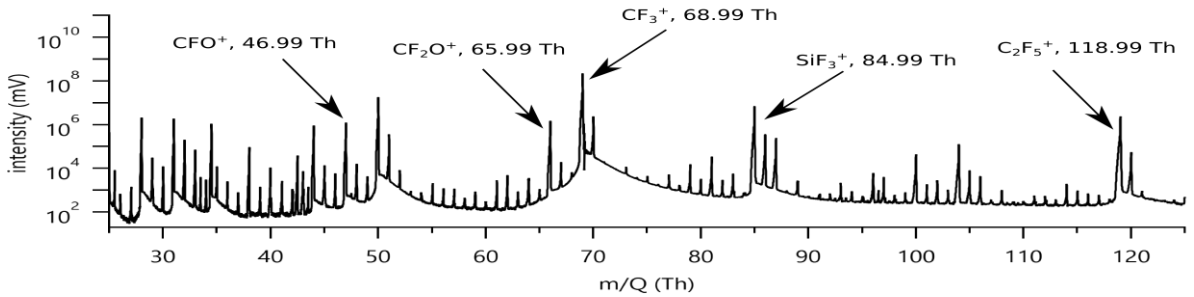
Mass spectra: analyte identification

- Unambiguous identification of species based on mass accuracy and isotopic distribution
- Example: identification of SiF_3^+:
  - Fitted curve (blue) for SiF_3^+ matches perfectly the measured spectrum (red)
  - Small mass difference between the measured peak and the calculated mass for SiF_3^+

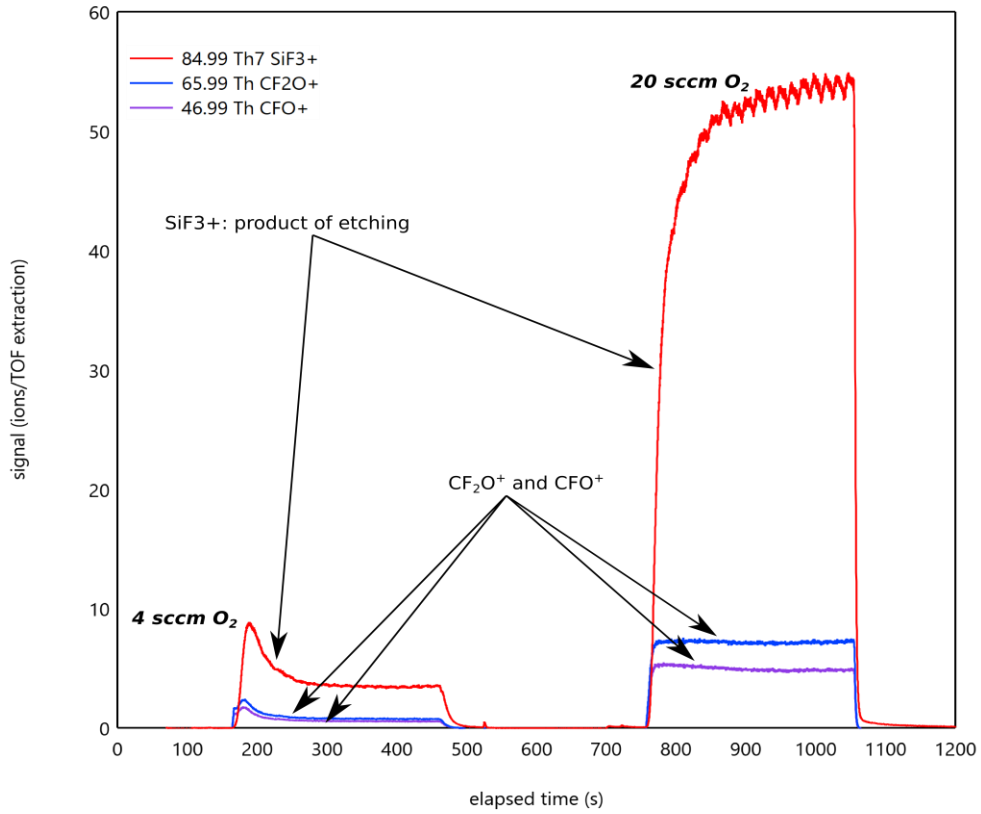


CF4 Plasma Etching of Si*

Typical Spectrum during an Etch run of Si in a CF_4/O_2 plasma



Time evolution of relevant species, Effect of O_2 addition on the Etch rate



- Real-time monitoring the evolution of etch gases and all reaction products
- Plasma diagnostics by screening time-traces of plasma species.
- High dynamic range permits monitoring of both abundant and trace level compounds.
- Sub-monolayer sensitivity
- Detection of etch rate changes/fluctuations due metrology tools malfunction/instabilities (i.e. O_2 flow oscillations)

***ETCH equipment provided by EMPA**

Time-Traces During Reactive Ion Etching (RIE)

Real time-trace of pertinent species

- Real time evolution of Plasma species and Etch products
- **Plasma diagnostics** during the Etching Process
- Screening **etch process dynamics:** different rise times of various species provide insight into key etch reactions and critical system's health parameters

At plasma ignition:

Higher etch signal (rate) and lower etch gas signal

During the process:

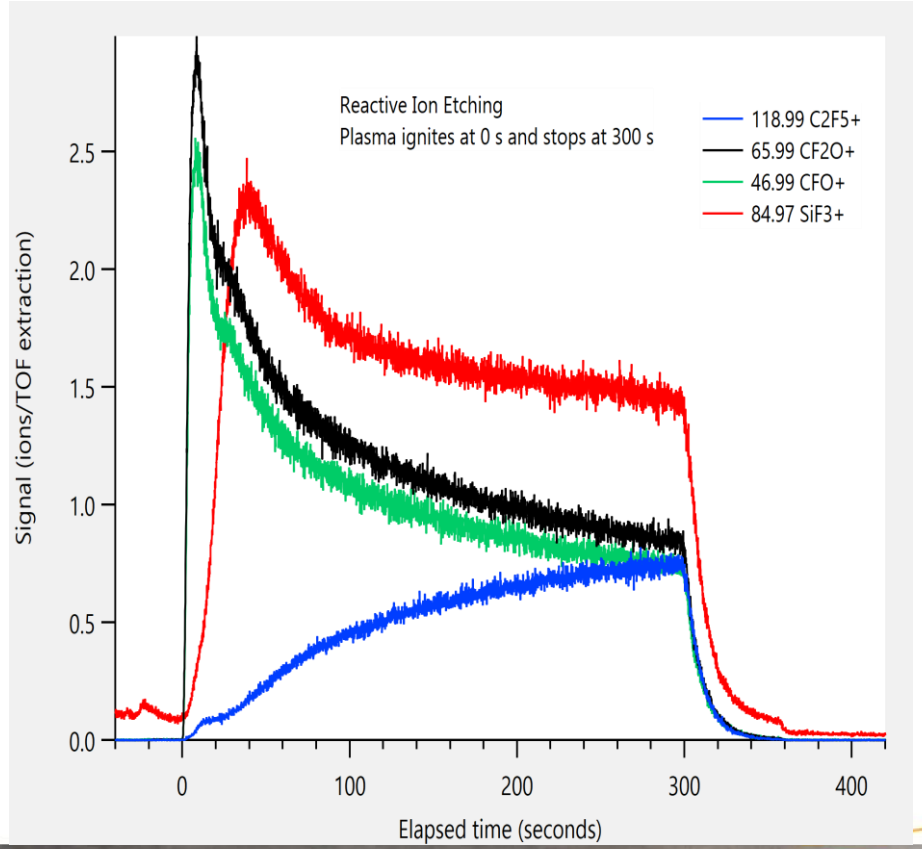
Etch signal drops while the etch gas signal increases

Insight:

The above behavior is consistent with an inefficient etch process due to non-volatile carbon products hindering the surface chemical reaction kinetics

Process Parameters:

- Chamber pressure: 405 mTorr
- O_2 flow: 0 sccm
- CF_4 flow: 100 sccm
- MW power: 300 W
- Pulsed plasma



Time-Traces During Remote Plasma Etching

- Following the time trace of pertinent species
  - Real time evolution of Plasma species and Etch products
  - **Plasma diagnostics** during the Etching Process
  - **Insight inside the etch process dynamics:** different rise times of various species provide insight into key etch reactions and critical system's health parameters

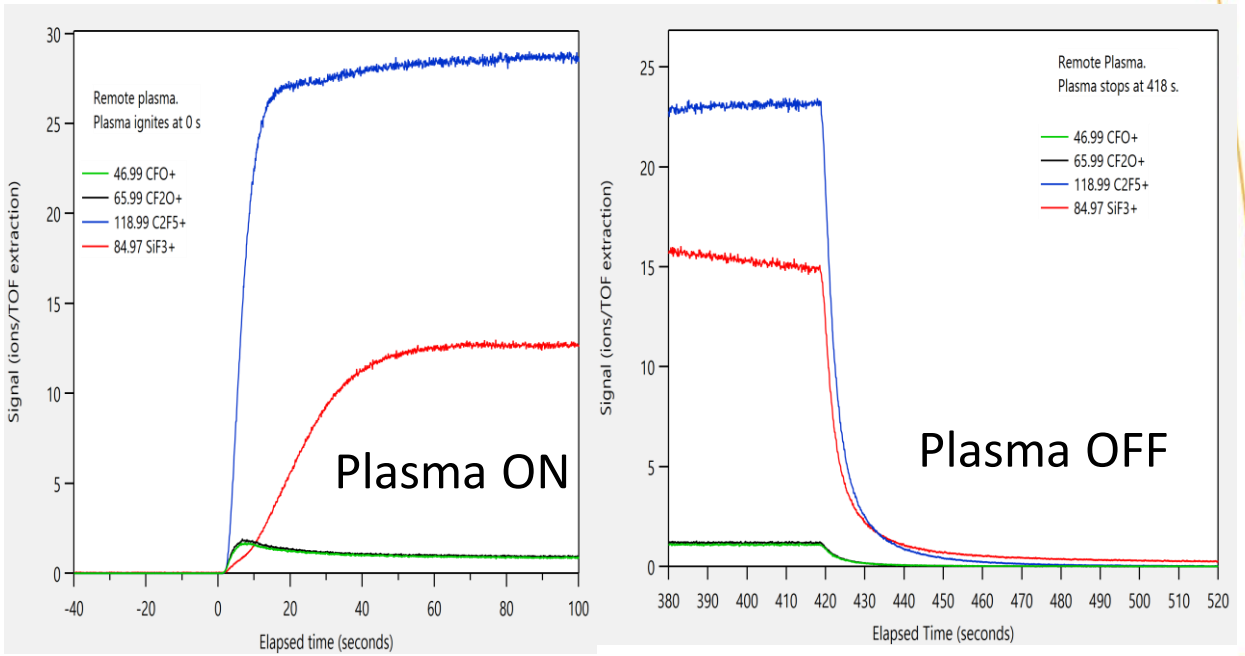
Process Parameters:
- Chamber pressure: 100 mTorr
- O_2 flow: 0 sccm
- CF_4 flow: 50 sccm
- MW power: 600 W
- Sample temperature: 50 °C

Observation:

The etch product and etch gas signals are stable throughout the process

Insight:

Higher etch radical density is present under these conditions

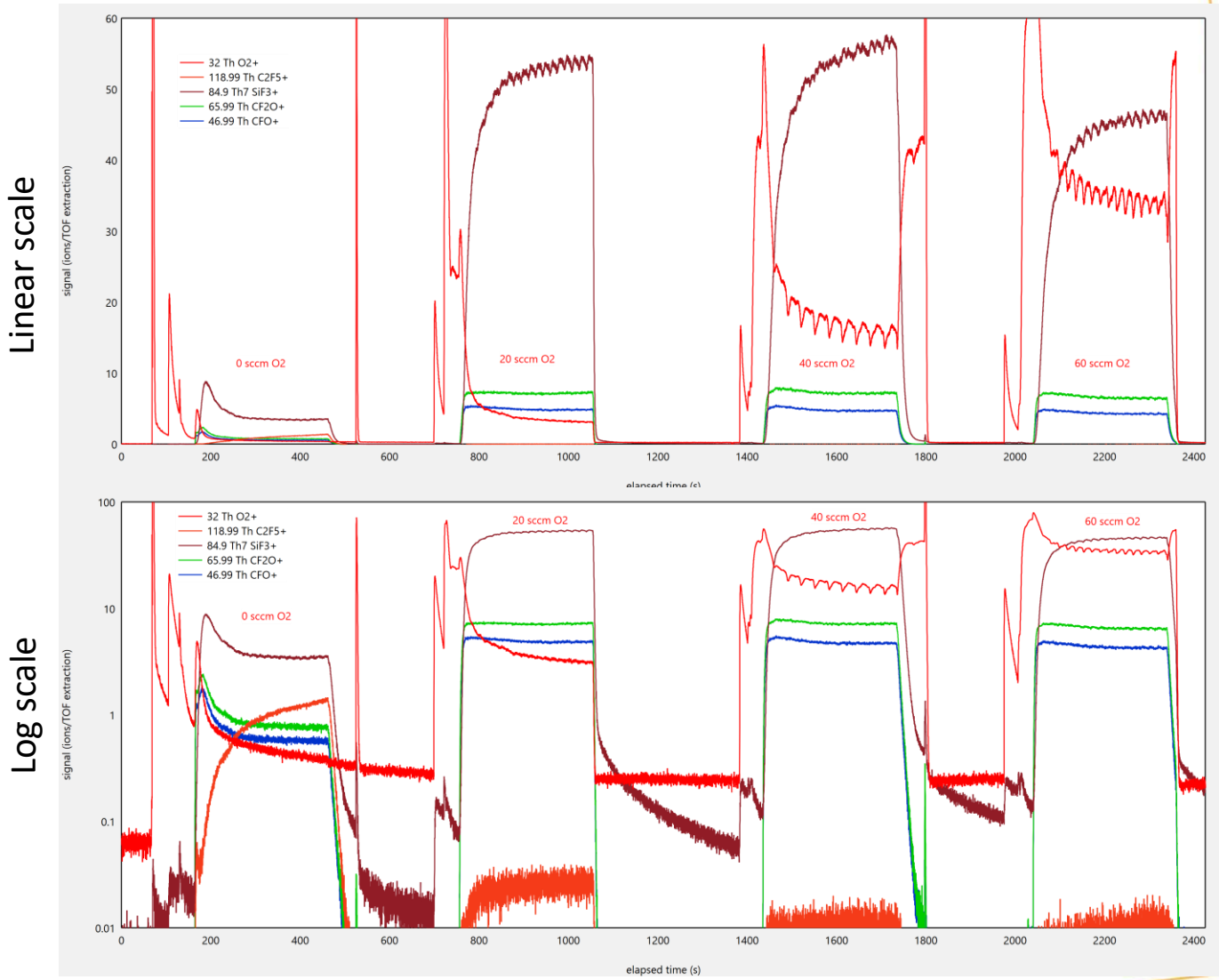


RIE: Effect of O_2 Addition to a CF_4 plasma During Si Etch

- Adding 20 sccm of O_2 in the CH_4 plasma greatly enhances the etch rate (>10 times)
- Further increase of O_2 content does not seem to further enhance the etch rate

Observations:

- O_2 signal shows spikes and oscillations (MFC issue?)
- Etch product (SiF_3^+) follows the O_2 signal fluctuation
- Etch gas signal ($C_2F_5^+$) drops significantly during the etch process under O_2 conditions



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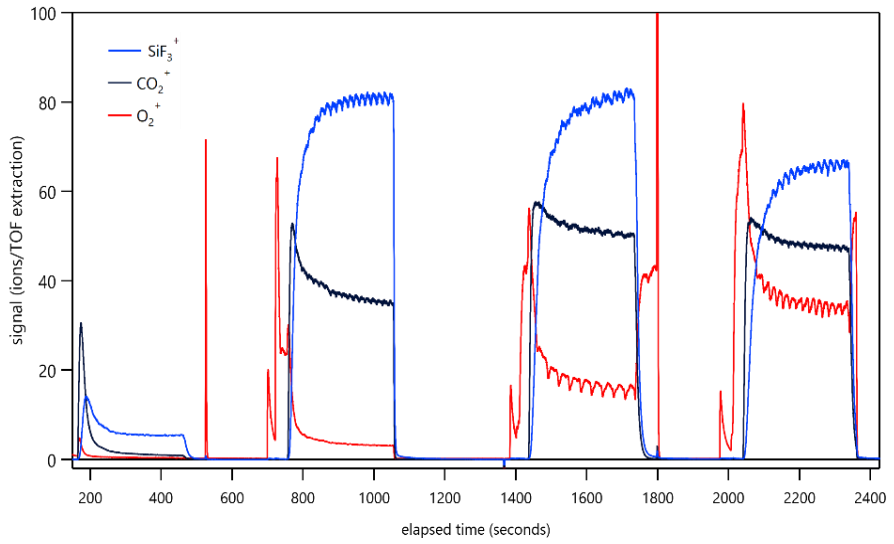
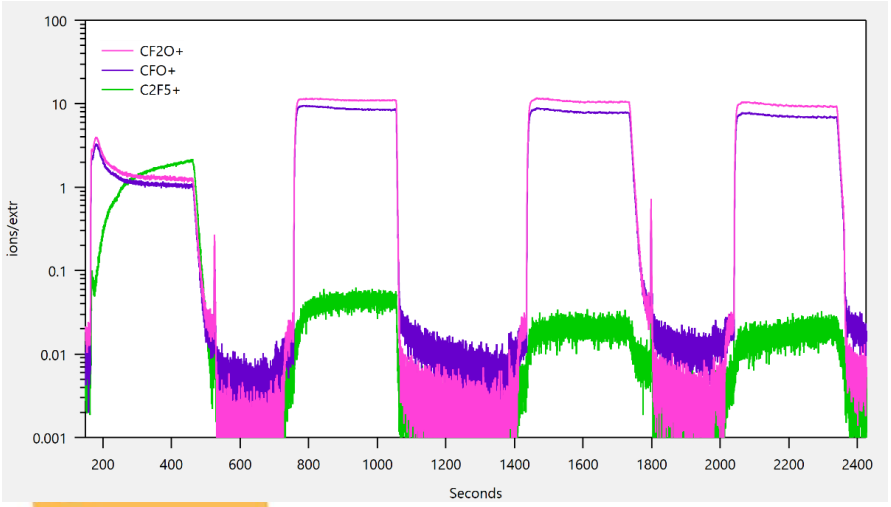




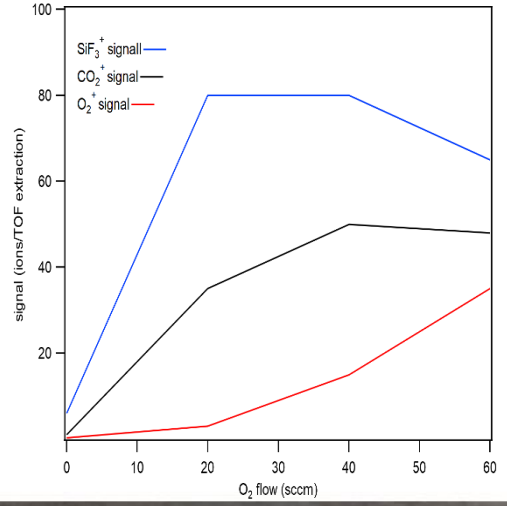
Observations:

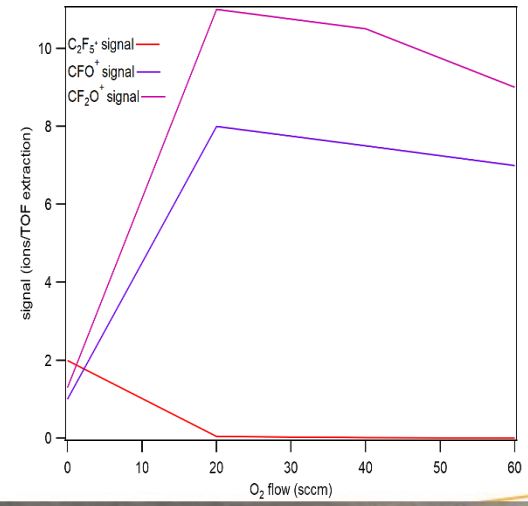
Addition of O_2 to a CF_4 plasma generates CO_2

- CO_2 signal increase initially then reaches a maximum as O_2 content increases
- Etch signal increases initially, reaches a maximum, then decreases as O_2 is added

Insight:

- O_2 turns non-volatile C compounds into CO_2
- As more O_2 is added, all C compounds are removed and etch reaches a maximum. Further increase of O_2 dilutes the plasma and lowers the etch rate .





Atomic Layer Deposition (ALD)

pgaTOF

- Sequential pulses of various precursors are used to form compounds that are both atomically flat and with tunable electronic and optical properties
- The above is only achievable if the growth mode is controlled to be in surface limited regime.
- To that end, the pulse width (flux) for each element needs to be precisely controlled so as to exactly and fully react the top surface layer; neither under nor over is optimal.
- By its very nature, this is a very slow process with some (device) stacks taking many hours to complete.
- In R&D, procedures to determine the self-limiting conditions is time consuming and requires many ex-situ measurements and iterations. This for each precursor, temperature and substrate.
- In production, slight variations in substrate temperature, flux variation or reactor conditioning state can lead to non ALD conditions and total run failure.

TOF Mass spectra monitoring tool

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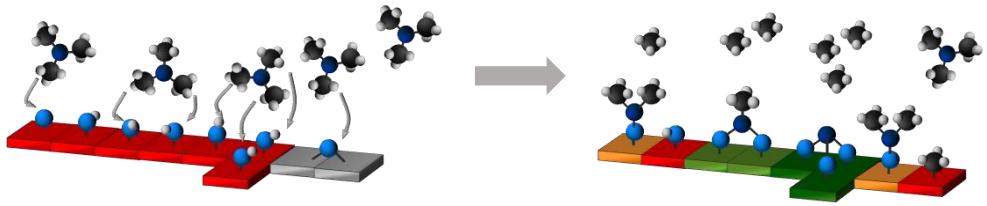
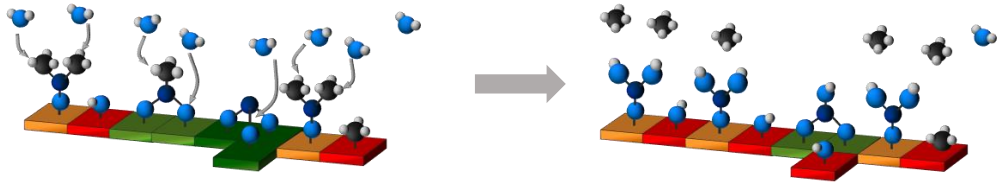
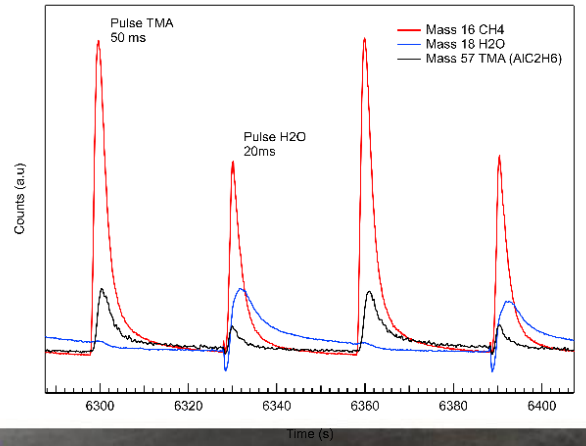
Pulse of TMA ($Al(CH_3)_3$) -in excess- and ligand exchange reaction with OH surface groups
Methane as by-product

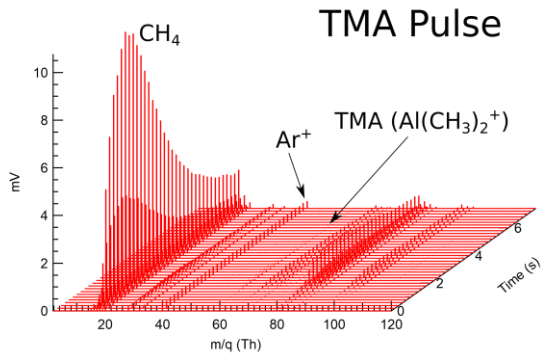


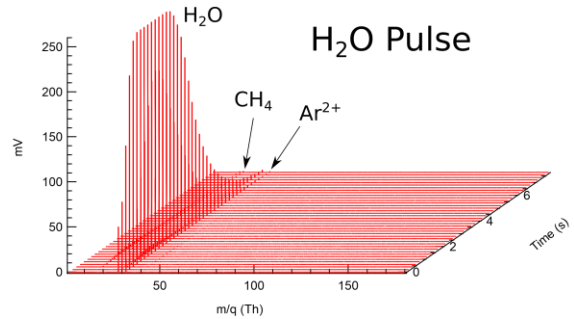
Pulse of H_2O–in excess- and ligand exchange reaction with CH_3 surface groups
Methane as by-product





Detection of the immediate appearance and the time to purge out the by-products (CH_4) and unreacted TMA or H_2O

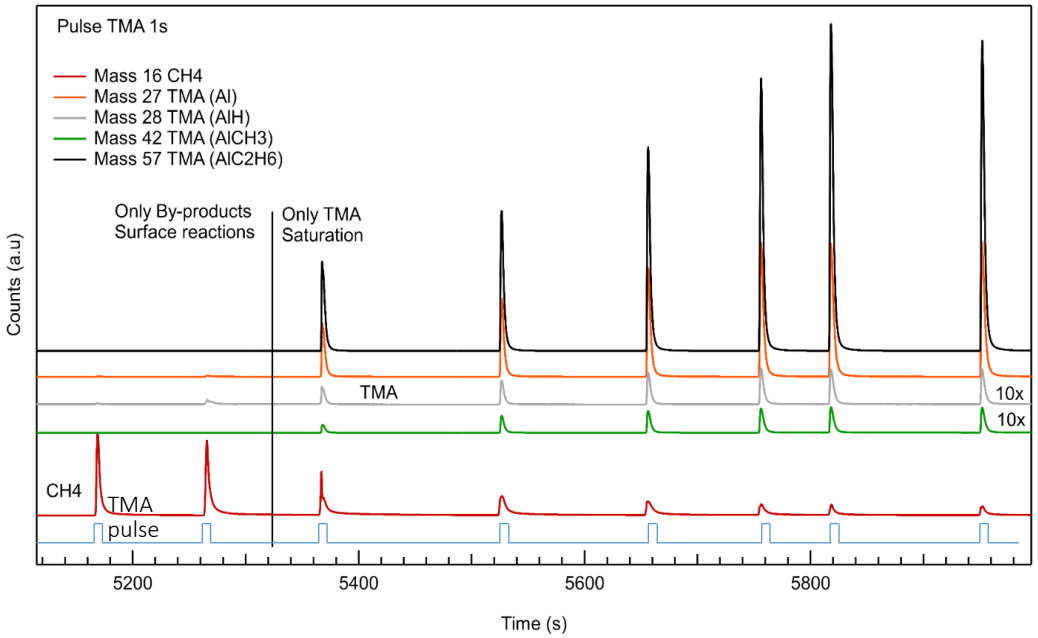


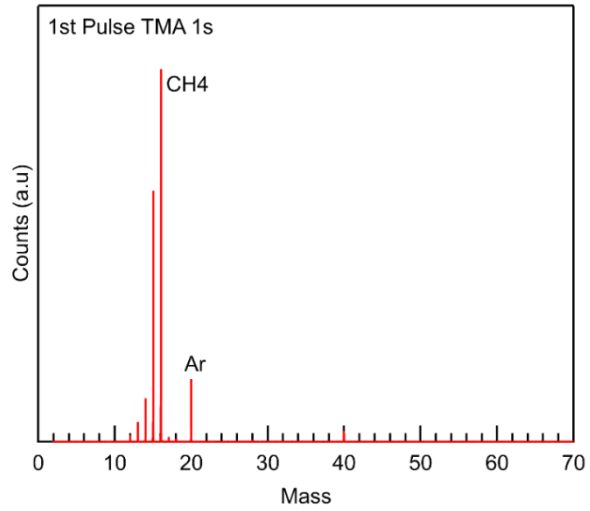


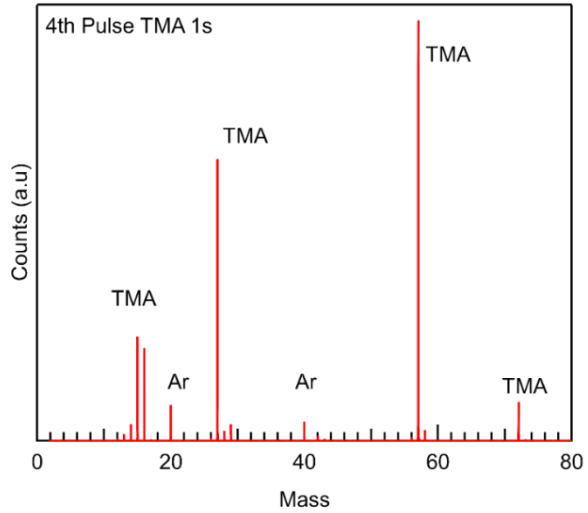
- Analysis of all masses in real time
- Detection of all by-products and gas precursors in every cycle in the deposition process
- Monitoring the evolution of the deposition process
- Detection of anomalies during the coating process by setting a benchmark spectra at the beginning of the process.

Consecutive Pulsing of TMA for saturation and self-limiting studies

- For every new precursor/process tested, saturation of the precursor inside the chamber needs to be guaranteed
- Figure bellow shows the amount of precursor needed to ensure the reaction with all of the available surface groups in the chamber







- 1st Pulse TMA: Only By-products (CH_4)- All TMA pulsed into the chamber is consumed by surface OH groups- no TMA fingerprint detected
- 3th Pulse TMA: CH_4 still produced but with unreacted TMA- All surface OH groups reacted with TMA and the unreacted TMA is detected
- After 4th Pulse TMA: Only TMA is detected because all of the OH groups have reacted.- Saturation is achieved and Self-limiting behavior of the process is evidenced
- ~3 s of TMA are needed to react with all of the -OH groups in the surface of the chamber.
- similar results are found for H_2O experiments

Real Time Mass Spectrometry as an ALD Process Monitoring Tool

pgaTOF

For a reliable production ALD process it is important to guarantee the saturation of the precursors in order to:

- Ensure a true ALD process (complete reactions, constant growth per cycle, self-limiting behavior)
- Dose the appropriate amount of precursor and purge the necessary amount of time to reduce precursor waste and deposition time (highly demanded in industry)
- Ensure the deposition process (reaction by-products and excess precursor) is homogenous from the beginning to the end. Some ALD processes take multiple hours. The mass spectra allows the detection of anomalies or deviation from optimum conditions during the coating process
- Saturation depends on every system used : Reactor dimensions, Reactor State of Health, Chamber pressure, Temperature, Pumping speed, etc.

As a research tool

- For every new precursor or material process it is important to know which by-products and their relative amount are produced during the precursor pulses (i.e., CH_4 ratio produced in the TMA/H_2O pulses) to model the reaction and growth mechanisms (How the gas molecules react with the surface and arrange during growth, and the growth per cycle.) The pgaTOF is a highly valuable tool to model the film growth for each new material. This helps understand the growth process, optimize the ALD mode for every precursor combination, as well as identify potential hazardous by-products.

Summary of Etch and ALD Experiments

pgaTOF

- Non-Invasive Configuration of a pgaTOF on a Semiconductor Etch/Deposition Tool Still Permits Important Real Time Insight into the Process Chemistry Dynamics
- Acquisition of all Relevant Masses with High Resolution is Key to Unequivocally Allocating the Correct Gaseous Species Present During the Process (Etch or Deposition)
  - Unambiguous species identification based on accurate mass and isotopic distribution
- High sampling rate of all masses is necessary to capturing process transients for process control and monitoring applications