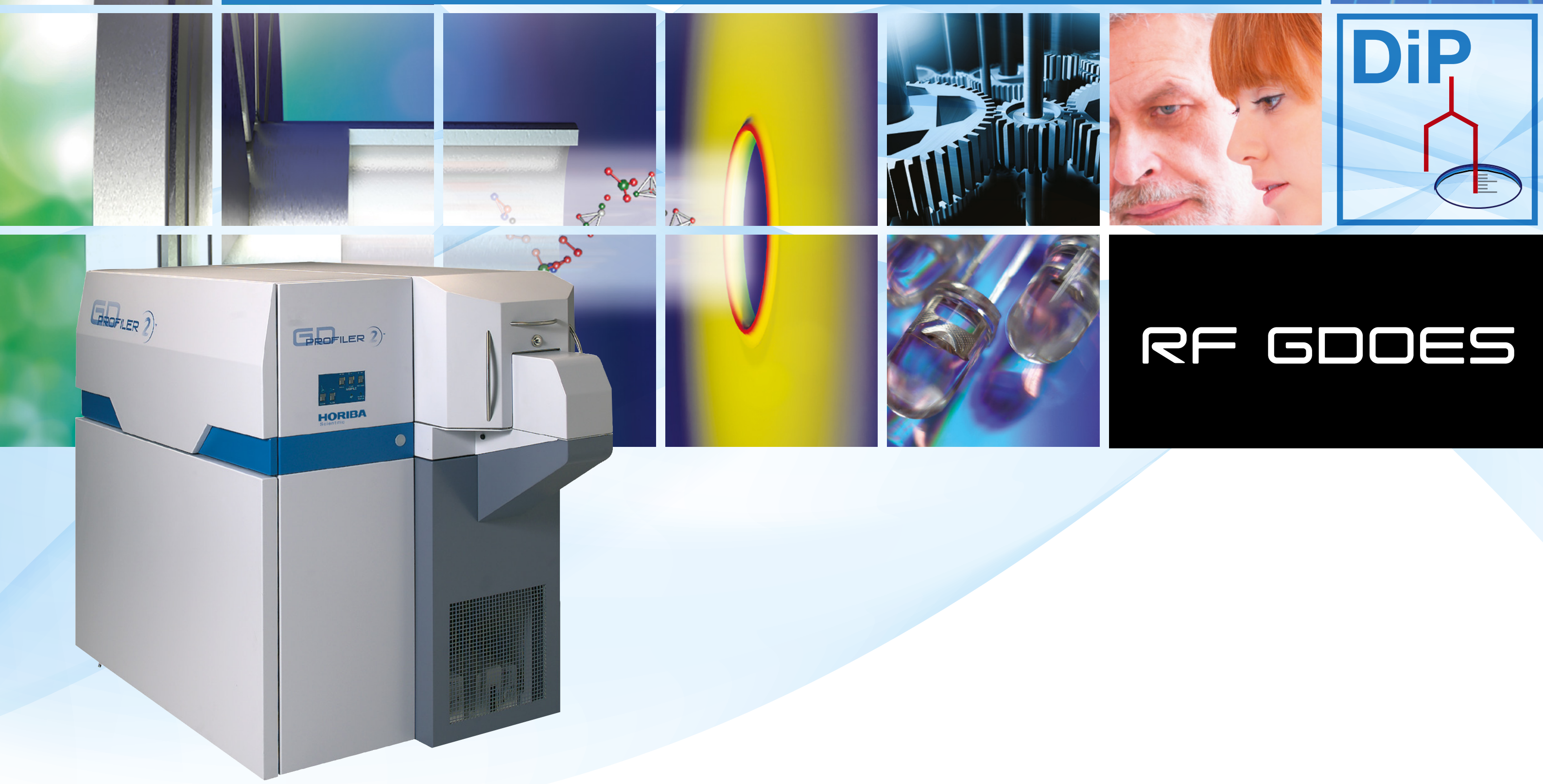
HORIBA
Scientific

GD-Profiler 2™

Pulsed RF Glow Discharge Optical Emission Spectrometer with Differential Interferometry Profiling



JOBIN YVON
Technology

Pulsed RF Glow Discharge Optical Emission Spectrometry with Differential Interferometry Profiling

GDOES: Multilayer elemental depth profile

Most materials today are multilayered (automotive bodies, LED, photovoltaic thin films, hard disks, electrodes for Li batteries, coated glasses, etc.) or they feature surface treatments and coatings in order to enhance performance, to improve mechanical properties or to strengthen corrosion resistance (nitrides, biocompatible surfaces, advanced oxides, etc.)

In this context, pulsed RF GDOES is the ideal analytical technique for studying layered materials as well as their process control. It offers ultrafast elemental depth profile analysis of thin and thick layers, conducting or isolating, with high sensitivity to all elements.

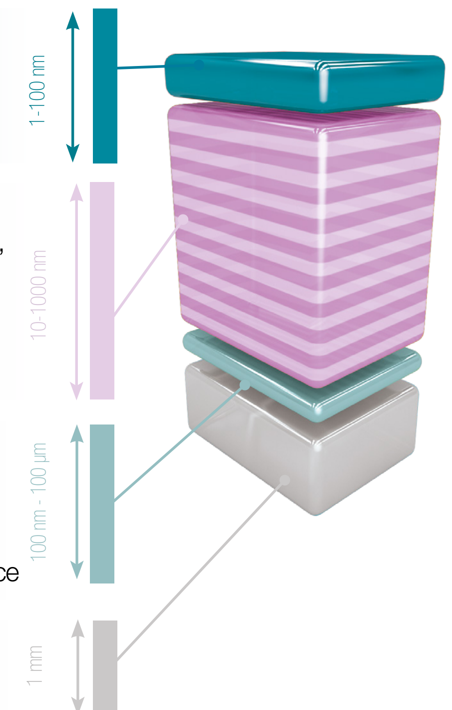
From multilayer sample to depth profile

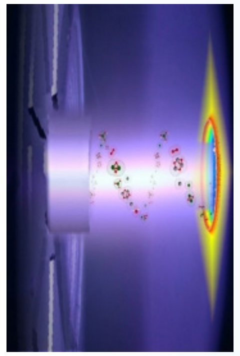
Protective coatings
- Native oxide (few nm)
- Corrosion protection
- Tribological improvement

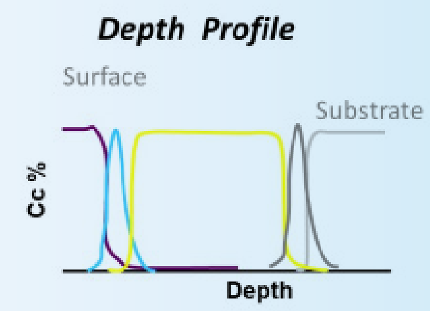
Complex coatings
- Structure: Multilayer, Gradient,
- Elemental composition
- Interface details
- Layer intermixing
- Compound formation

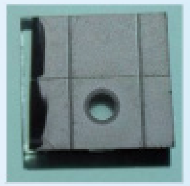
Intermediate layers
- Adhesion improvement
- Element inter-diffusion
- Substrate protection
- Contamination at a buried interface

Substrate
- Bulk composition









Large compartment

Some application domains

Li Batteries	Cationic Exchange in Glass
Nitriding	Coatings on Steel
LED	Polymers
Structured Materials	Hydrogen
Hard Disks	

DiP, Direct measurement of the depth as a function of time

With DiP, Differential Interferometry Profiling, a direct measurement of the depth as a function of time, with nanometric precision, is performed simultaneously with the GD analysis.

With a transparent Sapphire sample the two DiP beams can be observed.

Enhance productivity with the Sample Mapping Unit

Quantitative Elemental Depth Profile Analysis
From the First Nanometer Down to More than 150 Microns

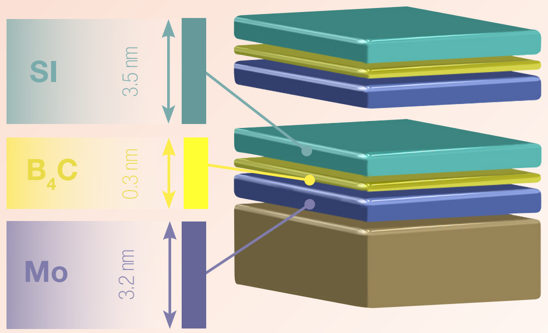
Speed & depth resolution

Ultra Fast

With a typical erosion rate of µm/min (2-10 nm/s), pulsed RF GDOES is ultra fast. Researchers and users are therefore encouraged to run multiple samples or do multiple measurements on any specimen. The immediate feedback allows them to check for material homogeneity, to optimize and control each stage of their evaporation, deposition or annealing processes and to quickly react to any observed variation. Even polymeric layers are sputtered ultra fast without damage, due to HORIBA's patented "UFS" system.

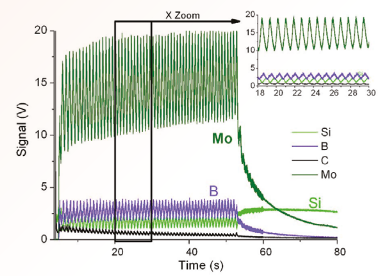
Nanometric depth resolution

Pulsed RF GDOES offers superb depth resolution, down to the nanometer scale or below, made possible by the unique characteristics of the advanced pulsed RF GD source and the patented High Dynamic Detection capability of the optical system.



Sub nm depth resolution Mirror for X-ray, thin multilayer material. Ref: Thin Solid Films 540 (2013) 96–105

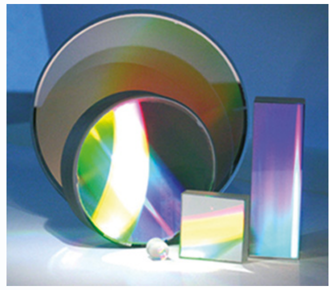
60 periods of 7 nm thick



The 60 layers of B_4C - each 0.3nm thick – are seen and resolved. The 420nm thick structure is sputtered in 1 minute!

Optimum spectral coverage

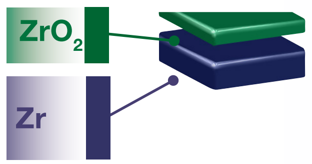
High Dynamic and Ultra-Fast Optical Detection allows simultaneous measurement of all elements of interest in the depth profiles from ppm levels to 100%. The proprietary HORIBA diffraction gratings allow optimum measurements of emission lines ranging from the VUV (120 nm for H and its isotope D, 130 nm for O, etc.), to the IR for Li (670 nm) and K (766 nm).

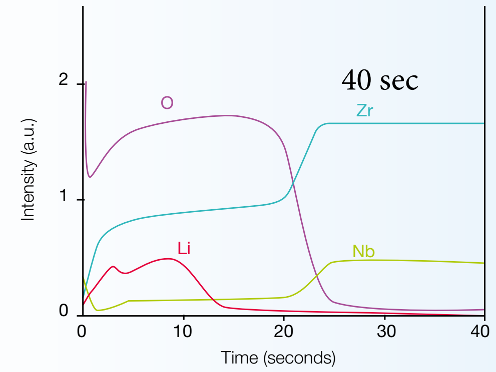


Absence of matrix effects

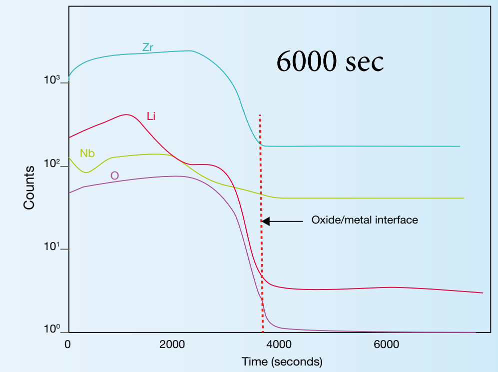
This example shows analysis of Zr exposed to oxidation conditions in an atmosphere containing traces of Li. Zr concentration naturally increases when going from the oxide to the Zr bulk. GD signals (left) follow the concentration changes, whilst conversely the SIMS signals (right) are much higher in the oxide layer.

The ionization process in SIMS is matrix dependent while the separation of erosion and excitation in the plasma gas for GD makes the GD nearly matrix independent.





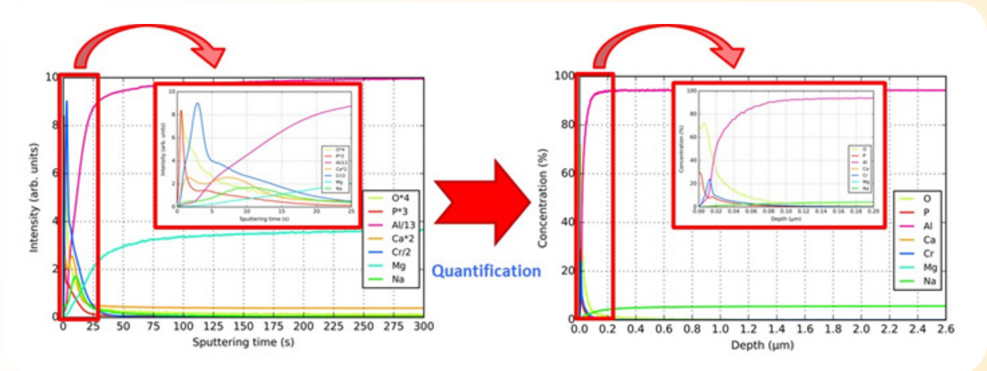
GD measurement



SIMS measurement

Qualitative and quantitative depth profiles of thin and thick films

Surface sensitive techniques (XPS or SIMS) are slow and fail to measure layers of more than 1 micrometre. For thicker layers, SEM EDX on cross sections can be used, but require tedious preparation and cannot measure light elements. Pulsed RF GDOES, on the other hand, rapidly sputters tens of micrometres of conductive and non-conductive materials, measures all elements and is therefore ideal both for thin and thick layers.
Within the pulsed RF GD source, erosion and emission are spatially separated. Erosion is material dependent and measured with DiP. Excitation takes place in the gas phase only and uniquely relates to the plasma conditions and emission lines intensities are directly proportional to the concentrations in the plasma. Conversion from measured signals (intensities vs time) to quantitative results (concentrations vs depth) is therefore straightforward.

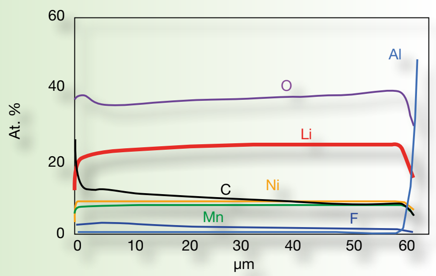


Large Spectrum of Applications

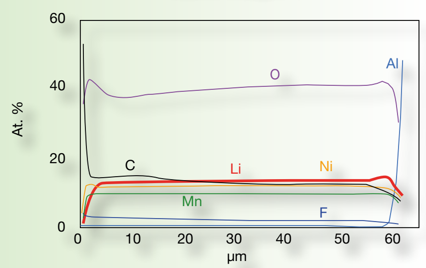
Li Batteries

Positive and negative electrodes, Thick layers and thin surface SEI. Air sensitive sample handling strategy with Li bell accessory.

Ref: HORIBA Scientific Application note n°18



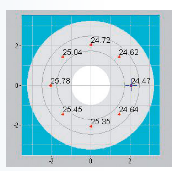
State Of Charge 0 %



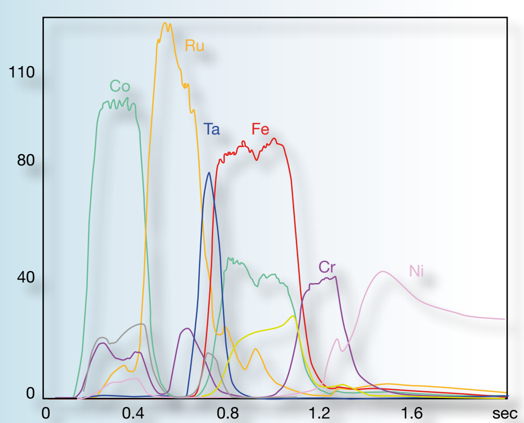
State Of Charge 100 %

Hard Disks

Depth resolution, uniformity check, repeatability



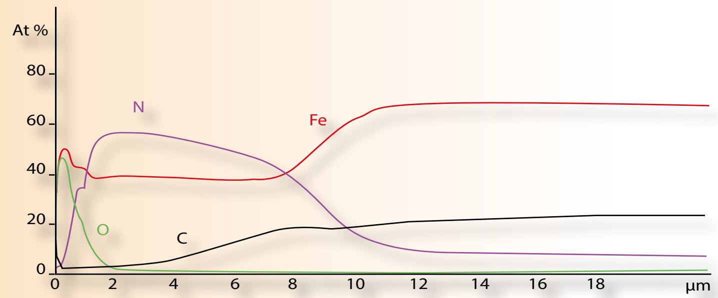
Ref: S. Liang, Seagate, 2013 SCIX US GD Workshop. Elements for illustration only, not actual.



Nitriding

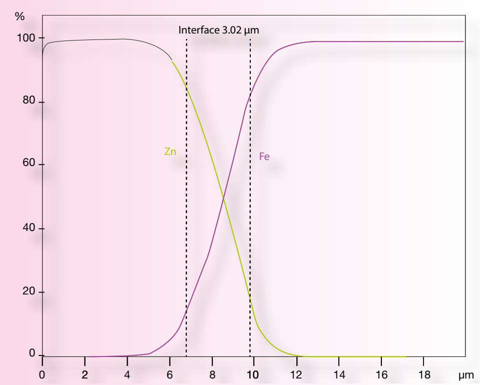
In depth N and C measurements

Ref: G. Mancuso, Colmegna, 4th GD Day



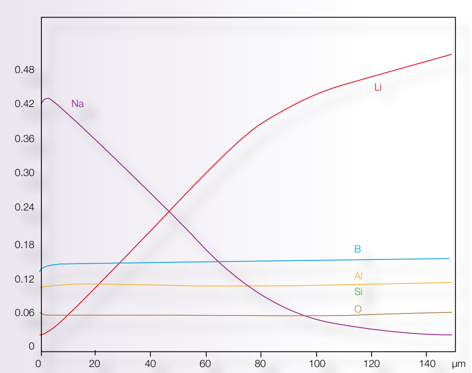
Zn Coatings

Compliant with ISO 16662
Thickness, uniformity of coating, defectology.



Glass Cationic Exchange

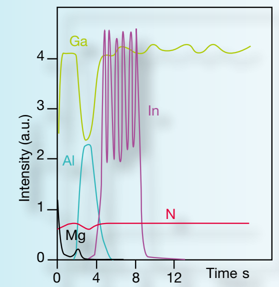
Pulsed operation to avoid thermal effects.
Deep craters.

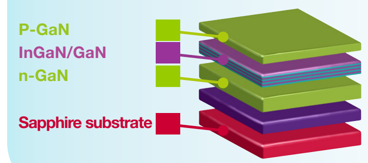


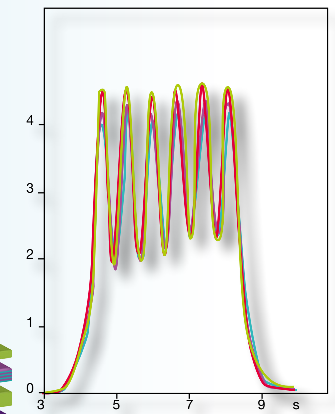
LED

Process control, depth resolution. Blue and red LED analysis, with possible automation using the Sample Mapping Unit.

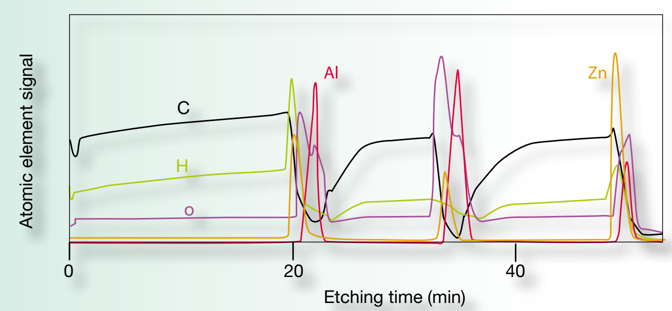
Ref: HORIBA Scientific Application note n°19

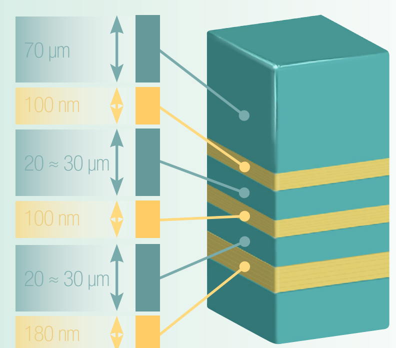






Polymers





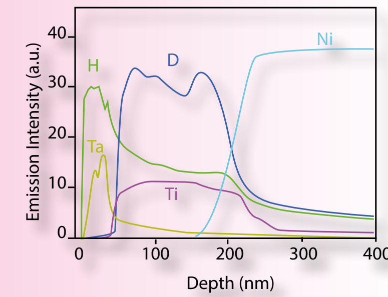
Patented UFS mode for Ultra-Fast Sputtering Plastic DVD with 6 embedded layers (100nm) resolved below a 70 µm polymer layer.

Ref HORIBA Scientific notes N° 28 & 36

Hydrogen

Direct measurement of H.
H and D can also be measured simultaneously.

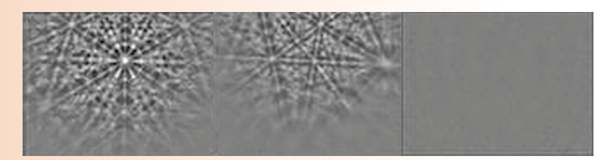
Ref: Fusion Engineering and Design 87 (2012) 1091– 1094



GD SEM/EBSD Sample Preparation

Patented application of GD plasma to prepare samples for SEM and EBSD.

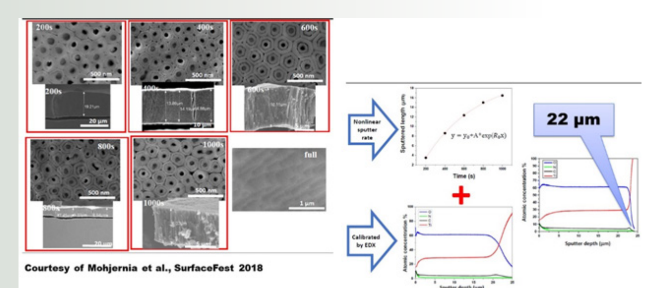
Ref: M. Penoy, Ceratizit, 6th International GD day.



GD: 10W - 3 sec *CP: 5 hours* Mechanical polishing

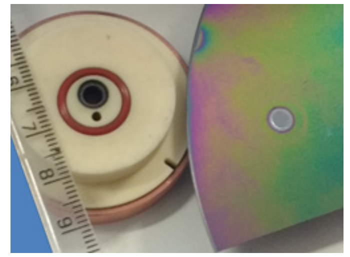
Structured Materials

Long TiO_2 nanotubes (over 20µm).
Structure maintained thoughout the whole erosion.



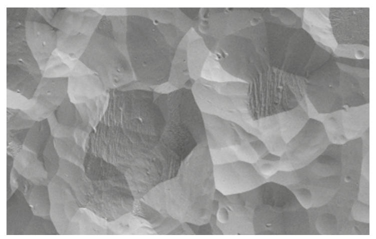
Plasma Source: It Makes the Difference

Source principle

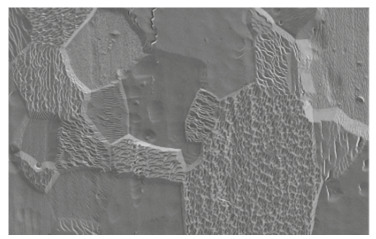


The source is central to the operation of the instrument and accounts for many of its specific characteristics.

- **Easy Operation**: sample is placed against the “O” ring and faces the anode tube in which the plasma is confined
- **Large Sample Compartment**
- **Low Pressure Plasma**, 13.56 MHz RF Plasma Source, Pulsable, no Ultra High Vacuum needed; low plasma gas consumption (<0.3l/mn)
- **Double Pumping**: the plasma source is pumped with 2 pumps (for optimum pressure control during the entire sputtering process – also mandatory in patented application of GD for SEM observation)

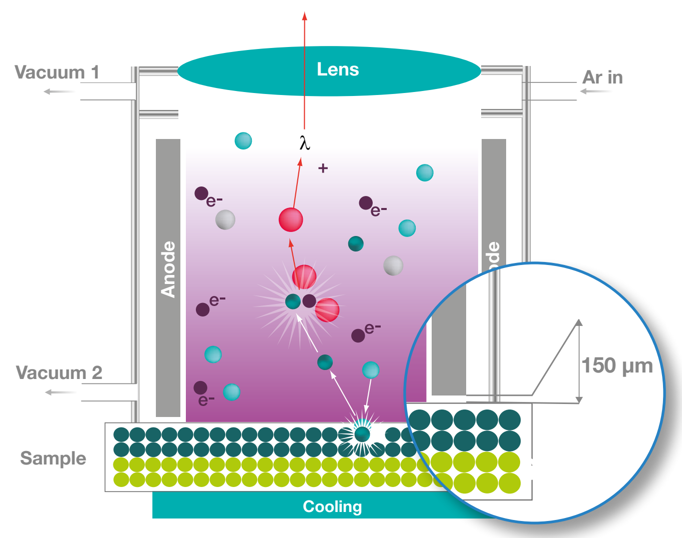


Without double pumping. Local pressure at surface is not uniform, resulting in poor sputtering.



With double pumping. Sample grain structure is well resolved

- **Capacitive Coupling**: ensured by real time auto-matching in non-pulsed and pulsed modes (patented). Mandatory for optimum measurement of multilayered samples.
- **Pulsed RF Operation**: provides higher instantaneous power without damage for fragile and heat sensitive materials
- **Plasma Cleaning**: only possible in Pulsed RF mode it minimizes surface contamination and is crucial for proper interpretation of extreme surface measurements (Ref: J. Anal. At. Spectrom., 2009, 24, 734–741)
- **Pulse Synchronisation Acquisition of optical signals**: enhances the Signal/Noise Ratio
- **Flexibility for Calibration**: the selection of calibration materials is easy with Pulsed RF as bulk and coated specimens – conductive, isolating or hybrid – can be used within the same analytical method



Principle of GD sputtering

Latest Innovations

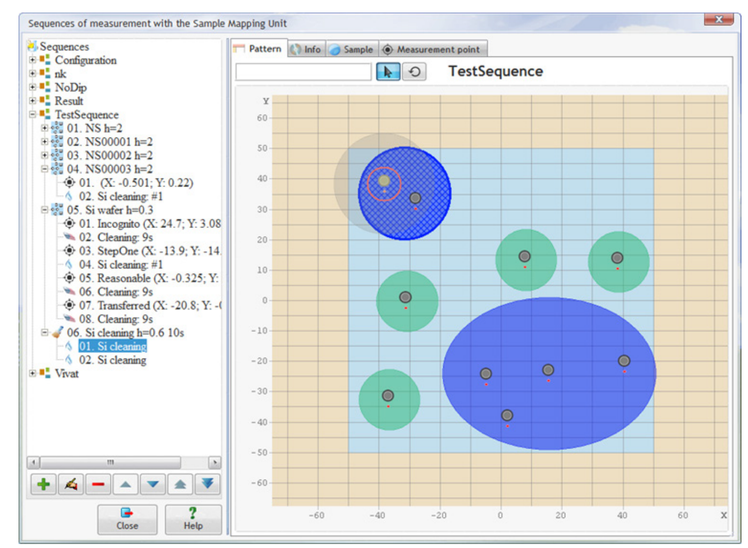
- **UFS Mode (patented)**: Ultrafast Sputtering of polymeric materials without sample damage
- **Differential Interferometry Profiling DiP (patented)**: built-in interferometer for real-time measurement of crater depth and erosion rates

Enhance Productivity with the Sample Mapping Unit

Pulsed RF GDOES is sometimes too fast that it requires a permanent presence near the instrument when multiple analyses are being made. Do you need to map a multilayer wafer (LED, hard disk, etc.) to check coatings uniformity or to measure a batch of thin samples in an unattended manner? The Sample Mapping Unit (SMU) is for you.

The SMU replaces the standard source compartment (it can be retrofitted onto existing units). With the SMU, manual and automatic operations are equally available.

Within the SMU, an XYZ stage allows the plate with multiple mounted samples to be precisely positioned for analysis. The plate also ensures that the RF coupling efficiency is uniform (patented). Automatic cleaning of the anode is done when the stage is in rest position. In this rest position, manual operation of the instrument is also possible, offering the same flexibility as in a standard instrument – the large chamber doors ensure easy access to the sample compartment.



Software screen showing a batch measurement of various samples with different shapes and thicknesses (colour change is linked to thickness). SMU measurements can be conducted with 2 and 4mm anodes.

Optics Made for GD

Spectral range and resolution

- Wide Spectral Range of 120-800 nm
- Optimised VUV/UV grating with proprietary MgF_2 coating
- Red/IR grating for alkali elements
- Nitrogen purge optics for long-term efficiency of the optical surfaces

Flexibility

- High-resolution monochromator with HDD detection
- Flexibility to measure any N+1 element tunable
- Full-spectrum coverage with Image

High Dynamic, Ultra-Fast Detection

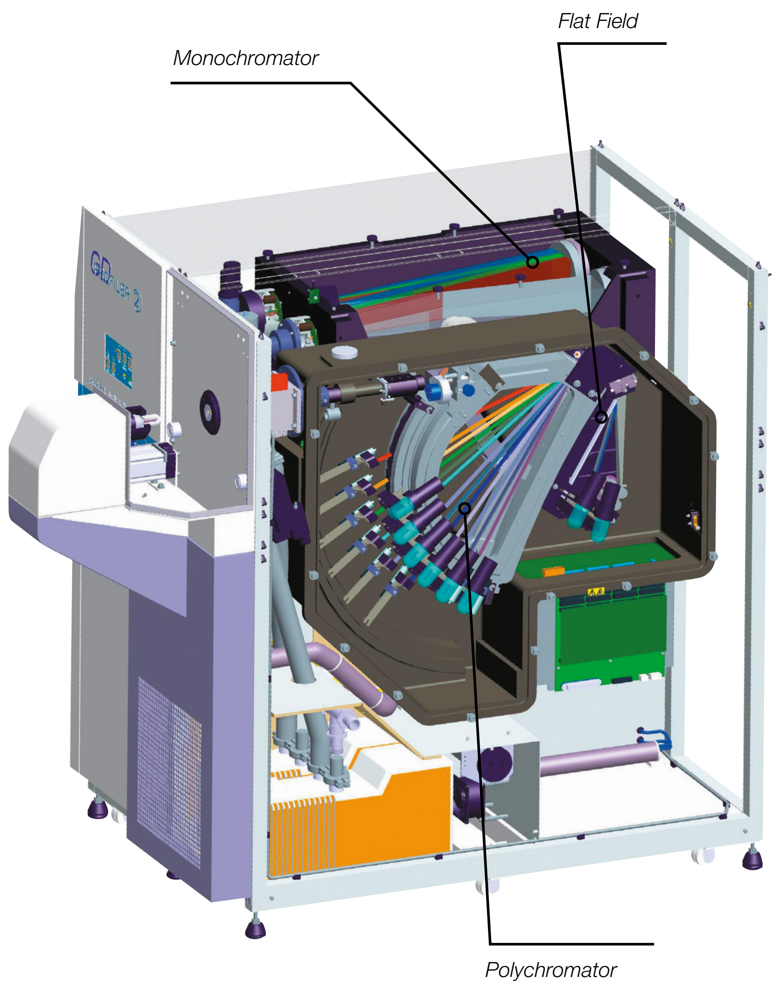
Patented High Dynamic Detectors for all lines

GD is fast. Reducing erosion rate degrades sensitivity, as the amount of light is directly correlated to the quantity of material entering the plasma.

Detection must therefore be much faster and should respond immediately to the rapid changes of concentrations from layer to layer.

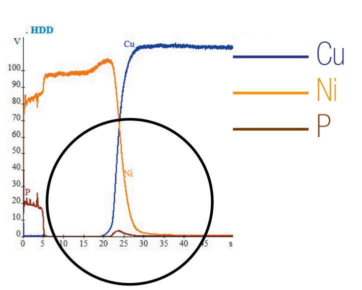
Only the patented High Dynamic Detector (HDD) offers a linear dynamic acquisition range of $5x10^9$ to measure all elements from sub ppm to 100% within depth profiles.

With HDDs pre-adjustments of voltages are no longer required prior to analysis or calibration, resulting in considerable time saving and ease of use.



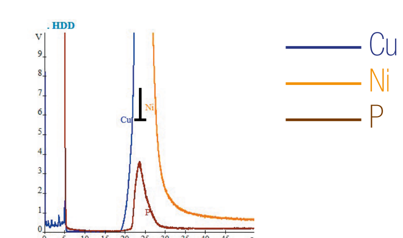
Optimum optical configuration with polychromator and monochromator

1



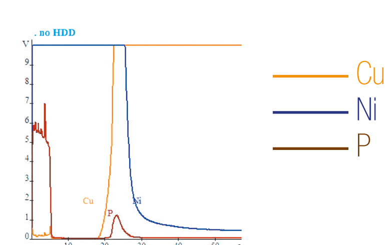
Ni/Cu sample. The top layer contains P and traces of Cu.

2



With HDD 1 & 2, both the low levels of Cu and the major levels are seen and dynamic range is above 109.

3

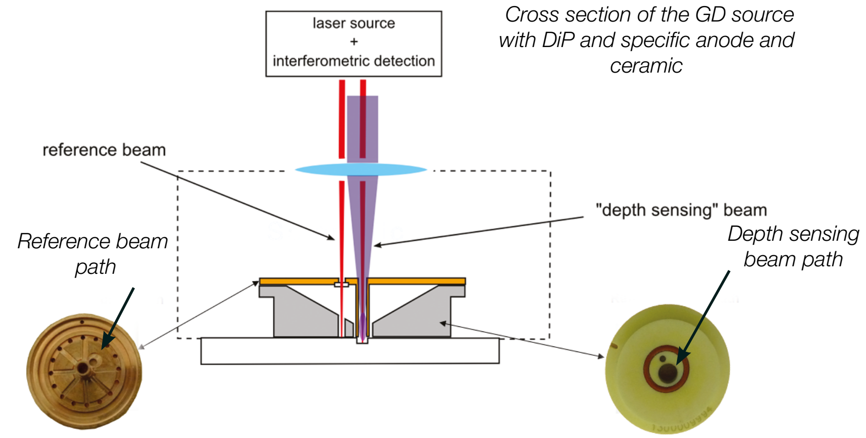


Without HDD 3, the measurement scale is limited to 0-10 V and signals of Ni and Cu appear saturated.

Differential Interferometry Profiling (DiP)

Erosion rates in GDOES are material dependent, and when multi-layers are measured, the erosion rates change with depth. Previously, estimating erosion rates could only be obtained from calculations (prone to uncertainties) or external measurements.
Thanks to DiP, a direct measurement of the depth as a function of time, with nanometric precision, is performed simultaneously with your GD analysis.

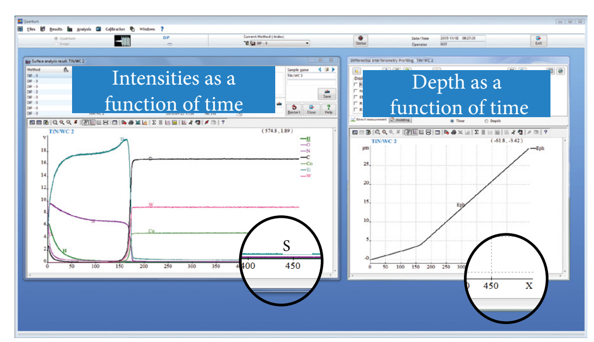
- Interferometer built in the GD source
- Crater depth and erosion rate measured
- Laser Class 1



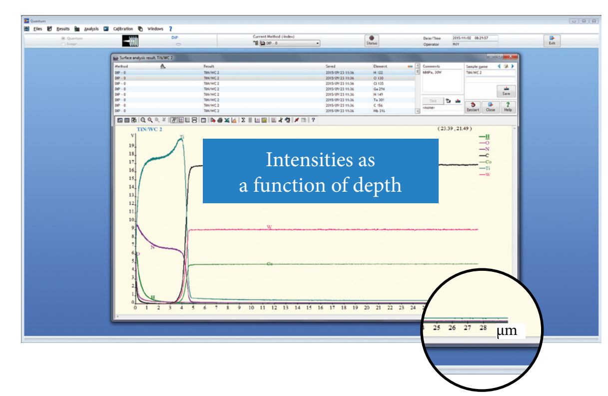
Cross section of the GD source with DiP and specific anode and ceramic

With a transparent Sapphire sample the two DiP beams can be observed.

Intensity as a function of time + **Depth as a function of time** = **Intensity as a function of depth**



Surface Measurement and DiP windows. In the DiP window (right) the changes of slopes reflect the changes in erosion rates between layers. These erosion rates are directly obtained by the interferometric measurement.



Measurement with time axis directly converted in depth using DiP in Quantum software.

Strategies for Handling Multiple Samples

GD operation does not require Ultra High Vacuum Sealing. Air-sensitive, small, porous or non-flat samples can therefore be measured using dedicated holders or mounting strategies.

Large Sample Compartment

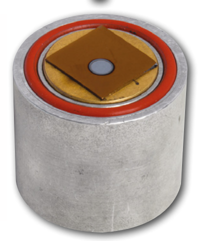
The large sample compartment helps you measure large samples but also allows the use of various accessories for handling multiple samples.

Li Bell

For air-sensitive materials or rough samples.

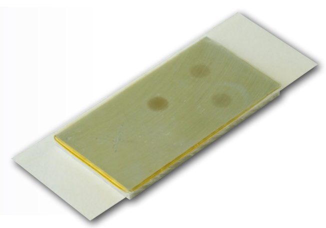
Small Sample Accessory

When samples are small. Also available: smaller anode diameters, Indium kit, etc.



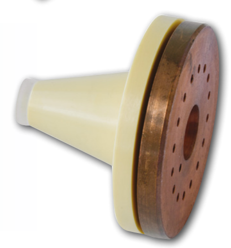
Methodology for flexible thin films

Coated PET film on Aluminium substrate.



Elephant anode

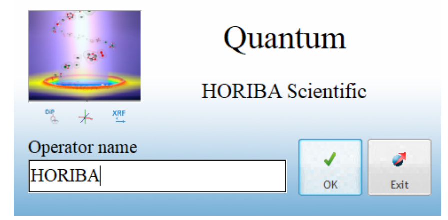
Strategies for non-flat samples to ensure proper distance anode/sample and vacuum seal.



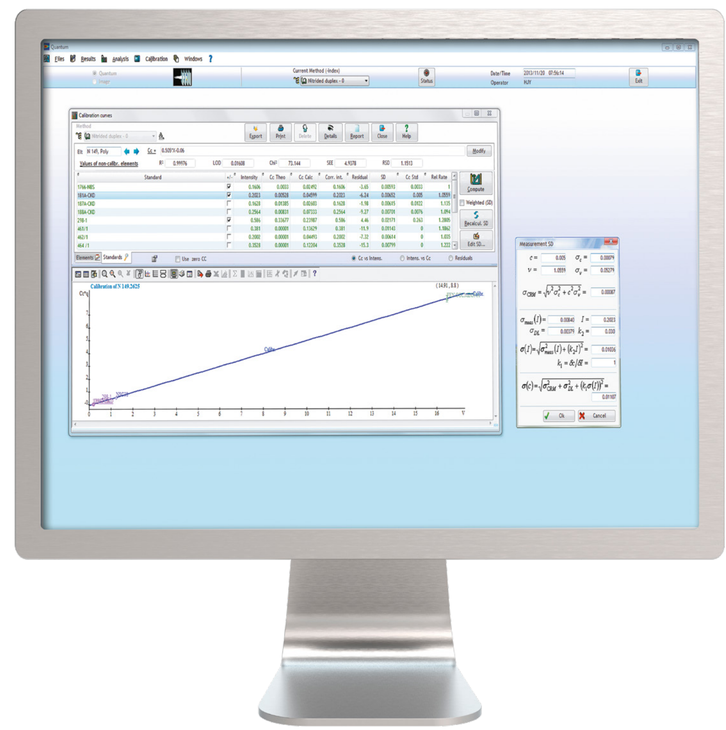
Sample holder for SEM cross-section preparation

The sample's cross section is sandwiched between 2 stainless blocks placed inside a vacuum-tight holder.

Quantum™: your GD Software Suite

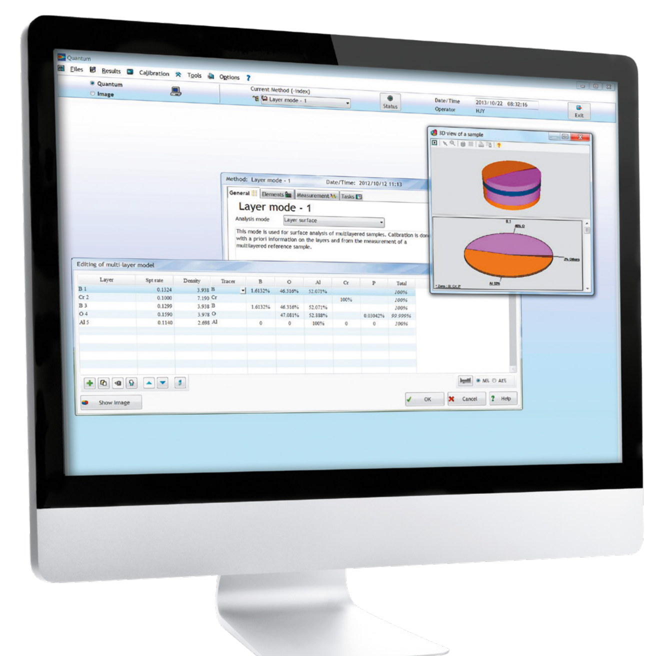


- IQ, Intelligent Quantification Models following ISO standards and the flexible Layer Mode, possible thanks to the flexibility of the pulsed RF source. Expression of results in M%, At%, depths, coating weights, layers thickness.
- Built-in libraries of reference materials, erosion rates and information on optical wavelengths
- Powerful data treatment functions (with task generation for batch treatment) and report generation



Multimatrix Linear Calibration of N with statistical information built in

- All functions included (no options)
- Emulation versions freely available for remote data treatment
- Time Plus function (increases measurement time during operation)
- Plasma Cleaning
- Pulse synchronisation detection

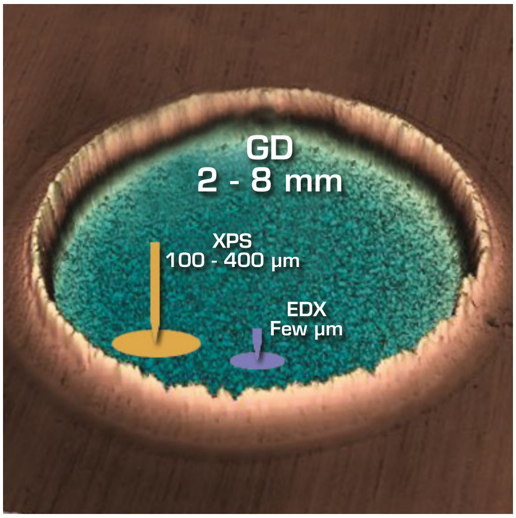


- XRF Link for direct correlation with XRF (or XPS) measurements
- Online SPC (Statistical Process Control module)

Surface and Beyond

We know GD and its multiple application possibilities!

The ISO Technical Committee TC 201 for Surface Analysis has already issued three international standards for GD. 6 reference books are available, and an annual rate of over 100 scientific papers published with GD data shows the vitality of the technique in all domains of material science. Our staff of application scientists provide dedicated solutions and full support.



Coupling of techniques with variable lateral resolution

Coupling to SEM, XPS or other surface techniques

The GD plasma sputtering, though Ultra Fast, is delicate. Incident particles have a low energy (50eV) and do not induce structural changes in the material. Coupling GD with other techniques offering different lateral resolution is therefore of great interest. XPS, Ellipsometry and micro-Raman measurements have been performed within GD craters, providing multiple and complementary information on the same materials.

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