Mass Spectrometric Methods

RGA and Charged Particle Analysis in Plasma Assisted Processes

HIDEN ANALYTICAL

Introduction

- Plasma for diverse range of applications
- Thin Films, Industrial Coatings, Plasma Spraying, Decorative Coatings, Etching
- Increased requirement for :
  - reduced device geometry's
  - enhanced yields
  - faster process transfer
  - improved reproducibility

Process Characterisation

HIDEN ANALYTICAL

Plasma Processes

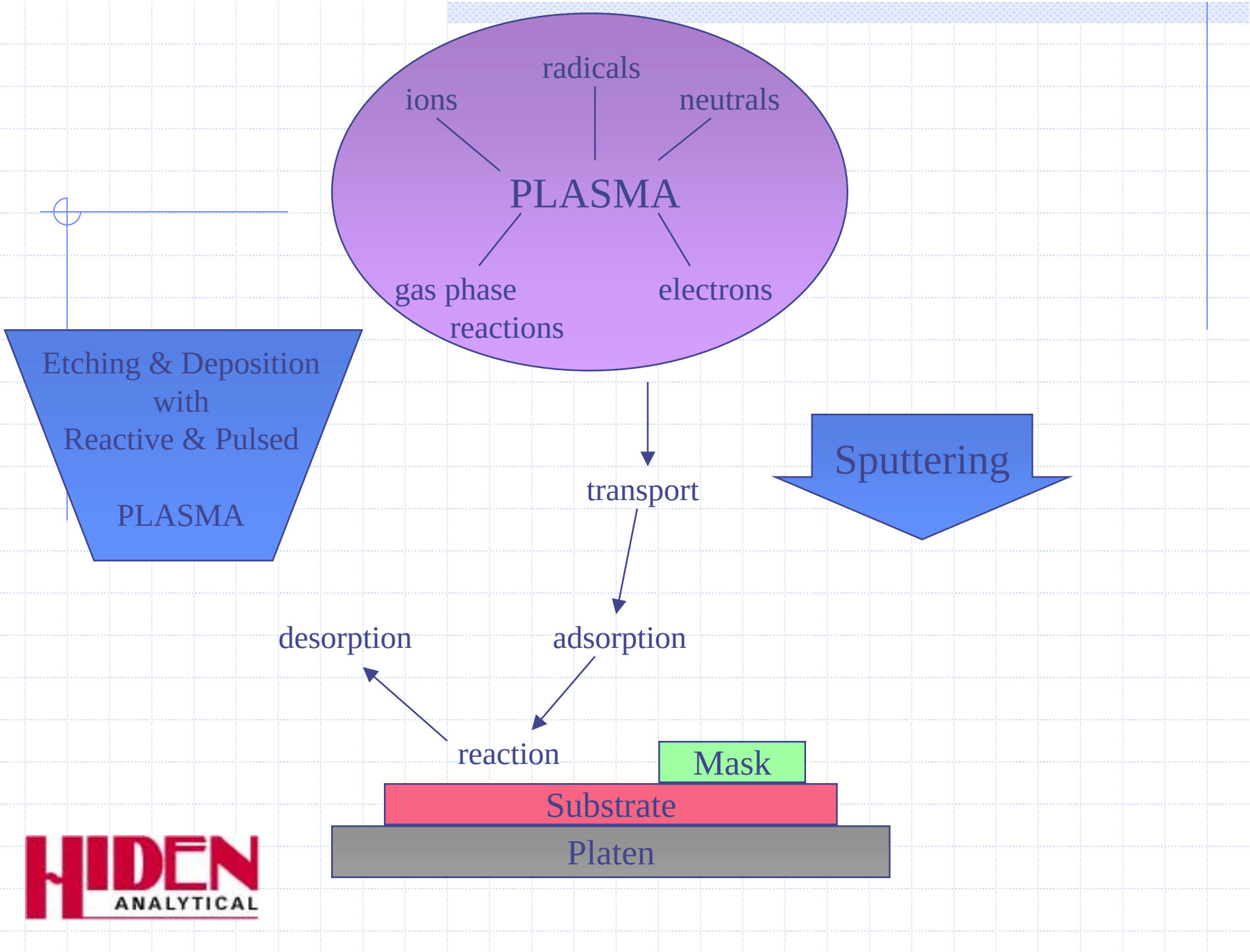
Techniques

- ECR
- DC Magnetron
- Pulsed Plasma & Laser Ablation
- RF Driven
- TCP/ICP

Applications

- PECVD
- Plasma Etch
- PVD
- Plasma Spray
- Hard Coatings
- Ion Implantation

HIDEN ANALYTICAL


radicals
ions
neutrals
PLASMA
gas phase
reactions
electrons
Etching & Deposition
with
Reactive & Pulsed
PLASMA
transport
Sputtering
desorption
adsorption
reaction
Mask
Substrate
Platen
HIDEN
ANALYTICAL

Plasma Constituents

Macroscopic

- Power Feeds
- Gas Supply
- Pressure
- Electric/Magnetic Fields
- Heating/Cooling
- View Ports

Microscopic

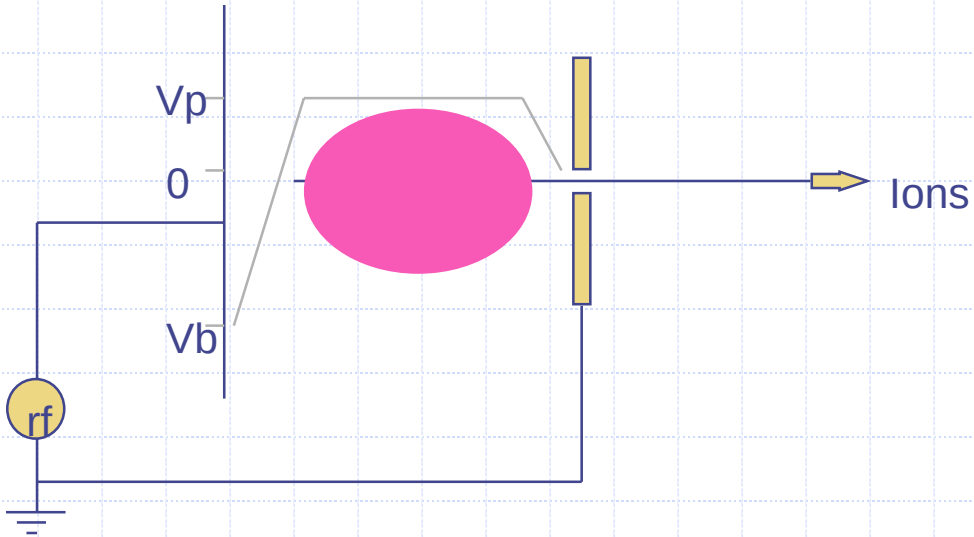
- Neutrals
- Positive Ions
- Negative Ions
- Electrons
- Radicals

Complex System To Predict

HIDEN ANALYTICAL

Measurement and Control

- Environment
  - chamber leaks, wall contamination
  - gas type, impurities, temperature, total/partial pressure, pumping
  - target material/substrate impurities
  - temperature, bias
- Plasma Constituents
  - particle flux
  - direction
  - energy, atomic state



HIDEN ANALYTICAL

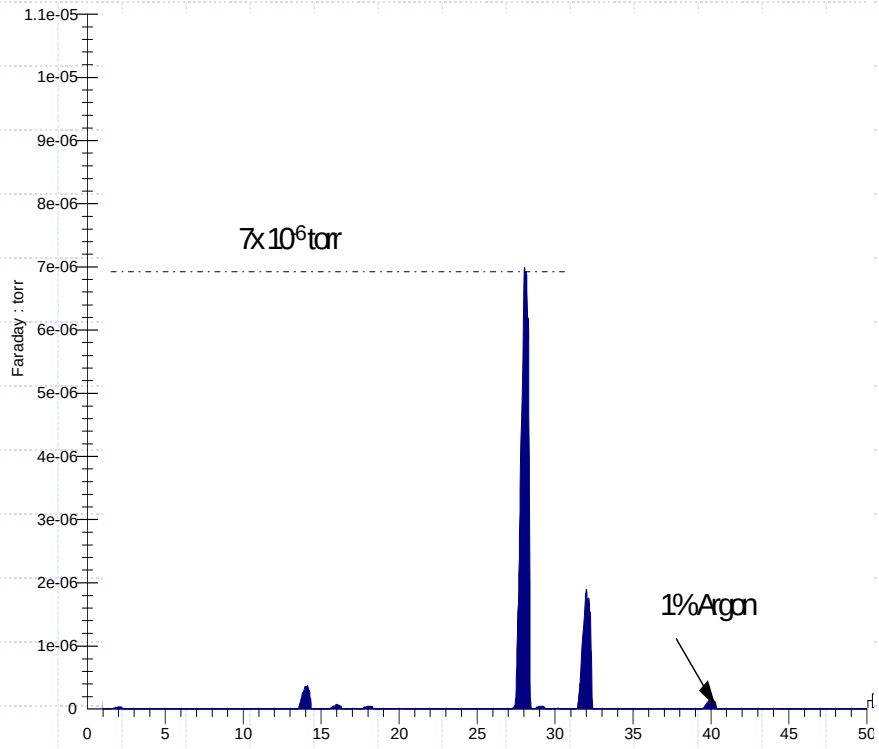
Plasma Process Monitoring

- Residual Gas Analysis
- Down-stream Process Gas Analysis
- Exhaust Gas Analysis
- In-situ Process Gas Analysis
- In-situ Plasma Characterisation

Quadrupole Mass Spectrometers

HIDEN ANALYTICAL

Residual Gas Analysis



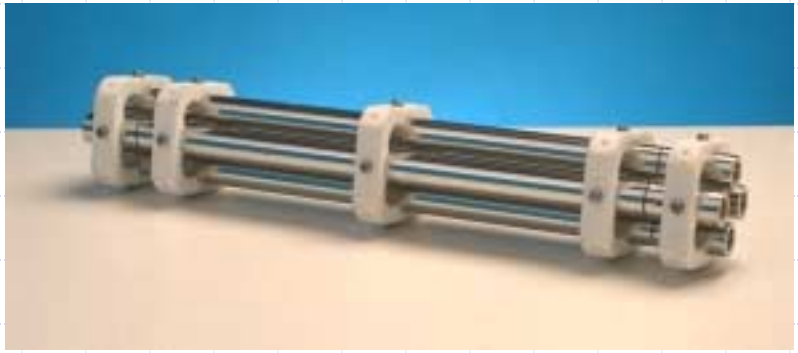
Plasma Off - Neutrals Analysis

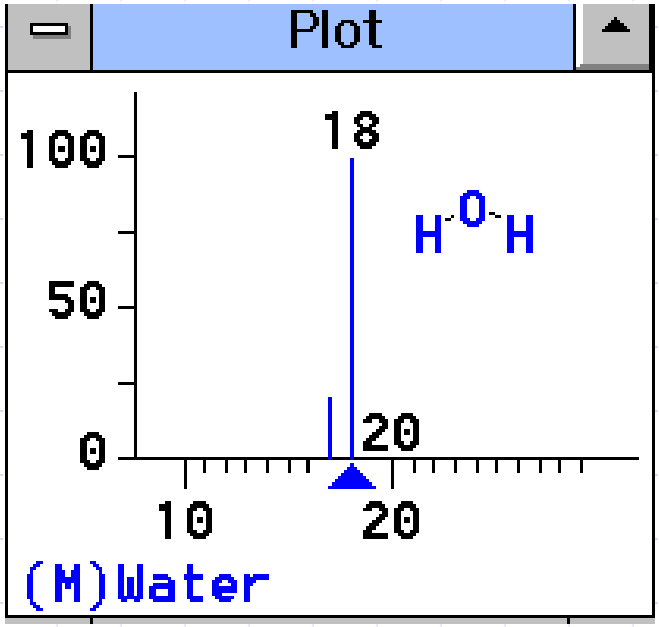
- Base Pressure Fingerprint
- Leak Detection
- Virtual Leaks
- Outgassing
- Bakeout Cycles
- Pump Performance

HIDEN ANALYTICAL

Water Vapour Detection

- **Water at m/e 18**
  - outgassing
  - bake-out
  - spectral overlaps



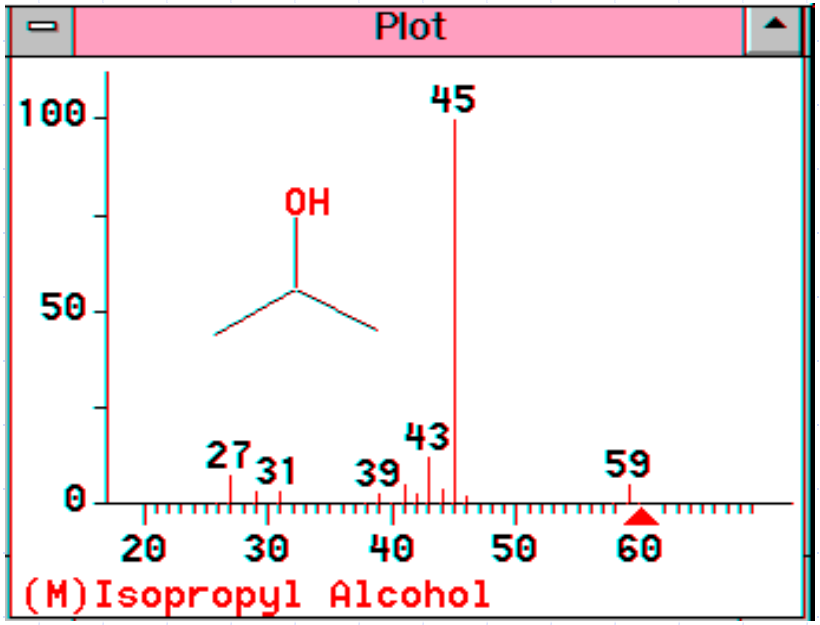


RGA Spectrum of Water

HIDEN ANALYTICAL

Hydrocarbon Detection

- Backstreaming of oil vapour
- Cleaning fluid residue
- Vacuum grease



RGA Spectrum of IPA

HIDEN ANALYTICAL

Down-stream Process Gas Analysis

Plasma On - Neutrals Analysis

- Process Pressure Analysis
- Gas Purity
- Contaminants
- Differentially Pumped
- Sample Valve/Orifice

Primary Issues

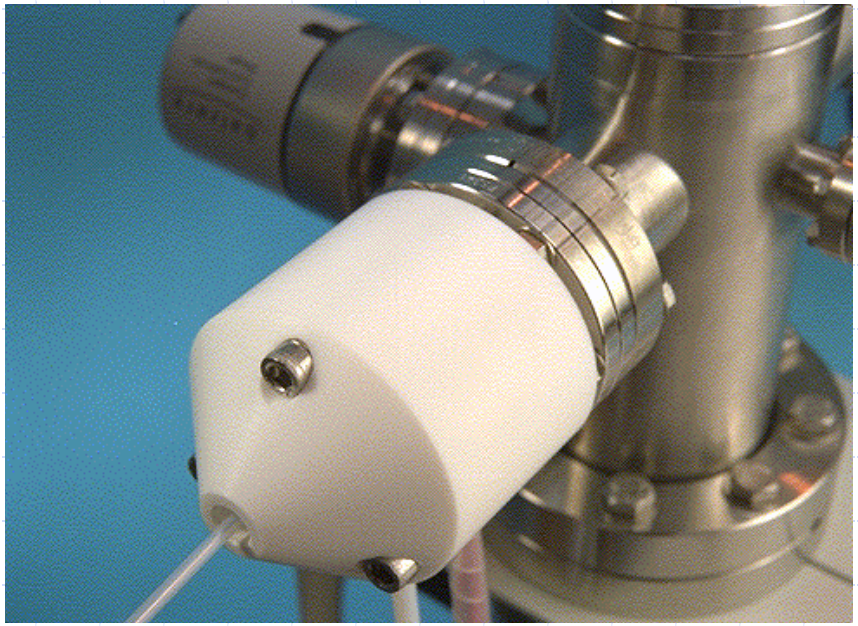
- Species Lifetime
- Detection Limits
- Recombination
- Response Time

HIDEN ANALYTICAL

Exhaust Gas Analysis

Plasma On - Neutrals Analysis

- Atmospheric Pressure Sampling
- Capillary Inlet
- PPB Detection
- Process Gas and Contaminants



HIDEN ANALYTICAL

PPM Detection

MASsoft - [MID Tabular view C:\HIDEN\H2HPPMAR.EXP View:3]

File Edit MassSpecs Tune Gallery System Views SPC Window Help

Parameters/Scans:	ppm Hydrogen 1	ppm Air 1	ppm Water 1	ppm Methane 1	ppm Oxygen 1	ppm CO2 1
Real time						
7:57:32 pm	31	3	4	0.7	0.4	0.7
7:58:42 pm	32	2	3	0.5	0.04	0.6
7:59:55 pm	33	3	3	0.7	0.5	1
8:01:14 pm	34	2	3	0.5	0.5	0.9
8:02:27 pm	37	4	3	0.5	0.3	0.6
8:03:40 pm	36	2	4	0.5	0.08	0.8
8:04:53 pm	32	3	3	0.9	0.2	0.9
8:06:06 pm	35	2	3	0.4	0.3	0.8
8:07:19 pm	34	2	3	0.7	0.4	0.5
8:08:32 pm	35	1	5	0.8	0.4	0.7
8:09:57 pm	37	2	3	0.6	0.3	0.7
8:11:15 pm	33	3	2	0.7	0.2	0.8
8:12:28 pm	34	3	3	0.7	0.2	1
8:13:41 pm	34	3	4	0.8	0.2	0.6
8:15:00 pm	32	2	2	0.9	0.1	0.8
8:16:19 pm	32	2	4	0.6	0.2	0.5
8:17:38 pm	33	3	4	0.6	0.2	0.6
8:18:51 pm	36	2	3	0.8	0.5	0.7
8:20:04 pm	31	3	4	0.8	0.3	0.8
8:21:23 pm	32	2	3	0.8	0.2	0.8
8:22:36 pm	35	3	4	0.5	0.4	0.7
8:23:49 pm	33	3	4	0.8	0.3	1
8:25:02 pm	37	2	3	0.8	0.3	0.8
8:26:15 pm	33	2	4	0.7	0.2	0.7
8:27:40 pm	31	2	4	0.5	0.3	0.8
8:28:59 pm	33	2	4	0.4	0.3	0.8
8:30:12 pm	37	3	2	0.5	0.2	0.9
8:31:25 pm	29	2	2	0.8	0.3	0.7

HIDEN ANALYTICAL

In-situ Process Gas Analysis

Plasma On -

Neutrals Analysis

Close Coupled

Sampling For :

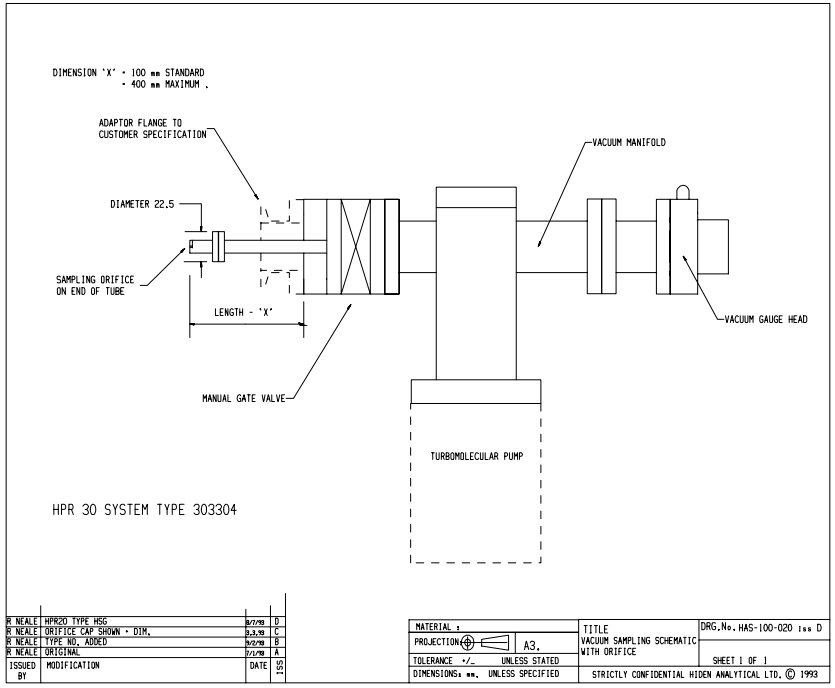
- Vacuum Diagnostics
- Pump Down Profiles
- RGA
- Leak Checking
- Process Templates
- Process Qualification
- SPC

HIDEN ANALYTICAL

Process Pressure Sampling

Sampling Configuration :

- >10^{-4} Torr
- Optimised Sampling
- Vacuum Isolation
- System Base Pressure



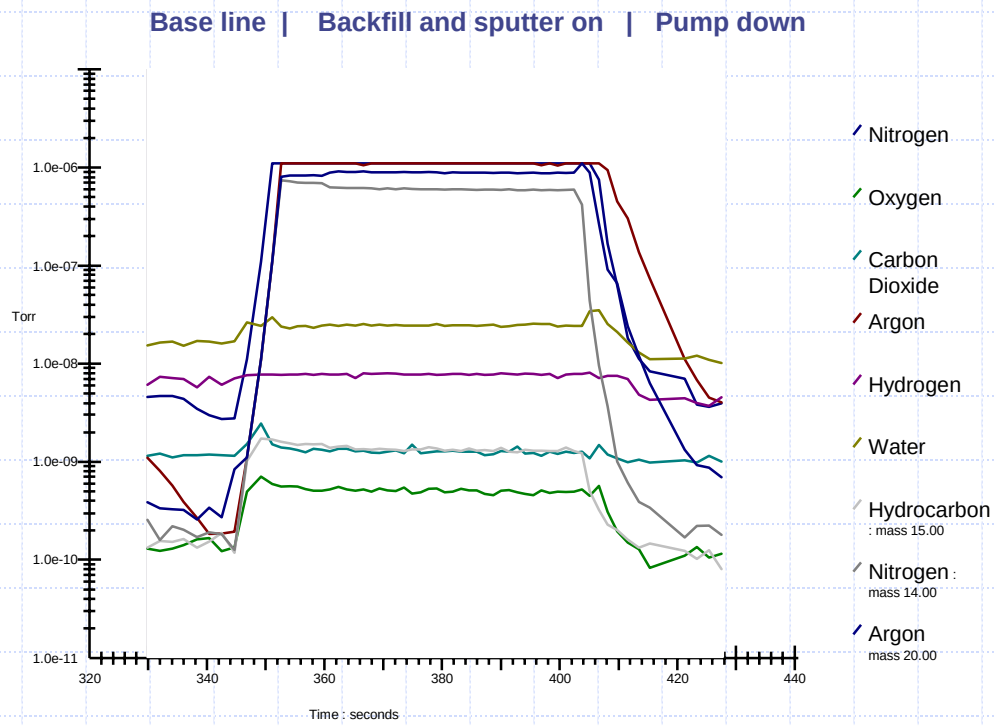
HPR 30 Vacuum Process Sampling System

HIDEN ANALYTICAL

TiN Deposition

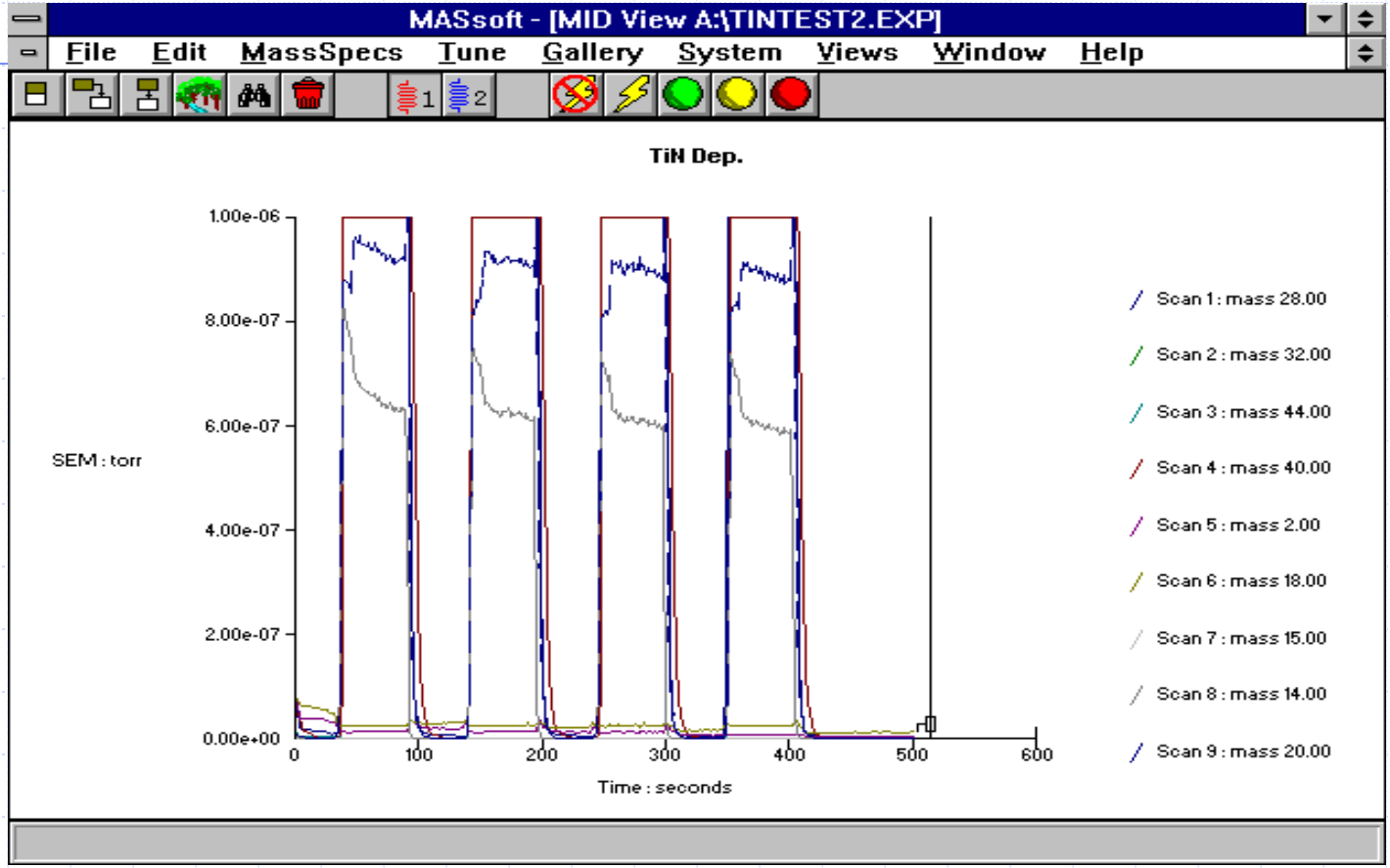
Single Wafer Cycle

- TiN Process Endura PVD
- Reagent Gas Levels Monitored
- Ultrapure Ti Target
- 60:40 N_2 to Ar
- 8mTorr Process Pressure



HIDEN ANALYTICAL

Multi-wafer Cycles



HIDEN ANALYTICAL

In-situ Plasma Characterisation

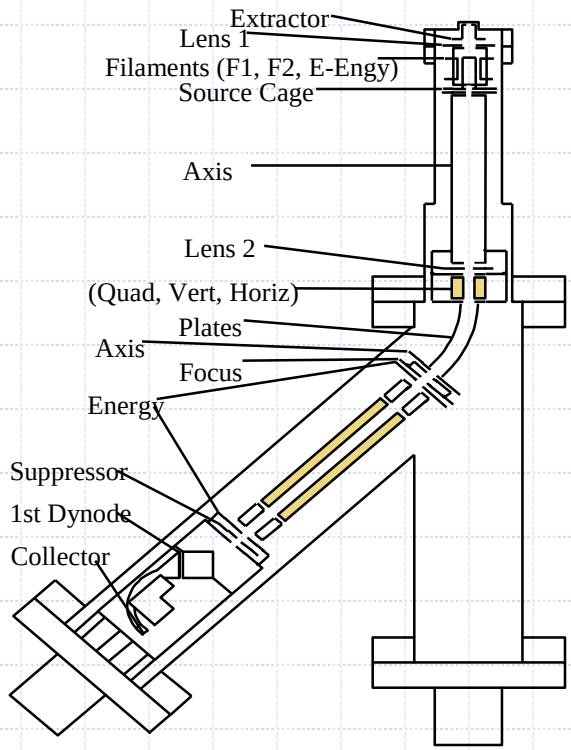
Plasma On/Plasma Off - Neutral and Charged Particle Analysis

- Gas Composition
- Process Trends
- Time Resolved
- End Point Detection
- RGA

- Positive Ion Distribution
- Negative Ion Distribution
- Thermal and Non-thermal Neutrals
- Radicals

HIDEN ANALYTICAL

Combined Mass And Energy Analysis



Hiden's EQP

HIDEN ANALYTICAL

Applications and Techniques

- 1. RF Plasma
- 2. Electron Attachment
- 3. End Point Detection
- 4. Pulsed Laser Deposition

HIDEN ANALYTICAL

1. Negative & Positive Ion Energies in RF Plasma in Nitrous Oxide

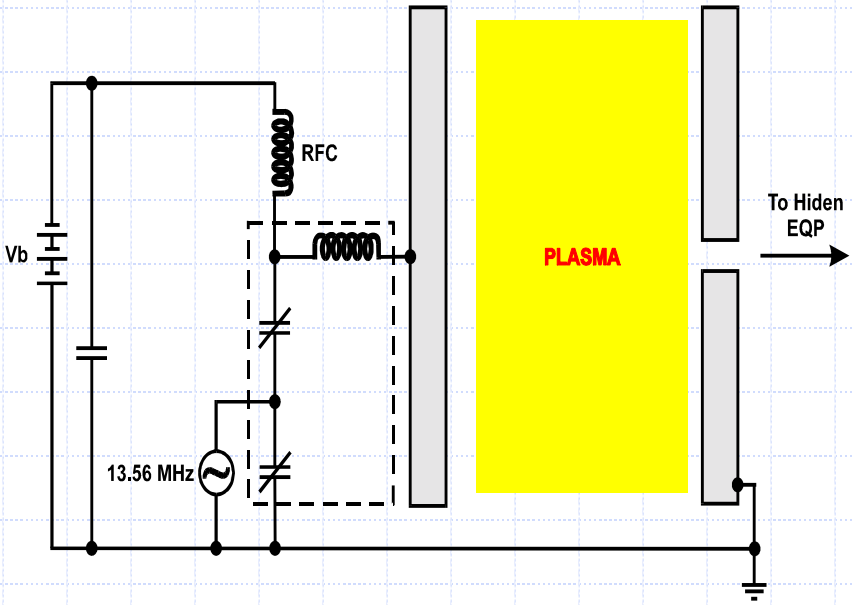
Abstract

- Negative ions important in the plasma oxidation of silicon & silicon nitride
- Nitrous oxide - growing interest
- Investigate O^-/N_2O^+ ions at grounded electrode in RF plasma

HIDEN ANALYTICAL

Experimental Conditions

- N_2O at 6 mTorr
- 13.56 MHz to 5 cm driven electrode
- 0 - 100 V DC bias
- 8 cm electrode spacing
- Grounded electrode forms entrance plane of EQP mass & energy analyser



HIDEN ANALYTICAL

Measurements

- Ions arriving at EQP mass identified
- Dominant species
  - Positive Ions: N_2O^+
  - Negative Ions: O^-
- N_2O^+ /O^- ion energies measured

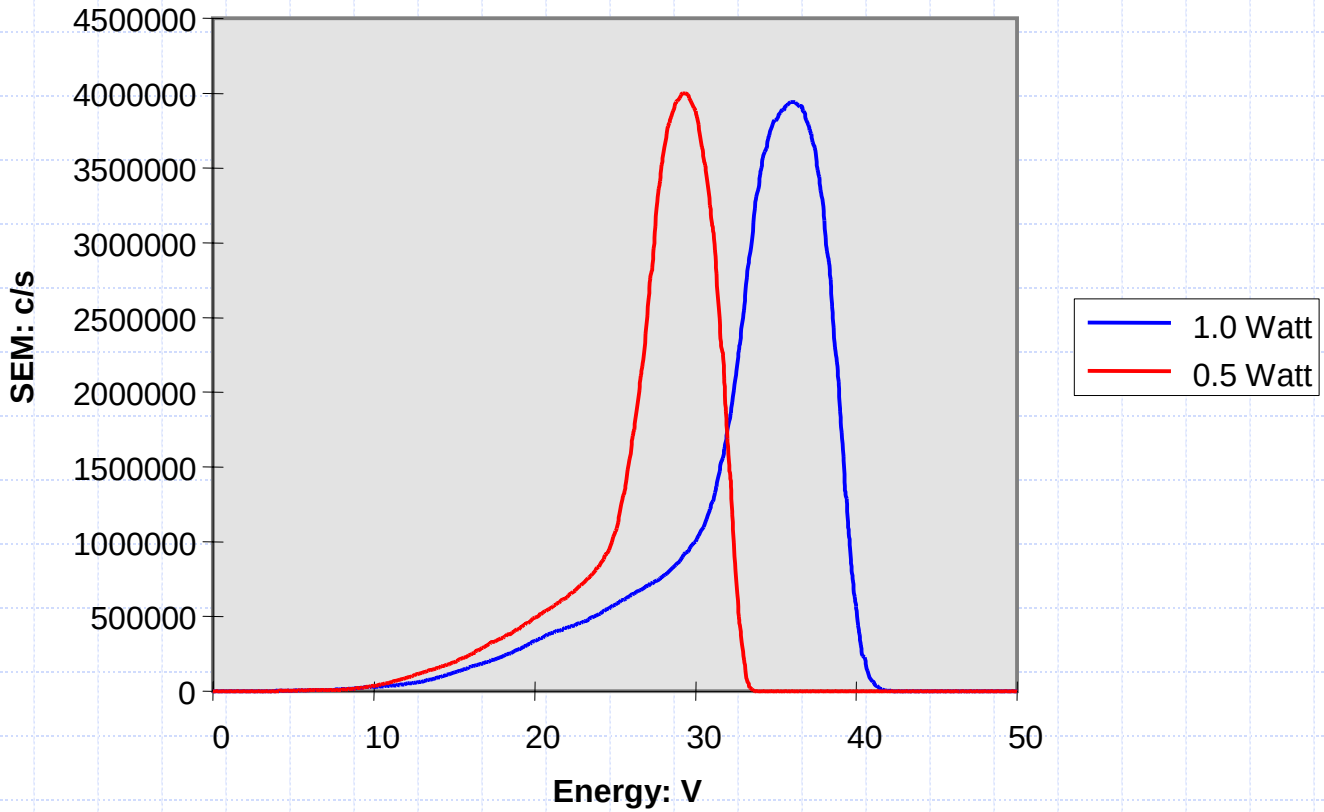
HIDEN ANALYTICAL

Positive Ion Energies

- N_2O^+ studied as a function of DC bias and RF power
- Maximum energy determined by plasma potential resulting from DC bias and RF input signal magnitude
- RF varied from 0.5 to 3 Watts
- DC bias set at -70 V
  - Observe ion energies increase with increasing power - increase in plasma potential
  - Peak splitting at highest powers - transit time across grounded electrode sheath comparable to RF period

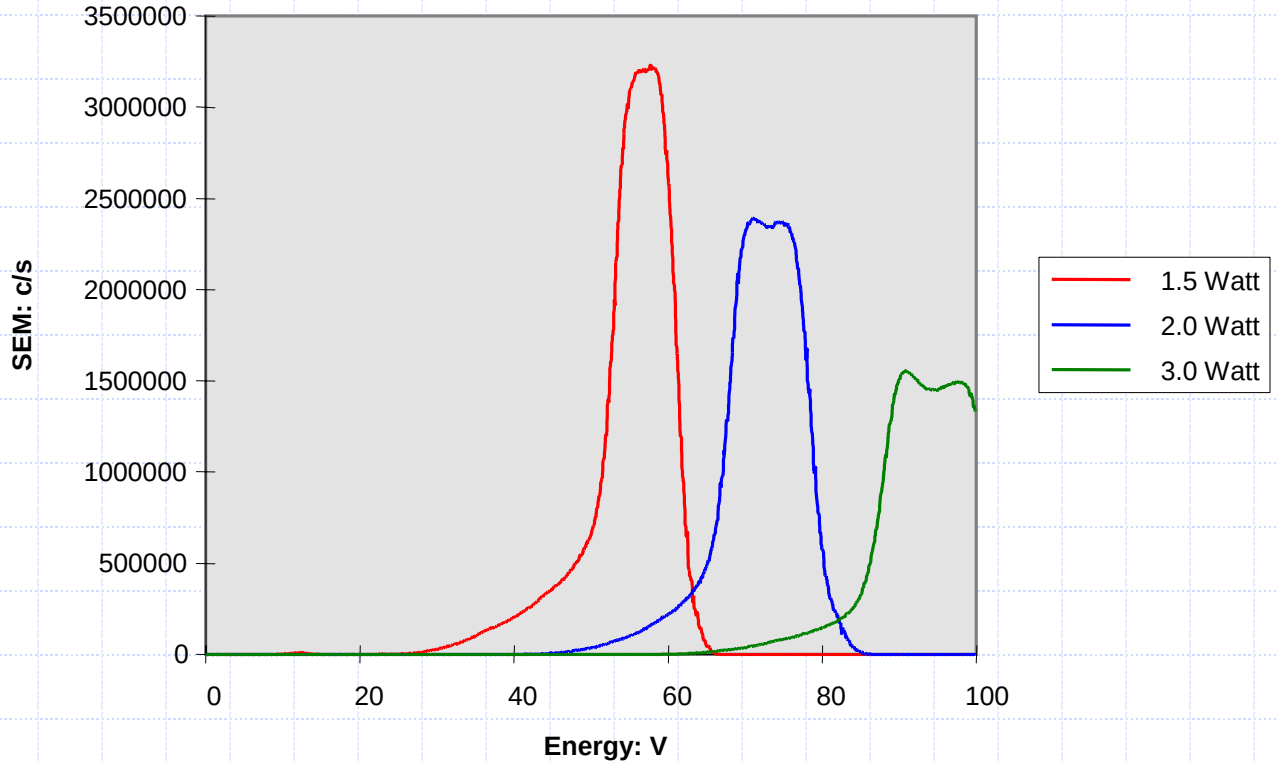
HIDEN ANALYTICAL

N_2O+ In N_2O.
Bias = -70 V, 6 mTorr.



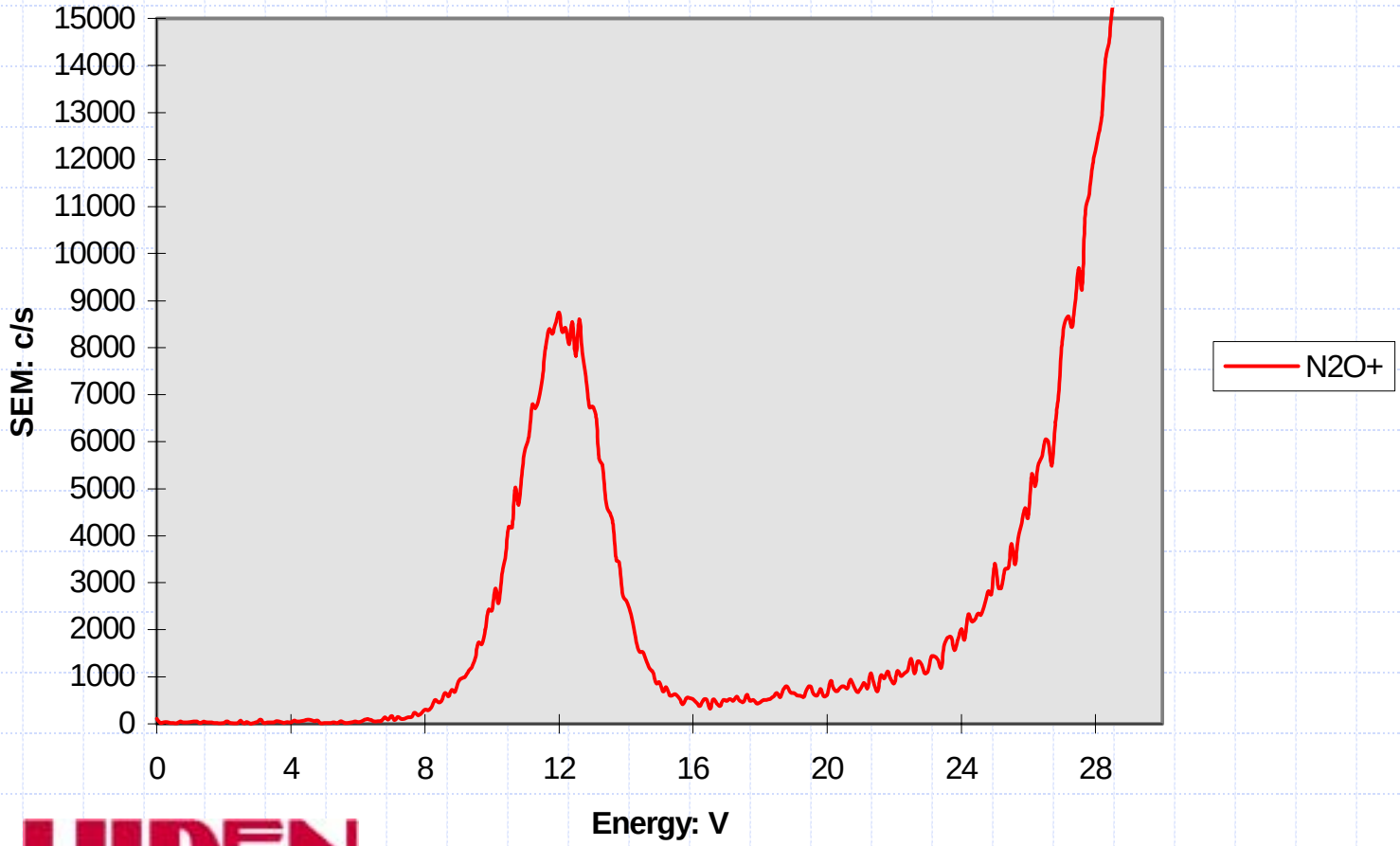
HIDEN ANALYTICAL

N_2O+ In N_2O.
Bias = -70 V, 6 mTorr.



HIDEN ANALYTICAL

N_2O+ In N_2O.
Bias = -70 V, 6 mTorr, 1.5 Watt.



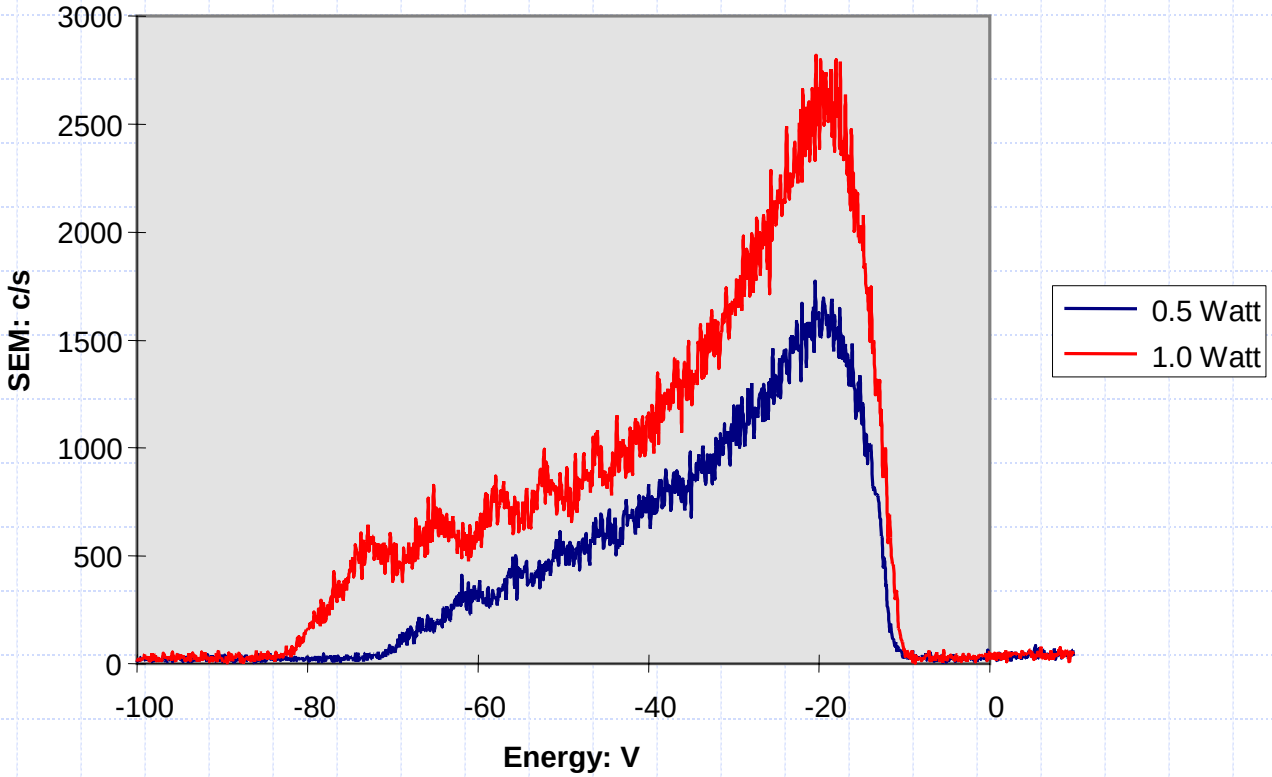
HIDEN ANALYTICAL

Negative Ion Energies

- O^- lower intensity than N_2O^+
- Generated by electron impact in the sheath at the driven electrode
- RF varied from 0.5 to 3 Watts
- DC bias set at -70 V
  - Observe ion energies increase with increasing power - RF pk-pk increases, applied RF and DC accelerates the ions through the sheath at the driven electrode

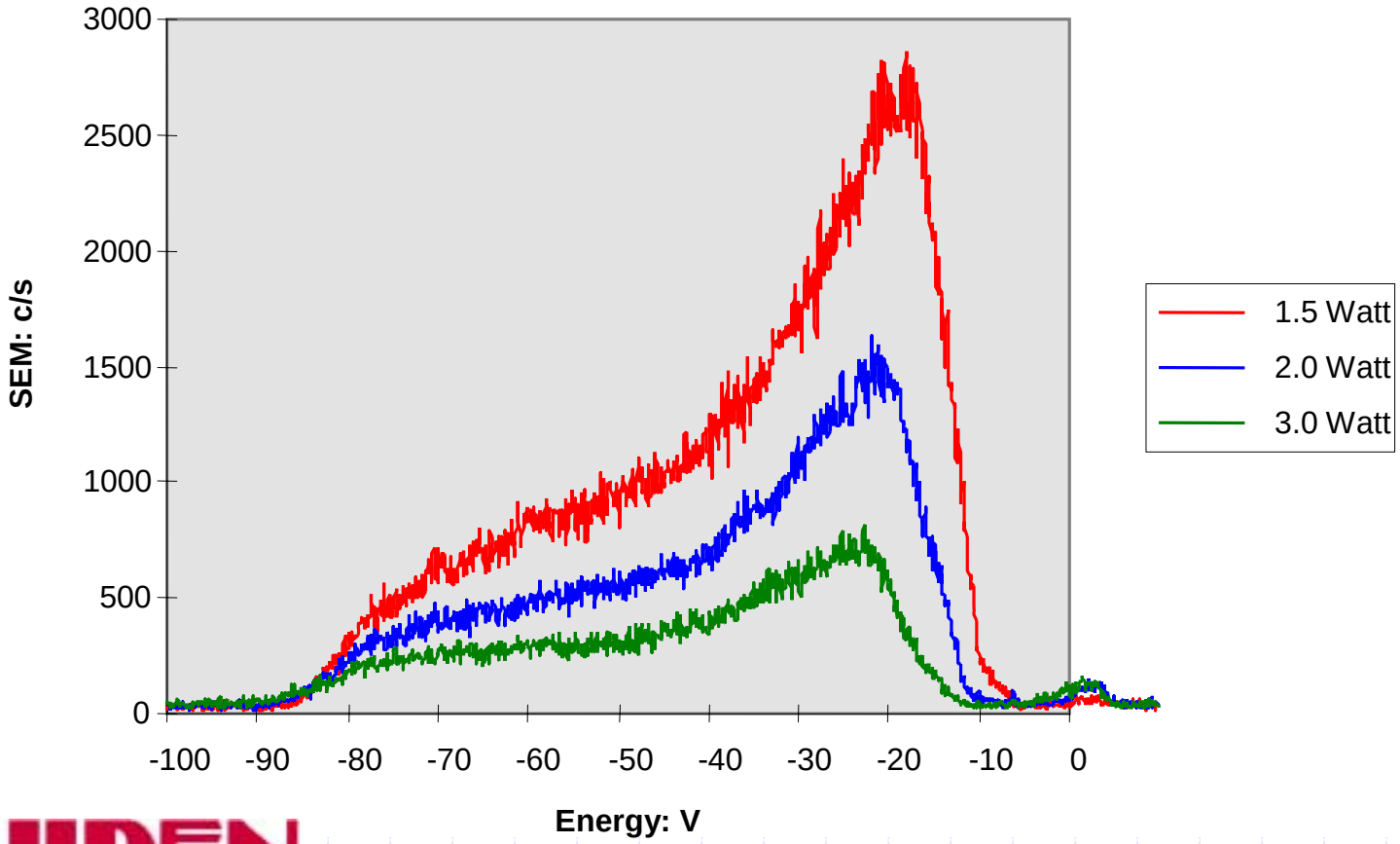
HIDEN ANALYTICAL

O- Ions In N_2O. Bias = -70 V.



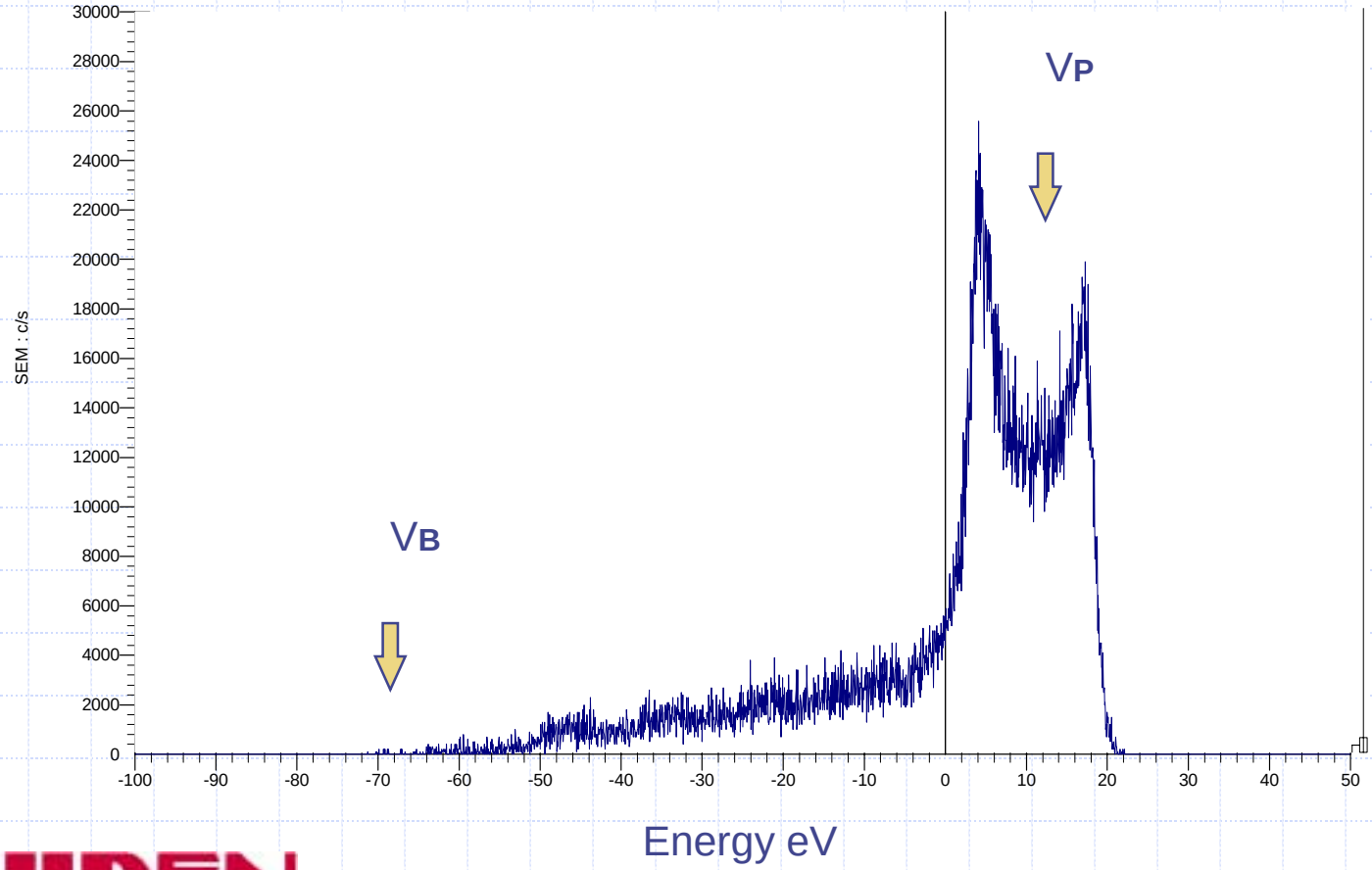
HIDEN ANALYTICAL

O- Ions In N_2O. Bias = -70 V.



HIDEN ANALYTICAL

Ar H^+ 10 mTorr



HIDEN ANALYTICAL

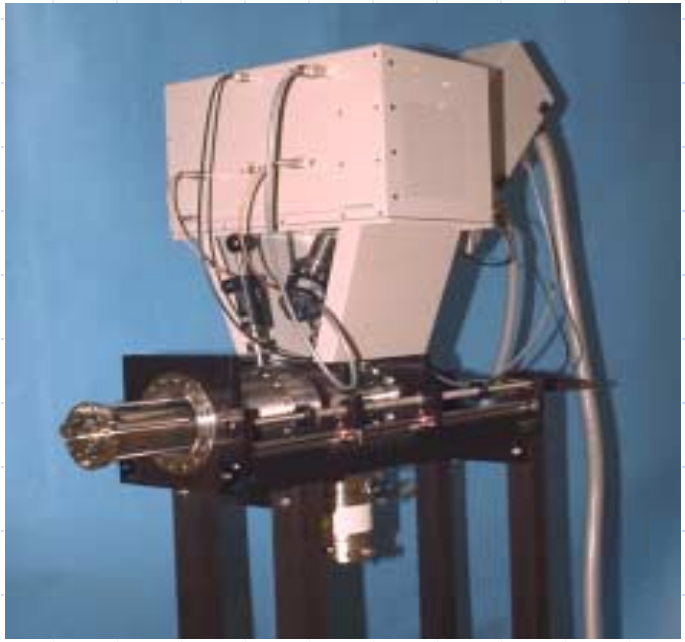
Conclusions

- Positive & Negative ions analysed
- Negative ions produced in the driven electrode sheath
- Negative ion energies strongly influenced by DC bias
- Positive ions strongly affected by RF amplitude
- Positive ion low energy tail - electron impact in grounded electrode sheath - to be determined

HIDEN ANALYTICAL

2. Analysis of Plasma Neutrals by Electron Attachment and Ionisation Threshold Techniques

- Surface/gas phase chemistry strongly dependant on plasma neutrals
- Complex mix for single/binary gases



HIDEN ANALYTICAL

Principle

- Neutral products resulting from collisional processes:
  - a) $e + M \rightarrow A + B + C + e$ E.I. dissociation
  - b) $e + M \rightarrow A^{+} + B + C + 2e$ E.I. dissociative ionisation
- Photon impact equivalents of a) and b) are also possible. Other products may arise from chemical reactions between the ions produced in the plasma and neutral constituents, including reactions such as:
  - c) $A^{+} + B \rightarrow A + B^{+}$
  - d) $A^{+} + BC \rightarrow AB^{+} + C$
- a)-d) repeated for electronegative gases

Carbon Tetrafluoride Positive Ionisation Thresholds

- Plasma Off - CF_3^+/CF_2^+ from CF_4 agree with published data

- Plasma On - CF_3^+ results from:
  - $e + CF_4 \rightarrow CF_3^+ + F + 2e$ and
  - $e + CF_3 \rightarrow CF_3^+ + 2e$
    - the CF_3 having been formed by dissociation of CF_4 in the plasma

HIDEN ANALYTICAL

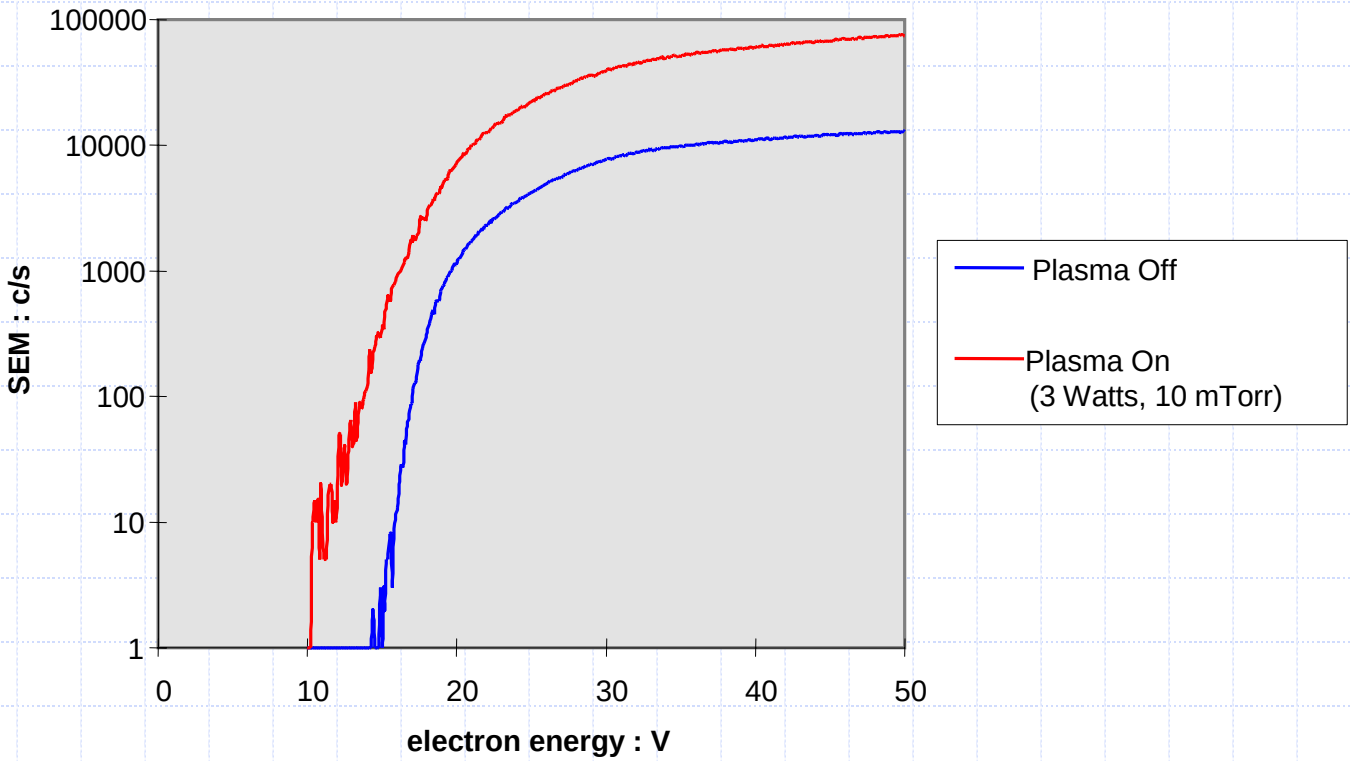
CF_4 Plasma

- Plasma Off - CF_2^+ from:
  - $e + CF_4 \rightarrow CF_2^+ + F_2$ (19.3eV) and
  - $e + CF_4 \rightarrow CF_2^+ + 2F$ (20.9eV)

- With the plasma turned on, extra CF_2^+ ions are expected from the additional processes:
  - $e + CF_3 \rightarrow CF_2^+ + F + 2e$ and
  - $e + CF_2 \rightarrow CF_2^+ + 2e$

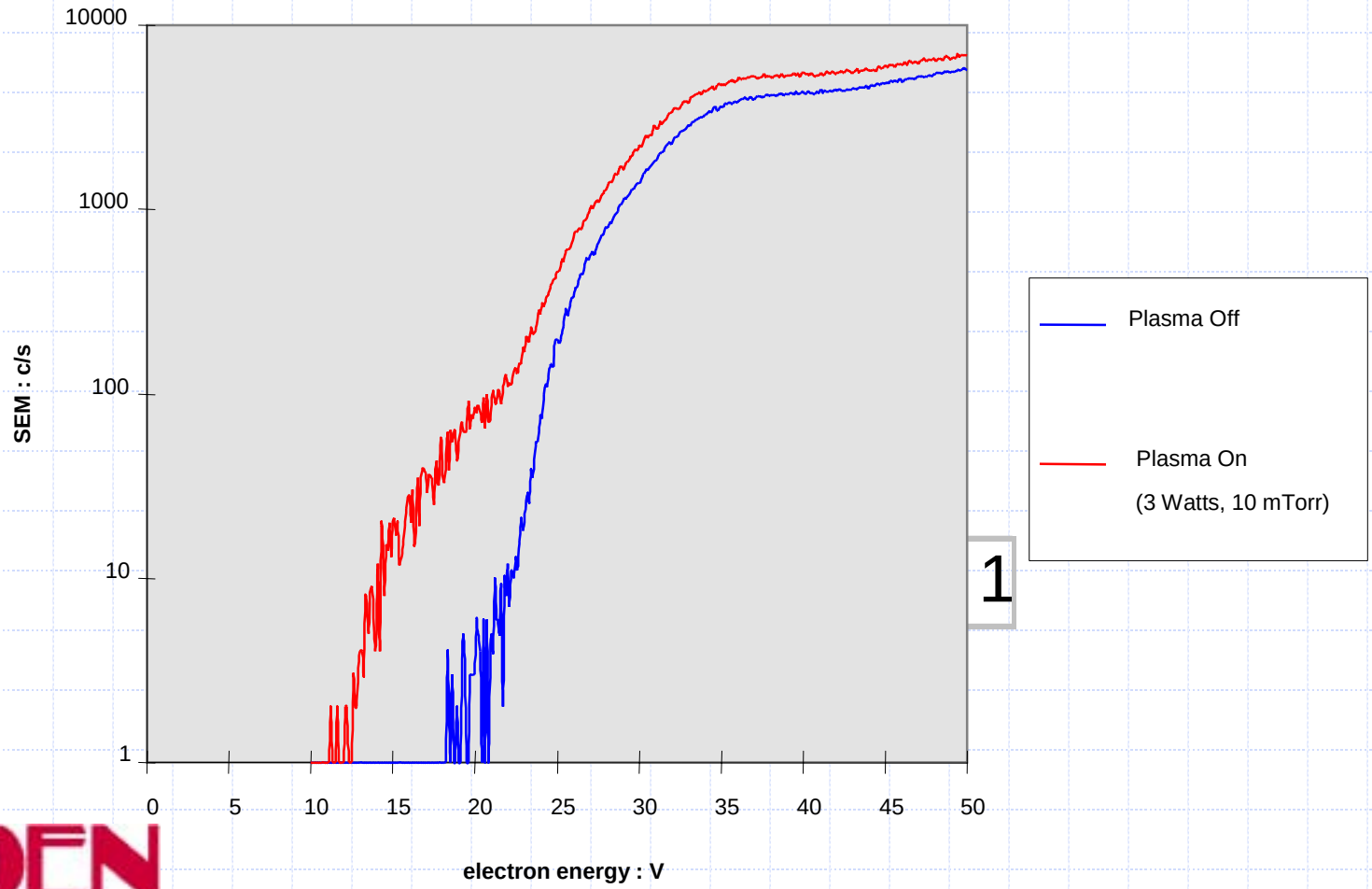
HIDEN ANALYTICAL

CF_3+ Ions



HIDEN ANALYTICAL

CF_2+ Ions

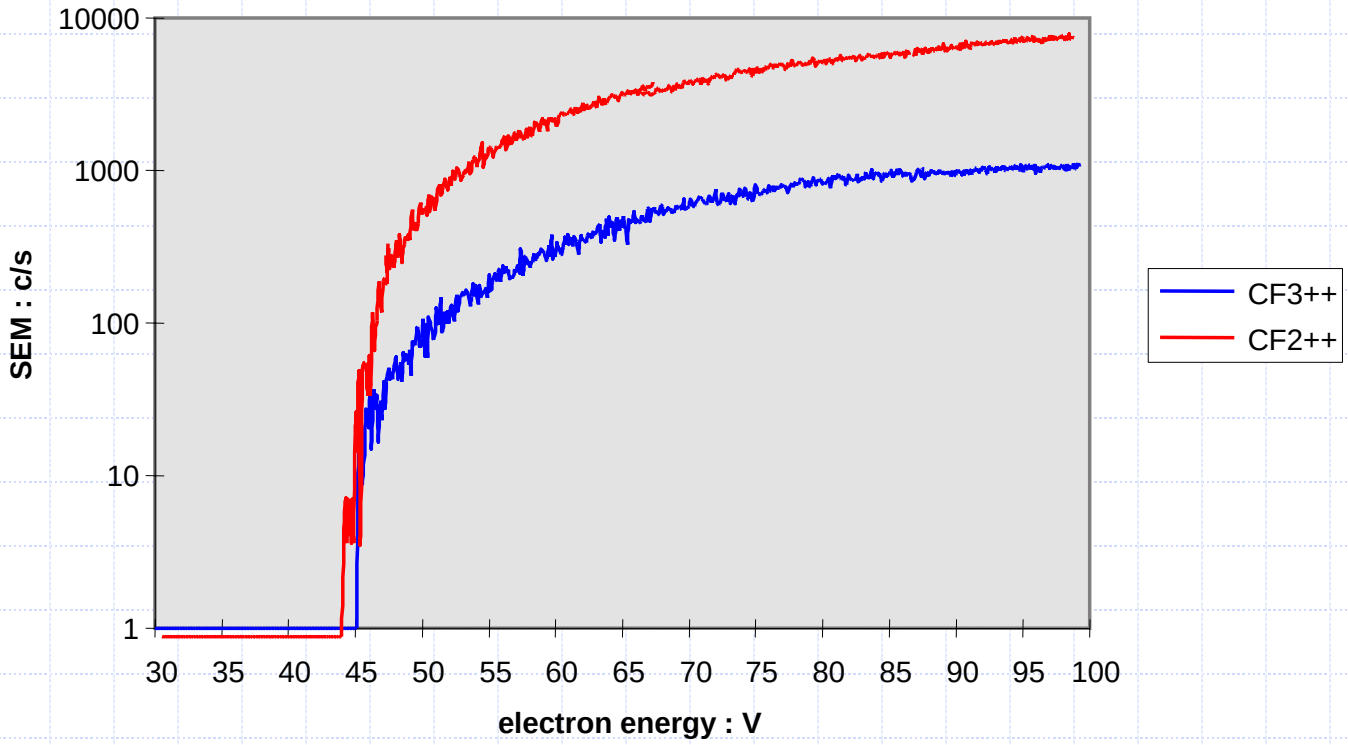


1

HIDEN ANALYTICAL

Appearance Potentials

(Plasma Off)



HIDEN ANALYTICAL

Negative Ion Formation

- The neutral species generated in a plasma may also be examined by studying the negative ions they yield in the EQP's ionisation source
- For CF_4 the dominant ions formed by electron attachment are F^- and CF_3^-, formed through the reactions:

$$e + CF_4 \rightarrow CF_4^- \text{ (ground state)} \rightarrow F^- + CF_3 \quad \text{(A)}$$

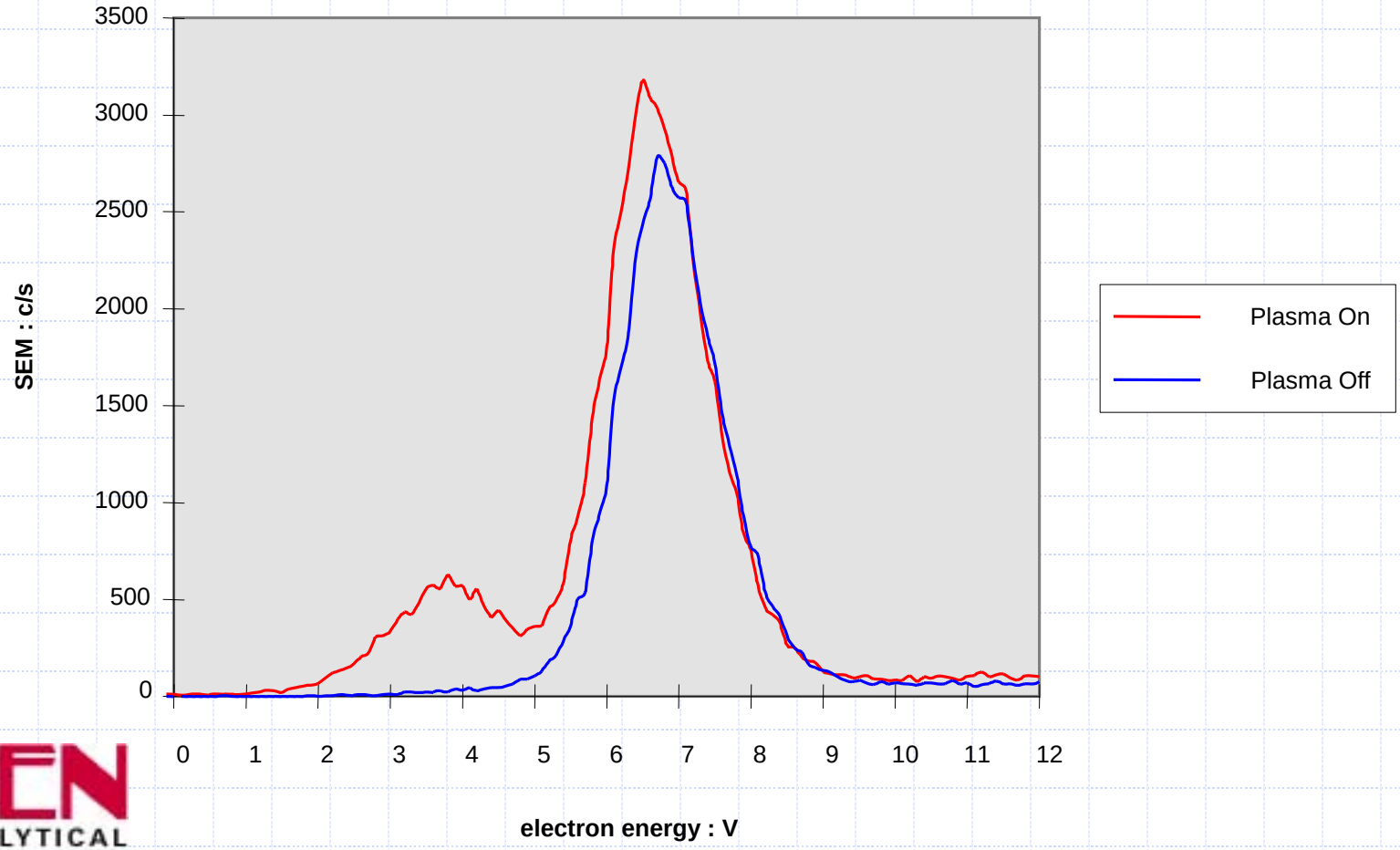
$$\searrow \quad CF_3^- + F \quad \text{(B)} \quad \text{and}$$

$$e + CF_4 \rightarrow CF_4^- \text{ (1st elect. excited state)} \rightarrow F^- + CF_3 \quad \text{(C)}$$

Only F^- ions are formed via reaction (C)

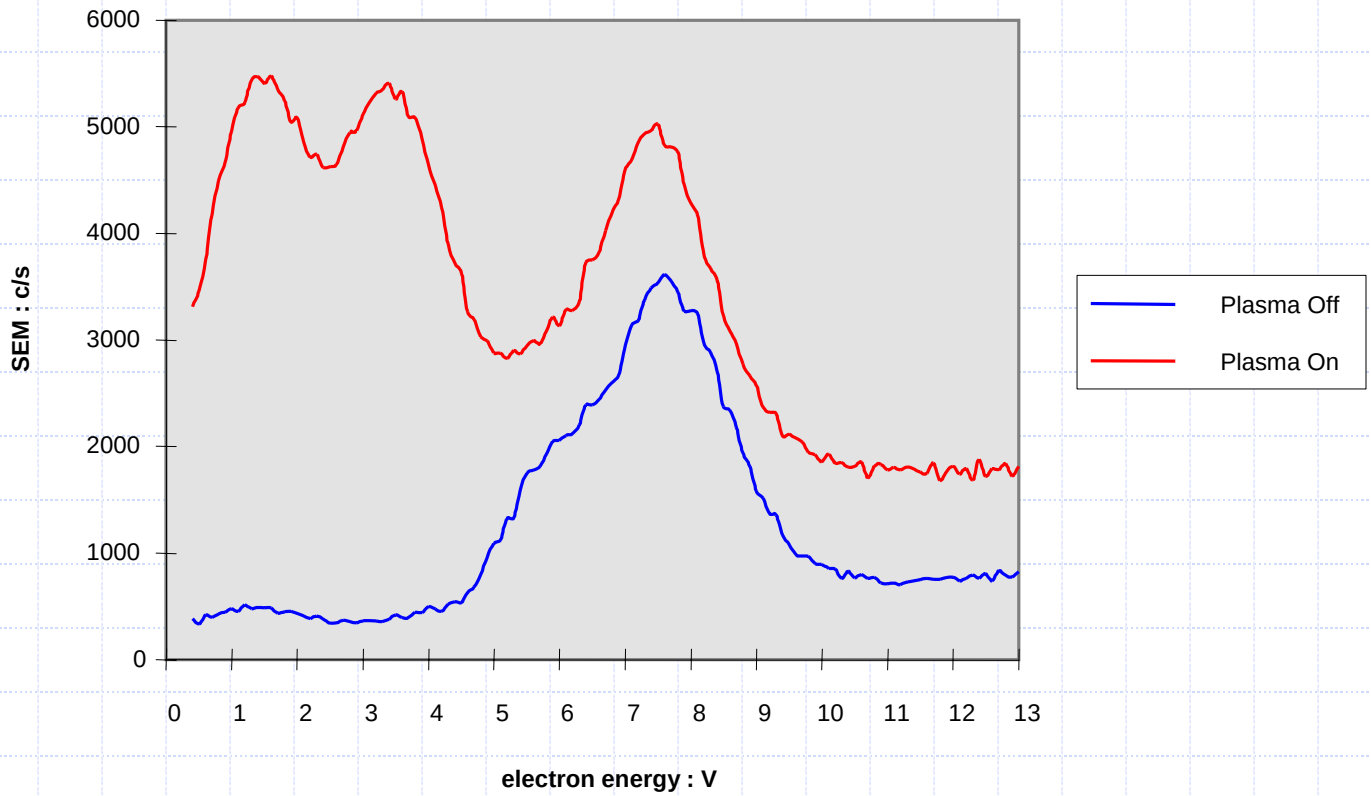
HIDEN ANALYTICAL

CF_3- Ions By Attachment In CF_4



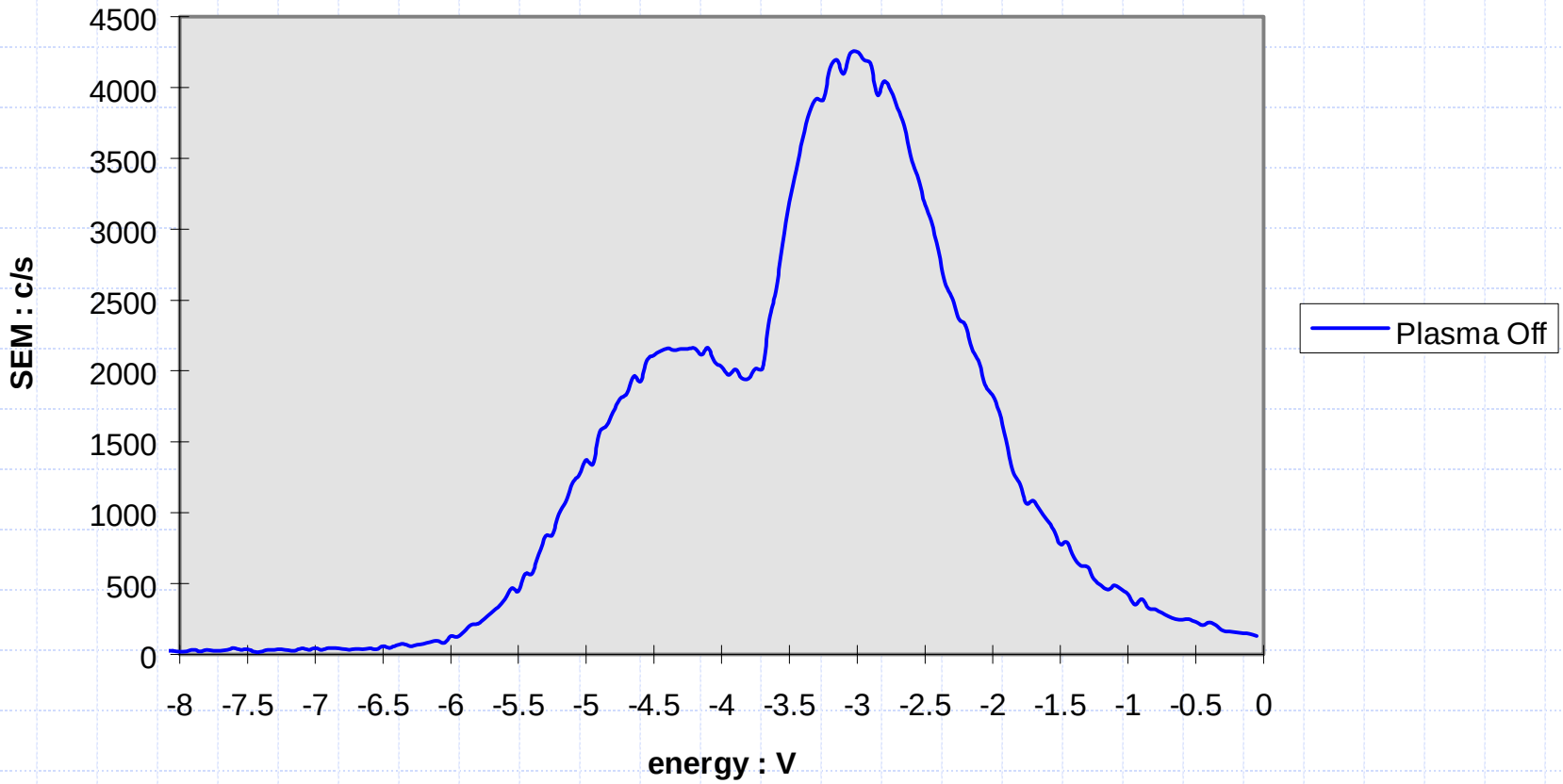
HIDEN ANALYTICAL

F- Ions By Attachment In CF_4



HIDEN ANALYTICAL

F- Ions By Attachment In CF_4 (Electron Energy = 6.5eV)



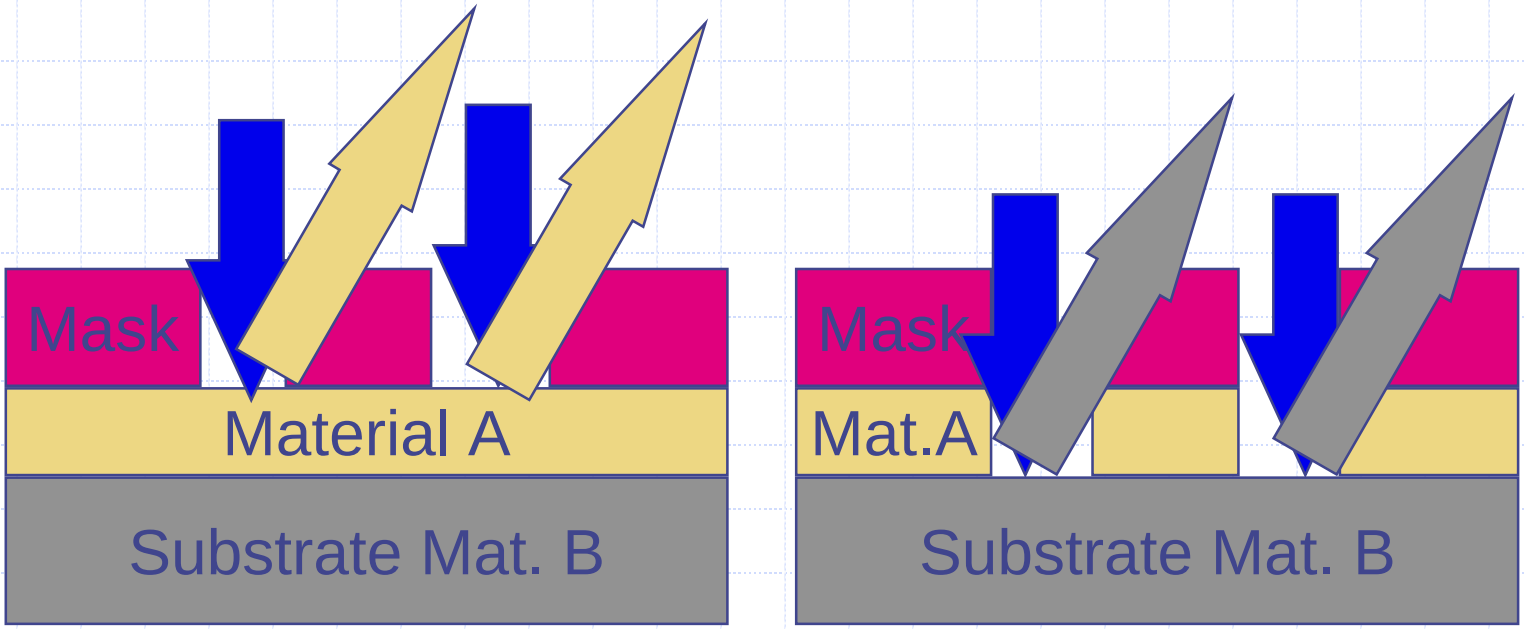
HIDEN ANALYTICAL

Results

- CF_3^-/F^- from neutrals in the EQP analysed
- CF_3^-, plasma off reflects electron attachment cross section for (B). Plasma on shows second peak 2.8 eV below main peak due to electron attachment to CF_3 fragments generated by the plasma
- F^- more complicated - analysing energy distribution at 6.5 eV electron energy helps. The 2 peaks correspond to F^- ions with near-thermal energies from (C) and F^- with higher translational energies from (A)

HIDEN ANALYTICAL

3. End Point Detection



Primary Ion Beam

Secondary Ions Mat.A

Secondary Ions Mat.B

HIDEN ANALYTICAL

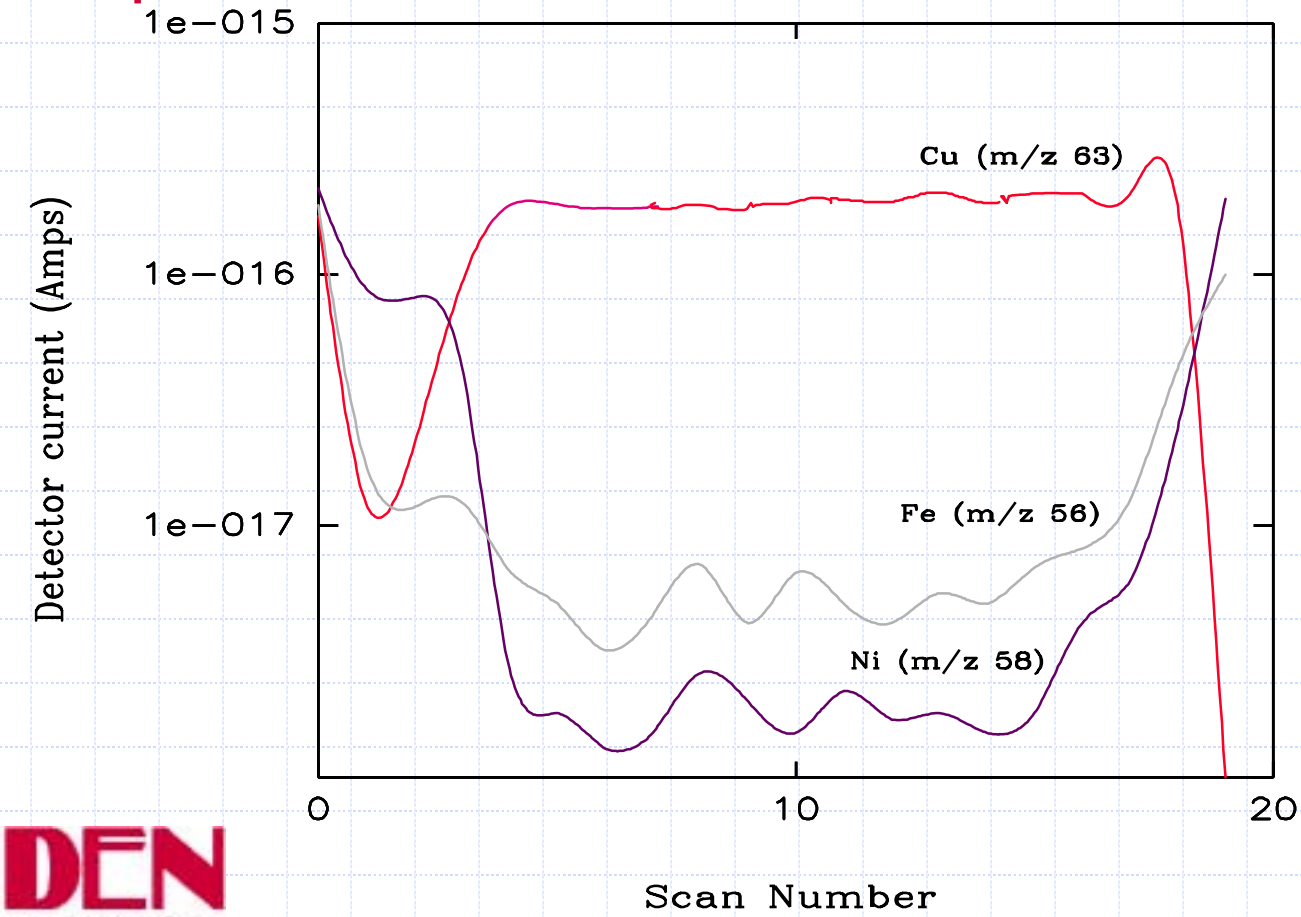
Materials Guide

INTERFACE	APPLICATION EXAMPLE
Si/Ga	Identification of SiO_2 interface on III-V semiconductor.
Au/Cr/Al	Au/Cr track identification on aluminium substrates.
Au/Ti/Ga	Precise definition of Au/Ti electrical contacts in GaAs.
Mo/Ge	Precise definition of Mo/Ge interfaces in multifilm Mo/Ge structures.
Al/In	Identification of the interface between two semiconductors Al In As/InP.
Al/Ga	To etch down to the interface between two layers of AlGaAs separated by a 79 Å GaAs well. The Al signal clearly identified the sandwich.
Y/Ba/Cu/MgO	Identification of separate layers in multilayer superconductor materials.
NiCr/Cu/NiFe/SiO2	Magnetic disc sensor head manufacture.

HIDEN ANALYTICAL

End Point Detection-

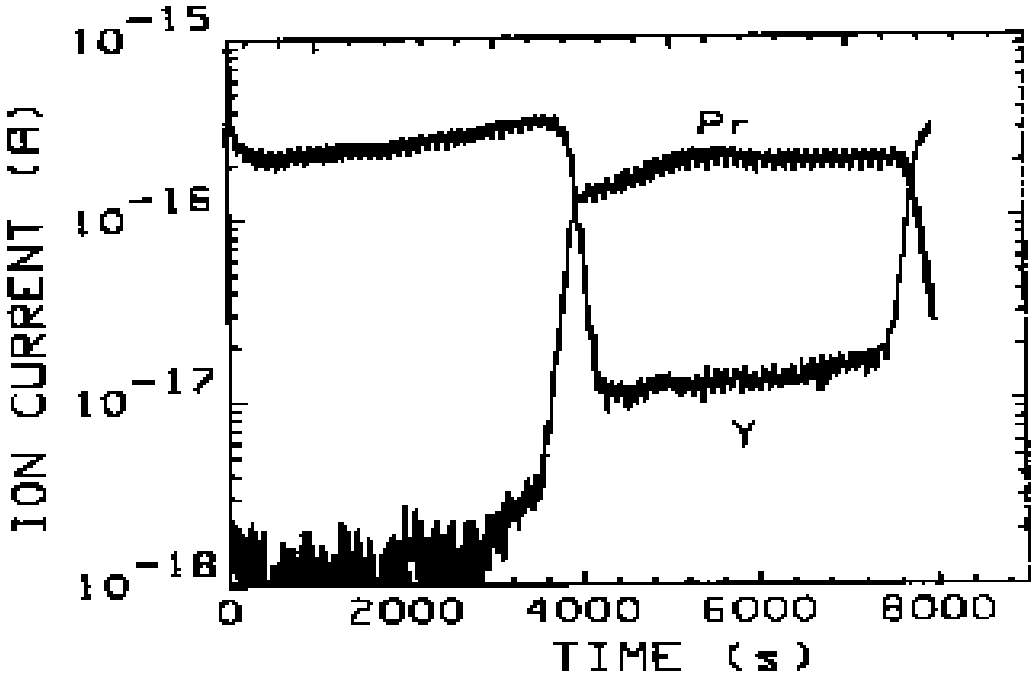
Etch profile for a Cu/NiFe layered material, with the objective to stop on the NiFe layer.
Sample was 99% masked



HIDEN ANALYTICAL

Tri-layer interface

YBa2Cu3O7-PrBa2Cu3O7-YBa2Cu3O7



HIDEN ANALYTICAL

End Point Resolution

The secondary ion signal defines the interface with high specificity, sensitivity and with resolution limited only by surface and etch process uniformity.

End points are routinely measured to within 10 Å in ion beam etch processes.

HIDEN ANALYTICAL

4. Pulsed Laser Deposition

The EQP system includes the following data acquisition facilities which provide for accurate determination of pulsed laser deposition species

- **Time Averaged Spectra**
- **Time Resolved spectra using gated acquisition**

These acquisition modes apply to the analysis of :
Neutrals Fast Neutrals +ve ions -ve ions Radicals

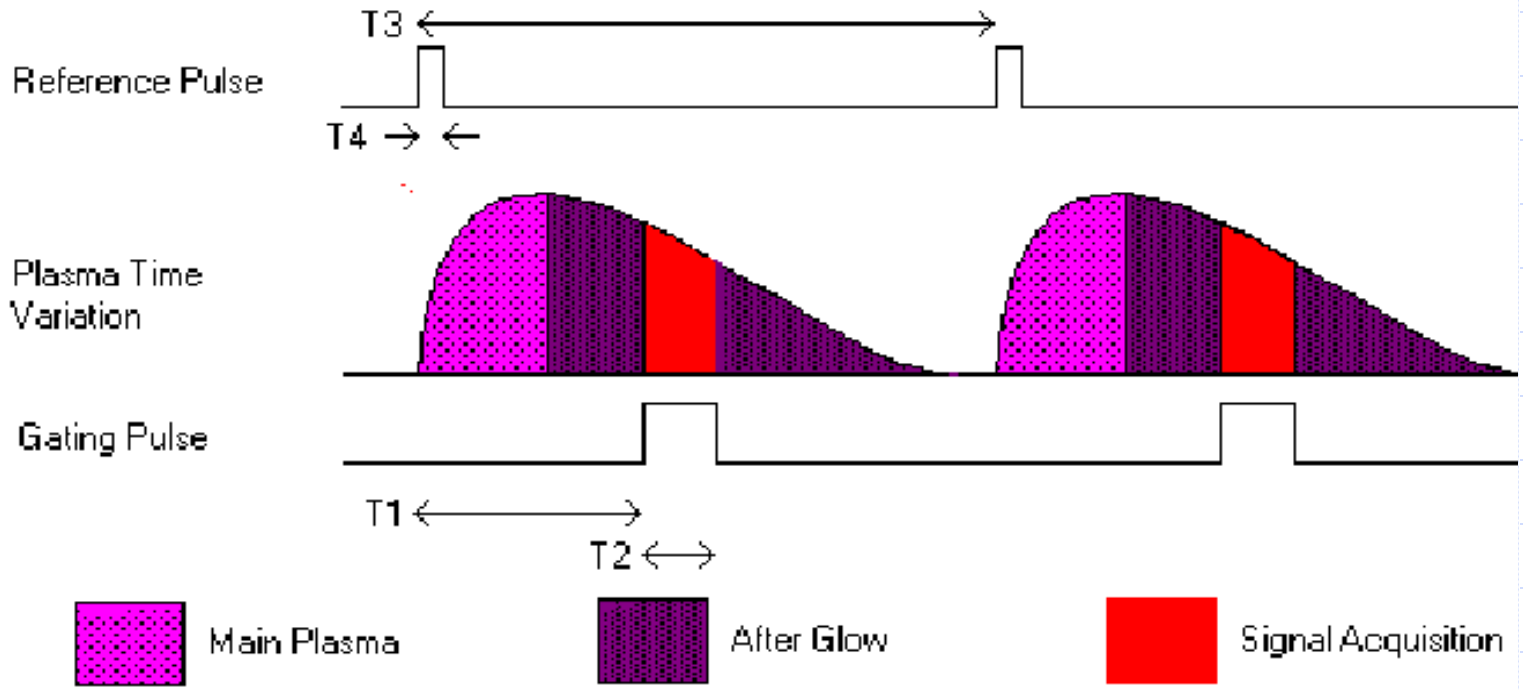
HIDEN ANALYTICAL

Time Averaged Spectra

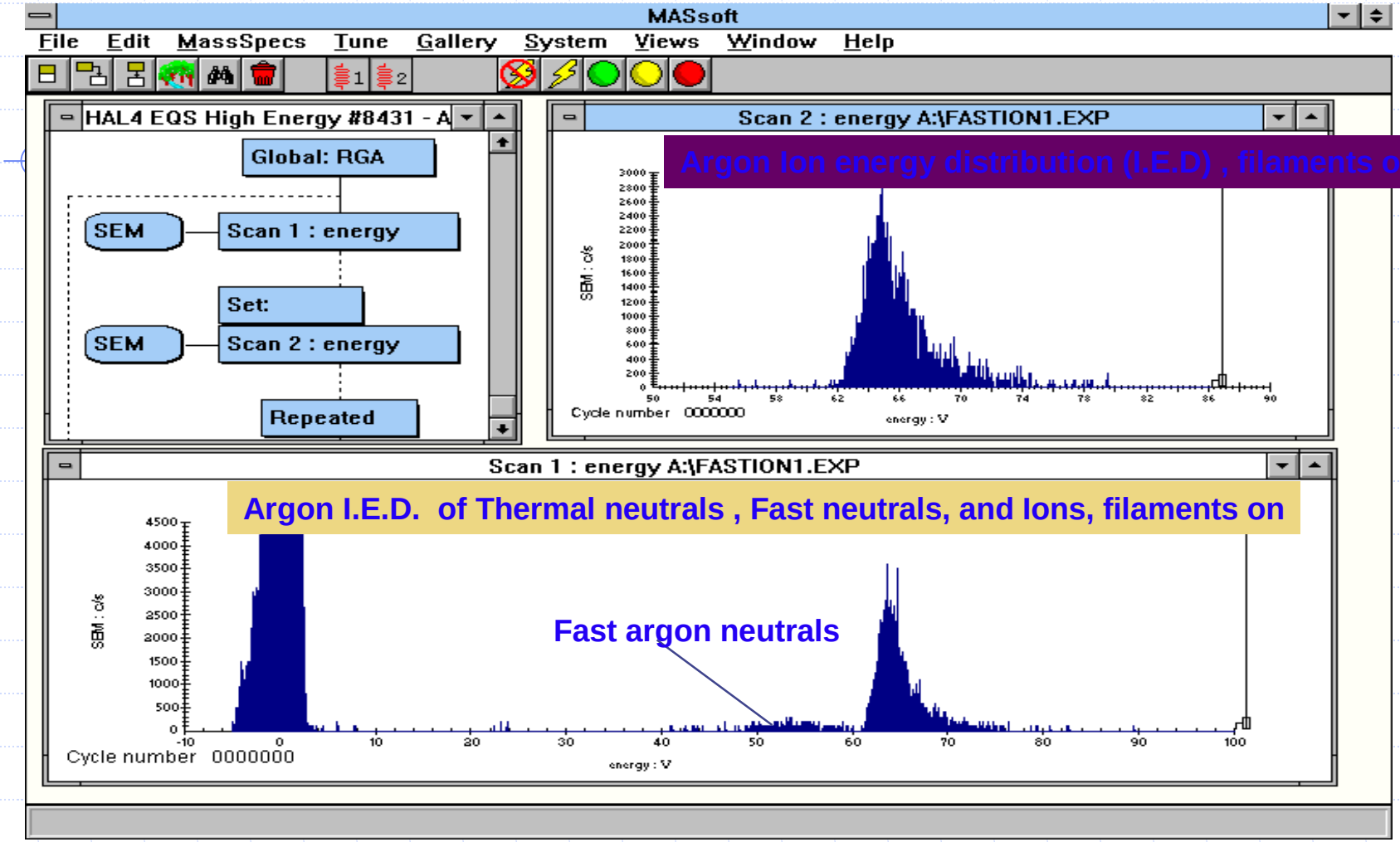
- In this mode the mass and energy spectra are accumulated over the desired acquisition time period.
- The instrument integrates the signal from scan to scan building a time averaged picture of the mass and energy distribution of the pulsed plasma products.

HIDEN ANALYTICAL

Time Resolved Data Acquisition From Pulsed Plasma



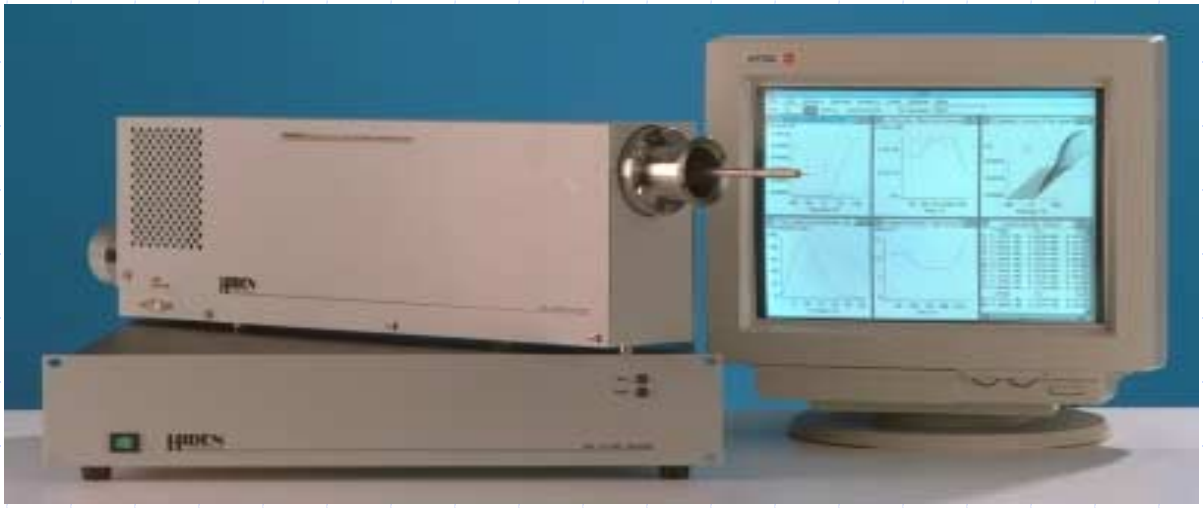
HIDEN ANALYTICAL



HIDEN ANALYTICAL

For The Future

- Quadrupole Mass Spectrometry/Langmuir Probe
- SPC Techniques
- Feedback Control - electron injection
- ..... To name but a few!!



HIDEN ANALYTICAL