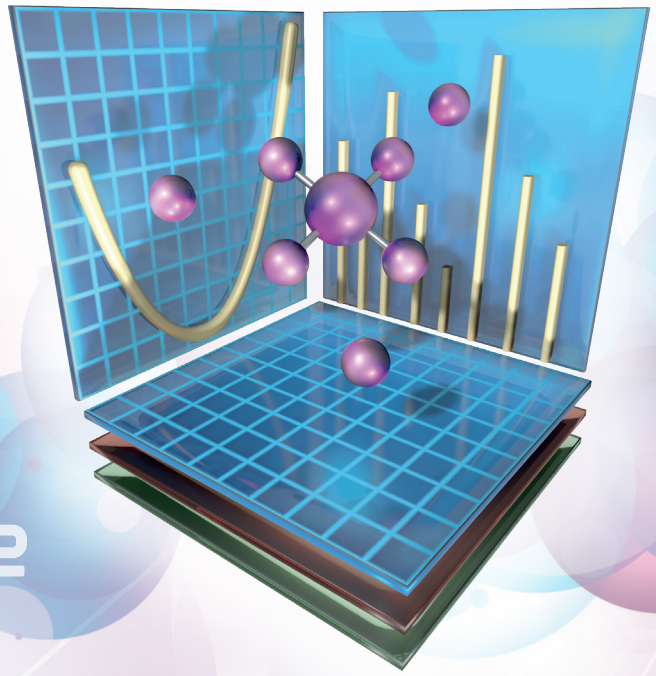
HORIBA
Scientific

# Plasma Profiling TOFMS

## Ultra Fast Thin and Thick films Depth Profile Characterisation



fast

sensitive

accurate

The full mass spectrum at any depth!

JOBIN YVON Technology

## Applications

- Photovoltaics
- Photonics rare earths
- Ion implantation
- Hybrid materials
- Electrodes of Li batteries
- Corrosion studies
- Materials science

The instrument is born from a EU project (“EMDPA”) coordinated by HORIBA Jobin Yvon which gathered 10 organisations from 7 countries with experts in material sciences, plasma physics/chemistry and plasma-surface interactions, renowned groups in GD-MS design, chemometrics and data handling and a provider of innovative TOFMS technologies. “EMDPA” partners have co-authored the chapter Analysis of Thin & Thick Films in the Handbook of Mass Spectrometry published by Wiley in 2012 (Lee editor).

Ultra Fast Depth Profiling

# Time of Mass Spe

## The Plasma Profiling TOFMS instrument (PP-TOFMS™) offers Ultra Fast depth profiling of advanced materials

made of conductive and/or non-conductive thin or thick layers down to the nanometre scale and allows direct simultaneous quantitative measurement of all elements, isotopes and compounds at any depth.

1-100 nm

**Protective coating**
Native oxide (few nm)
Corrosion protection
Tribological improvement

10-1000 nm

**Complex coating**
Structure: Multilayer, Gradient,..
Elemental Composition
Interface details
Layer Intermixing
Compound formation

100 nm - 100 µm

**Intermediate layer**
Adhesion improvement
Element Inter-diffusion
Substrate protection

1 mm

**Substrate**
Element Inter-diffusion

For all materials by Plasma Profiling

# Flight ctrometer

## Fast and direct analysis

A rapid erosion plasma combined with an ultra fast detection is the key to analyse samples in minutes. In addition samples are measured direct without any preliminary preparation or transfer into a UHV chamber.

## Thin to thick layers

The high density plasma results in high sputtering rate and allows for measuring thick layers up to 100 µm.

## High depth resolution

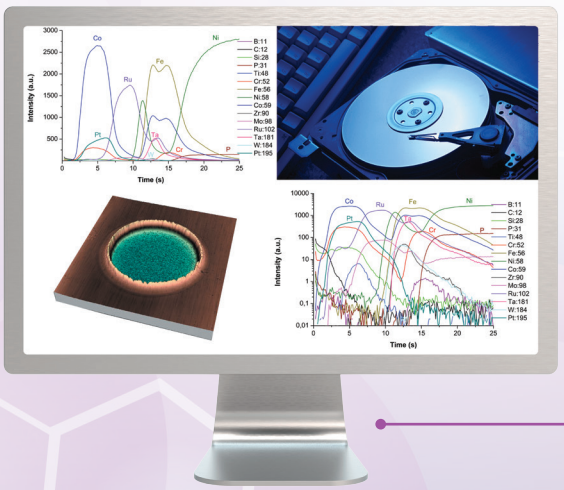
Despite the mm size crater formed, layers as thin as 1 nm are measured.

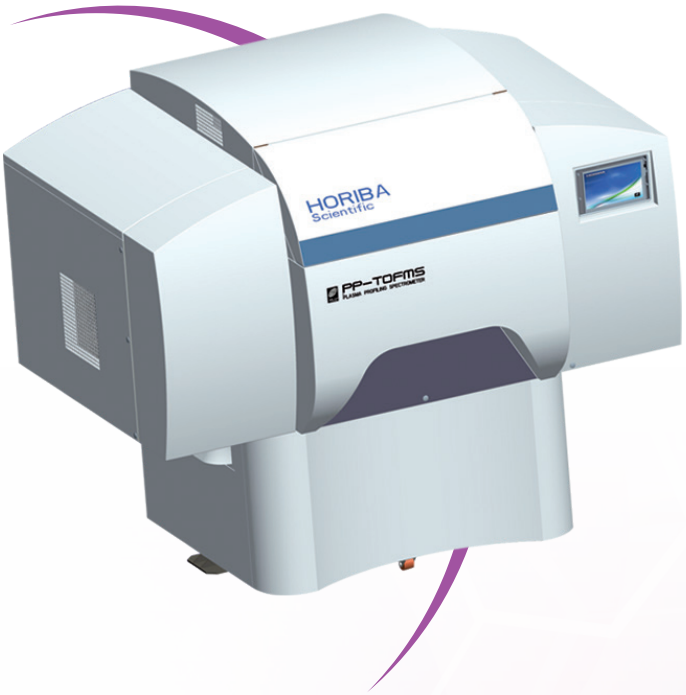
## Minimal Matric Effects

The separation of sputtering and ionisation processes in the discharge volume gives the capability of a calibration free semiquantitative analysis.

## All types of materials

The use of pulsed RF excitation permits the analysis of conductive and insulating, inorganics, organics, and hydrides materials or layers, e.g. thin layers on thick glass substrates.





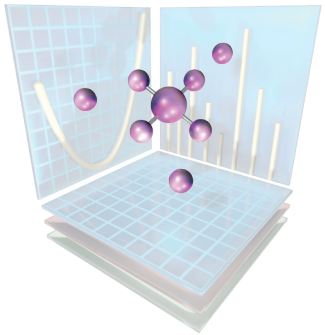

## Full mass coverage

In contrast with sequential mass spectrometers, TOFMS offers full mass spectrum at any depth, offering elemental (from H to U) and molecular information, including isotopic monitoring.

## Unique 3D data

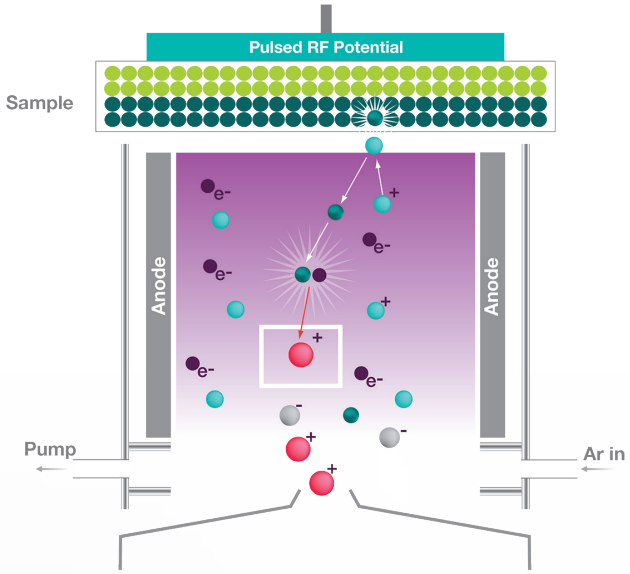
The glow discharge is operated in a patented pulsed RF mode thanks to an innovative matching system combined with high performance acquisition electronics and software. The temporal ion response over the RF source period is capitalised for high sensivity and to avoid isobaric interferences.

Ultra Fast Depth Profile of a hard disk (in linear and log scales) and associated erosion crater (4 mm diameter). New hard disks may feature up to 18 layers on the first 100 nm that are sputtered in less than 20 s. The instrument is used for detecting potential contaminants in the layers and at the multiple interfaces, and to evaluate the homogeneity of the composition over the entire hard disk area.

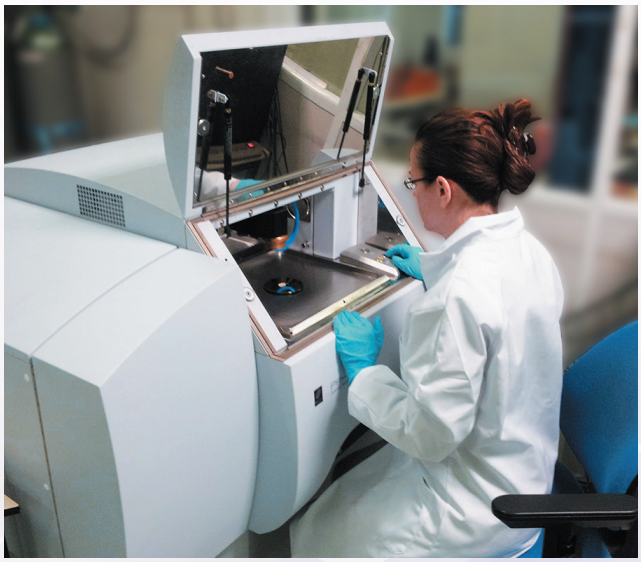


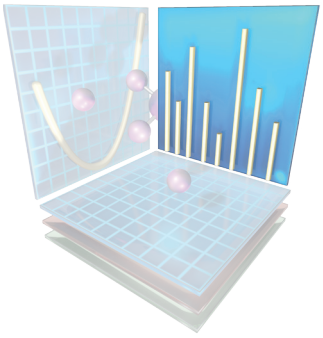
# A multiFunctional Glow Discharge Source

## at the heart of the PP-TOFMS™




- The Glow Discharge (GD) Source is a low pressure, high density plasma ($10^{14}$ /cm$^3$) that provides **very fast** (several nm/s) and **uniform** sputtering of solid materials.
- Pulsed RF operation allows that **conductive and isolating materials or layers** can be readily measured.
- The auto-matching in pulsed mode allows users to automatically tune the source in real time as it sputters through multiple layers and coatings that vary in impedance.
- The plasma gas ions involved in the sputtering process have a low energy (50 eV), causing negligible surface damage; as a result the GD plasma sputtering is also ideal to prepare samples for SEM observation or EBSD measurements.
- At the same time the plasma assures **the ionization of the sputtered species in the gas phase** away from the sample surface (no matrix effect).
- The speed of sputtering is therefore directly linked with sensitivity, the more materials enter the plasma per unit of time, the more signals can be collected.
- The stability of the ionisation mechanisms in the plasma allows for **calibration free semi quantification** (IBR) or **easy quantification** through RSF or «Layer Mode» Calibration. Concentrations range goes from sub ppm to 100%.
- This on going dynamic process (sputtering, ionisation, collection of the ions, evacuation of the neutral species) allows **real time measurement** of all elements with the Ultra Fast TOF Mass Spectrometer.



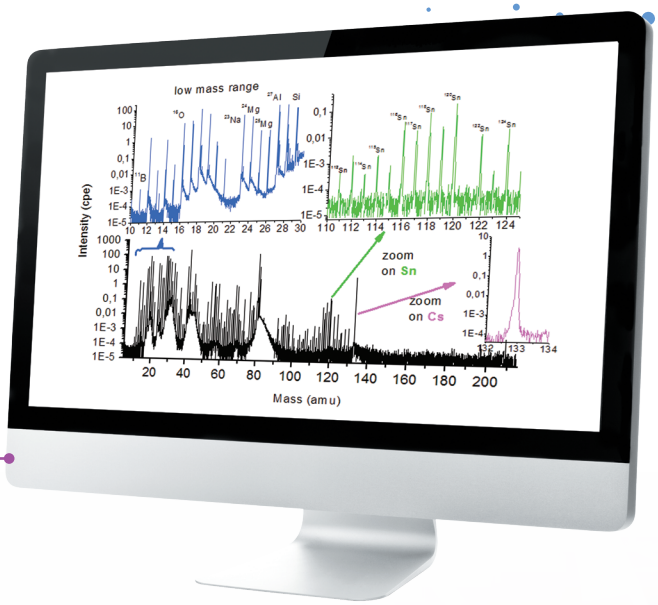


# All masses at once

## for depth profiling

A Mass Spectrometer measures elements and compounds according to their mass to charge ratio m/z. Compared to Optical Detection which is simpler, Mass Detection is the technique of choice for sensitivity.

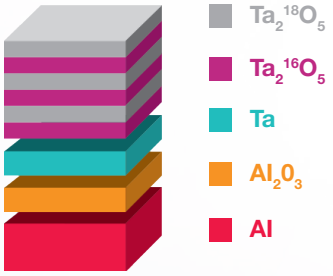
Compare to sequential mass analyser, Time of Flight (TOF) records a full and continuous mass spectrum thereby providing constant monitoring of all species throughout the depth profile.

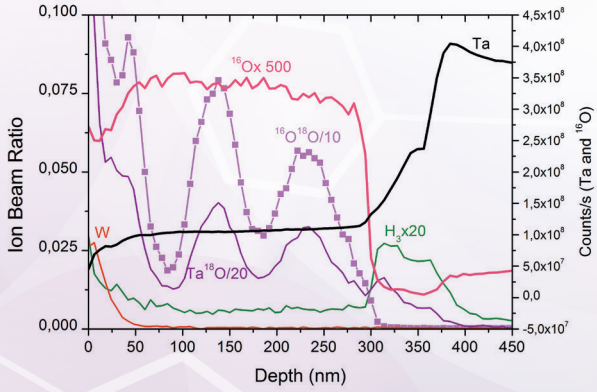



Mass spectrum of a glass bulk sample containing Cs. The dynamic range allows measuring matrix, major and traces.

# Isotopic Measurement

Isotopic labelling is often used in corrosion science to provide unambiguous determination of the presence and diffusion of species within a material.




Example of isotopic profile.
Ref: A. Tempez et al, Surface and Interface Analysis, 41, 966 (2009)

## Positioning of the PP-TOFMS™

vs SIMS (TOF-SIMS): Speed, ease of use, sample handling and throughput, absence of matrix effect, ease of quantification, no need for charge compensation, averaging of larger erosion zone

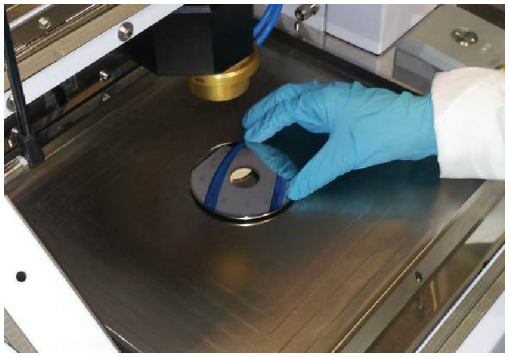
vs GD-OES: Higher sensitivity, isotopic and compounds measurement, calibration free semi quantification

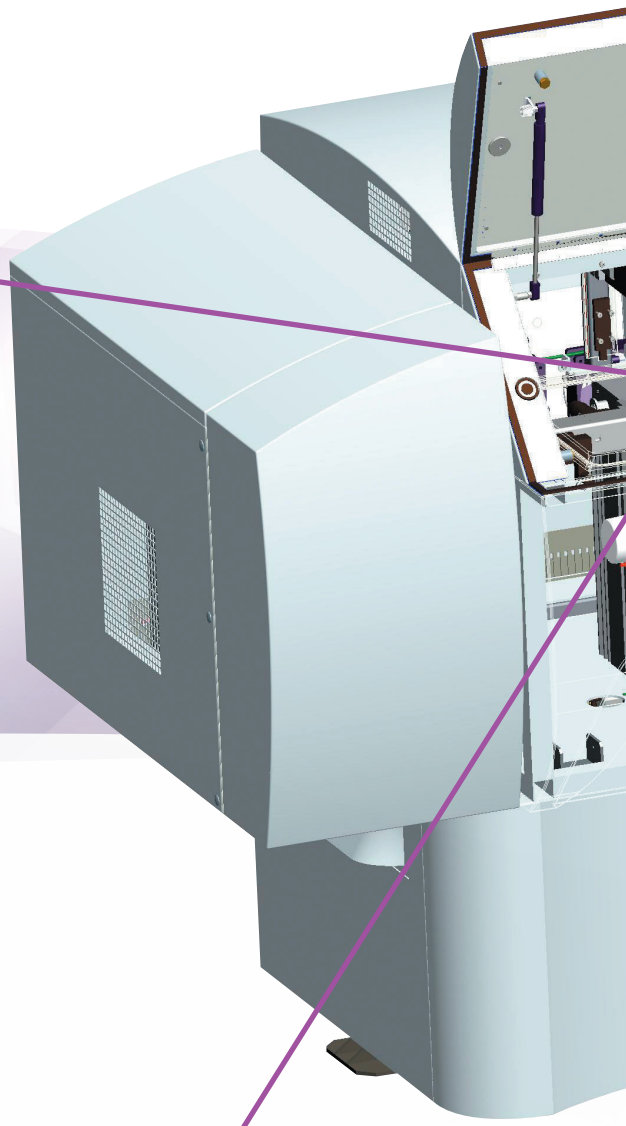
vs traditional GD-MS: Focus on depth profile, thin and thick films, entire mass spectrum at any depth, conductive and isolating layers

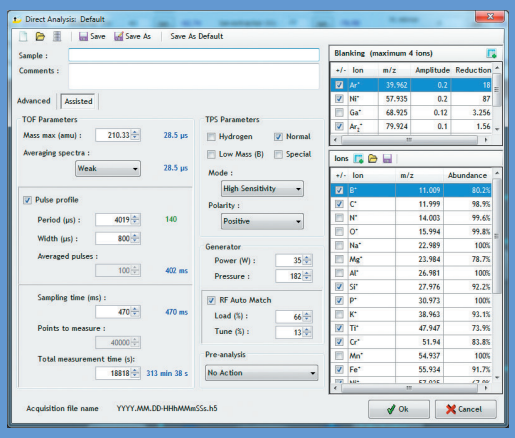
# The PP-

## at a g

- Easy sample mounting. No UHV chamber, horizontal positioning, large samples possible.
- Easily dismountable GD source and sampler for fast cleaning.
- Various holders for foils or small samples.







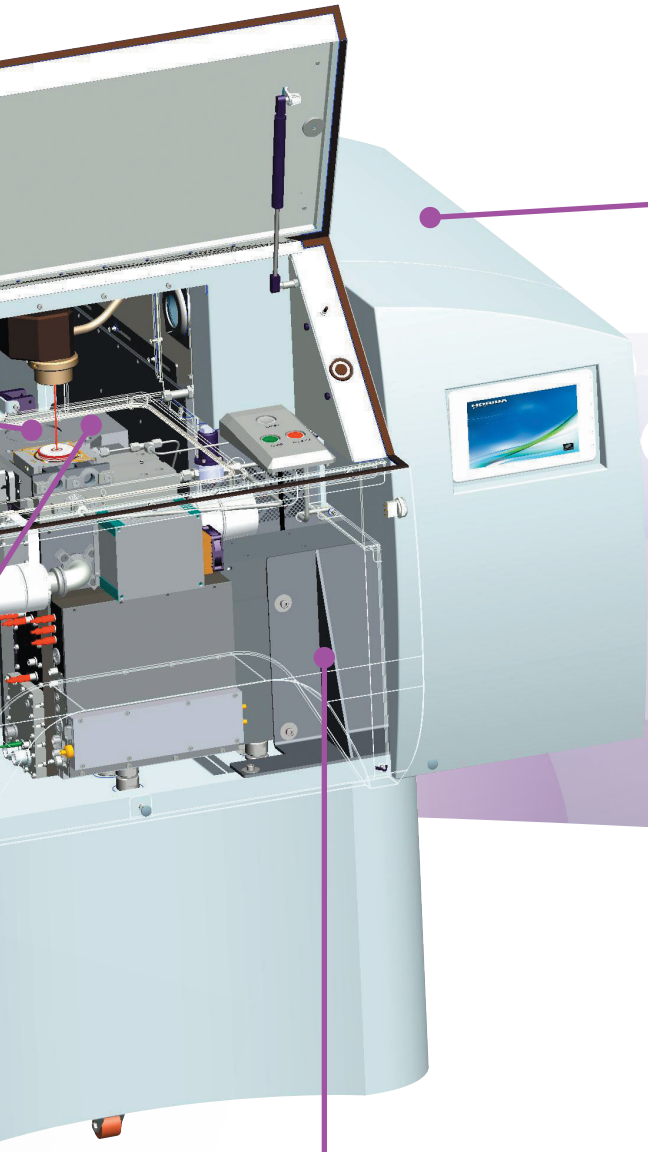

## Comprehensive software for

- Analytical tasks creation and optimisation
- Data handling
- Full control compatible with remote operation

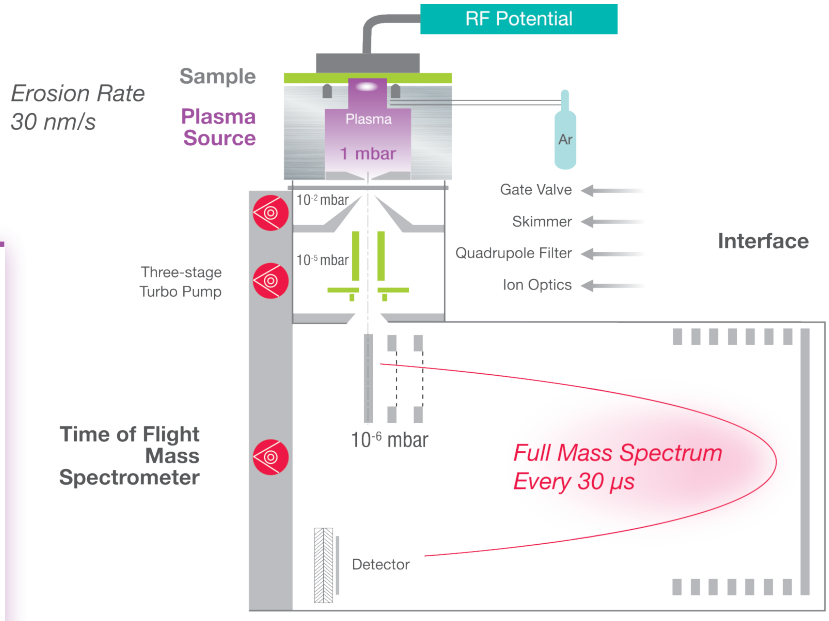
Patented interface with flexible "blanking" capability to lower signals of major ions for enhanced dynamic range and to avoid detector saturation.

# -TOFMS

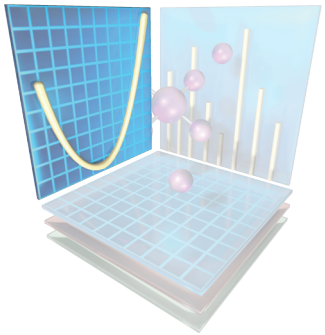
## glance



- Patented Pulsed RF source with auto-matching in pulsed mode for optimum measurement of multilayered materials.
- Patented UFS device for fast sputtering of polymeric layers.
- Possible addition of magnetic fields around the plasma chamber for enhanced performance (patented).




- Fast switching gate valve to isolate the TOF and vacuum interface stages.
- Multistage differential pumping.
- Ultra Fast Time of Flight Mass Spectrometer in orthogonal configuration allowing for measuring transient ion signals generated from RF pulsed plasma.
- MCP detector for high dynamic real time measurement of all elements at any depth.



# Enhance signal to noise ratio

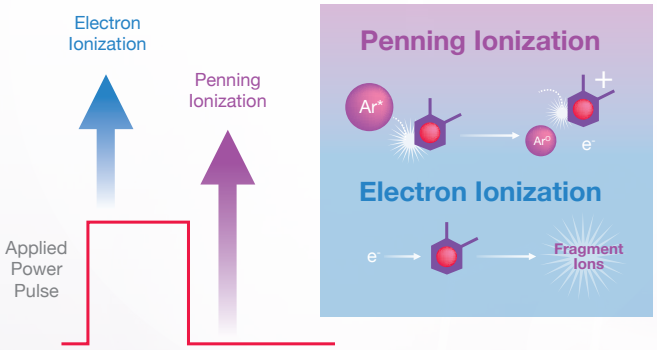
## The pulse timing effect

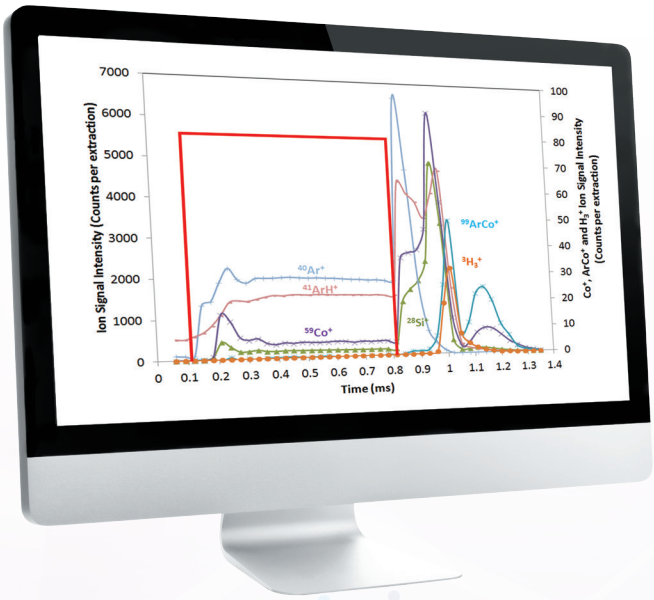
With millisecond pulsed RF operation appears a unique feature that is central to the operation of the Plasma Profling TOFMS instrument.

Various ionization mechanisms take place at different moments of the RF period. Since TOFMS acquires a full spectrum every 30 µs, TOFMS is perfectly adapted to monitor transient signals of the pulsed plasma over the RF period (few ms) with a pulse which can be varied from 0.3 ms to few ms. A time-resolved source profile is thus generated and an optimum time window may be selected per element to create the depth profile.

The analytical signals are usually taken in the afterglow region when the plasma is extinguished (Penning ionization zone) and can be temporally separated from possible recombinations.

### Pulsed Glow Discharge : A tunable source



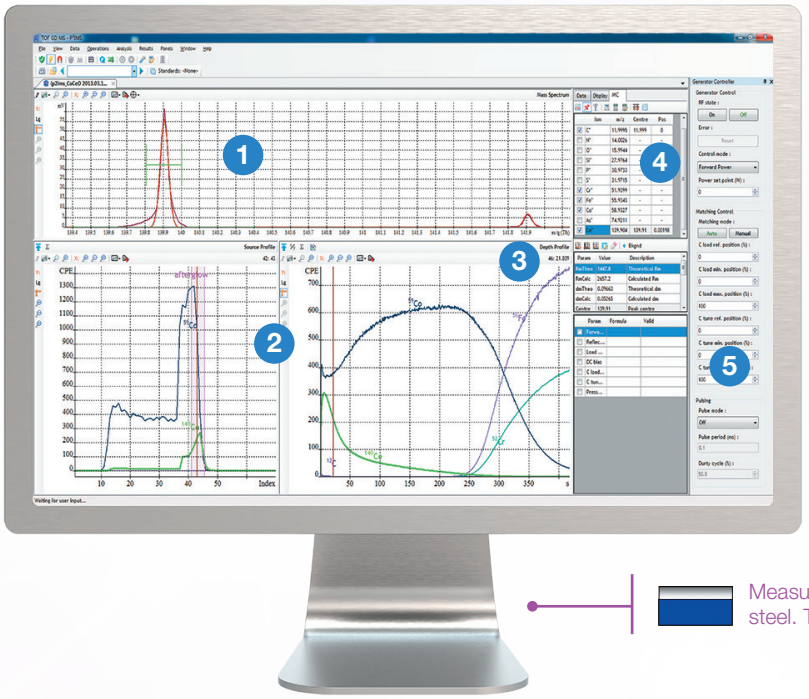

**The use of an orthogonal TOF configuration allows to decorrelate the pulsing of the source and the faster pulsing of the acquisition. It is therefore possible to acquire the entire mass spectrum at any time in a pulse.**

- Optimisation of sensitivity per element
- Time resolved minimisation of isobaric interferences
- Studies of plasma/material interactions and plasma chemistry
- Molecular depth profiles* and speciation studies

* N Tuccitto & al, Rapid Commun. Mass Spectrom. 2009; 23: 549–556

# Multidimensional Software

**TOF Viewer: The entire mass spectrum at any depth and any time in the RF period.** Optimisation of the analytical signals per element.




## Depth Profile/ Source Profile, Mass Spectrum, Isotope table/ Operating parameters

1. Mass spectrum
2. Source profile
3. Depth profile
4. Elements & Isotopes table
5. Operating parameters

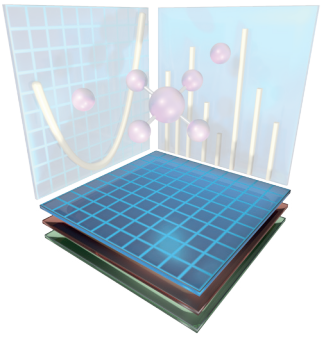
Measurement of a Co layer containing nanoparticles of $CeO_2$ on ferritic steel. The dynamic range allows measuring matrix, major and traces.

## Full control of operating parameters

Check up and control of voltages and vacuum levels

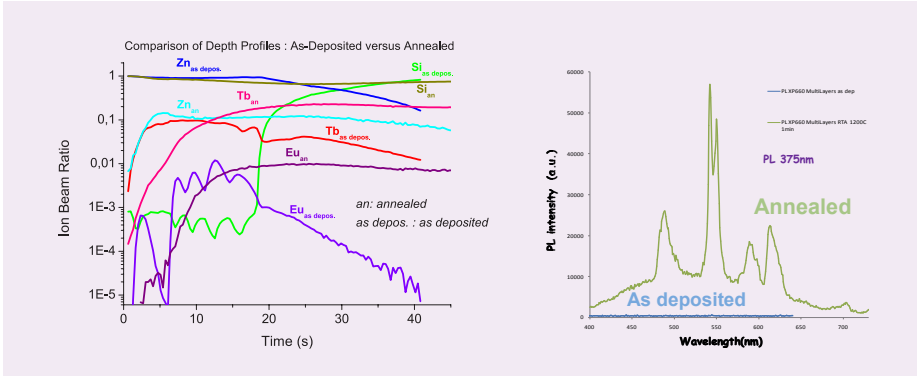
## Data handling and reporting

Each analytical result is saved in a HDF5 format file that contains the entire data set for potential reprocessing and detailed information on the operating parameters used for reporting.



# Applications

## Speed / Depth Resolution / Sensitivity




## Photonics

Study of Tb & Eu co-doped ZnO layers for white LEDs

[Eu,Tb:ZnO/Eu:ZnO] Multilayer 50 nm each layer by RF magnetron sputtering

Annealing effect - *Correlation between depth profile and PL data: change of matrix ZnO to $ZnSiO_3$ more favorable to the luminescence of rare earth*
Courtesy of CIMAP (Ions, Materials and Photonics Research Center), University of Caen.

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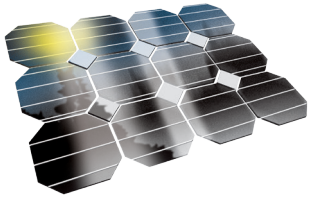
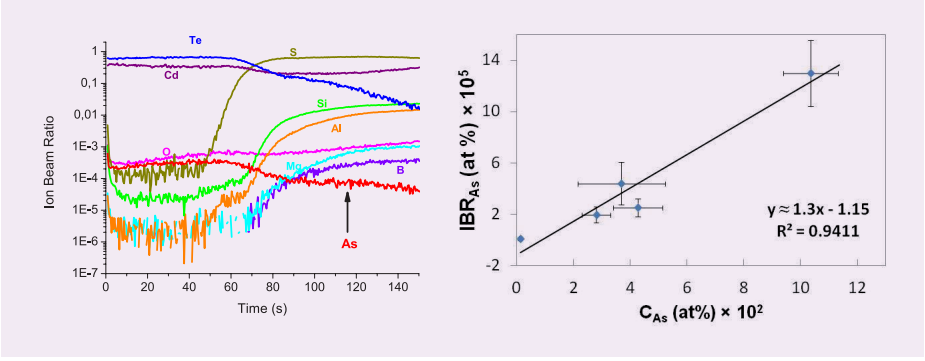


## Solar Energy

Study of As doped CdTe deposited on glass in a horizontal AP-MOCVD reactor




*Quantification of As • Comparison with SIMS • Good agreement down to $10^{17}$ atoms/cm$^3$ • Fast Control Tool (1 µm film in 60 s)*
PVSat 2013 Proceedings, Kartopu et al, CSER, UK.

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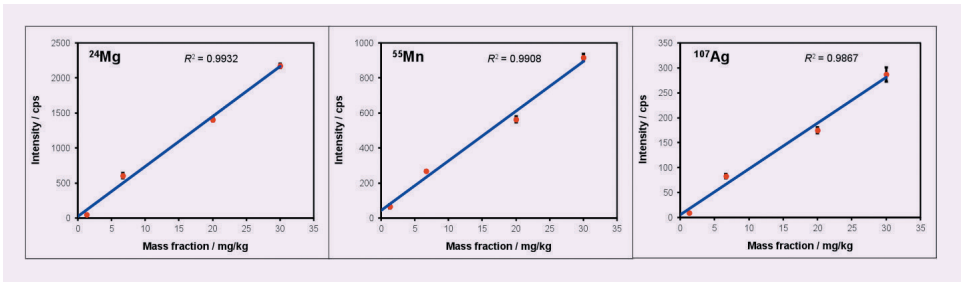


*R. Matschat et al., Anal. Bioanal. Chem., 386 (2006) 125 -141; T. Gusarova et al., Spectrochim. Acta Part B 66 (2011) 847–854*

## Bulk

Application of solution doped powder pellets for the analysis of pure copper

Calibration Curves of Mg, Mn, Ag
H. Traub et al, German GD User Meeting in Duisburg April 2013

# Specifications of the Plasma Profiling TOFMS

**Ultra Fast and Sensitive Depth Profile and Bulk Elemental and Ultra Fast Sensitive Depth Isotopic measurement of conductive and non conductive materials and layers. Simultaneous measurement of all elements and compounds from mass 1 to mass 250 – and above if needed – at each depth (for depth profile).**


- Compact instrument WxDxH 140 x 90 x 110 cm, weight 296 kg
- Easy sample handling (no need for UHV chamber, horizontal positioning)
- Nanometre Depth Resolution
- Dynamic range of $10^{10}$ for the simultaneous measurement of major, minor and trace elements in each layer and at interfaces
- Double "TPS" for optimized ion transmission all over the full mass range
- Glow Discharge Source for sputtering and ionization in the gas phase
- 13.56 MHz RF generator pulsing
- Pulsed RF powering (ms typical pulse frequency) with automatic matching in pulsed mode
- Ultra Fast Sputtering Mode of polymeric layers
- High Resolution orthogonal Time of Flight Mass Spectrometer (3500 or 5000 at m/z 208)
- Mass accuracy 40 μThTh$^{-1}$
- Positive and negative modes
- Ultra Fast acquisition rate (33 kHz to cover al elements up to U – a full spectrum every 30 μs)
- Time resolved measurements recording transient signals of the pulsed plasma to select for each element the optimum time window
- Interface with differential vacuum stages and flexible blanking capacity (up to 4 ions)
- Multidimensional software allows display in real time and records the depth profile, the pulse profile and the corresponding mass spectrum
- OS Windows 7
- Full control of operating parameters and remote control capability for on-line customer support


**The Plasma Profiling TOF MS instrument is manufactured in our new facility on the "Paris Saclay campus" – at the heart of the major French scientific cluster - and continues the HORIBA Jobin Yvon tradition of innovation.**

Other techniques of interest from HORIBA Jobin Yvon for surface and interface characterisation are Raman-AFM, Glow Discharge Optical Emission Spectrometry and Spectroscopic Ellipsometry.


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