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Mass and Energy Spectrometry of Processing Plasmas

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Hiden Analytical, Warrington UK.

November, 2011.

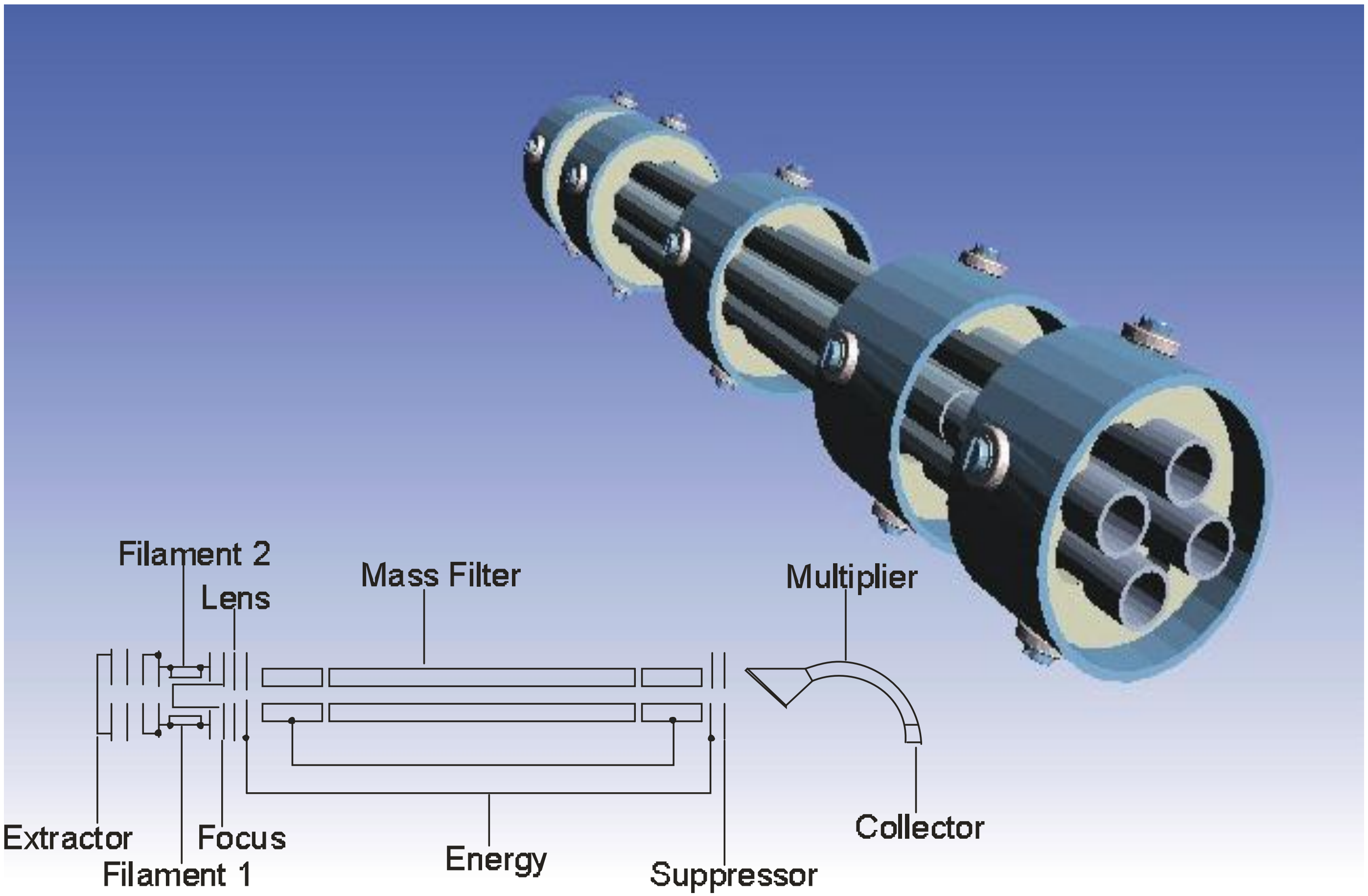
Hiden Analytical

Diagnostic equipment for 4 main areas:

1. Mass spectrometry
2. Surface analysis
3. Catalysis
4. Plasma diagnostics

Key component of much of the equipment is a quadrupole mass spectrometer.

Quadrupole mass spectrometer.



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Hiden TPD Workstation

A complete experimental system for UHV temperature programmed desorption (TPD) studies

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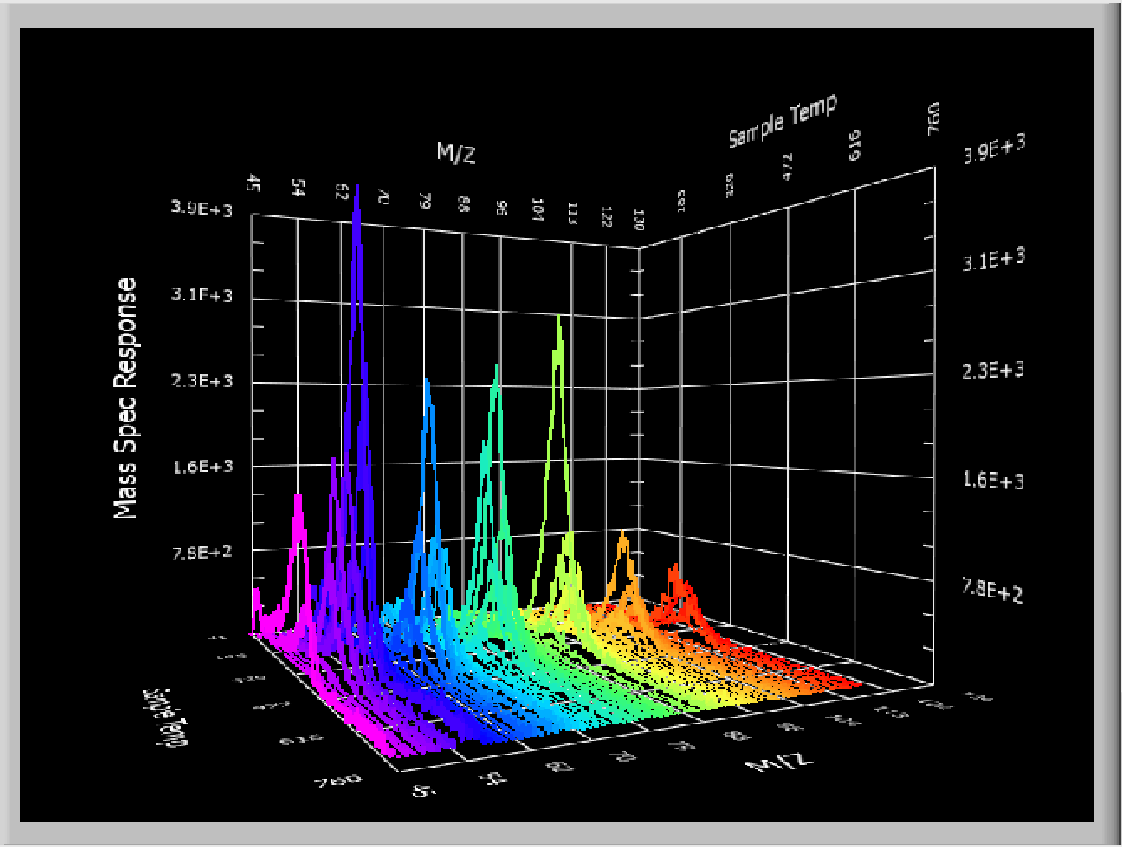
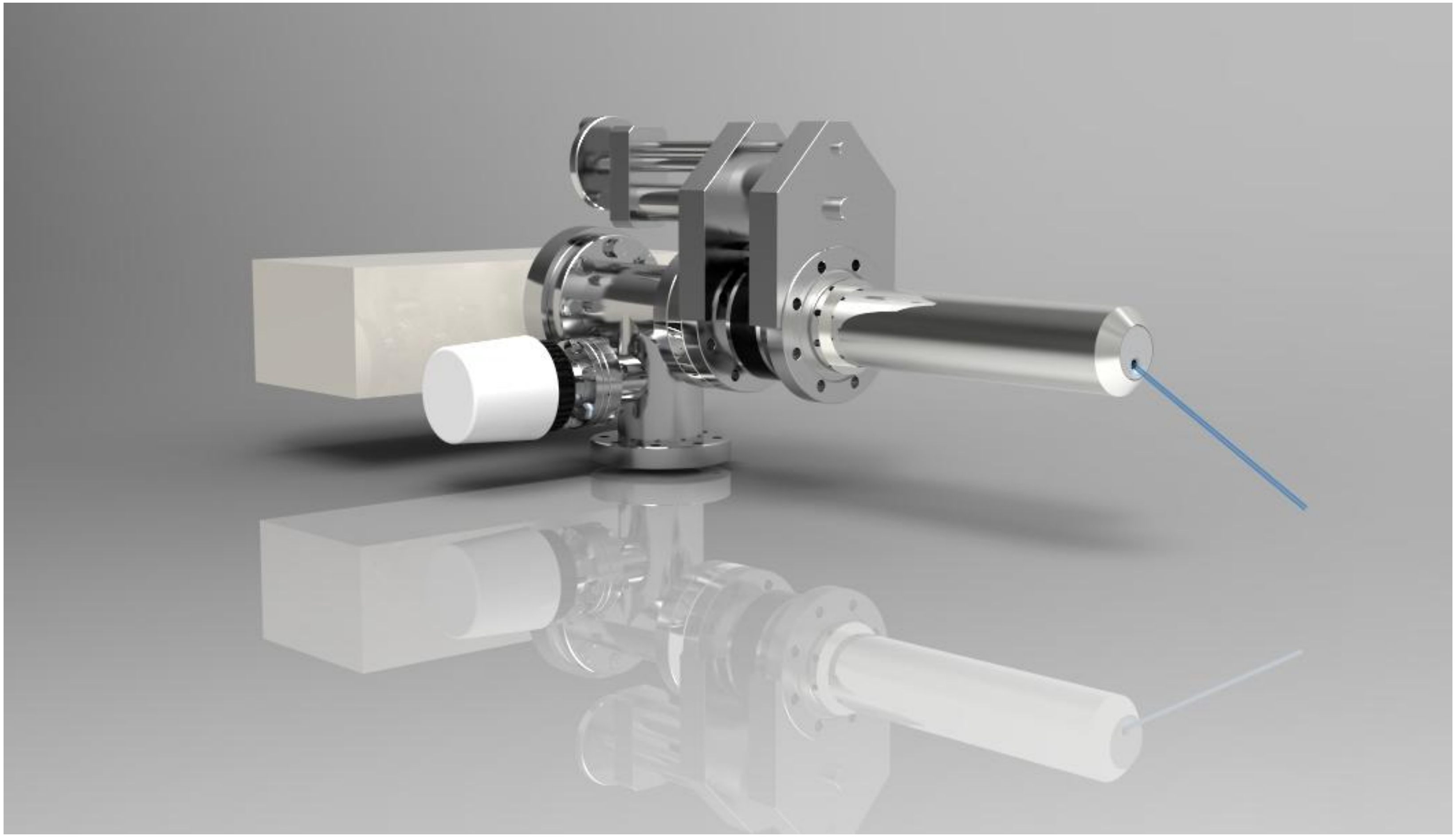
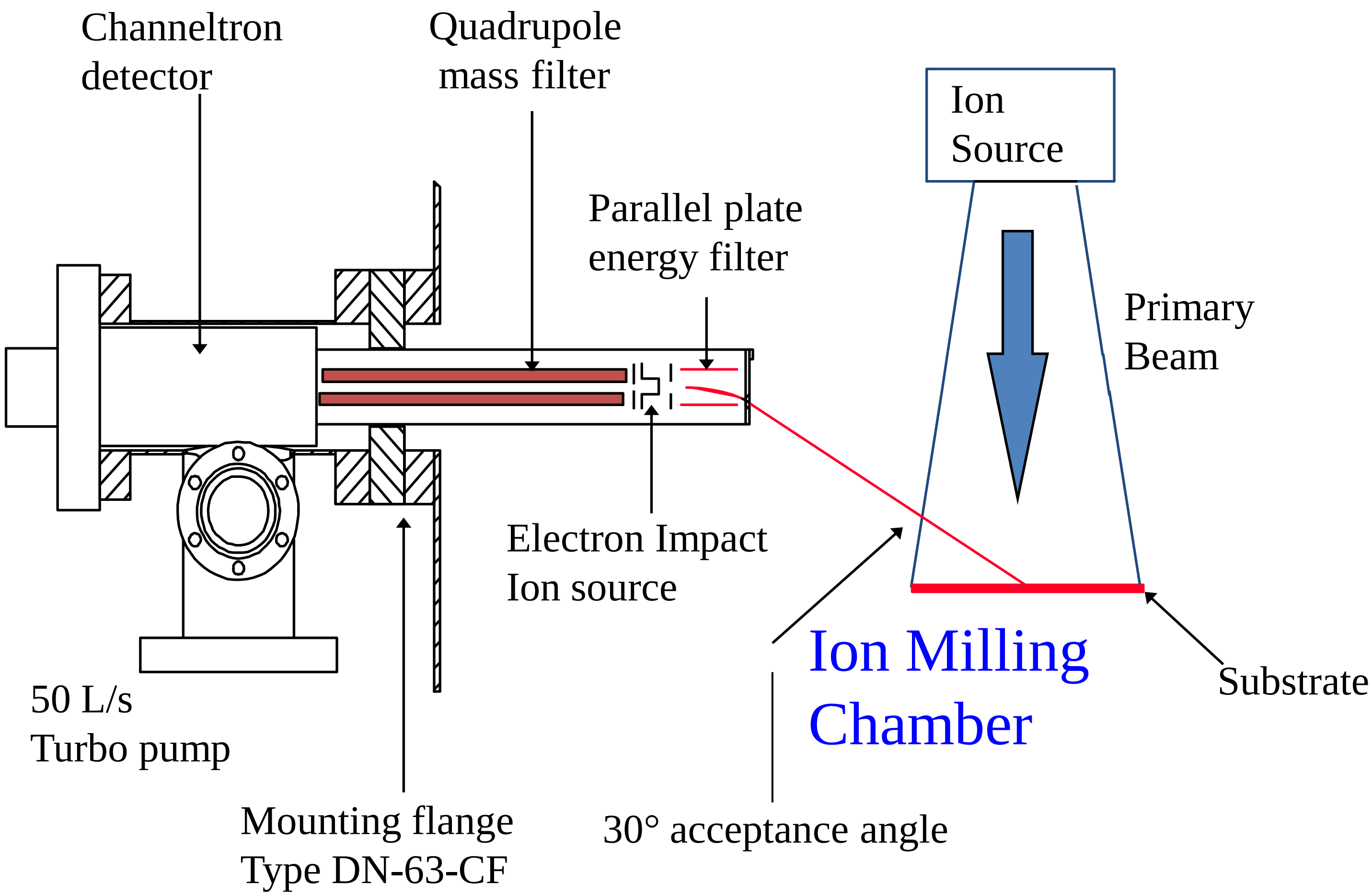
Example : desorption data from surface modified Si wafer



Ion Milling Probe.



Ion Milling Probe



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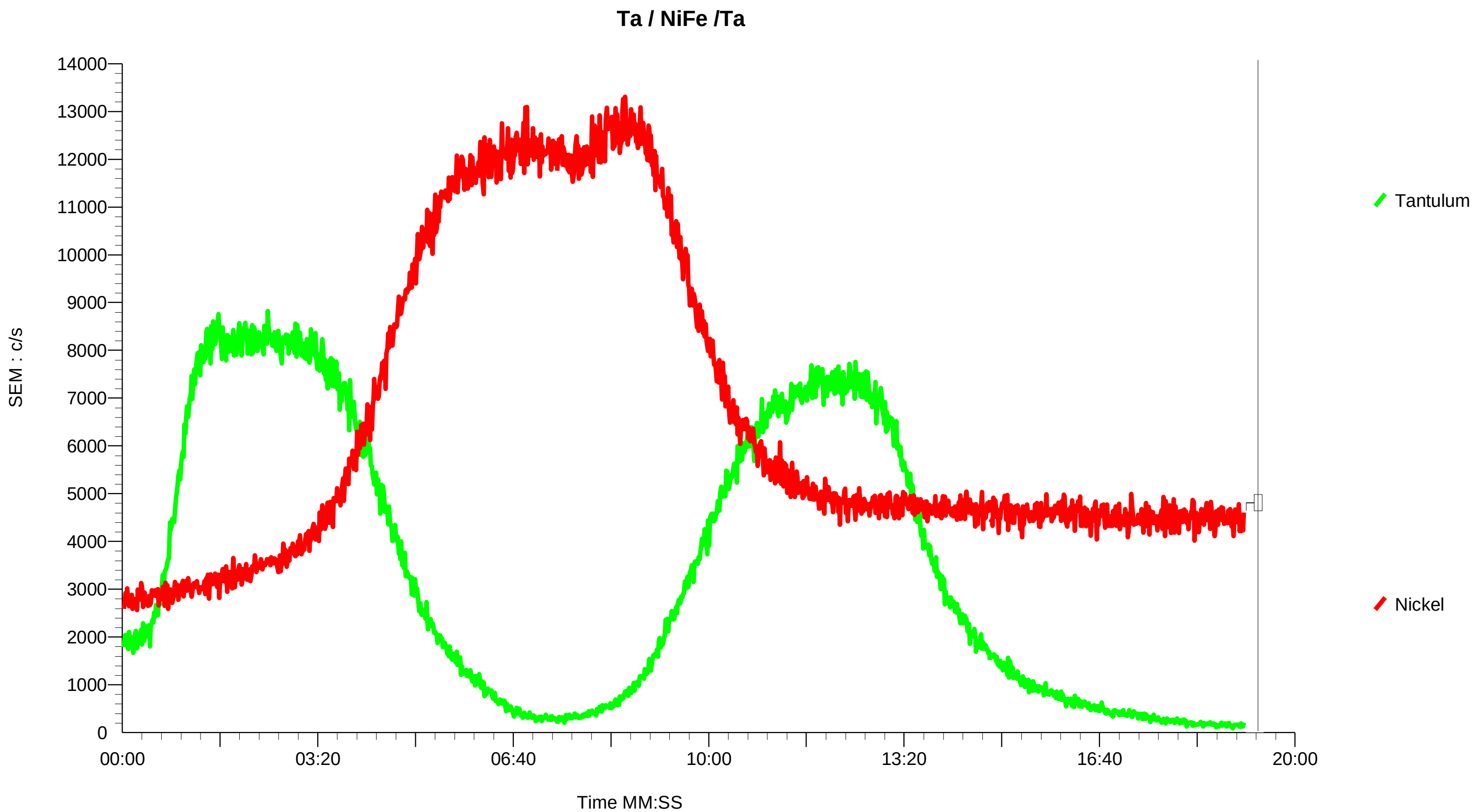
Sample data : Ta/NiFe/Ta



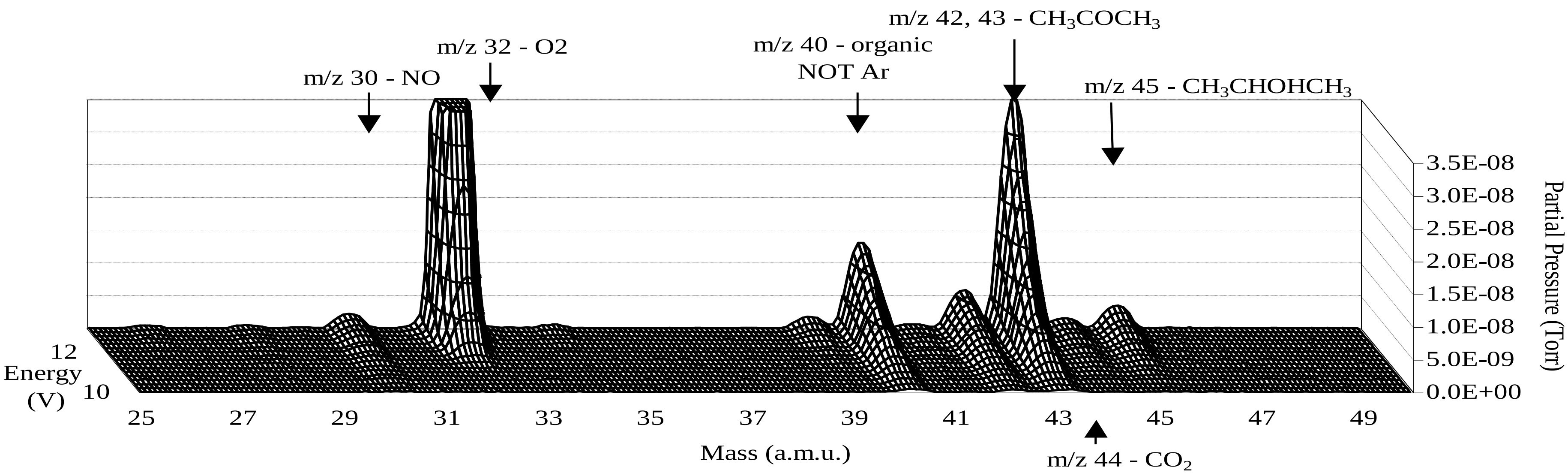
Trace Impurities

For traces of materials with low ionisation potentials ‘SOFT IONISATION’ techniques can be used

e.g. for traces of organic vapours in air

The electron energy in the ionisation source of the mass spectrometer is set to a low value (typically 10 to 15eV) instead of the more usual 70eV

MS Surface of an Acetone / Isopropyl Alcohol / Air vapour stream at Electron Energies of 10-13V



Threshold ionisation measurements are also useful in plasma diagnostics e.g. for looking at plasma dissociation of the working gas.

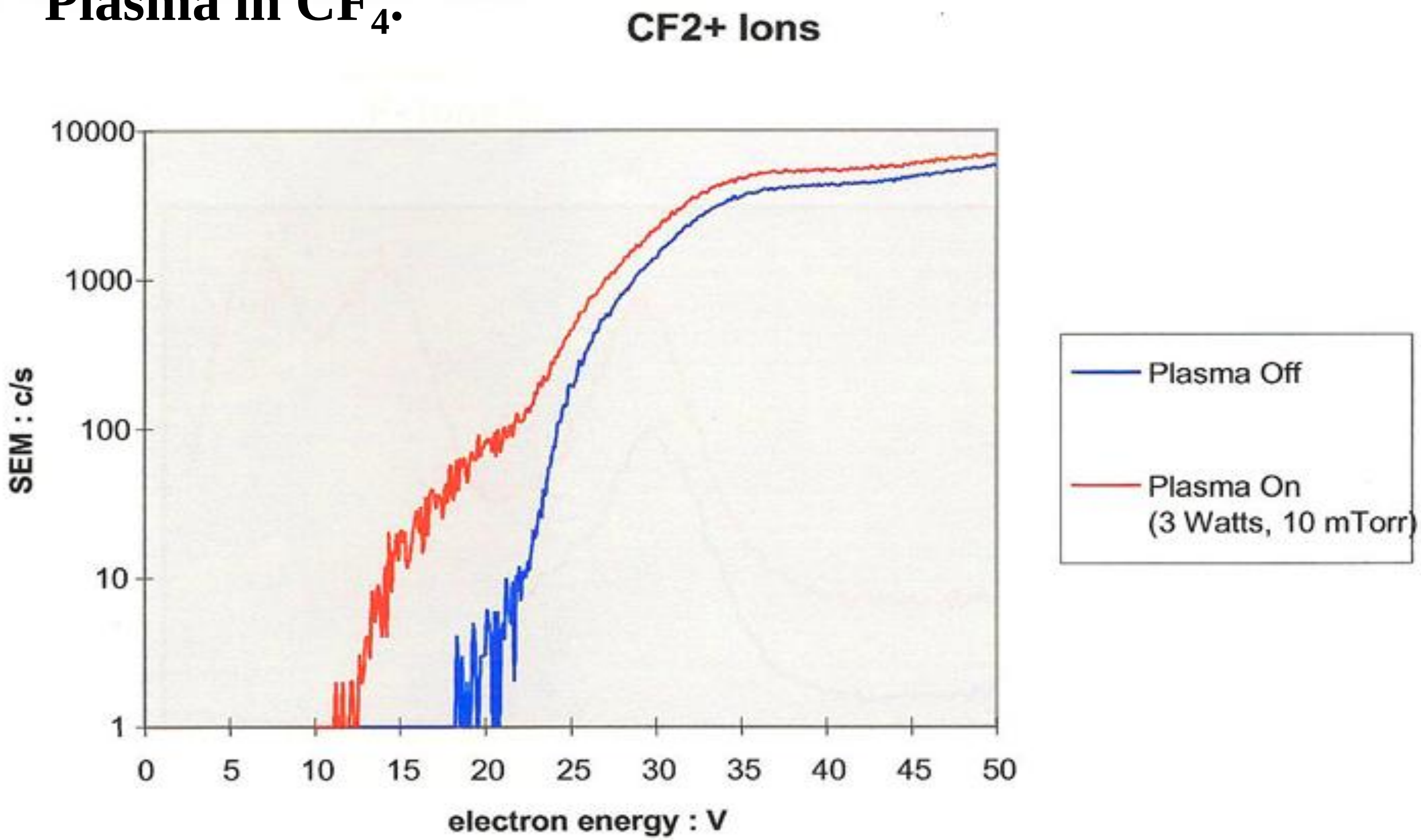
Such measurements have been made for over 10 years.

The main requirement s are:

(1) the ability to scan the energy of the electrons in the mass spectrometer source and

(2) the ability to prevent ions from the plasma from entering the mass spectrometer.

Plasma in CF_4.



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)

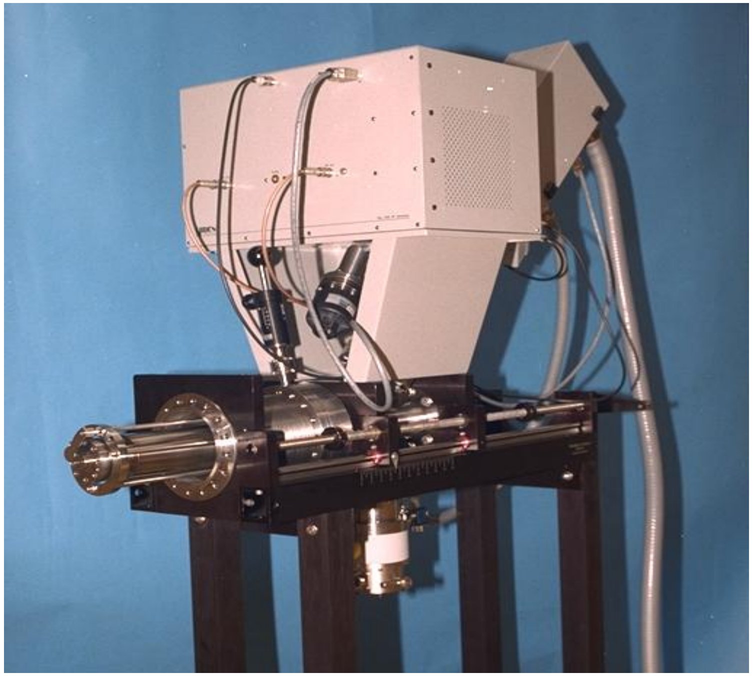
- With the plasma turned on, extra CF_2^+ ions are expected from the additional processes:

  $e + CF_3 \rightarrow CF_2^+ + F + 2e$

  $e + CF_2 \rightarrow CF_2^+ + 2e$

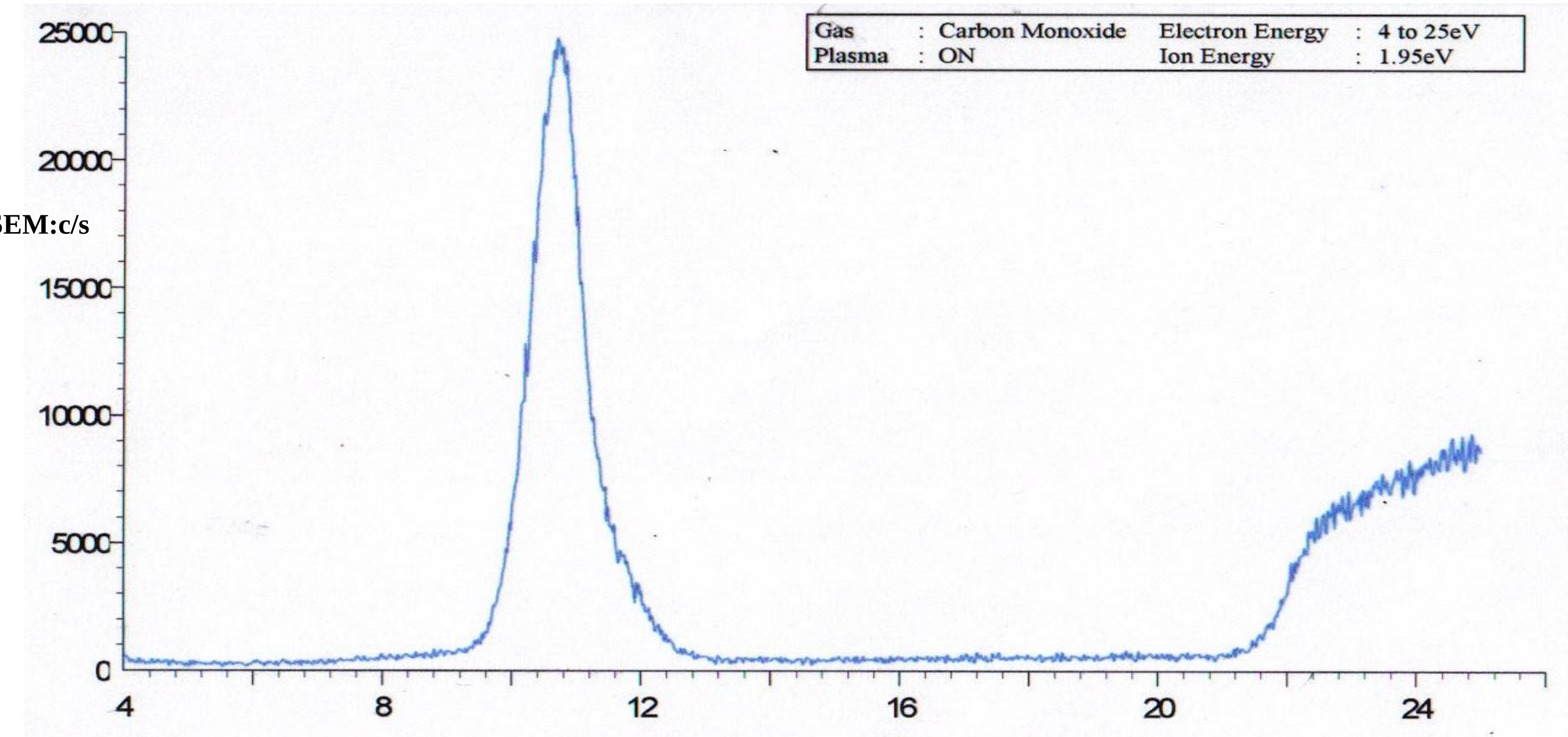
Analysis of Plasma Neutrals by Electron Attachment.

- Useful technique for electro-negative gases
- The ‘Finger print’ is often simpler than the more usual positive ion mass spectrum.

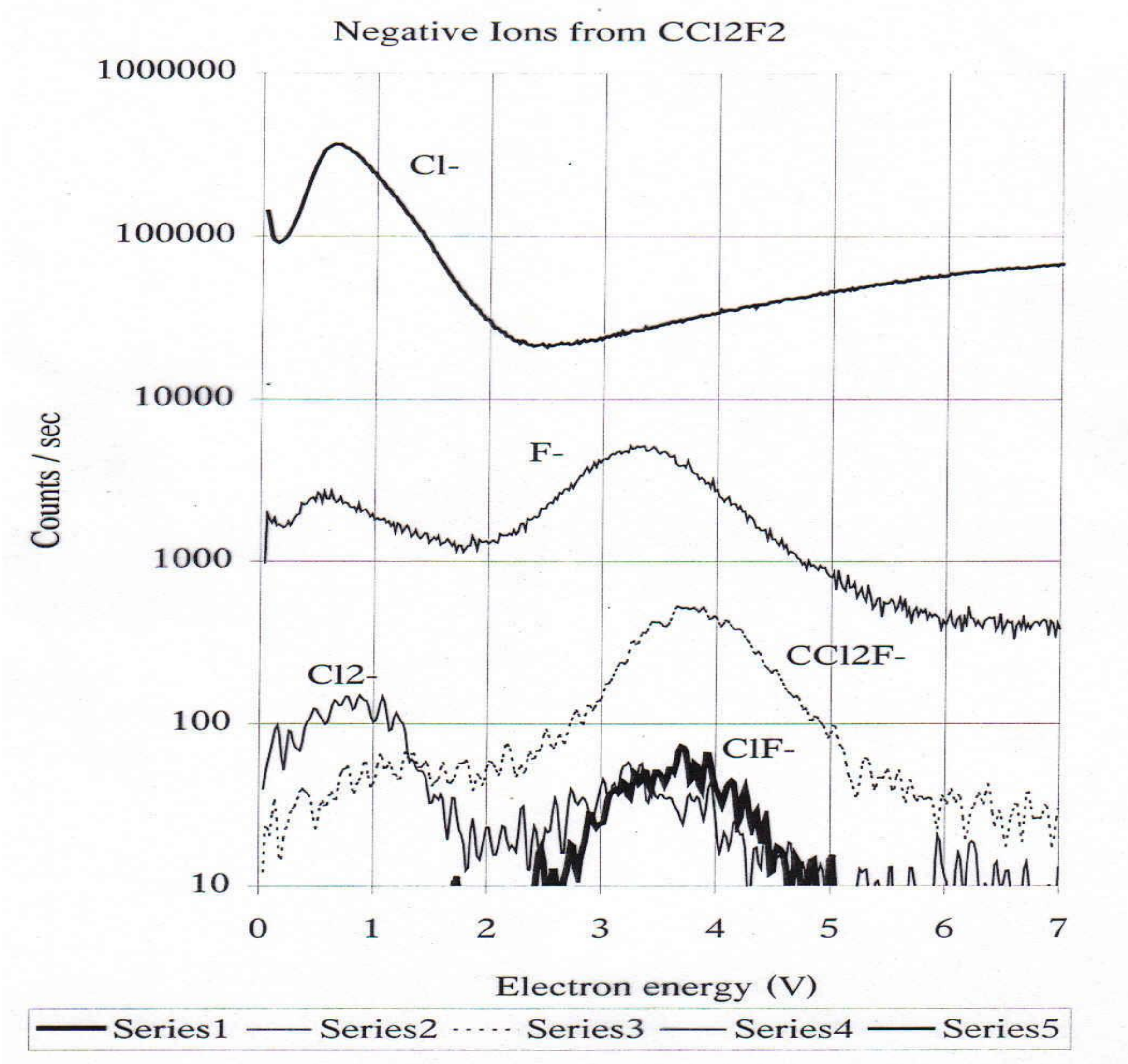


O^- ions from CO at 1×10^{-6} Torr

SEM:c/s



Electron-energy: V

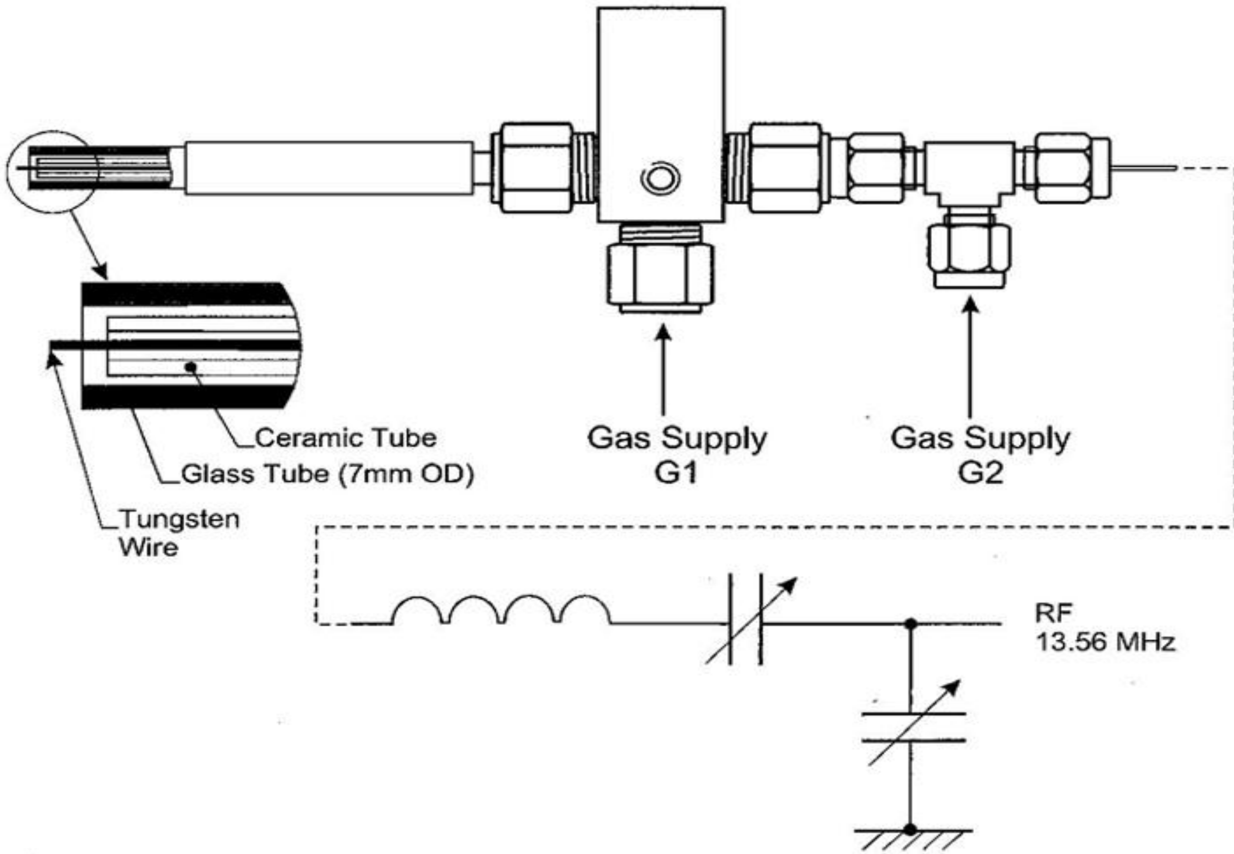

Negative Ions from CCl2F2
1000000
100000
10000
1000
100
10
Counts / sec
Cl-
F-
CCl2F-
Cl2-
ClF-
0
1
2
3
4
5
6
7
Electron energy (V)
Series1
Series2
Series3
Series4
Series5

PLASMA DIAGNOSTICS for high pressure plasmas (e.g. atmospheric pressure plasmas).

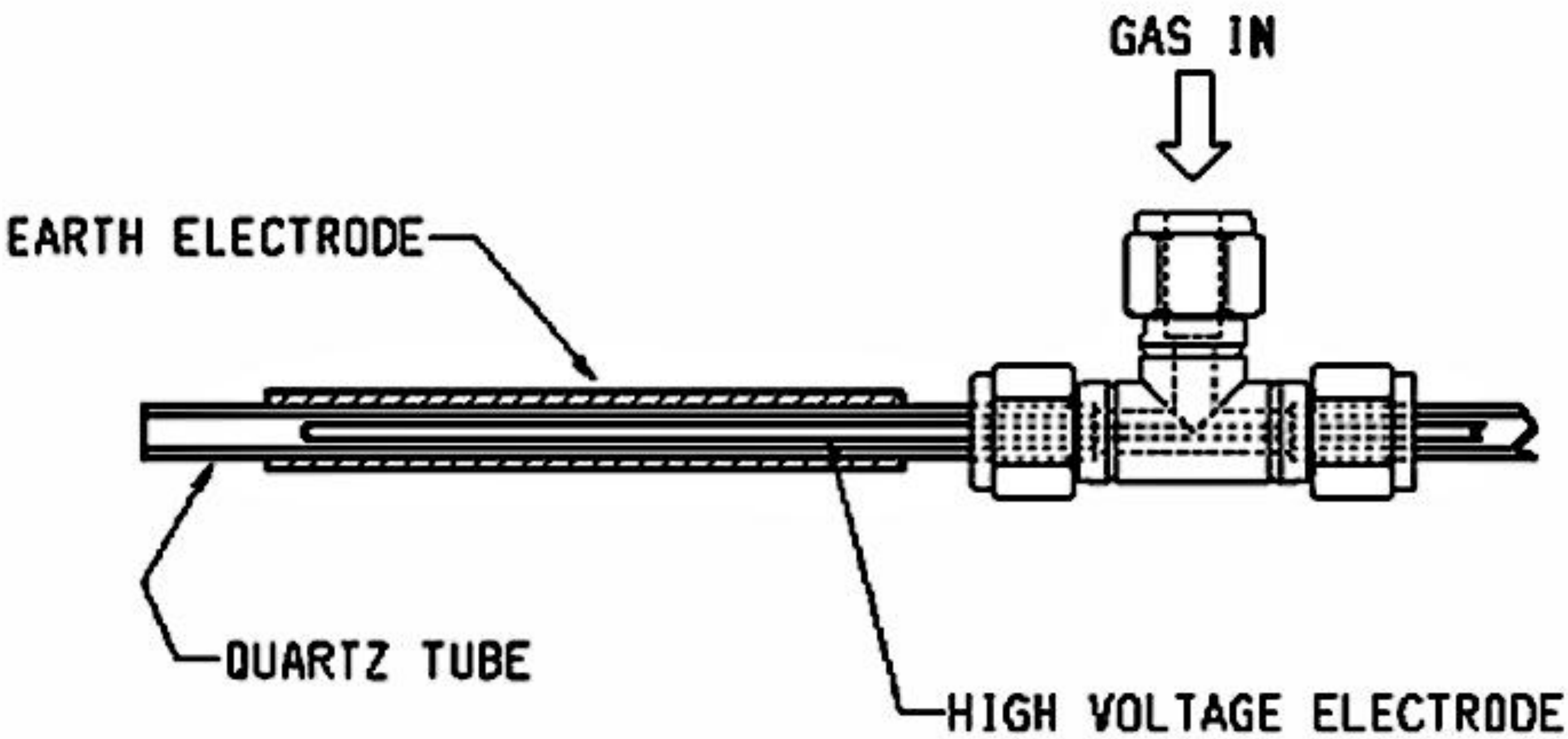
HPR 20 and 60 instruments.
HPR 20 instruments are for neutral analysis.

HPR 60 instruments incorporate *either*
EQP *or* PSM mass/energy analysers primarily
for work on plasma ions.

Sketch of plasma needle

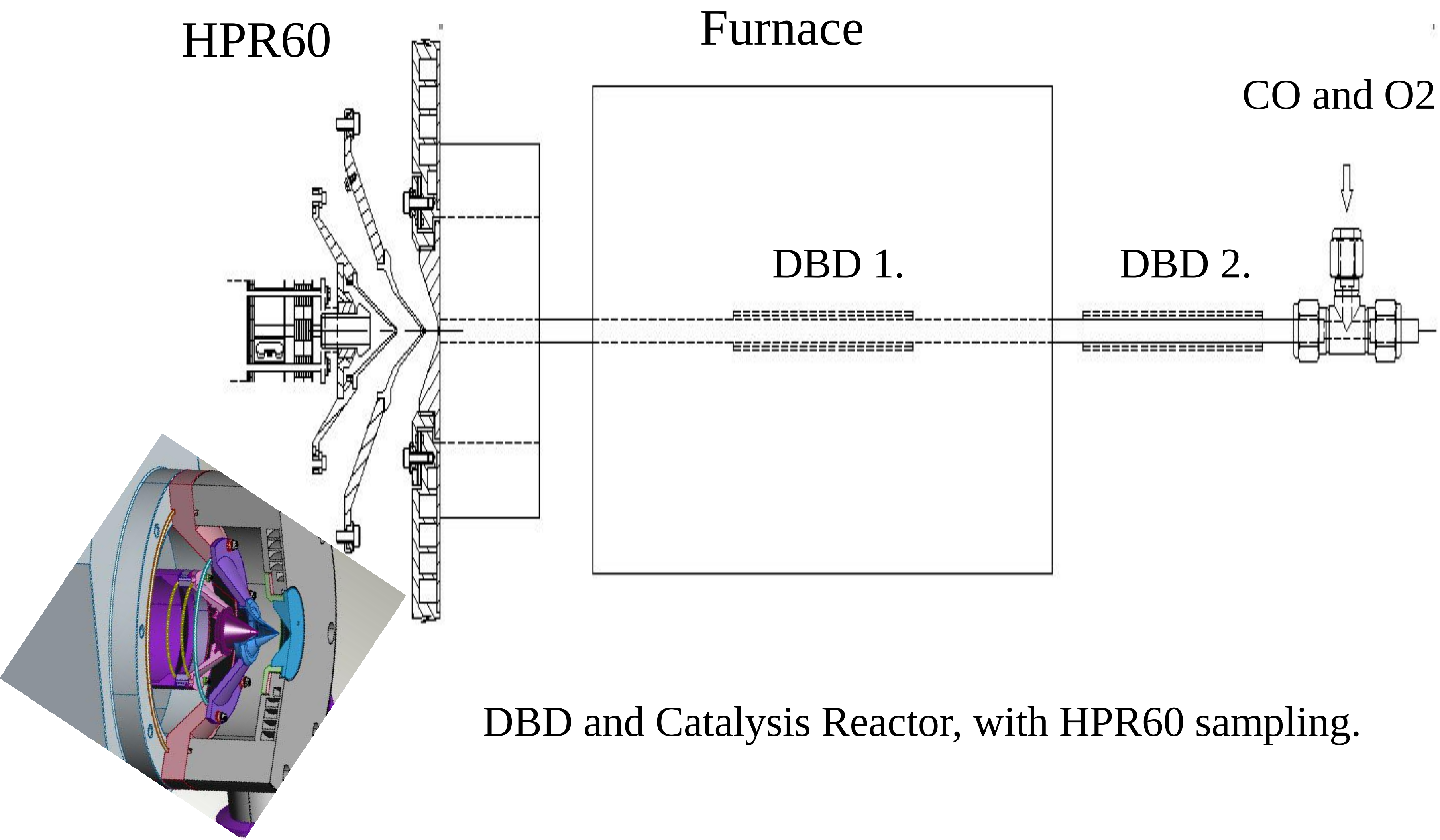


Sketch of small DBD reactor.

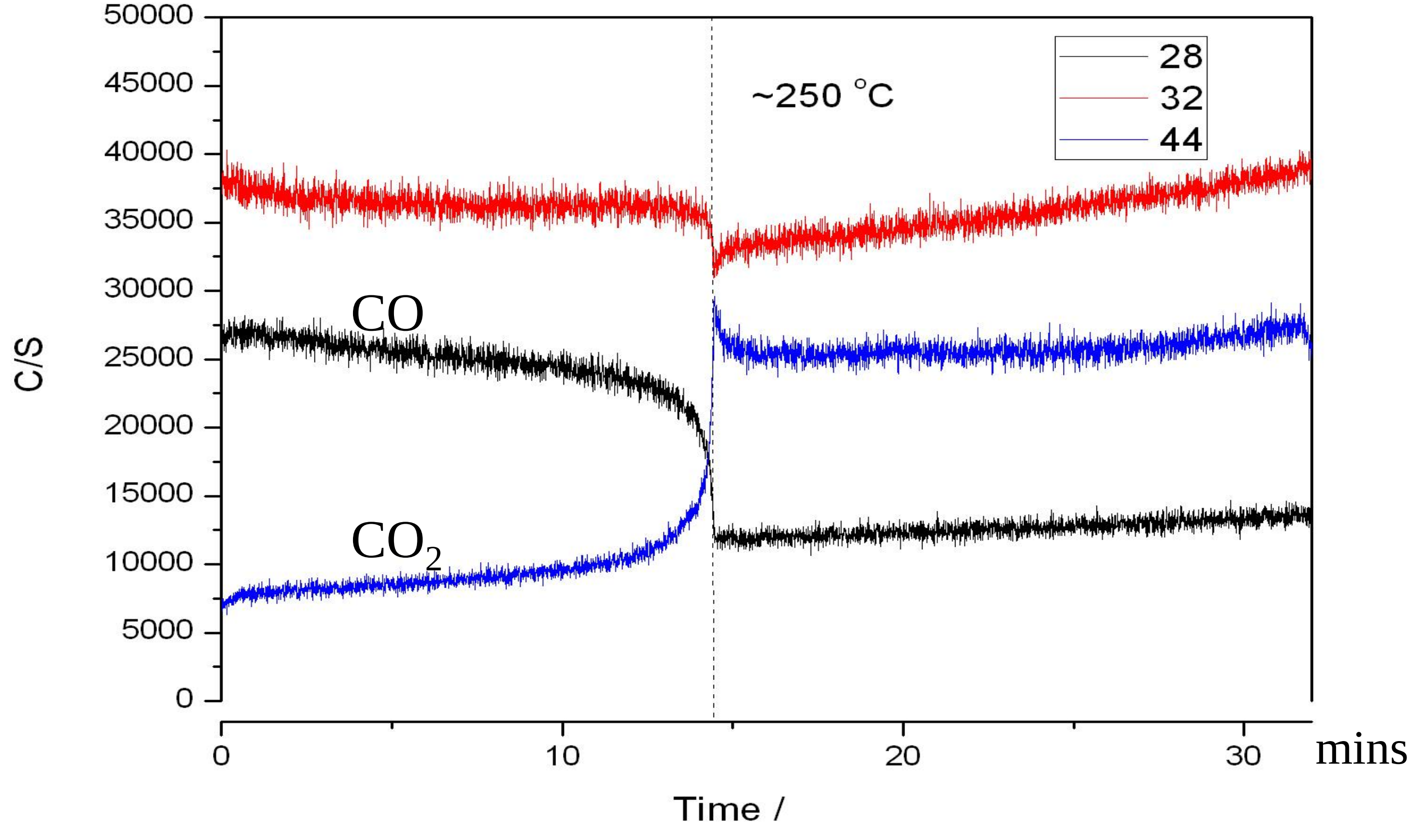


Typical areas of application.

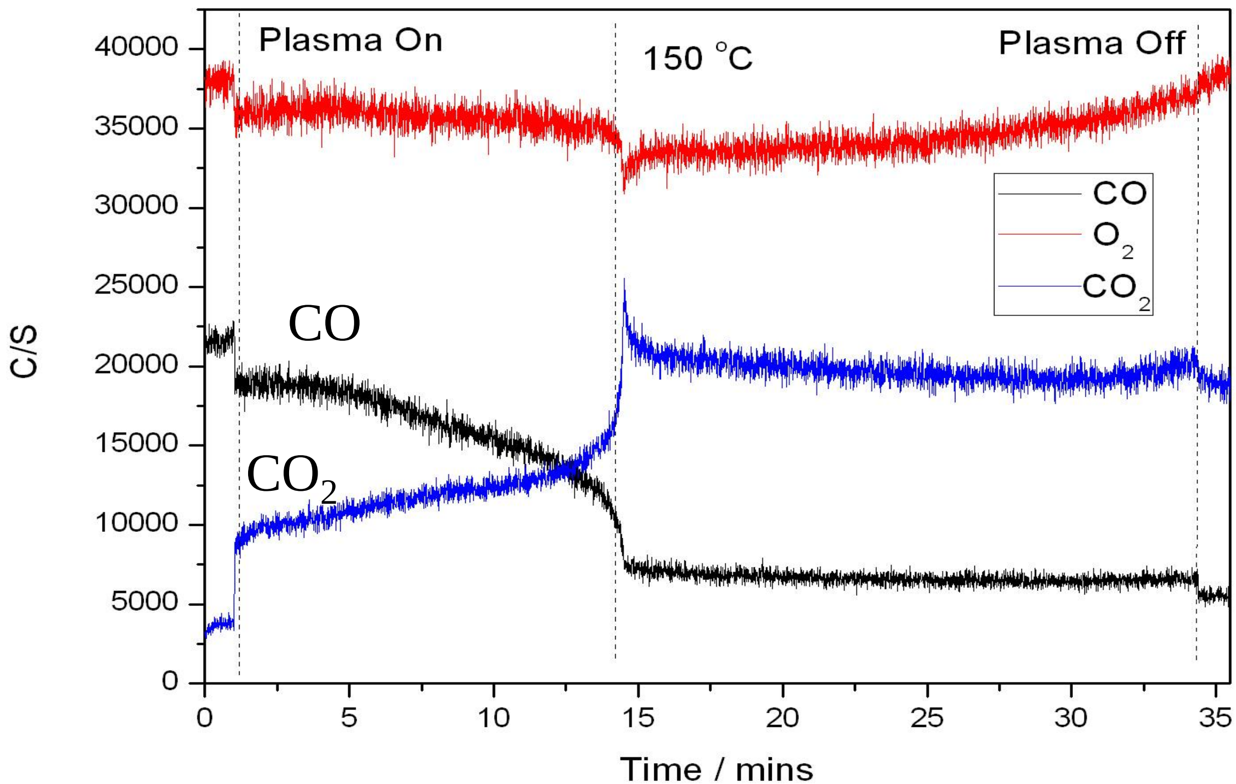
1. **Medical applications, e.g. Deactivating bacteria, tissue treatment/removal, nitric oxide production, etc.**
2. **Functional surfaces, e.g. hydrophobic coatings.**
3. ***Plasma-assisted catalysis.***
4. **Surface analysis.**



DBD and Catalysis Reactor, with HPR60 sampling.



Catalyst only.



Catalyst plus Plasma.

Diagnostic information for:

- Reactor System Environment
- Working Gas Composition

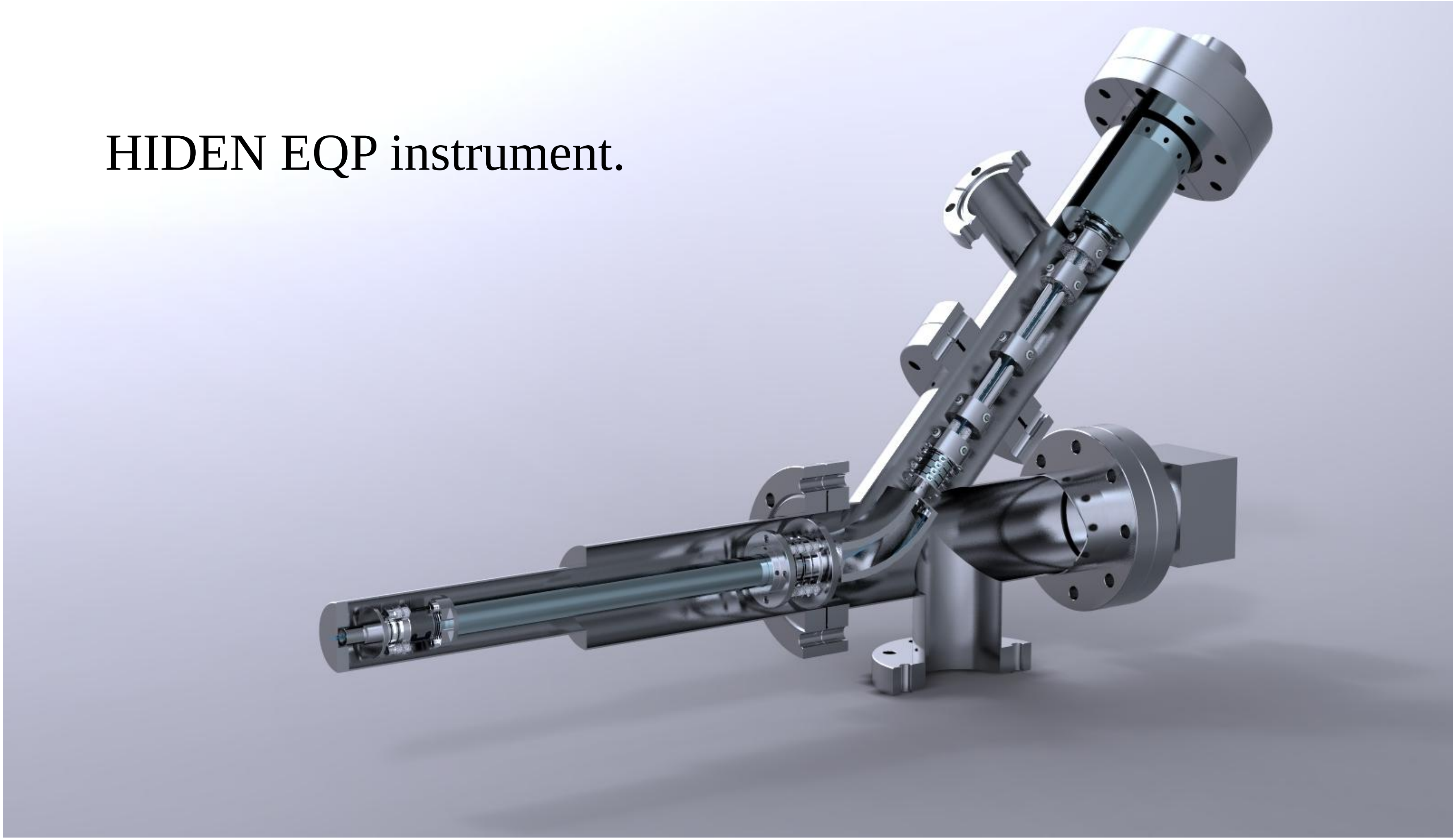
- Plasma neutral constituents a) Electropositive
  b) Electronegative

- **Positive and negative Plasma Ion constituents**

- **Ion Energy Distributions**
- **Neutral Energy Distributions**

- **Time-resolved studies**

HIDEN EQP instrument.



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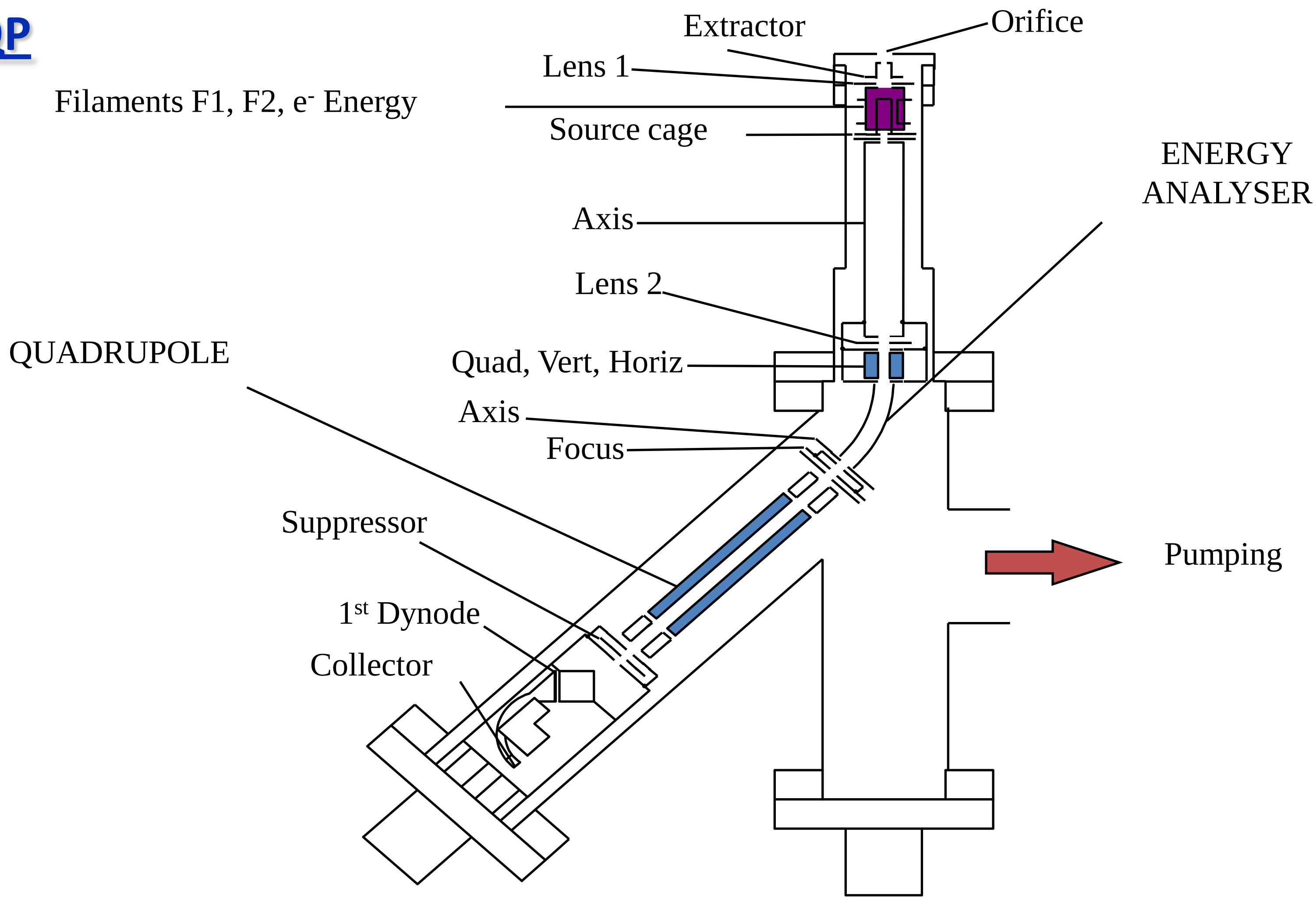
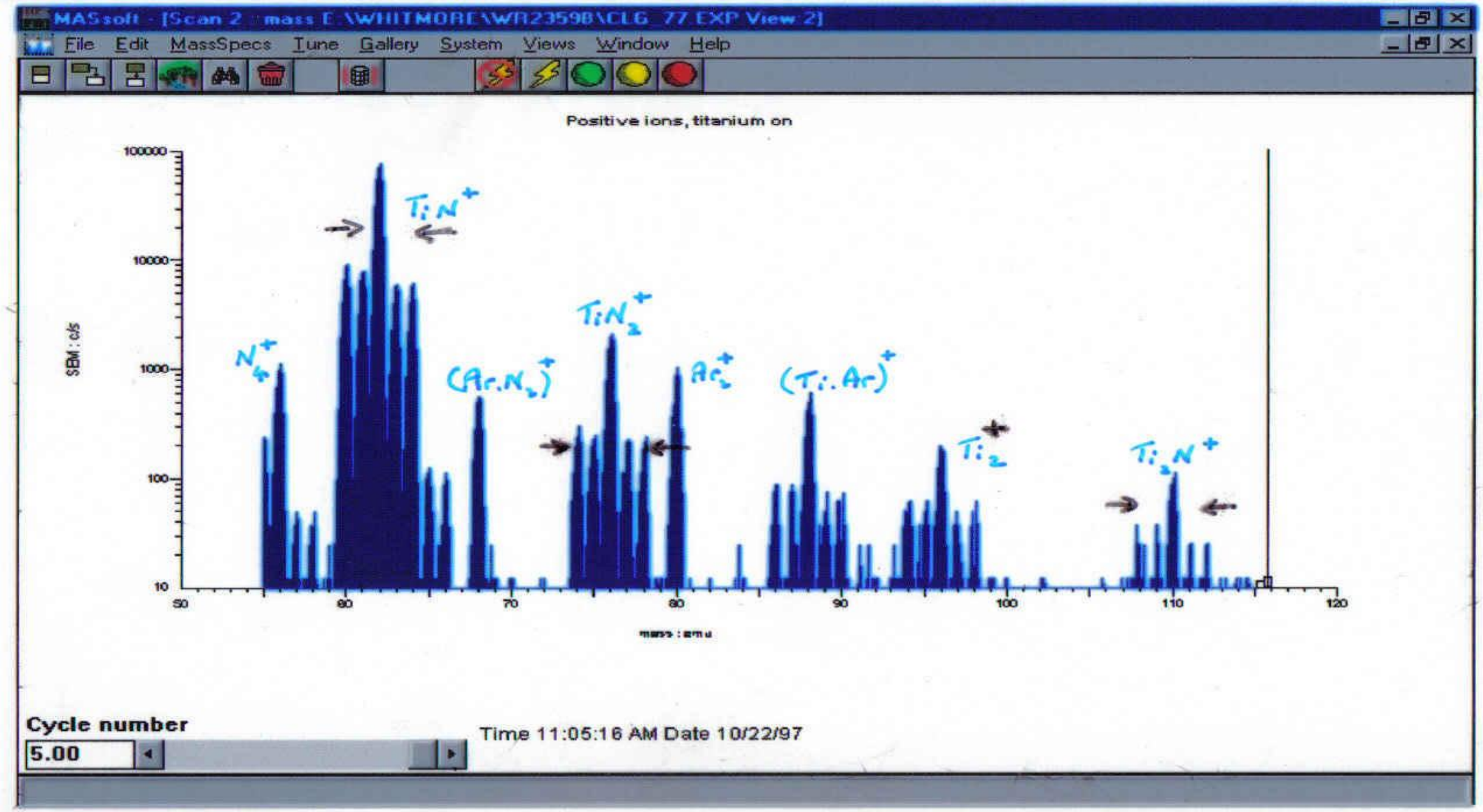
EQP

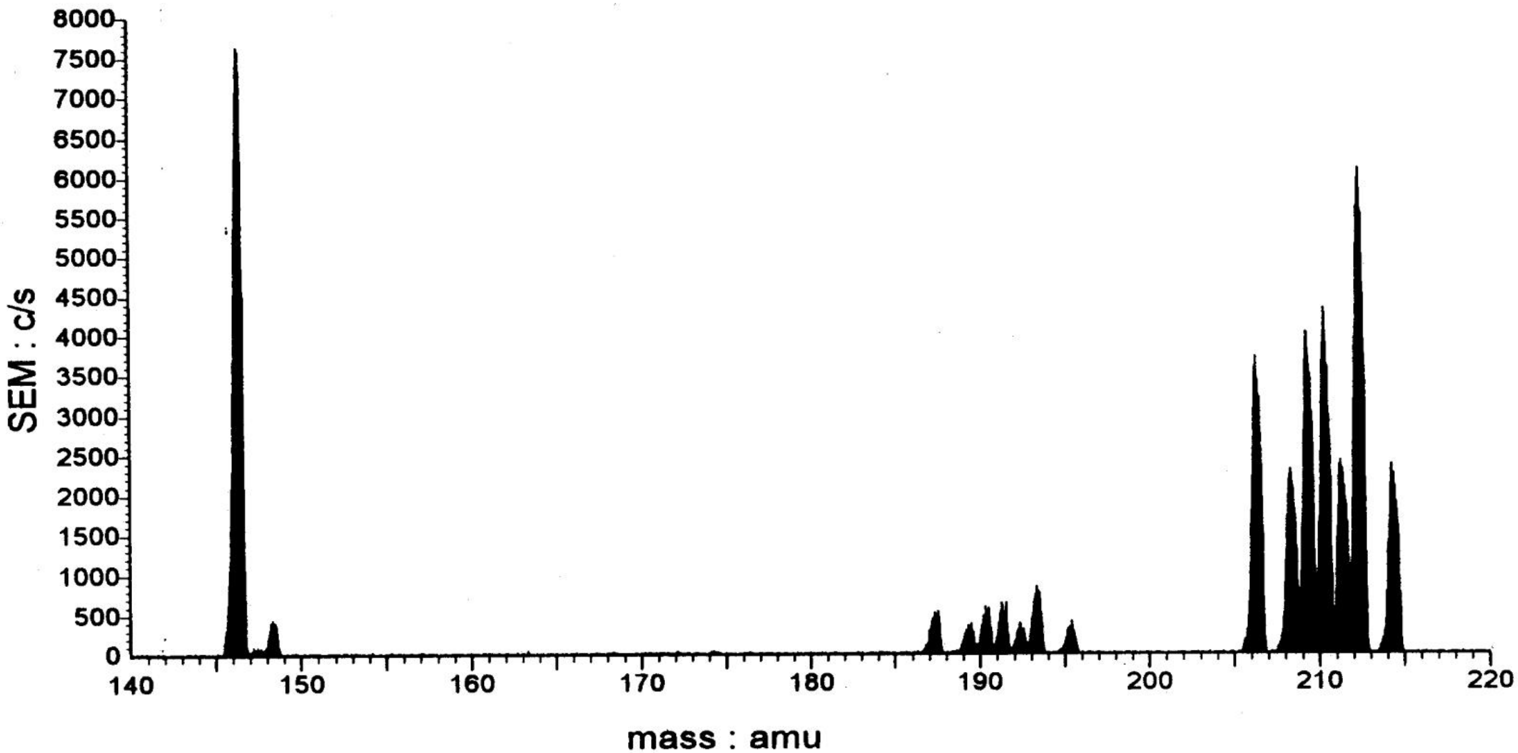




Note the date!! Early data from Hughes Research.

Negative Ions. Molybdenum Cathode. Sulphur Hexafluoride Gas.

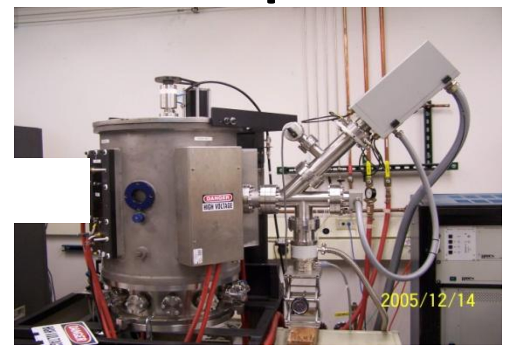
Mass Spectrum, 140 to 220 amu, Showing SF_6^-, MoF_5^- and MoF_6^- Ions.



Early C.S.M. Experimental Setup

System	Deposition	P-CFUBMS
	Plasma Examination	Hiden EQP
Film Deposition	Target Power [Watt]	Cr (200) Al (800)
	Pulsing Parameter	60-350 kHz 0.4-5.0 μs
	Substrate	AISI 304 coupon Si (100) Wafer
	Substrate to Chamber Wall Distance [inch]	8
	Working Pressure [mTorr]	2
	Substrate Bias [V]	-50
	N2 to Ar flow ratio	75:25
	Deposition Temperature [ºC]	150~250

Side View

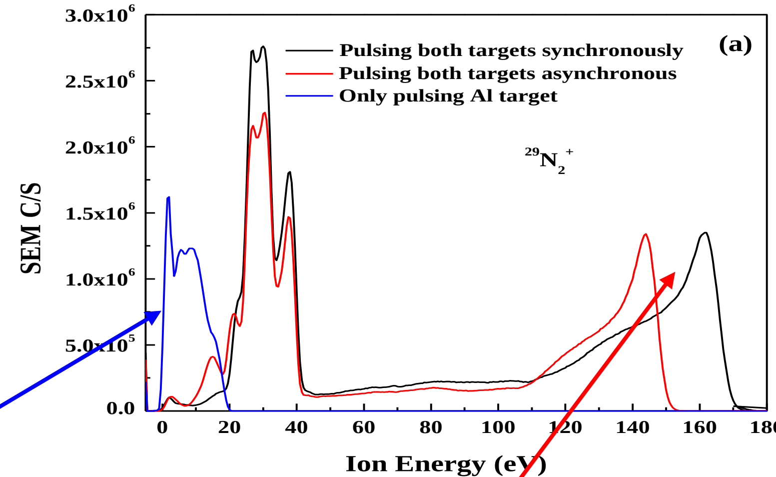


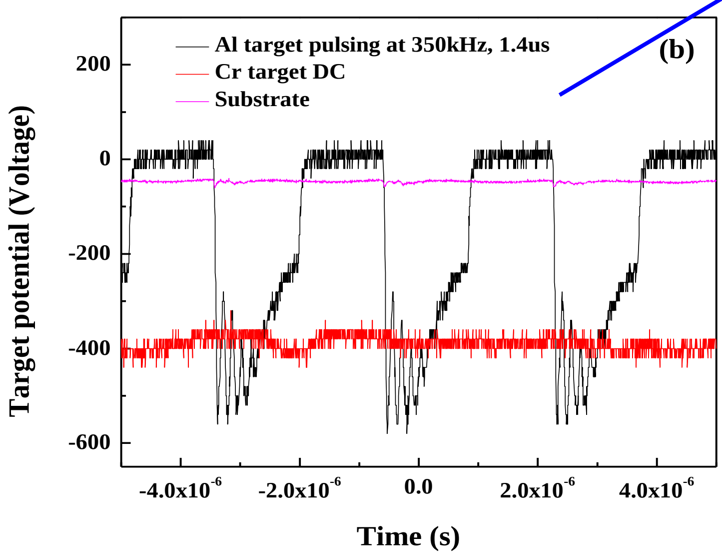
Top view

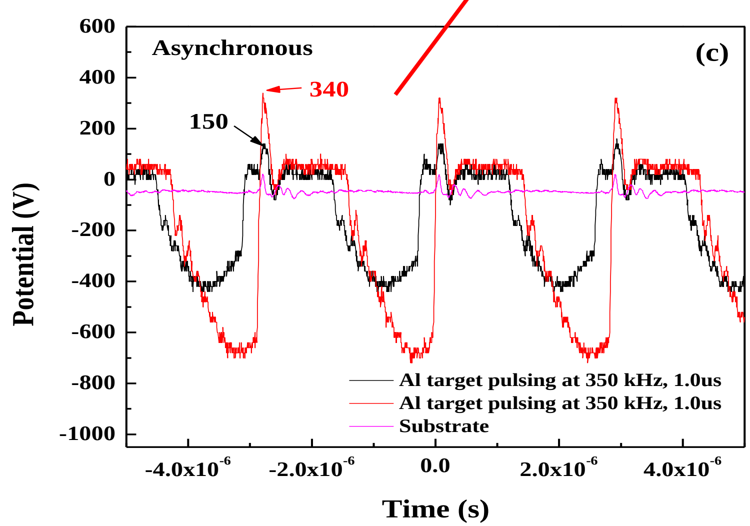
The Hiden mass/energy electrostatic quadrupole plasma analyzer (EQP) was used to measure the ion energy distributions (IED) in an effort to understand the effects of pulsing configuration and parameters on the energy and flux of the ions arriving at the growing film.

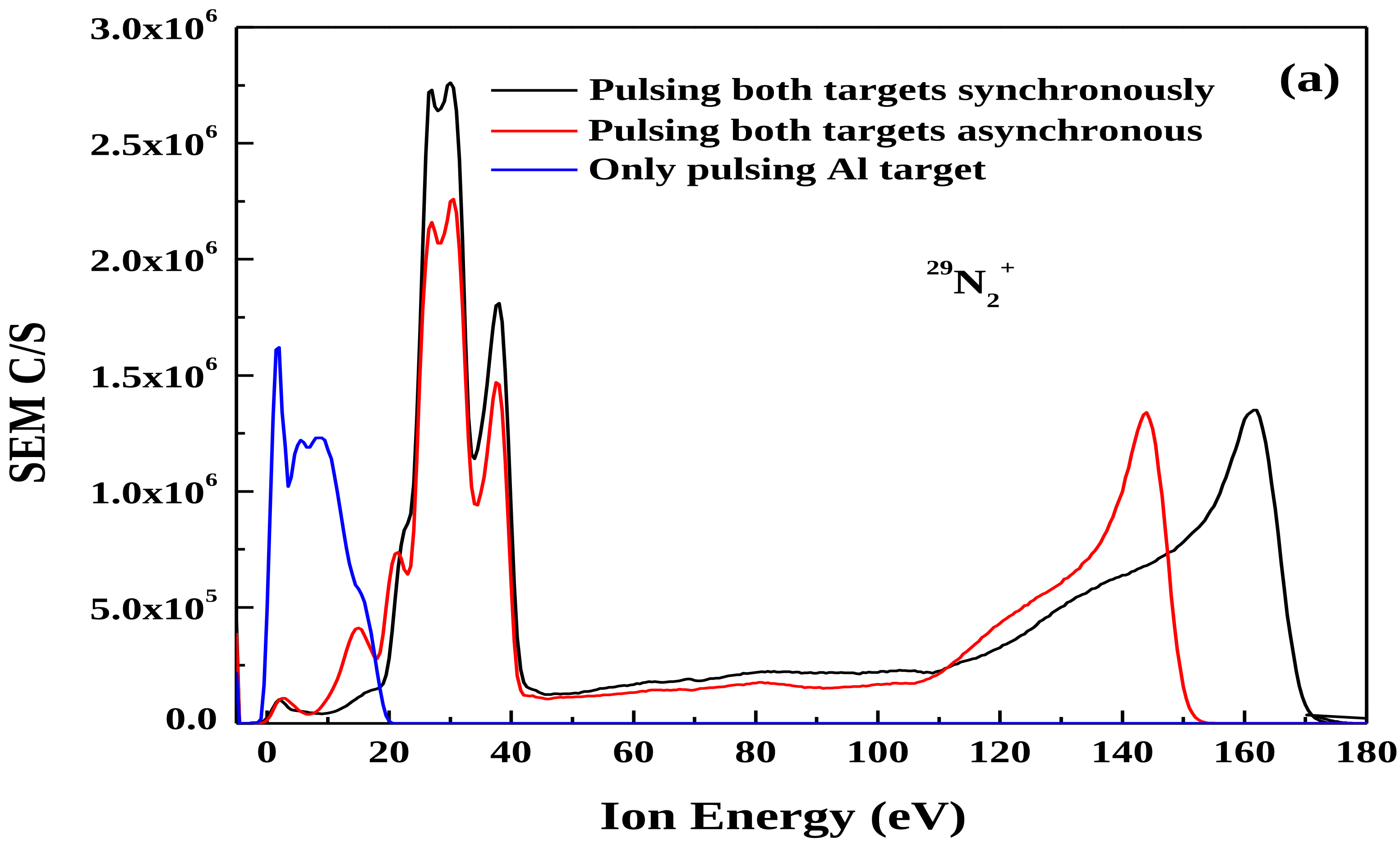
Effect of Pulsing on the Plasma Ion Energy and Ion Flux Change

- Pulsing both targets asynch. and synch
- . gives much higher ion energy and flux.
- The positive voltage overshoot at the
- beginning of the reversed positive pulse
- period increases the ion flux and energy
- in the plasma



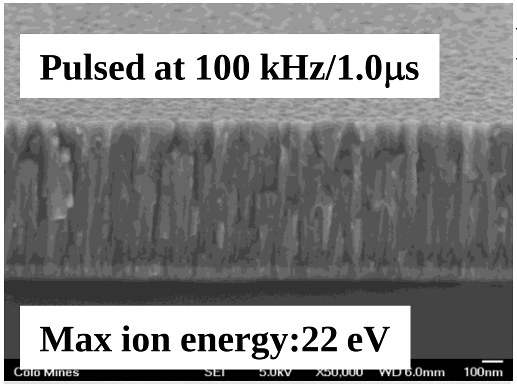


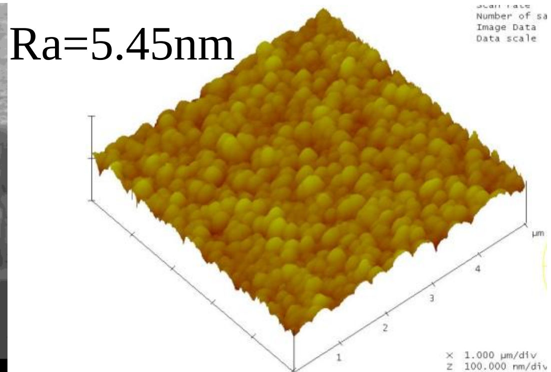


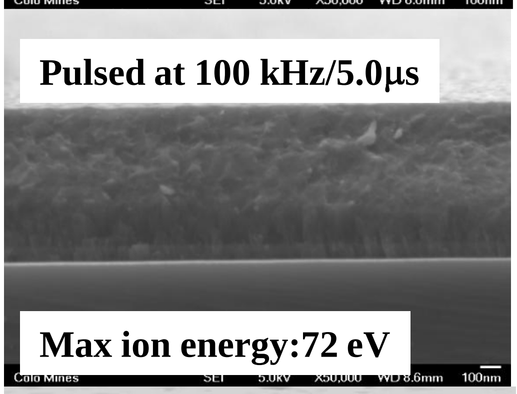


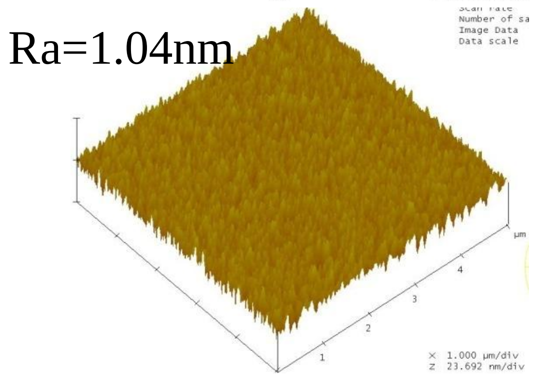
3.0x10^6
2.5x10^6
2.0x10^6
1.5x10^6
1.0x10^6
5.0x10^5
0.0
SEM C/S
0
20
40
60
80
100
120
140
160
180
Ion Energy (eV)
(a)
Pulsing both targets synchronously
Pulsing both targets asynchronous
Only pulsing Al target
$^{29}N_2^+$

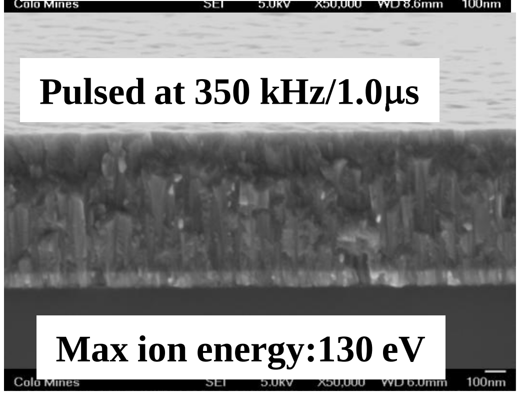
FESEM and AFM Micrographs

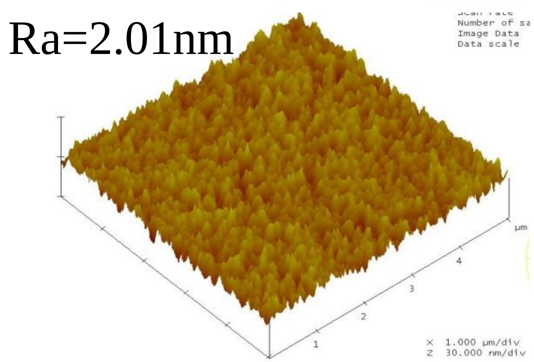


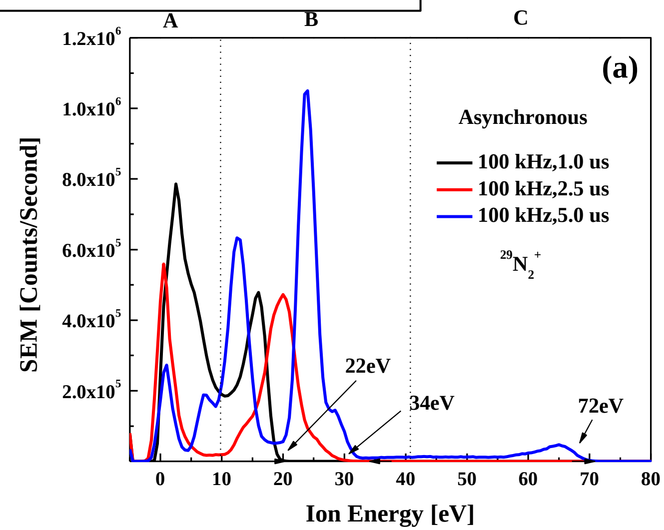


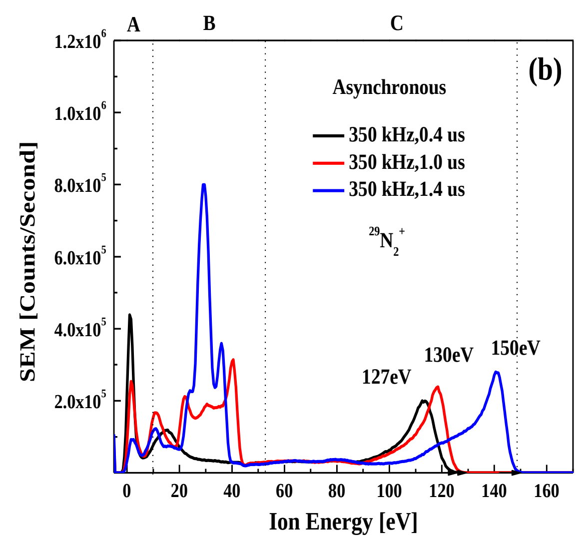






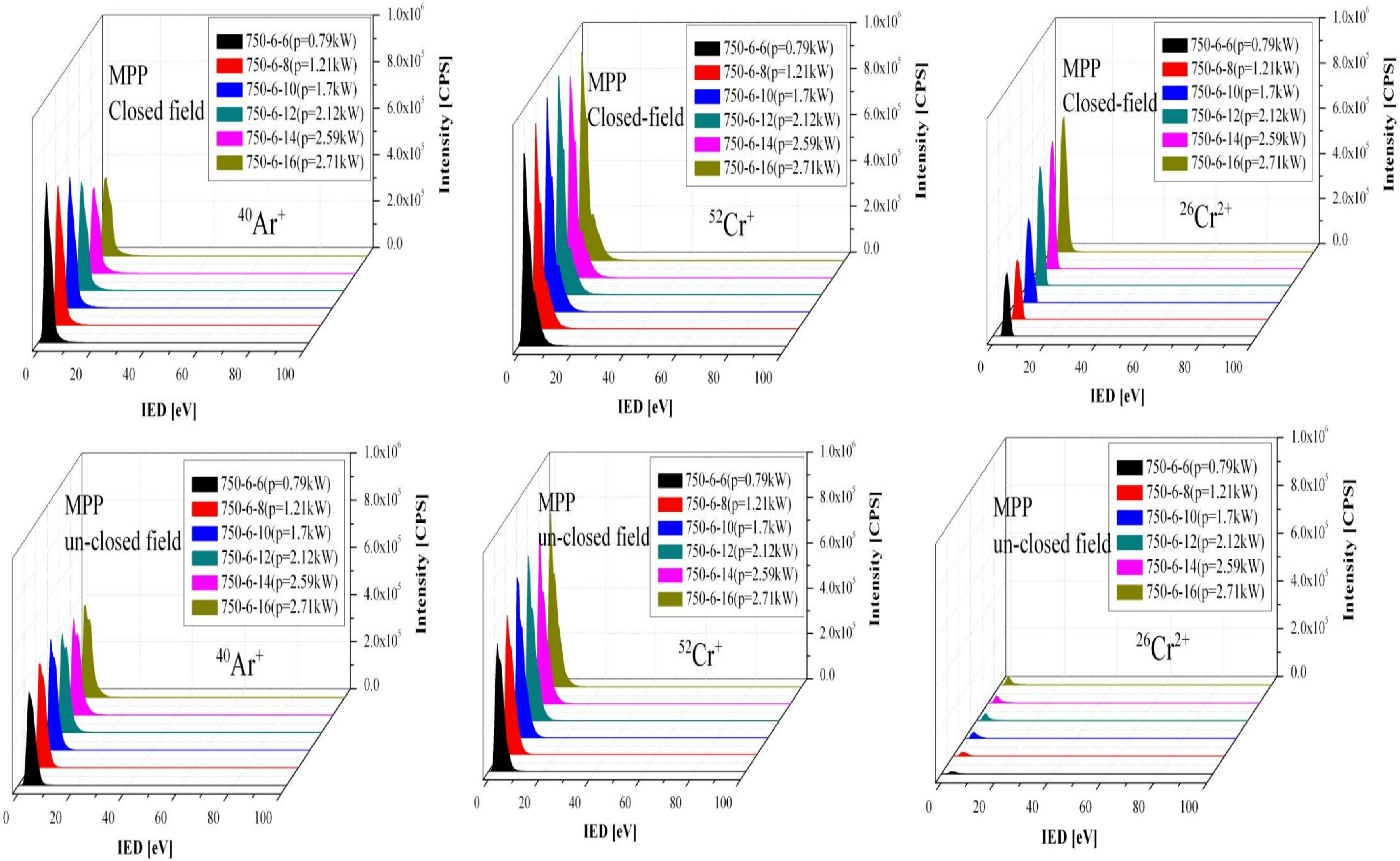




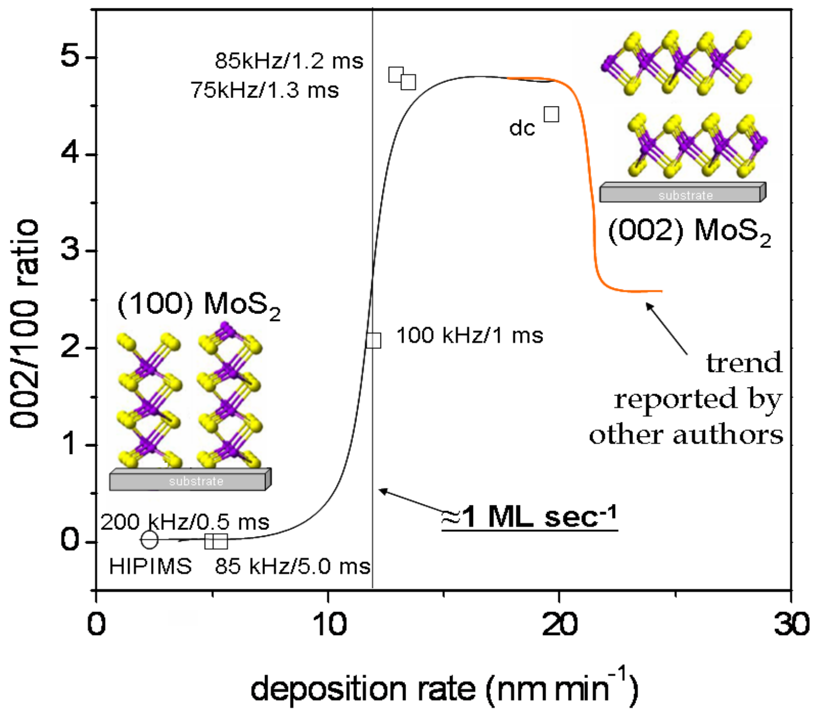


"The EDF is hence defined by the voltage-time characteristic of the pulsed dc generator used. One of the implications of this work is therefore that different pulsed dc generators with different voltage-time characteristics result in different EDFs of the electronegative species. In the thin film growth literature, experiments are often compared at similar average voltages or power densities. Our results indicate that this strategy may be of limited use since *the voltage-time characteristic determines the EDF*". (from paper by J M Schneider)

IEDs of MPP plasmas ---closed and un-closed magnetic fields



additional structure control in pulsed sputtering

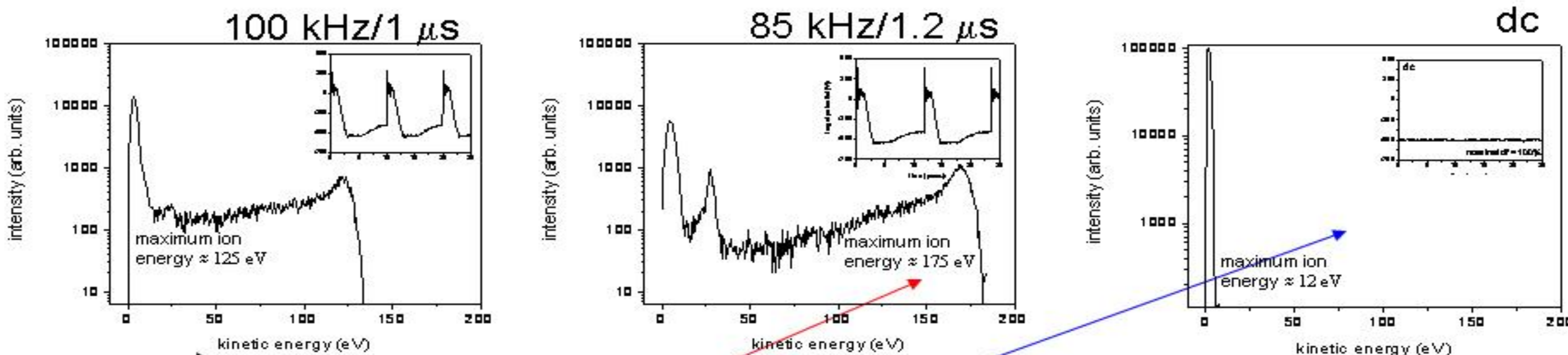


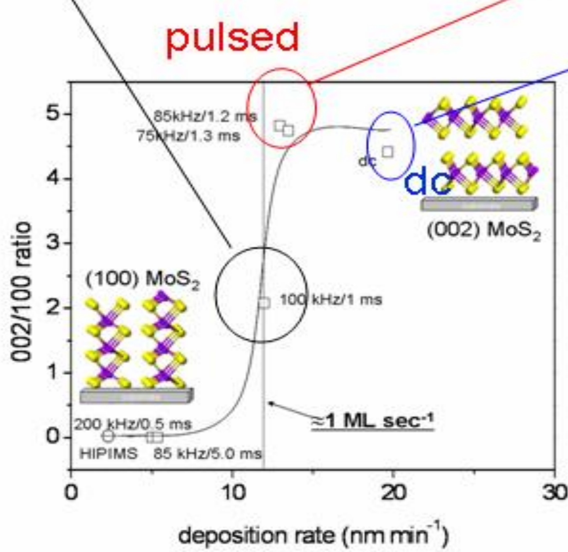
for deposition rates above 1 MLsec^{-1}, the observed data follows the expected trend

-reduced deposition rate prolongs time for deposited atoms to diffuse to find minimum surface energy site before burial

-increased incident ion energy in pulsed dc process promotes (002) crystal growth

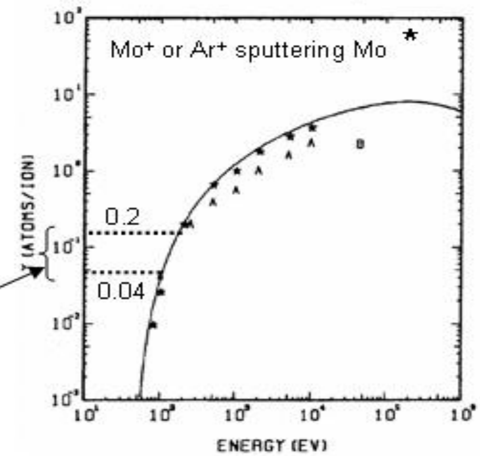
ion energy distributions in pulsed plasmas and their effect on orientation and growth rate of MoS_2 films





higher energy ions at 85 kHz favors growth of crystals with [002] orientation

small increases in ion energy in the 100-200 eV range have a strong effect on defect production



an order of magnitude increase in sputter yield for the energy difference observed above

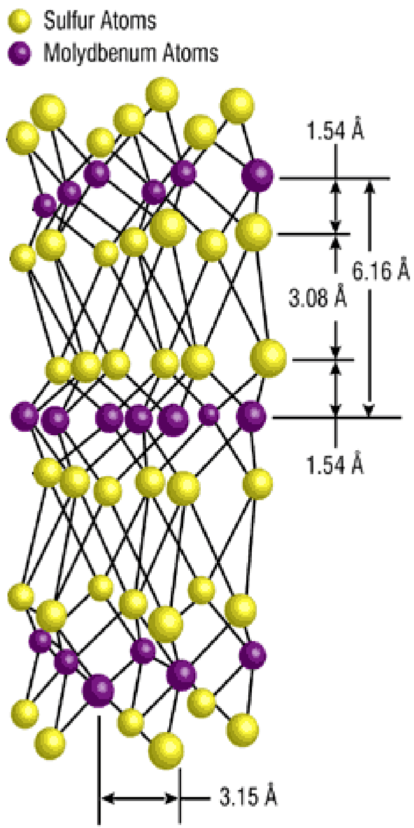
*Yamamura and Tawara, *Atomic Data and Nuclear Data Tables*, **62** (1996) 149

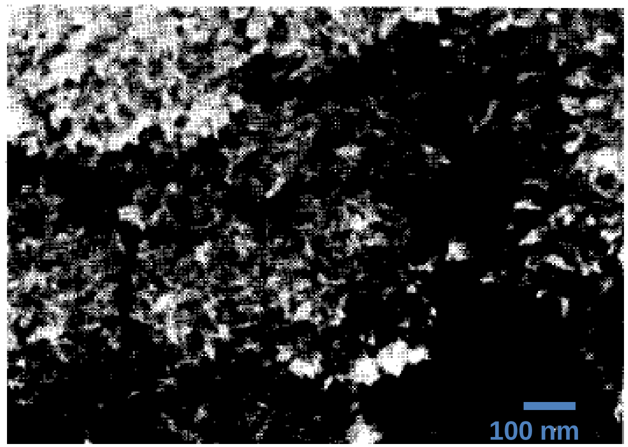
C Mutatore et al SCT 163, 2003, 12.

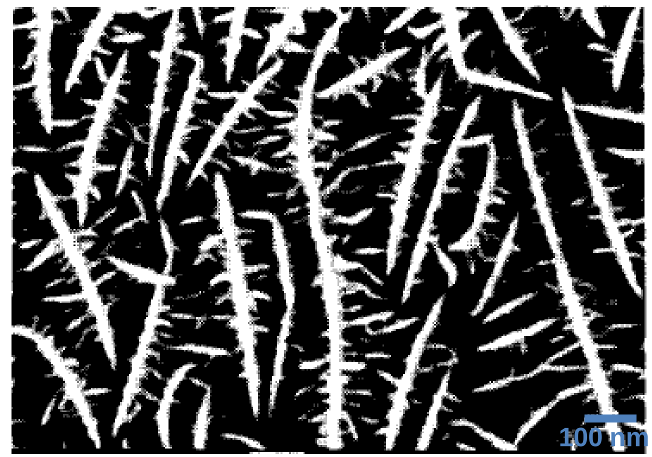
MoS_2 surface roughness dependence on orientation

less sensitive to ambient environment

more sensitive to ambient environment

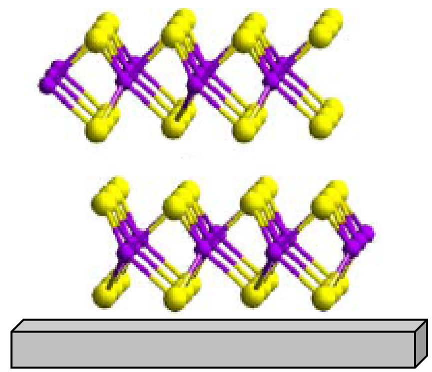


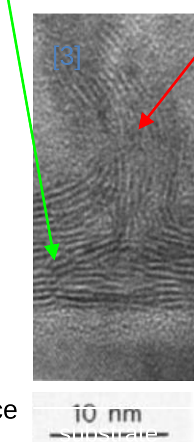


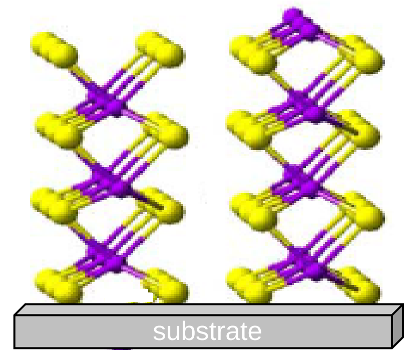


smooth (002) oriented MoS_2[1]

rough (100) oriented MoS_2[1]







inert surface [2]

surface energy = 250 mJ m^{-2}

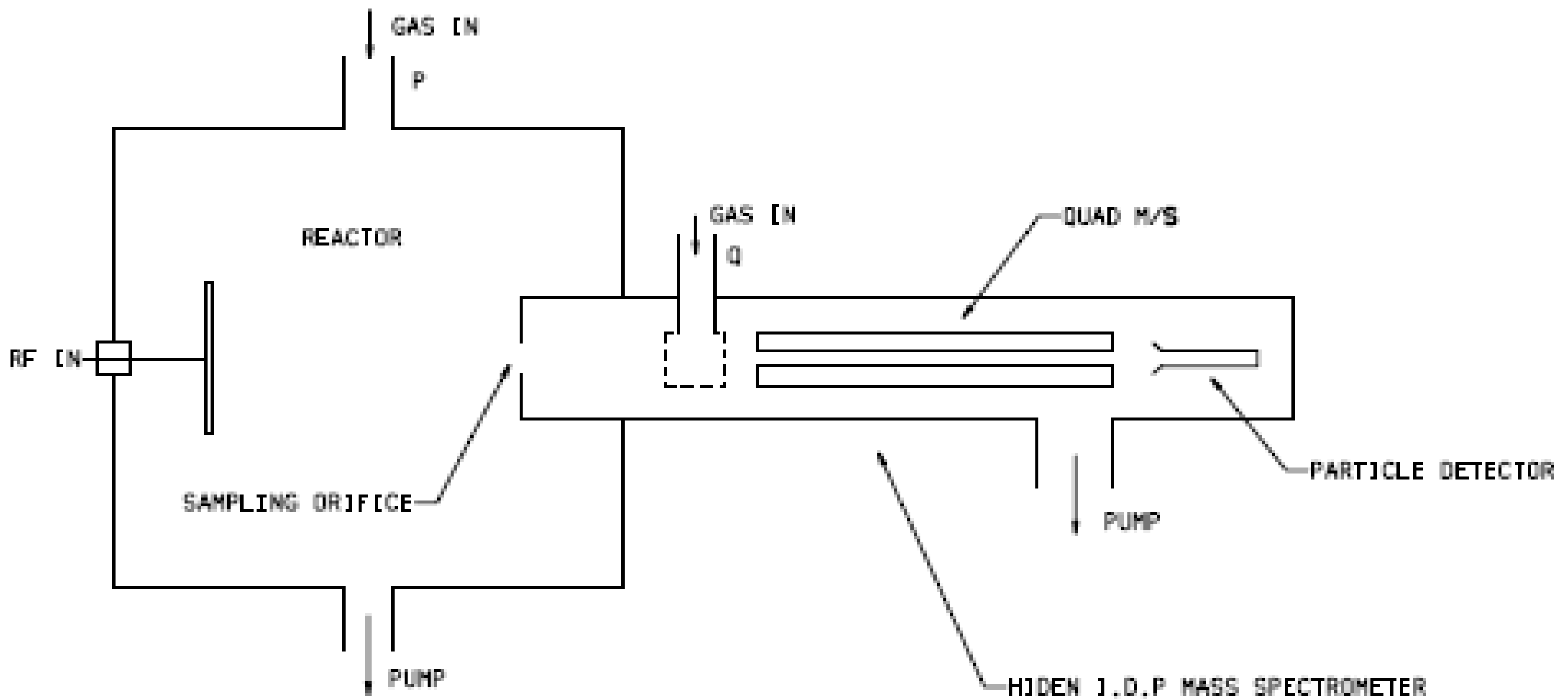
reactive surface [2]

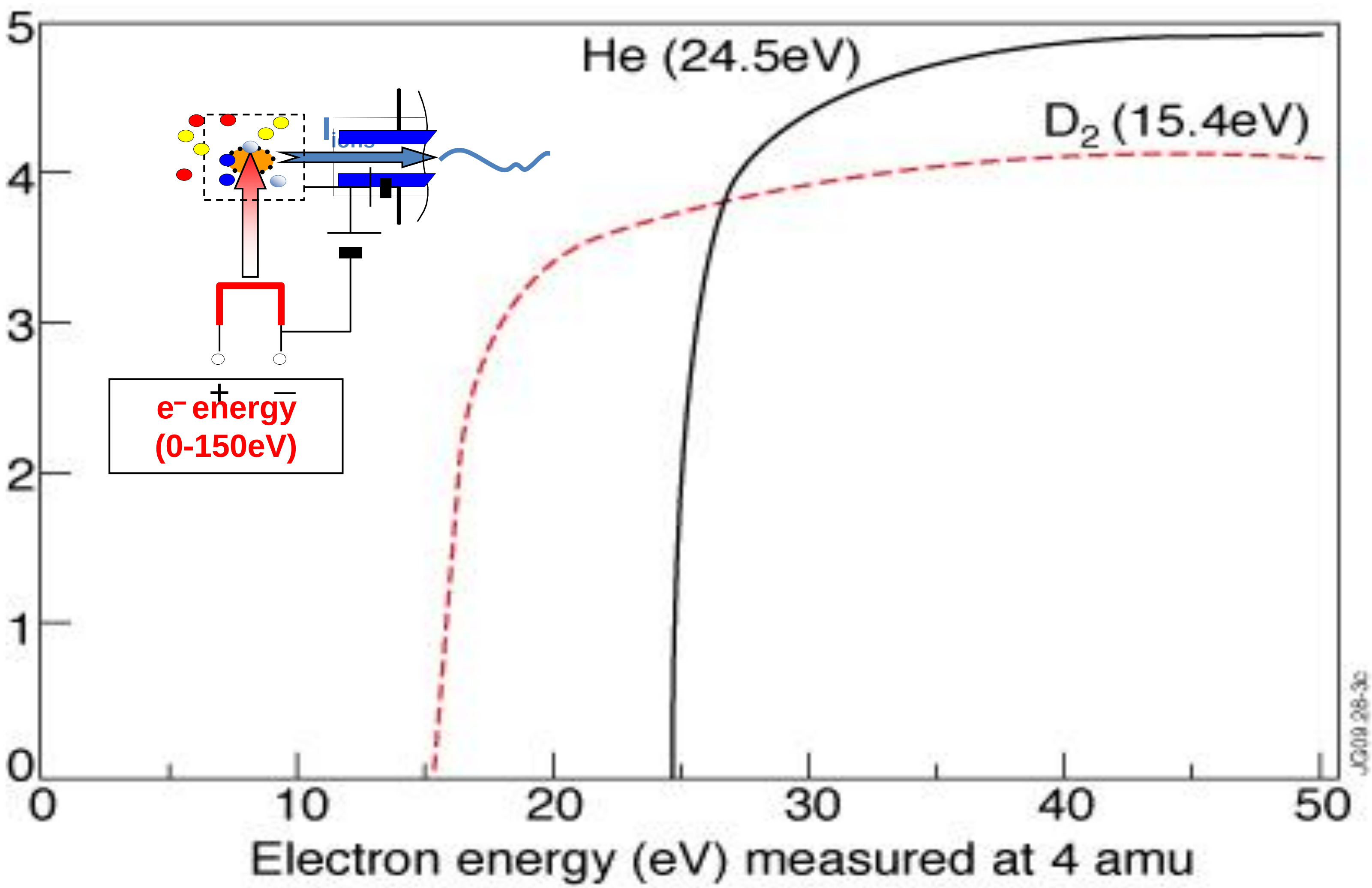
surface energy~25,000 mJ m^{-2}

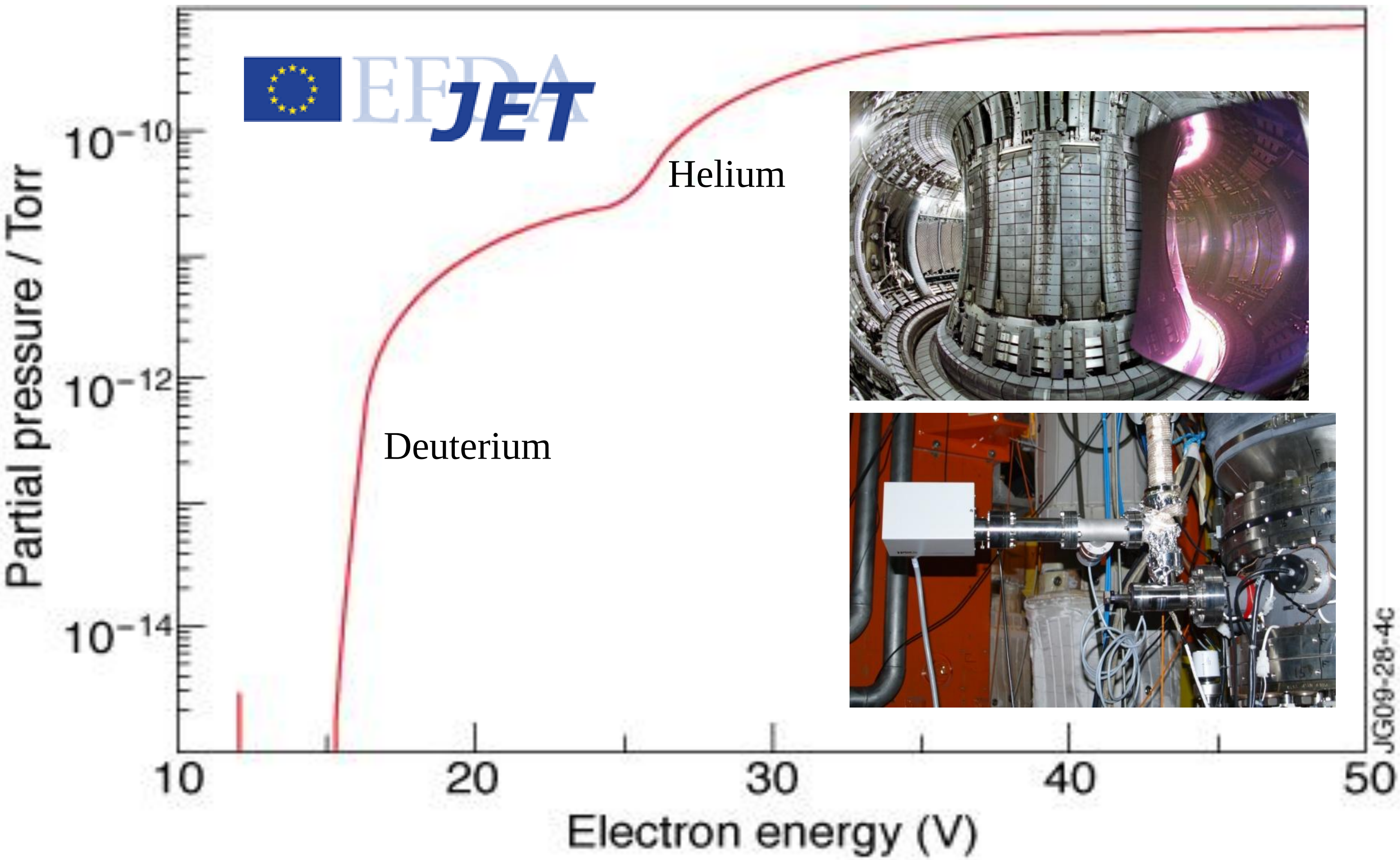
Diagnostics at higher mass spectrometer source pressures.

With the availability of particle detectors that tolerate ambient pressures of up to 5.10^{-4}Torr, it has become possible to operate mass/energy analysers at pressures which are about a factor of 100 higher than was previously the case.
For example, recent experiments at Hiden using rare gases have given interesting results which suggest new applications for customers.

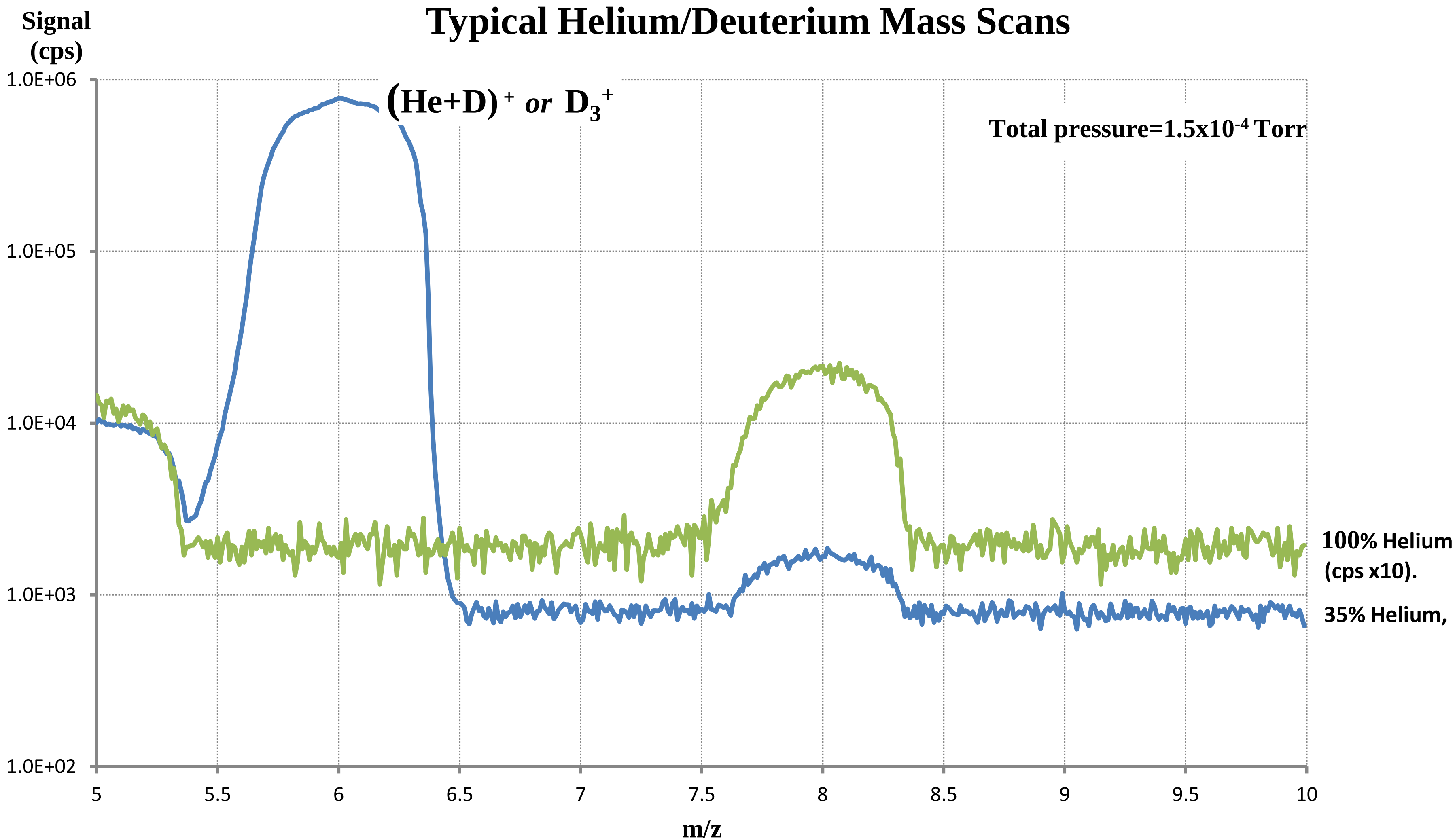
Experimental system.

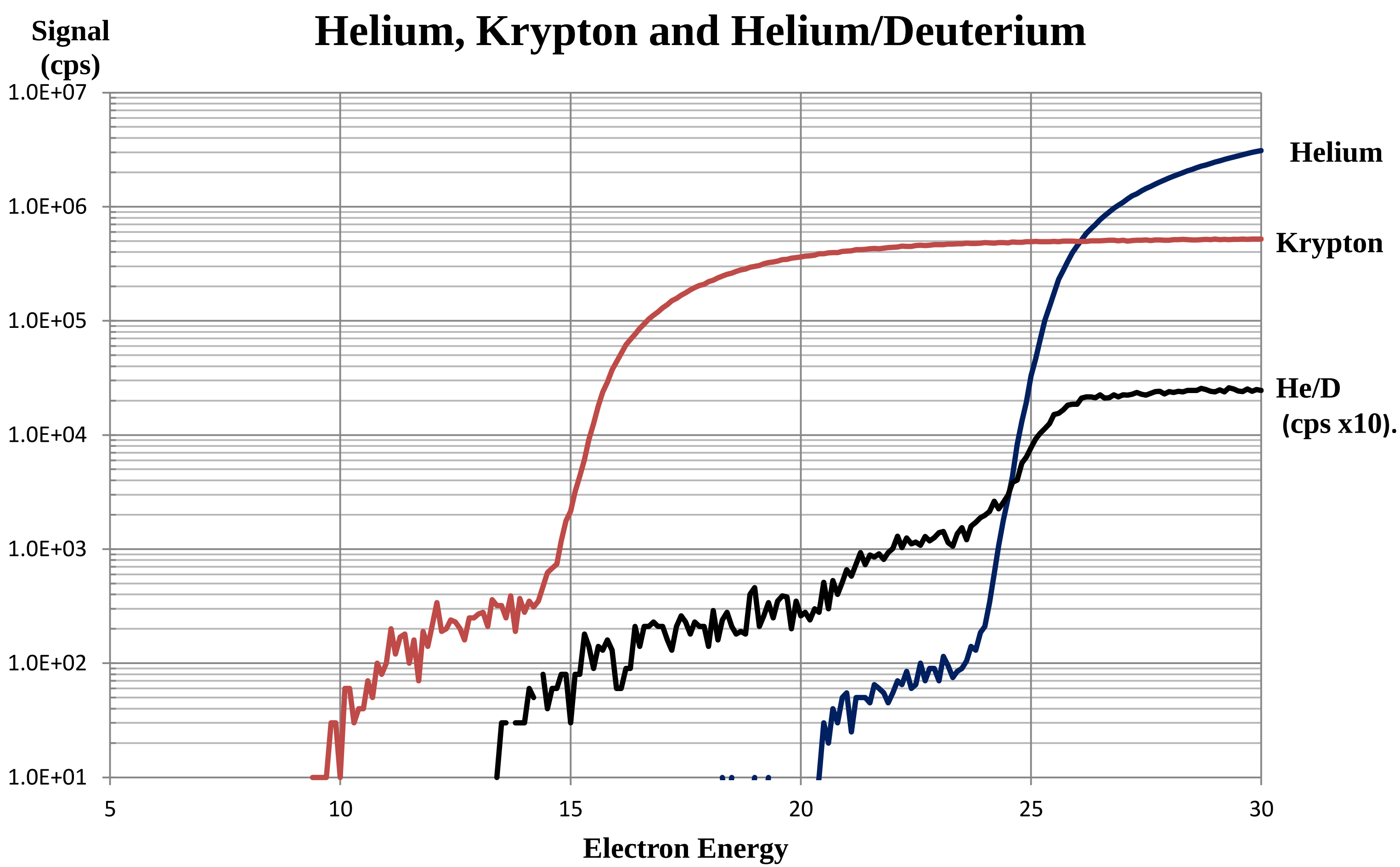



He (24.5eV)
D2 (15.4eV)
e⁻ energy
(0-150eV)
+
–
0
1
2
3
4
5
0
10
20
30
40
50
Electron energy (eV) measured at 4 amu

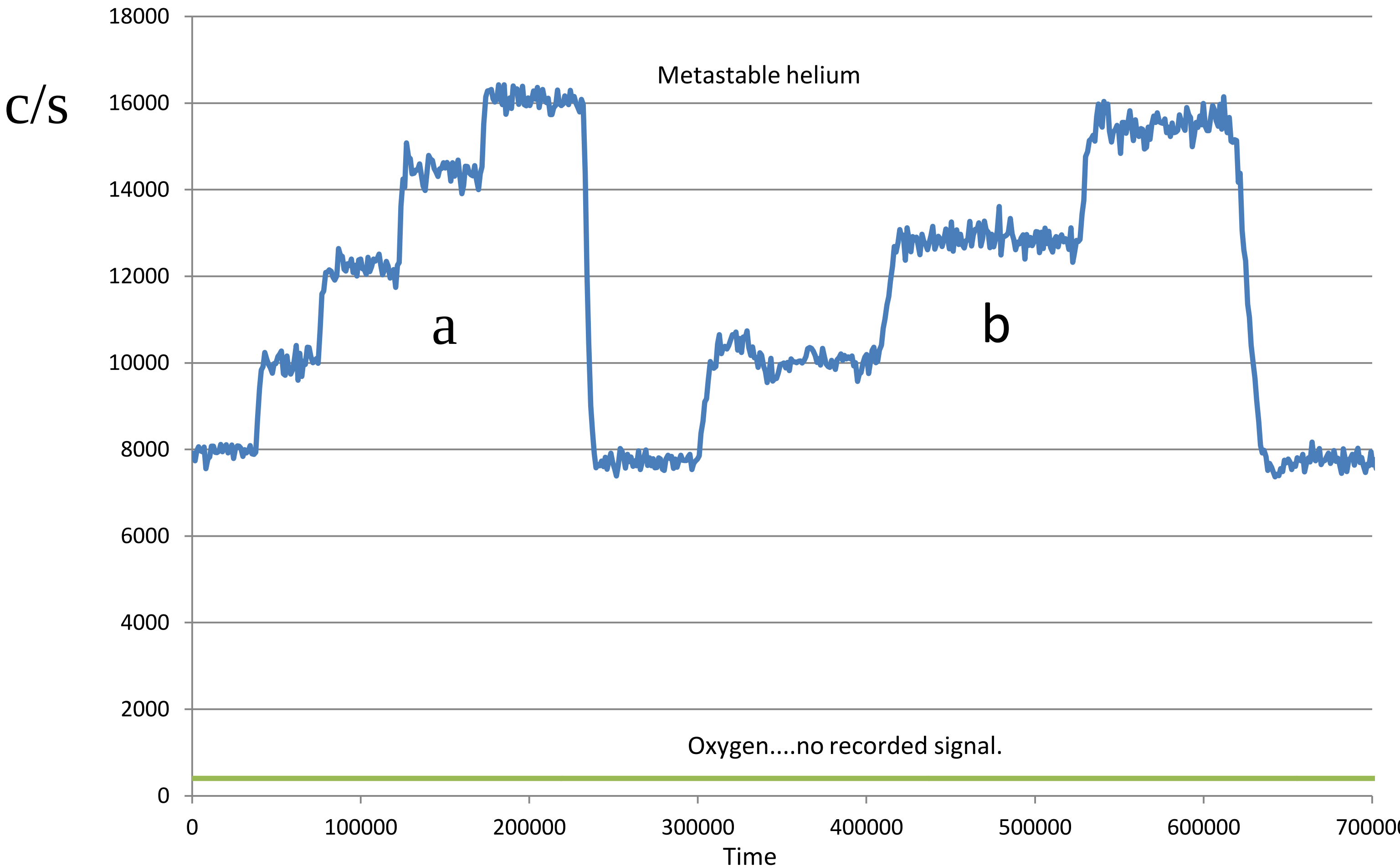

EFDA JET
Helium
Deuterium
Partial pressure / Torr
10^{-10}
10^{-12}
10^{-14}
10
20
30
40
50
Electron energy (V)
JG09-28-4c

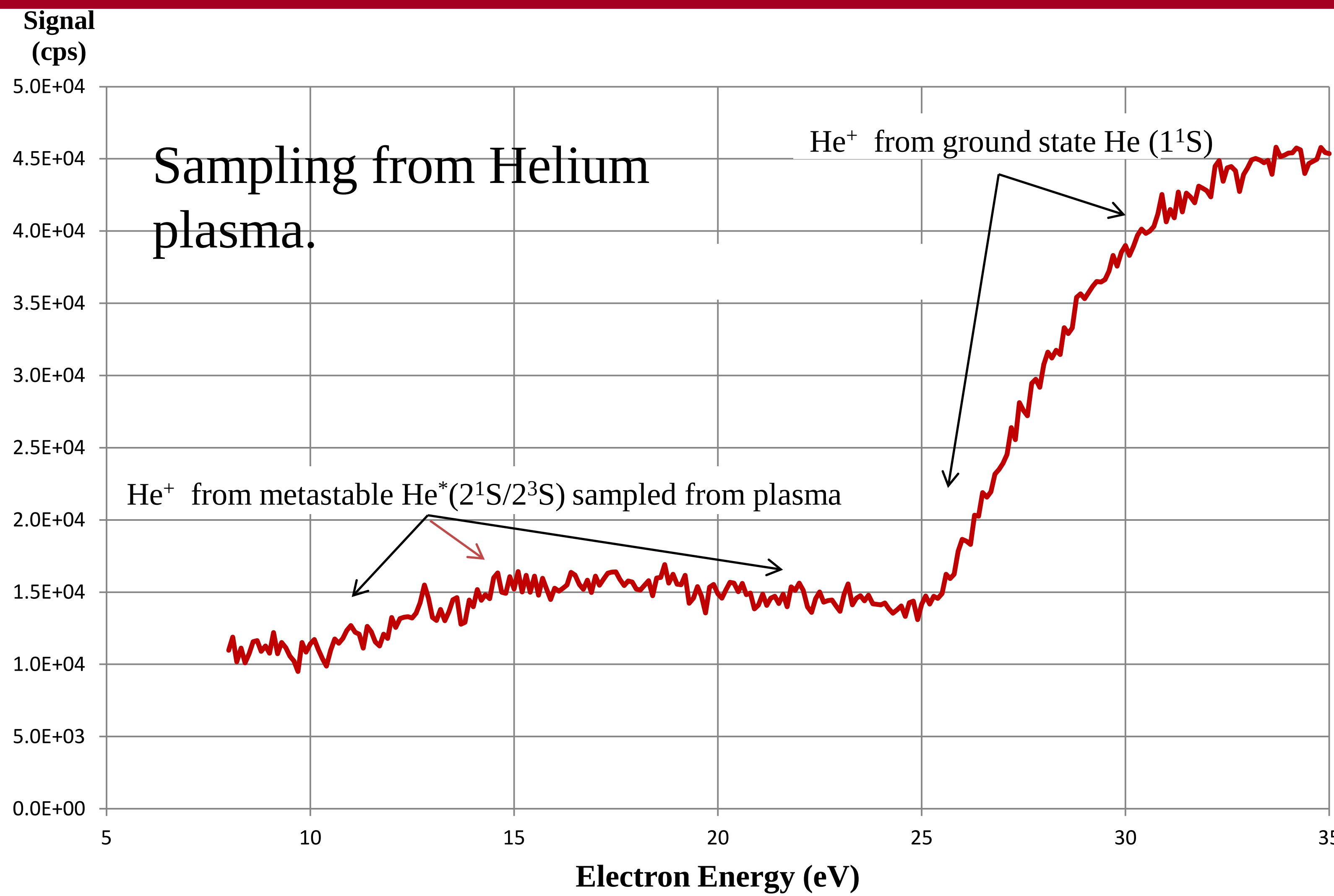
Typical Helium/Deuterium Mass Scans




Signal (cps)
Helium, Krypton and Helium/Deuterium
1.0E+07
1.0E+06
1.0E+05
1.0E+04
1.0E+03
1.0E+02
1.0E+01
5
10
15
20
25
30
Electron Energy
Helium
Krypton
He/D (cps x10).

a) plasma power=3,5,7,9,11 Watts at 2x10^{-5} Torr.
b) pressure=2,3,4,5x10^{-5} Torr at 3 Watts.




Sampling from Helium plasma.
Signal (cps)
5.0E+04
4.5E+04
4.0E+04
3.5E+04
3.0E+04
2.5E+04
2.0E+04
1.5E+04
1.0E+04
5.0E+03
0.0E+00
5
10
15
20
25
30
35
Electron Energy (eV)
He+ from ground state He (1¹S)
He+ from metastable He*(2¹S/2³S) sampled from plasma

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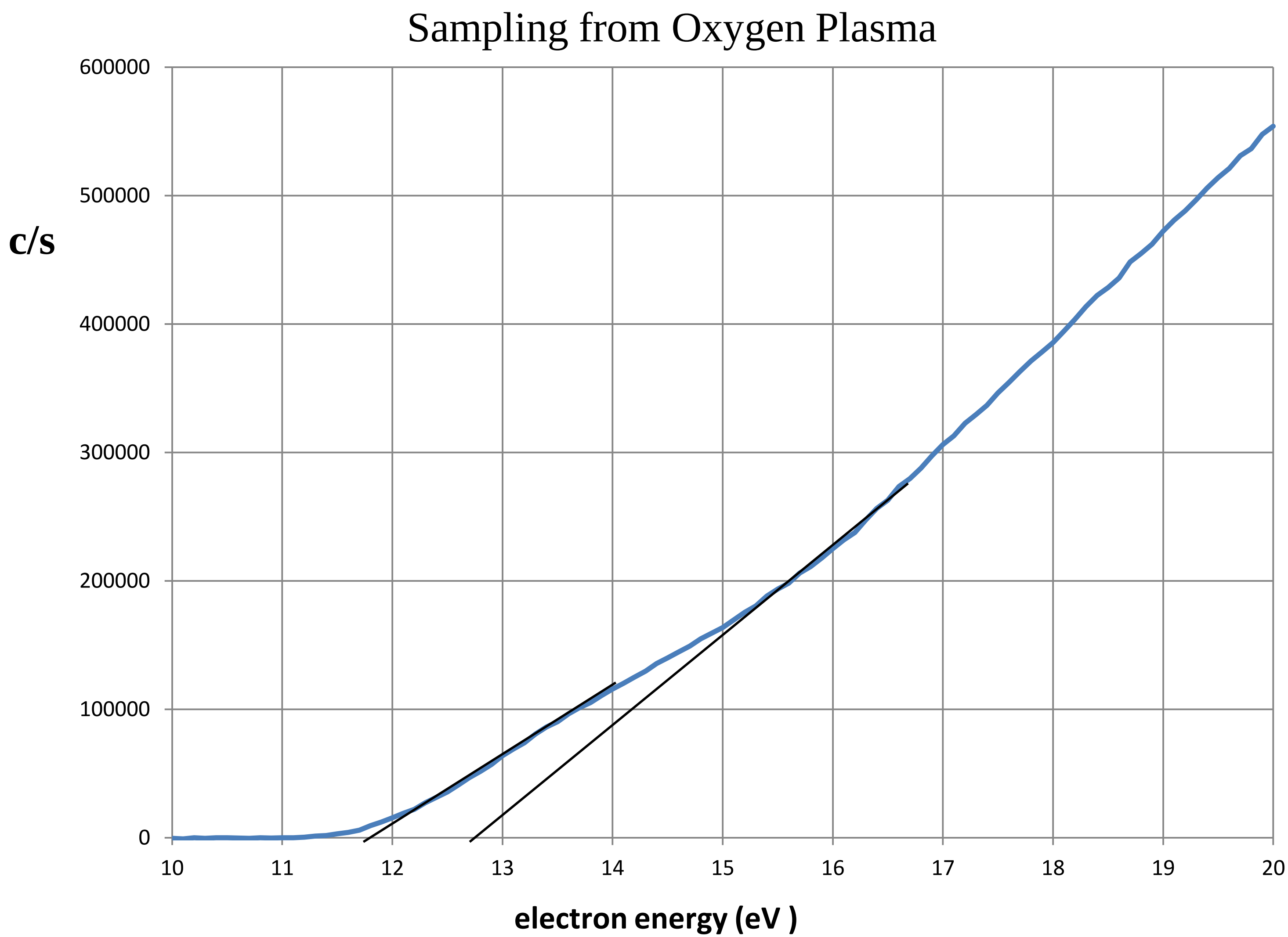
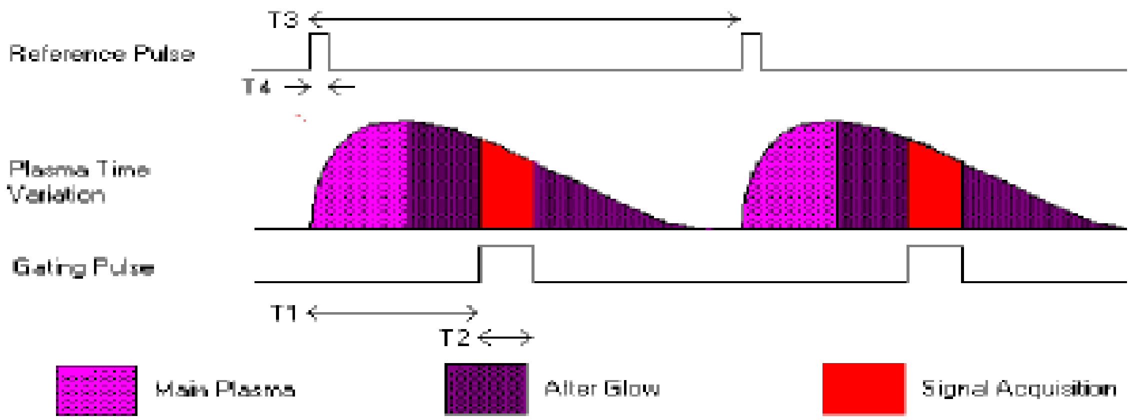


Time Resolved Acquisition from Pulsed Plasmas.



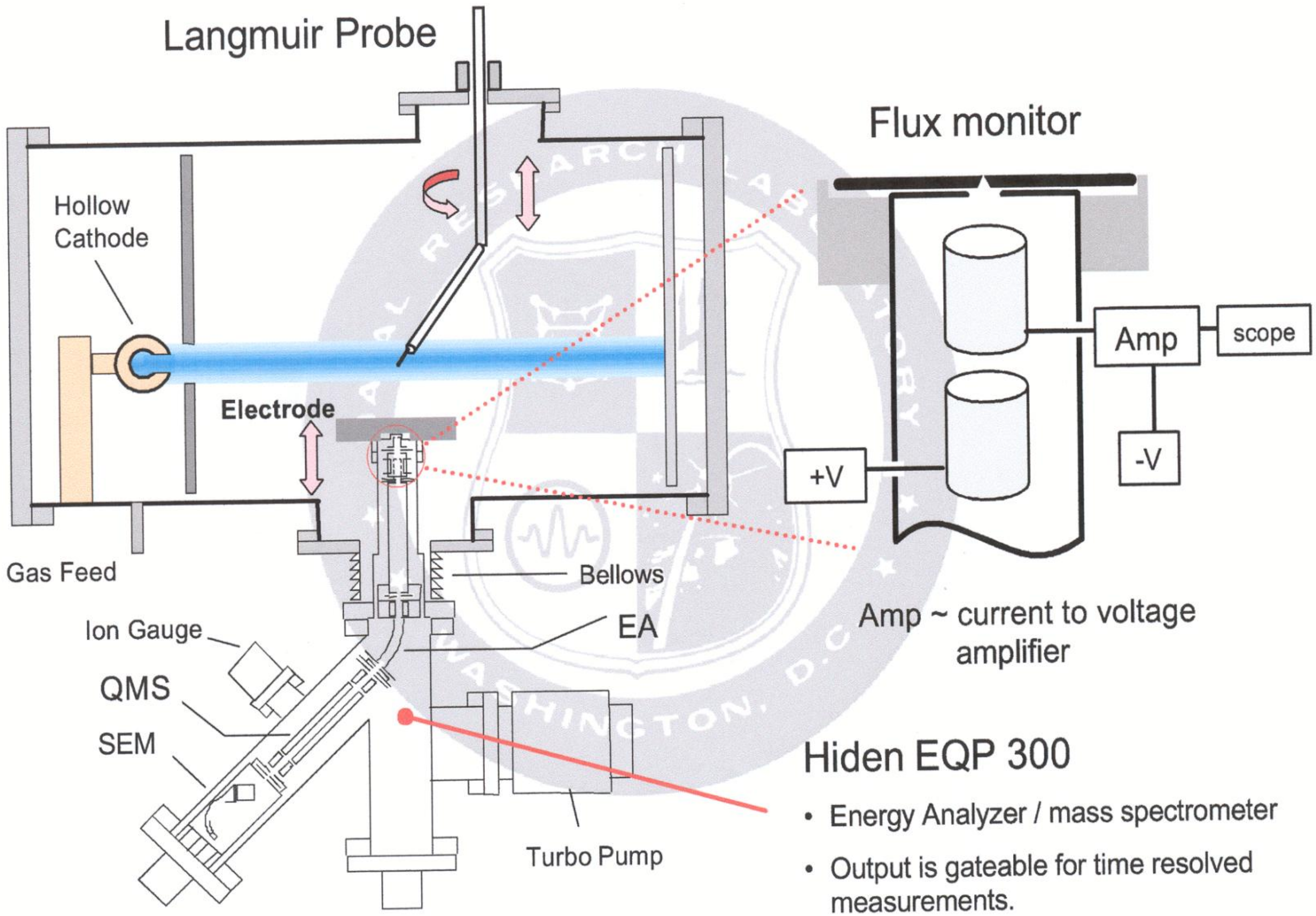
Programmable signal gating with foreground and background detection.

A gating system for time resolved measurements and to monitor differences between two time zones relative to a repeated event, enabling automated data acquisition during beam on and beam off cycles in modulated molecular beam studies for example.

Both the foreground delay and background delay timing may be scanned, enabling an automatic scan of the monitored time period across an event period

Minimum gate width selectable is 100 nano seconds.

LAPPS diagnostics chamber



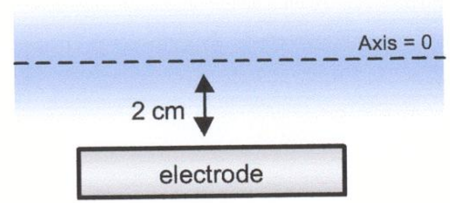
Hiden EQP 300

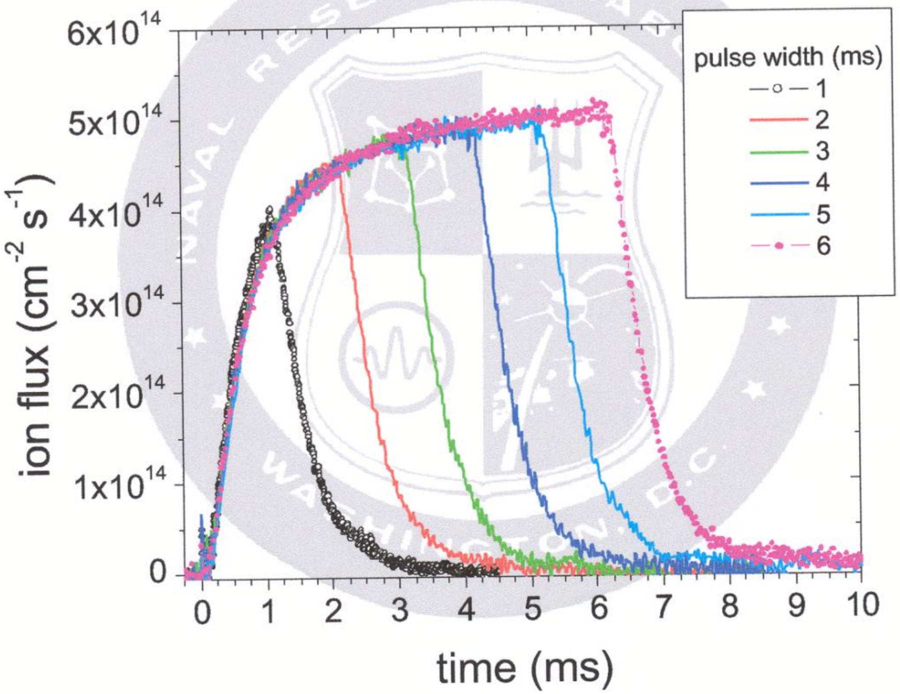
- Energy Analyzer / mass spectrometer
- Output is gateable for time resolved measurements.

Temporal profile: total ion flux

Gas: 50 mTorr **Argon**

e- beam pulse: 10 % duty factor

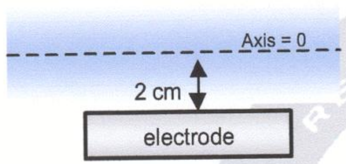


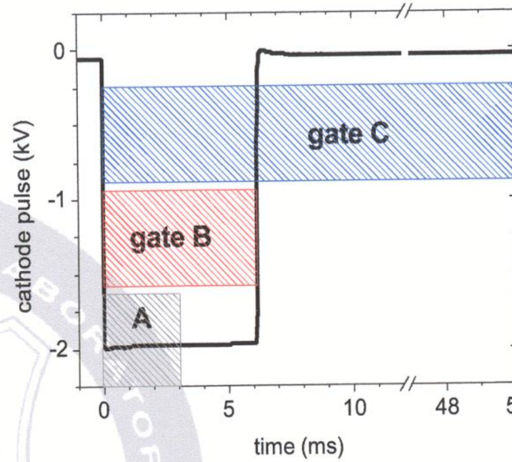


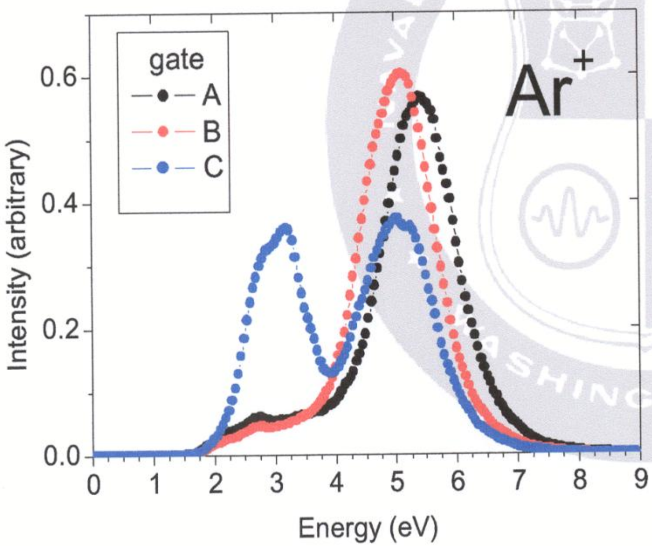
Temporal profile: IED and flux

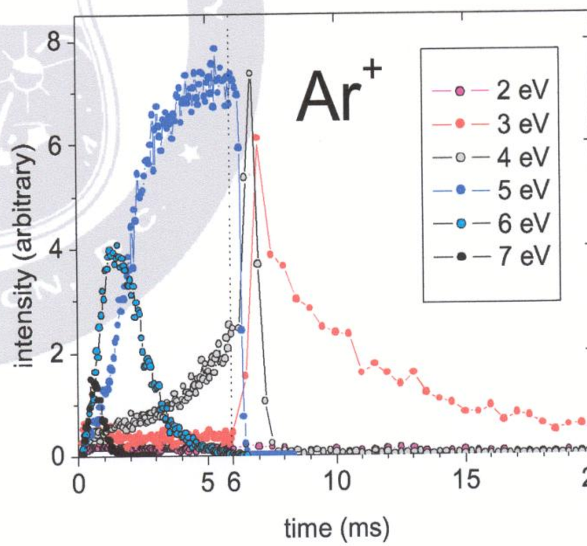
Gas: 50 mTorr **Argon**

e- beam pulse: 6 ms, 10 % duty factor

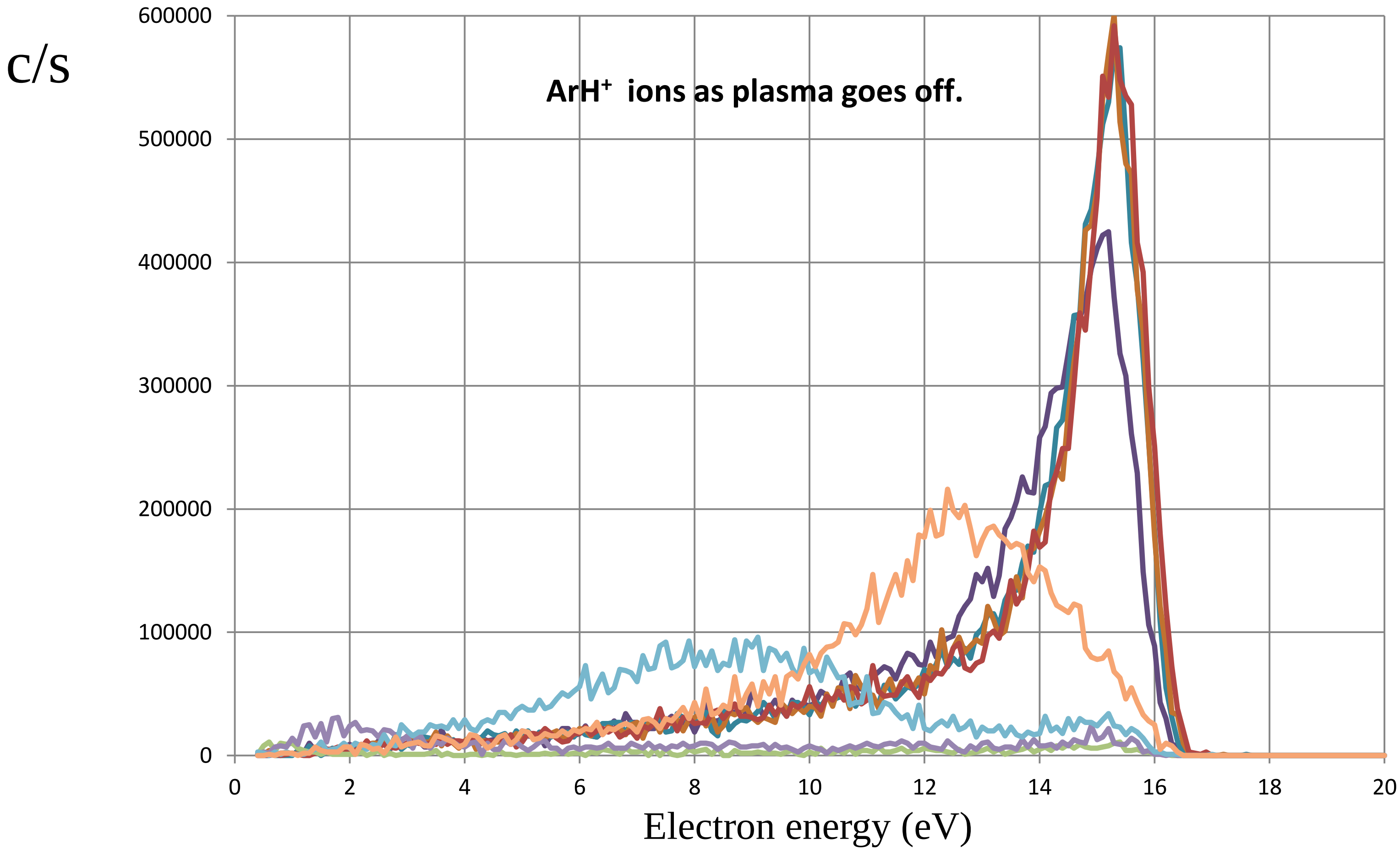








S.G. Walton *et al.*
2003 SVC Technical Conference


c/s
ArH+ ions as plasma goes off.
600000
500000
400000
300000
200000
100000
0
0
2
4
6
8
10
12
14
16
18
20
Electron energy (eV)

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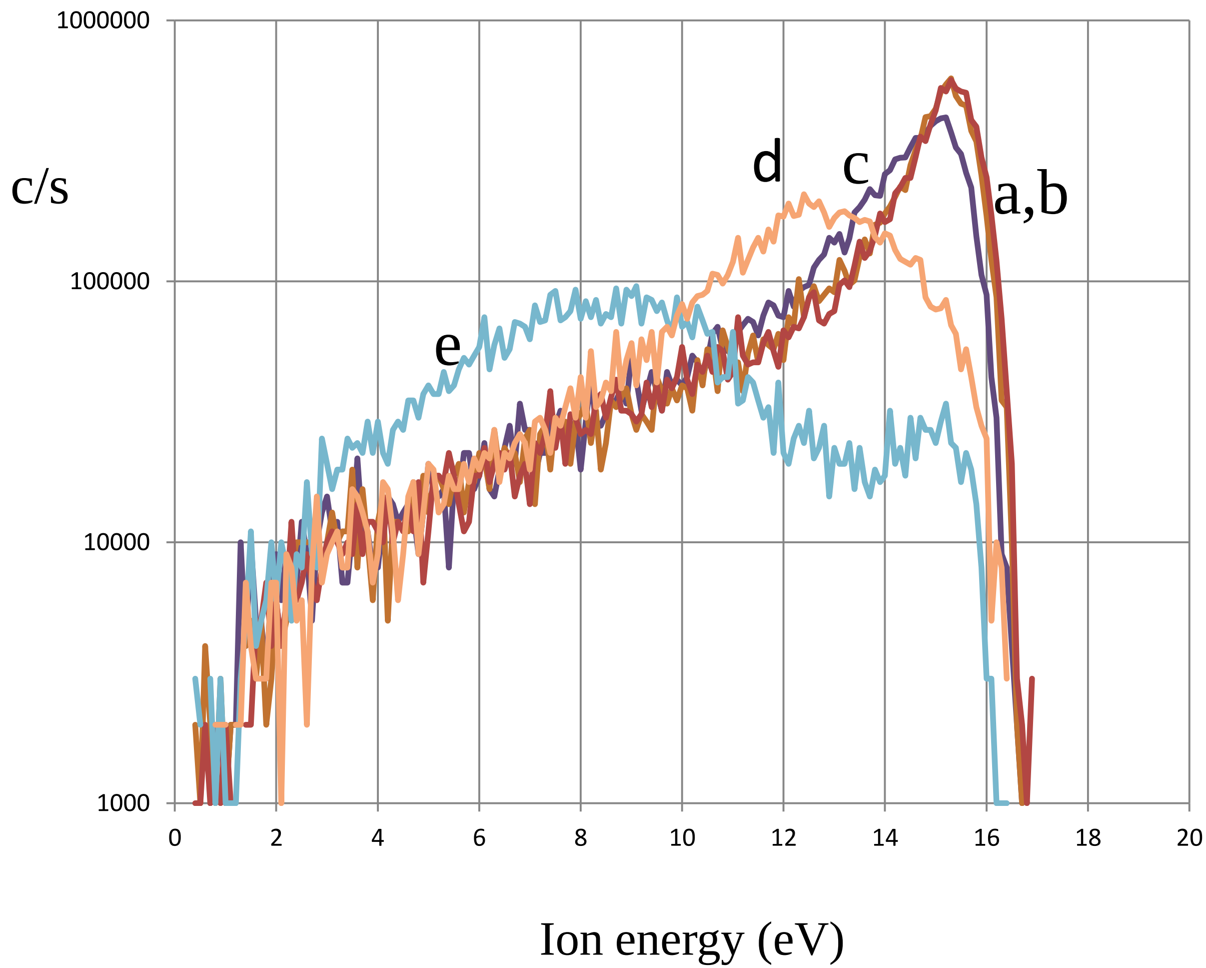
ArH+ ions as plasma goes off.



a t_{off} - 20usec
b t_{off}
c t_{off} + 60usec
d t_{off} + 100usec
e t_{off} + 130 usec

Conclusions

A. Possible Measurements include:

1. Identification of positive and negative ion species , including multiply-charged species, and neutrals, arriving at substrate.

2. Energy distributions for positive and negative ions, and neutrals.

B. Correlations with properties of deposited films are instructive.

C. Optimisation of plasma processes improved.

Acknowledgements .

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Dr Chris Muratore, (U.S.A.F. Research).

Dr Scott Walton, (U.S. Naval Research)

Many other Hiden customers.

Plasma Applications Group Meeting. Nov 10th 2011. Santa Clara.

J A Rees et al Hiden Analytical. Notes for slide presentation.

Slide2. Four instrumentation areas which may be of interest.

Slide 3. Common component is a quadrupole mass spectrometer.

Slide 4. Example 1 = Temperature Programmable Desorption Equipment.

Slide 5. Sample data .

Slides 6 and 7. Ion Milling probe. Slide 8 = Typical scan for Ta/NiFe/Ta wafer.

An useful feature of the ionisation source in the mass spec is the ability to scan the electron energy from as low as 1eV .This allows " Soft Ionisation" /" Threshold Ionisation". Slide 10 shows data for organic traces in Air with much improved relative sensitivity. Slides 11,12, and 13 show simple example for plasma dissociation of carbon tetrafluoride.

Another feature of the Hiden Mass spectrometers is their ability to perform NegativeIon RGA. Slides 14,15, and 16 show examples for CO and $C\,Cl_2\,F_2$.

In recent years diagnostics for plasmas at high pressures (often atmospheric pressure) has been of growing interest. (See J A Rees et al Plasma Processes and Polymers,2010, 7, 92-101). Two instruments for such applications are the HPR20 and HPR60 machines. See Slides 17 to 20.

Slides 21,22, and 23 show example of Plasma enhanced catalytic conversion of Carbon monoxide to carbon dioxide.

The reminder of the talk (see slide24) is devoted to the identification of positive and negative ions and long-lived metastable species from plasmas and the measurement of time- averaged and time- resolved ion energy distributions for mass identified species. A key instrument is the EQP shown in Slides 25 and 26.

Slide 27 is very early data from a titanium nitride, DC magnetron deposition system. Slide 28 shows part of a mass scan for negative ions in a different application . The titanium isotopes are seen clearly.

Slides 29, 30, 31, and 32 are another magnetron application at Col. School of Mines (Surf and Coatings Tech 201, 2007, 6960.). The detailed waveforms of the (positive) pulsing of the magnetron cathode are crucial. Slide 33, from a different laboratory, is strongly endorsed by the EQP measurements.

Slide 34 is also C.S.M. data but for their MPPS (a form of HIPIMS/HPPMS) magnetron system. Some of the data were presented here in Santa Clara (SVC Tech Con meeting , May 2009. W.D.Sproul et al.) An important feature was the identification of multiply-charged ions. Any such ions clearly “punch above their weight” in terms of energy carried to growing films.

Slides 35,36, and 37 by C. Muratore et al are another EQP investigation of pulsed magnetrons.

Recent work at Hiden (UK) has included exploration of the benefits of fitting particle detectors which tolerate ambient pressures of up to 4.10^{-4}Torr.(Slide 38).

Slide 39 is a sketch of the system. Previously, with a weak mixture of deuterium in helium admitted directly into the mass spect. source, Slides 40 and 41 show how Threshold Ionisation may be used to find the proportion of deuterium (T. Coyne et al . 36th Int Conf Plasma Science and Symp on Fusion Engineering). The analysis of traces of helium in deuterium is less tractable, but high source pressures in the mass spectrometer offers a way forward. Slide 42 shows formation of He^+.He.

Slide 43 shows formation and detection of long-lived metastable helium etc in the mass spectrometer source,while Slide 44 shows metastable helium sampled from a plasma in the reactor of slide 39.

Slide 45 shows formation of helium ions from metastable and ground-state helium sampled from the plasma (any ions produced in the plasma were carefully excluded). Sllde 46 suggests a similar plasma in oxygen produced metastable 0ne-delta-g which is also long-lived but only has an energy of about ieVabove the ground state.

Slide 47 shows the basis of time-resolved measurements with the EQP.

Slides 49and 50 show early data for the pulsed plasma reactor (Slide 48) at NRL (S G Walton et al Phys Rev E 65, 046412-1/4 2002). Slides 51 and 52 show in-house test data from Hiden for a decaying, pulsed RF plasma in argon. It is important to be able to carry out such measurements for mass identified ions, including multiply-charged ions if these are present in the plasma.