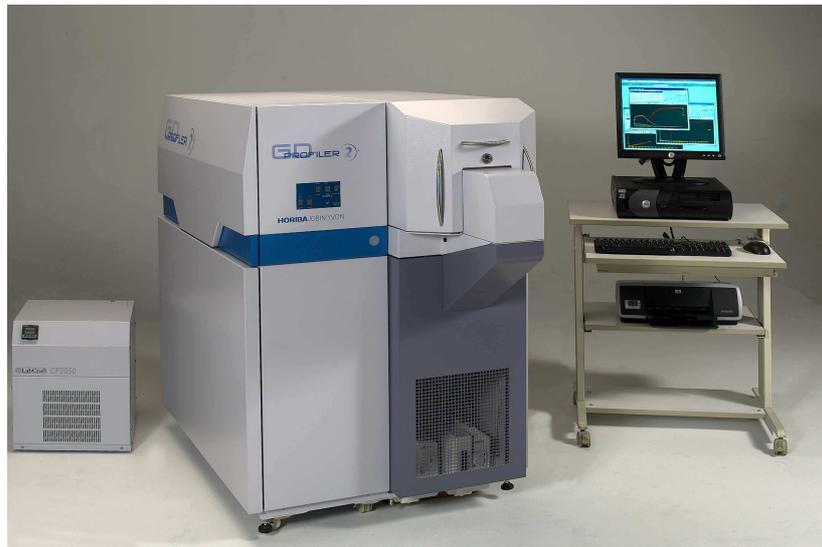
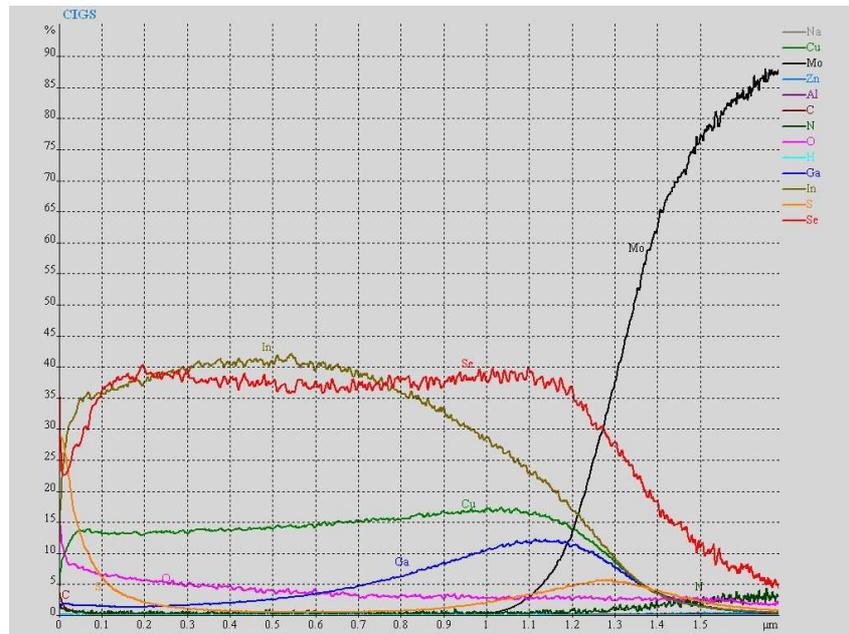


## Application of the GD-Profiler 2 to the PV domain



*GD Profiler 2*

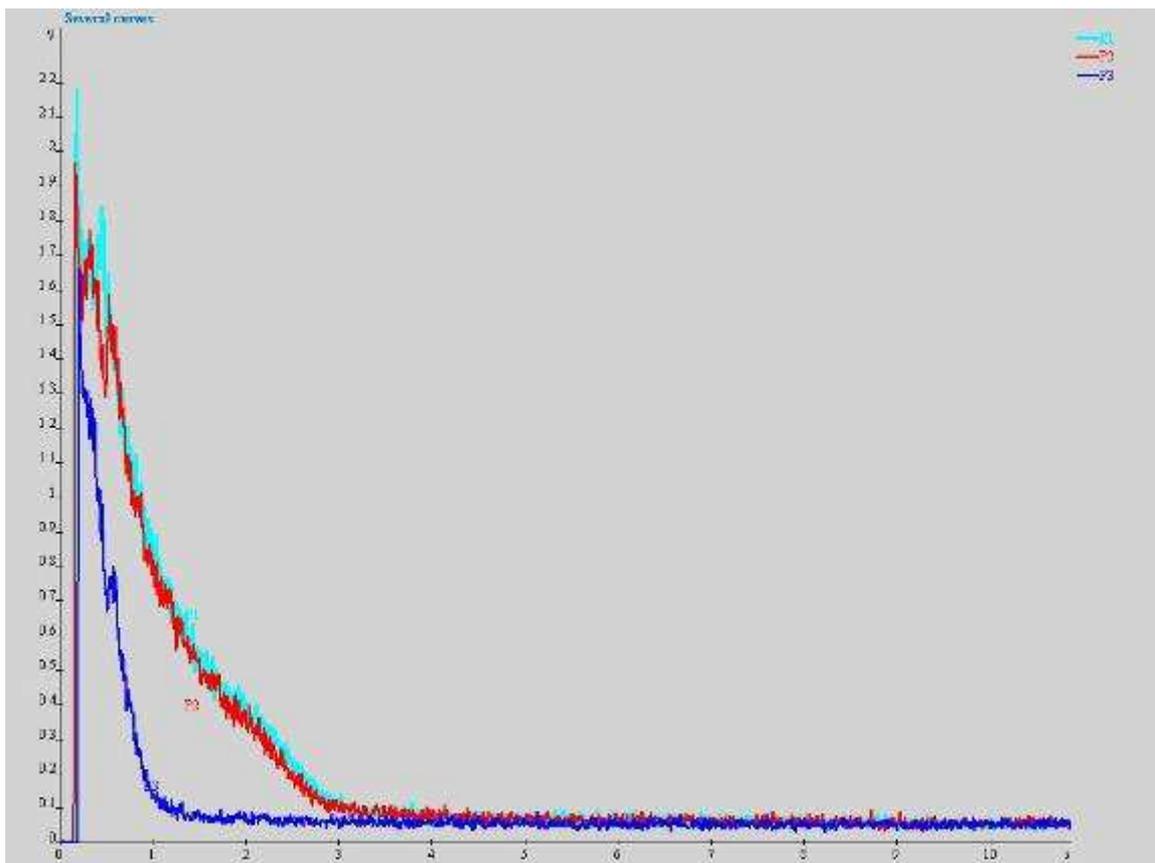
RF GDOES permits to follow the distribution of the elements as function of depth. This is an ultra fast characterisation technique capable to measure all elements of interest in thin films.



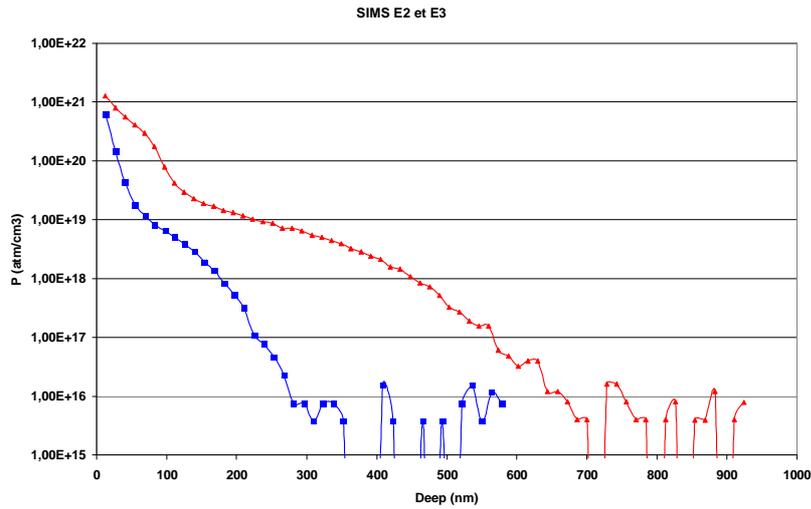
*Example of application in CIGS*



*GD crater on a Si PV sample doped with P*



*Depth profile of P (comparison of 2 samples an reproducibility). Dark blue (sample 1), light blue and red (sample 2)*



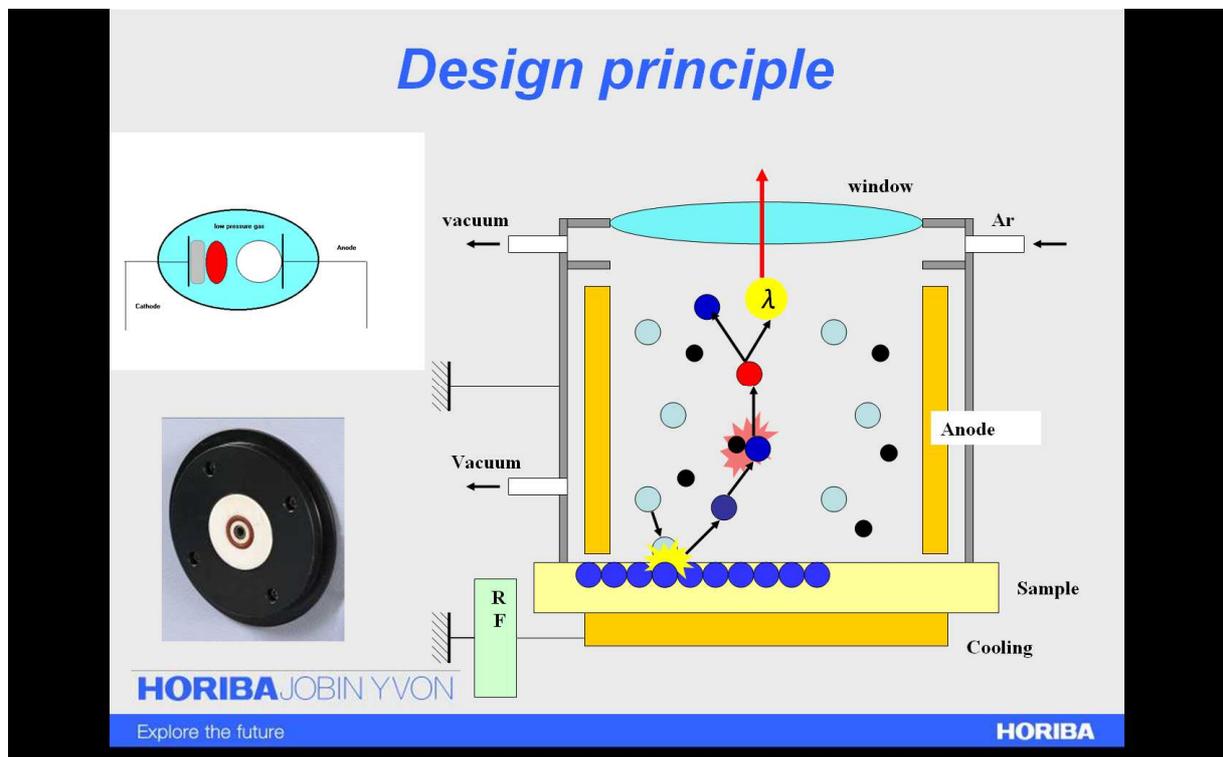
*SIMS data for comparison*

As the name suggests, the instrument combines an RF GD source for sputtering of the material and the excitation of the sputtered species and an Optical Spectrometer for detection.

RF GD Source

In a GD instrument the positioning of the sample is straightforward. Sample is simply positioned against the “lamp”. It seals the chamber operating at primary vacuum and low pressure gas and it is one of the electrodes of the plasma.

The instrument does not require UHV operation which contributes greatly to its **ease of use**.

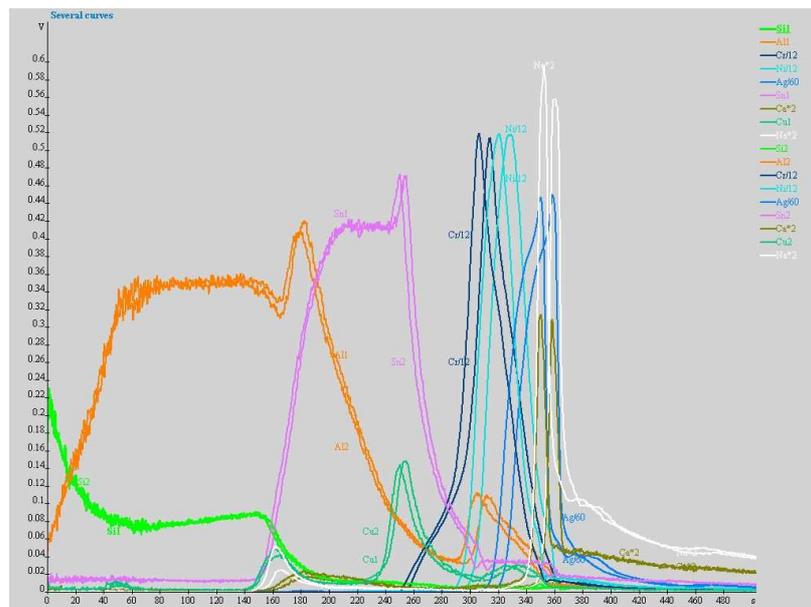


*Principle of GD design*

The typical **anode diameter is 4mm**. Other diameters are available 2, 7 etc. Reducing the diameter minimizes the amount of light collected which affects sensitivity of the technique.

The unique features of the instrument are related to the special GD plasma characteristics. The energy of the incident Ar ions is low (around 50eV) minimizing surface damages but the plasma density is high ( $10^{14}$ ) contributing to the high sputtering rate (about 1 micron/minute depending on the operating conditions).

RF GD OES is therefore an **Ultra Fast Elemental Depth Profiling Technique**. This allows to perform multiple analysis on a sample to check for instances the homogeneity of a coating.



*Overlay of 2 measurements done on a coated glass*

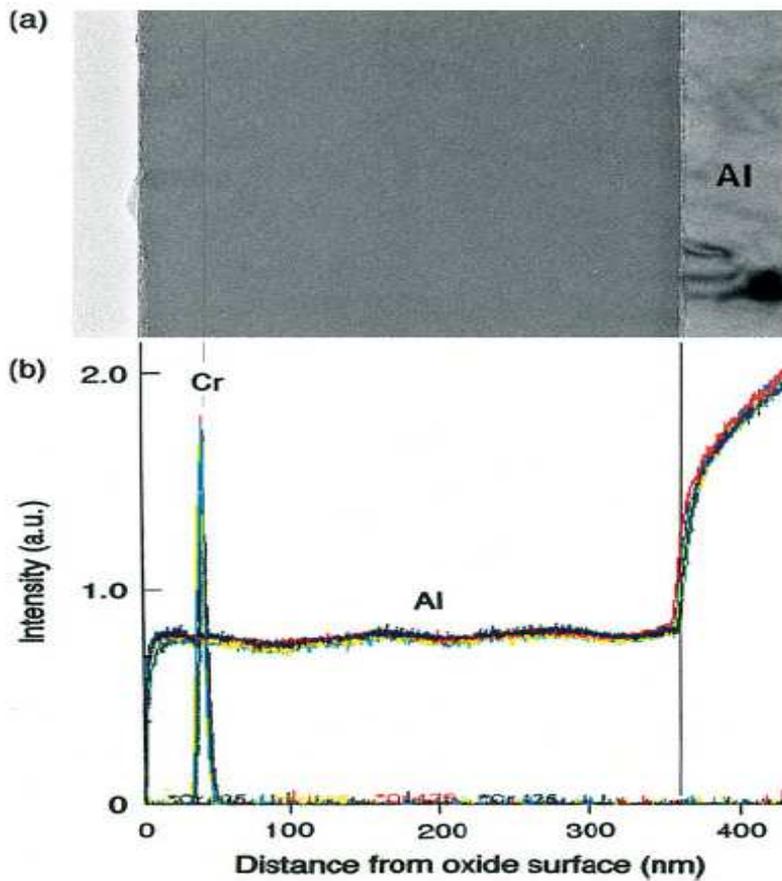
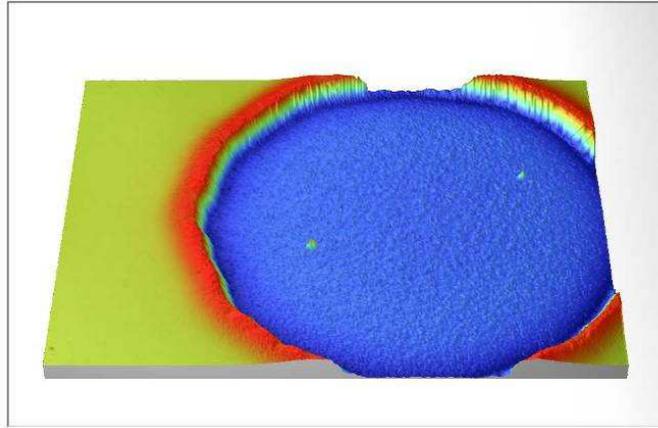
The RF source operates at 13,56MHz and allows pulsed operation. The pulsed operation mode is crucial for fragile and heat sensitive materials. Coatings on glass and polymers are readily analyzed with pulsed rf operation.

If the material is flexible, a straightforward mounting strategy is needed – samples are glued or fixed on a rigid substrate.



*Coating on PET film glued on an Al substrate*

The instrument is capable of **excellent depth resolution**. GD craters can be flat if operating conditions are selected properly. If sample is therefore flat a nanometre depth resolution is readily achieved.

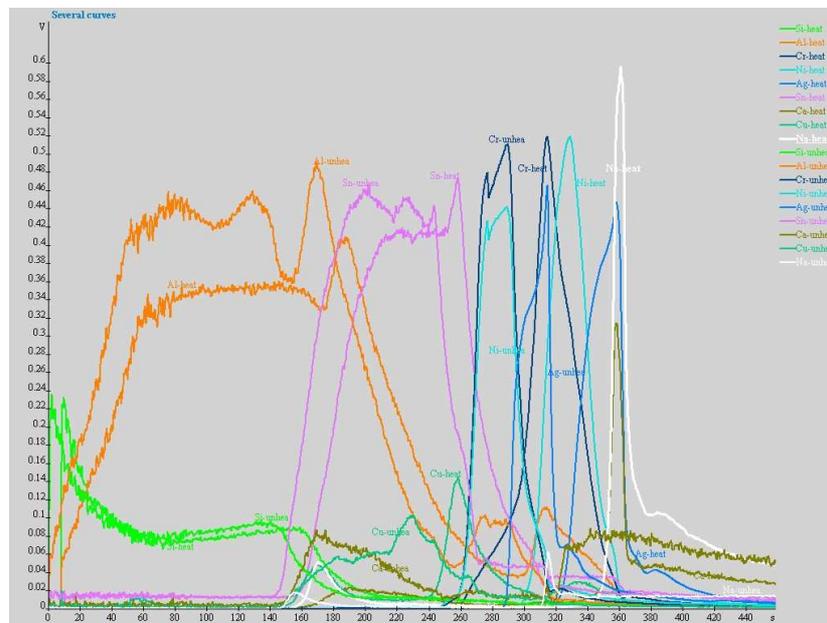


*Anodised Al sample with Cr delta layer. Overlay of 5 measurements*

If sample is rough, as the GD operates on a large surface and the signals recorded being the average of this surface the depth resolution is affected.

There is however a way in practice to get significant and useful information: it is to use the GD for what it is: **a comparative instrument** and therefore compare a sample before and after a diffusion process and overlay the 2 results.

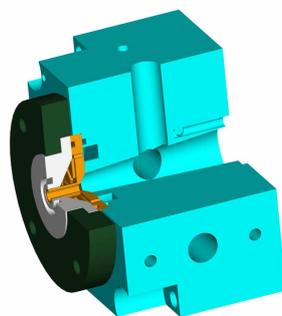
If we consider again the glass sample with the multilayers on top shown above, here is the overlay of the results before and after heat treatment.



*Overlay of 2 measurements before and after heat treatment*

The GD lamp uses a **differential vacuum system with 2 pumps**, one pumping the inside of the anode, one the gap between anode and ceramic. The pressure of the gas is kept constant in the lamp during the analysis. This is the preferred mode of operation notably for thin films.

The double differential vacuum and the pressure control allow the possibility to use the GD lamp **for sample preparation for Scanning Electron Microscope – patented application**. A book published by Springer and authored by K Shimizu describes in length the benefits of the RF GD operation for sample preparation in microscopy.

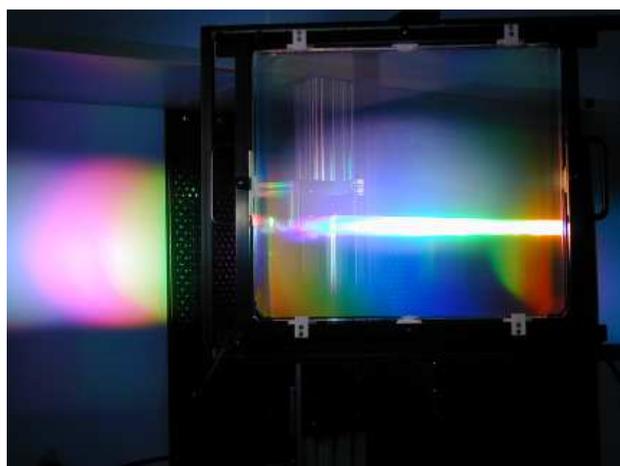


The source offers the **plasma cleaning capability**. This operation mode, unique to RF minimizes surface contamination prior to the analysis. The plasma cleaning concept was first

presented in a paper published in JAAS by HJY and HJY partners. Pumps are standard rotary pumps, the plasma cleaning concept minimizing all sort of contamination but dry pumps are available on request.

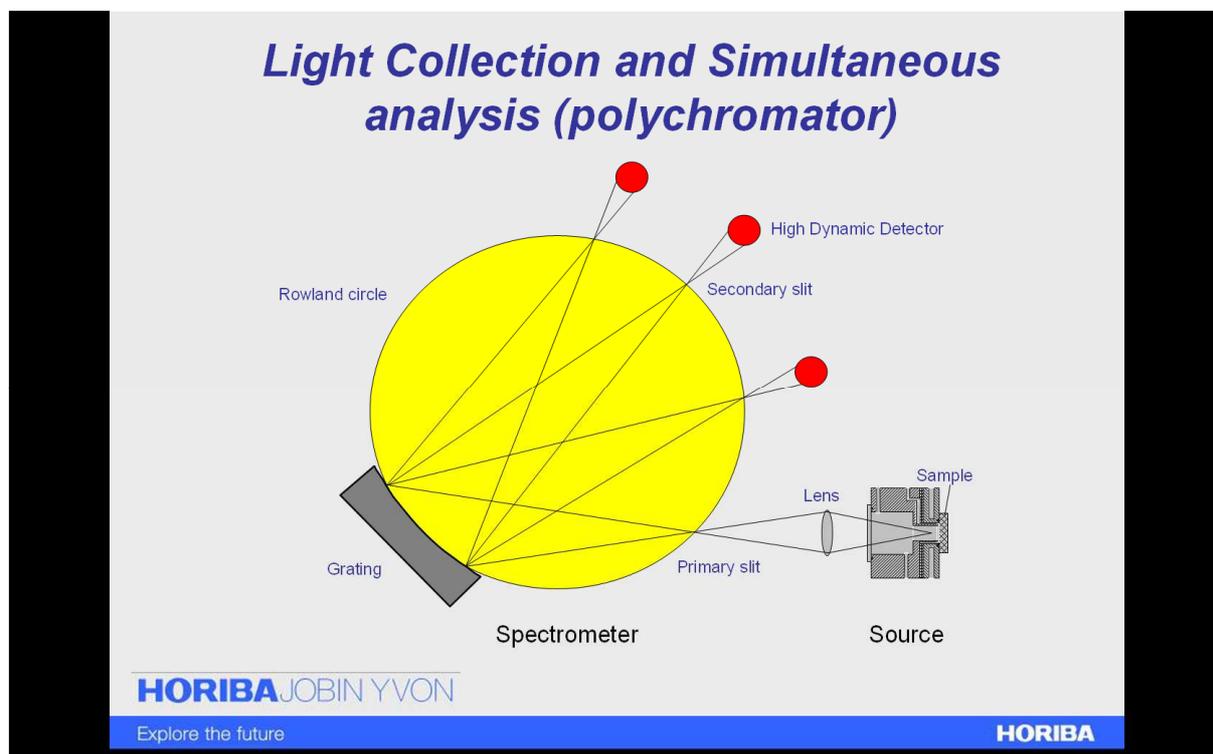
Cooling of the sample by application of a cooling block is provided. A close circuit without risk of leaks is used.

### Optical system



*HJY gratings*

The instrument includes the HJY holographic gratings with enhanced efficiency by ion etching recognized for their high efficiency and low stray light.

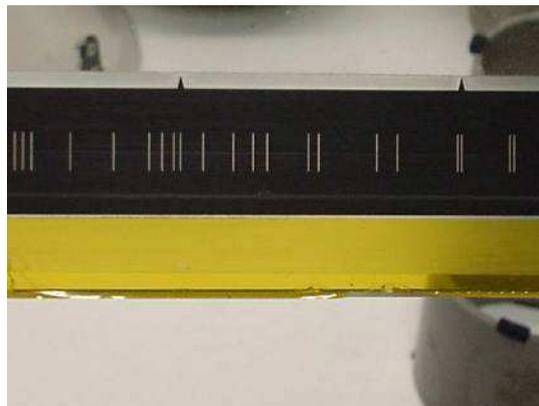


*Principle of the optical system*

The speed of sputtering requires the simultaneous detection of all elements of interest. The optical system is therefore a polychromator.

The main grating is covering the VUV and the visible range (120 to 520 nm). It is a **grating with 2400gr/mm operating in 3 orders**. A second grating for the IR (notably the alkali) with 1200gr/mm can be mounted from the beginning or added on site later on, without affecting the performances of the main poly.

The configuration is defined at the beginning but it can be extended at any time as we use a mask with about 230 secondary slits premounted.



*Partial view of the mask*

Below is a typical optical plan for PV with some comments. Of course the number of elements can be changed, reduced or extended.

## GD-Profilier 2

ELEMENT	LAMBDA	ORDRE	NFENTE	PM	REFPM	FILTRE
H	121,567	2	4	B	R8487	
O	130,217	2	10	M	R8487	
Sn	317,505	1	47	PM	R6350	
Cu	324,754	1	52	PB	R6350	
C	165,701	2	58	PH	R6354	
Zn	334,502	1	62	PM	R6350	
N	174,272	2	78	PB	R6354	
S	180,734	2	92	PM	R6354	
Fe	371,994	1	103	PH	R6350	WG305
Mo	386,411	1	114	B	1P21	
Se	196,09	2	117	PM	R6354	
Al	396,152	1	122	PH	R6350	WG305
Ga	417,205	1	144	PB	R6350	WG305
In	451,132	1	172	M	1P21	
Cd	228,802	2	179	B	R166	
B	249,678	2	197	PH	R6354	
Si	288,158	2	214	B	1P28	UG11
Na	589,592	1	219	M	R446	OG550
Fi	999	1	500	PM	R6354	TOTAL

## LIGHT

PRIM

F1

This proposed OP contains 18 elements. F1 is the total light which gives an indication of the sputtering rate. Prim is the channel corresponding to the primary slit control.

2 elements are in the VUV range: H and O.

C and N are of low analytical importance but present to detect contaminations, or leaks. Other elements correspond to the description received, we have added a few other lines classically demanded in CIGS applications.

Of course this OP is preliminary, it permits to prepare a quote.

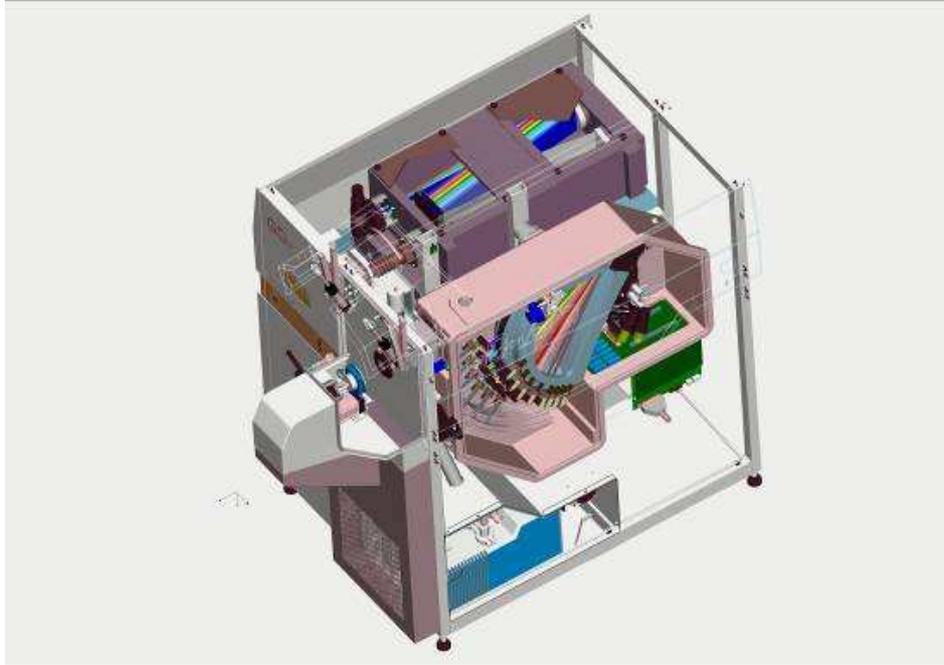
K could be of interest, it will require the addition of the flat field.

The polychromator of 0.5m focal length is equipped with the patented Polyscan feature. This device permits to move the entrance slit of the polychromator in a controlled way along the Rowland circle and therefore to shift the entire spectrum. For instances the polyscan is permitting to measure D (Deuterium) using the H detector.



*Patented Polyscan system*

The polychromator is nitrogen flushed, not evacuated (no vacuum) for optimum protection of the optical components. The purge makes the polychromator free of any oil vapour contamination risk. A Nitrogen generator can be provided if needed.



*Schematic view of the GD Profiler 2*

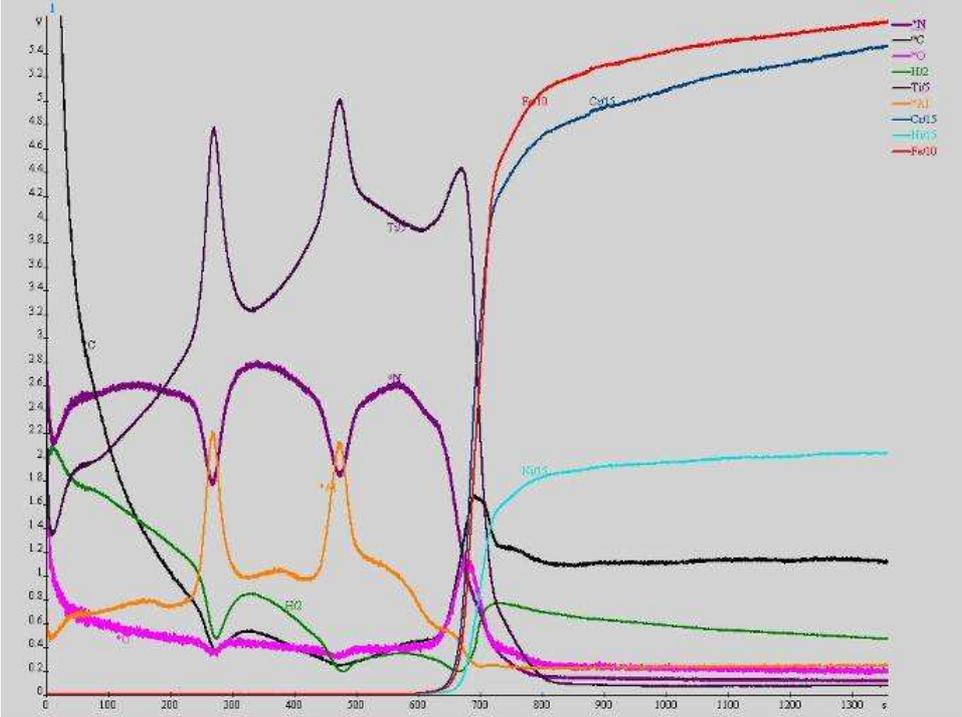
An additional monochromator can be added from the start or later on. It permits the simultaneous measurement of any  $n+1$  element in depth profile and of extra lines in bulk. It can also provide the scanning of the full spectrum without any saturation of the detector. This is the patented Image operation.

#### Detection system and calibration

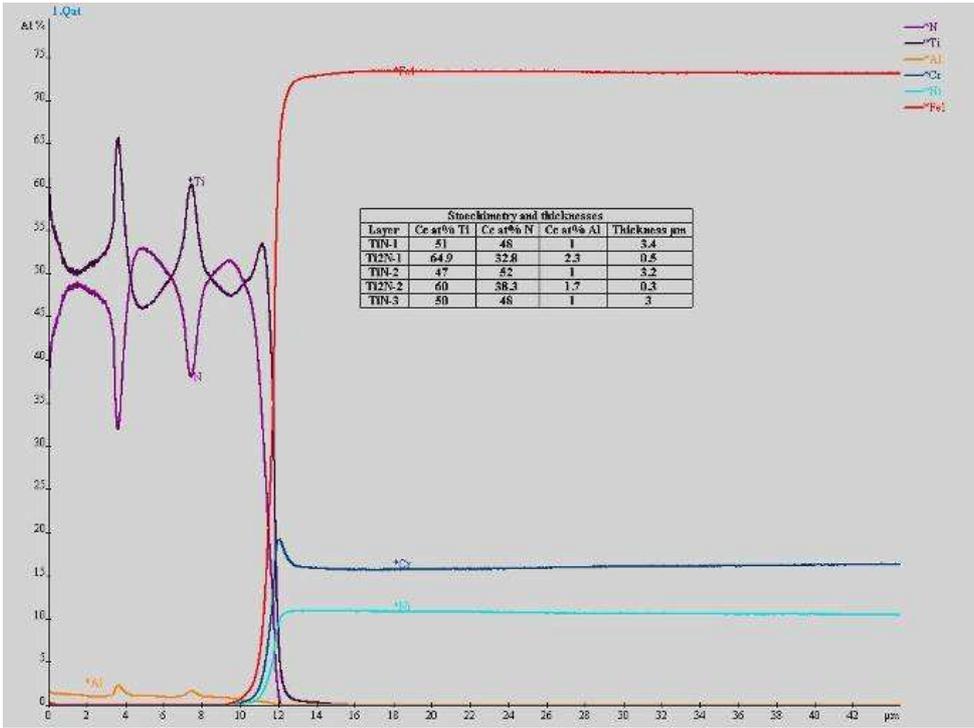
The dynamic of the measurement is at least of  $10^9$  for all lines without any preadjustment of the sensitivity of the detectors. This is the patented HDD system. The “HDD”, high dynamic detection is absolutely decisive for GD operation.

Thanks to HDD, only 1 line per element can be used in depth profile without saturation of the detectors and no presetting of the HV of the detectors is needed before operation.

GD-OES is a comparative technique. Direct results are intensities vs sputtering time. Conversion into quantified data is done after calibration.



Qualitative results



Quantitative results

Quantification provides at the same time concentrations and thicknesses of the layers.

It requires a selection of materials of known concentrations and sputtering rates to build calibration curves. As there are not yet reference materials available in the field and as NDA agreements do not permit to use for a customer, samples made by another one, here is the procedure we apply which requires work in common.

The following screen shows the selection of standards used in Japan to quantify CIGS layers, Calibration samples mix CRM bulk samples available from HJY and coated ones and include some materials from the customer with known thickness and composition.

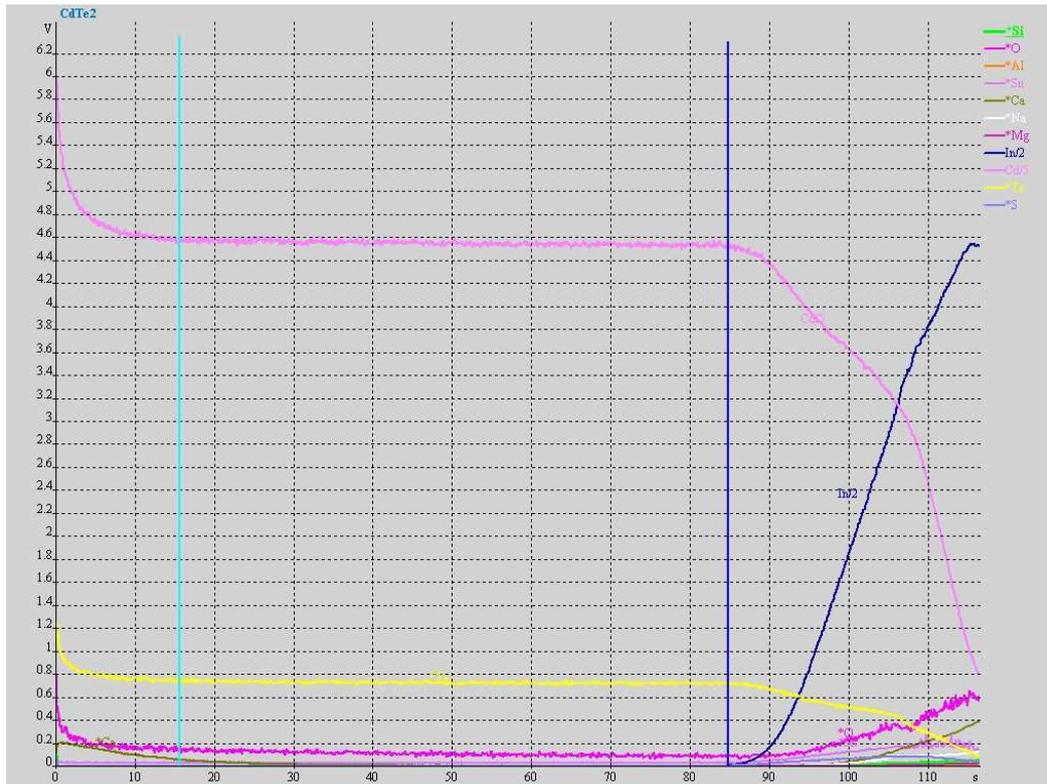


Standard	Family
13X_N5D1_B	Stainless Steel
1761_SR/M	Low Alloy Steel
CU_BULK_HK16	Cu
NILACO_CU	NILACO
NILACO_MO	NILACO
OXYGEN2	oxygen
SI_BULK_1	Si pure
SSO_2G	CIS
SSO_32T	CIS

Samples can be coated ones. This offers a large flexibility in the choice of materials.

Below is shown a GD profile of a sample featuring a CdTe layer. Such coating being very flat is ideal for calibration. If we know the concentrations of Cd and Te in the layer we can quantify these elements.

If we know the thickness of the layer we can also estimate its erosion rate.



For Na, we could use some bulk samples containing Na (glasses or aluminium) but the intensities that such samples will give are very low (low cc in Al, low sputtering rate for glasses). In order to get, at least, a high point in calibration the use of a reference sample featuring a Na peak with known concentration will be required. This can be obtained by cross section and EDX measurement.

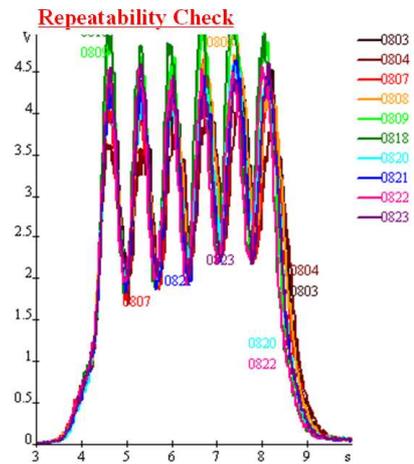
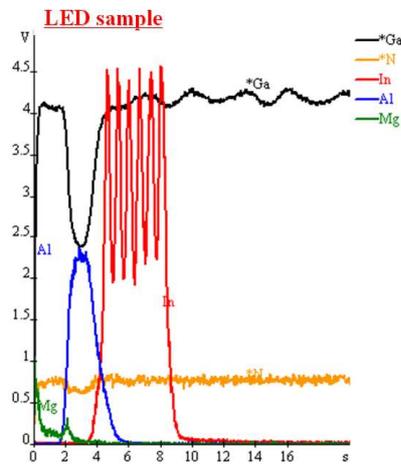
Thicknesses are usually derived from the calibration but they can also be derived precisely from the analysis times – considering the changes in SR. So if a reference sample is available we could estimate the thicknesses from the erosion times.

However the GD does not provide a direct measurement of thicknesses and therefore some correlation with SEM/TEM on cross sections is needed at the start for optimizing the results and regularly for checking.

Considering the uncertainties, a precision of 5% in the depth is achievable using such procedure.

Then if the intensities measured on a test sample are stable with the time, both concentrations and thicknesses will be stable. This is the principle of an optical spectrometer.

The example below is from a production site of blue LED. The rf GD OES is used to control the production and assess the stability in thickness and composition of the thin layers corresponding to the quantum dots.



Explore the future

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## Conclusion

HJY offers several characterisation techniques to parallel the development of the PV domain.

RF GDOES has for itself the speed and ease of use and is providing elemental composition as a function of depth to characterize coatings, detect contaminations at the interfaces and evaluate diffusion.

This is a comparative technique that operates on a relatively large area of the sample which is a statistical advantage when sample is not homogeneous.

## Characterization of Thin Films in Solar Cells with Complimentary Spectroscopic Methods

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### Introduction

The solar industry uses a wide range of materials for the manufacturing of solar cells. In most cases these materials are deposited as thin films in the nm- $\mu$ m-range.

For both the development of new materials and for quality control in established processes a full characterization on an elemental, molecular and structural basis is necessary.

This can be achieved by spectroscopic methods which allow rapid measurement, speed and do not require large photo- or sample preparation. Furthermore measurements with spectroscopic methods are in most cases non-destructive.

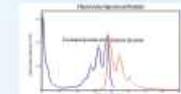
### Spectroscopic Techniques

#### ◆ Spectroscopic Ellipsometry

Principle: change in state of polarization  
 - thickness from sub-nanometer to several  $\mu$ m  
 - optical constants



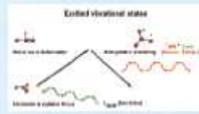
#### ◆ Steady State and Time Resolved Photoluminescence



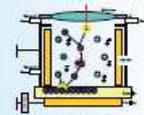
Principle: optical emission after optical excitation  
 - molecular identification "fingerprints"  
 - optical environment  
 - optical band gap

#### ◆ Raman Spectroscopy

Principle: inelastic scattering of light  
 - molecular identification "fingerprints"  
 - molecular composition  
 - morphology  
 - molecular environment



#### ◆ Glow Discharge - Optical Emission Spectroscopy (GD-OES)



Principle: optical emission after plasma excitation  
 - elemental composition  
 - molecular identification (e.g. Li)  
 - sensitivity ppm - 100%  
 - depth resolution: several nm

### Applications

#### ◆ Film Thickness

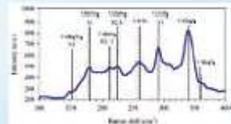
Determined by Ellipsometry for:  
 - multilayers  
 - optical layers  
 - dielectric films  
 - roughness / porosity



Open model and simulated data of a typical PV cell

#### ◆ Molecular Composition

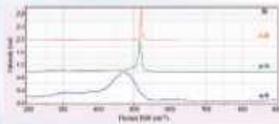
Raman spectroscopy to measure composition ratios of many materials such as CuInGa, CuInGaSe, CuS. Penetration depth is determined by the laser wavelength.



Raman spectrum of CuInGaSe grown on glass (CuInGaSe/P. Seitz et al., Thin Solid Films, vol. 516, No. 22, 2018, pp. 4897)

#### ◆ Crystallinity

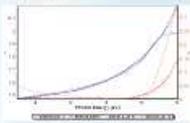
Raman spectroscopy is used to measure the degree of crystallinity in thin films. Monitoring the degree of crystallinity in  $\mu$ -Si is an essential process on thin film solar production lines.



Monosilane is sputtered in a glow discharge cell and deposited on SiO<sub>2</sub> film

#### ◆ Optical Constants

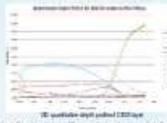
Determined by Ellipsometry in a wide spectral range from the optical constants to further material properties can be deduced  
 - refractive index  
 - transparency  
 - absorptivity  
 - porosity



Quantitative of the absorption coefficient

#### ◆ Elemental Composition

GD-OES is used to determine elemental composition profile throughout layers and films.



This is important for doping profiles and monitoring of defects.

#### ◆ Stress distribution in layers

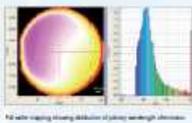
The stress distribution in Si layers can be determined by Raman spectroscopy with the Si-Si vibrational mode. Stress in crystalline Si layers has a strong influence on carrier mobility in the devices.



Stress in crystalline Si layers has a strong influence on carrier mobility in the devices.

#### ◆ Band Gap

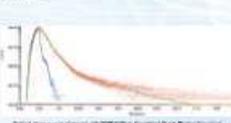
Photoluminescence to measure bandgap of semiconducting materials.



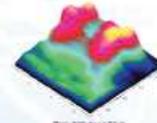
PL with mapping showing distribution of doping strength distribution

#### ◆ Efficiency

Time-resolved photoluminescence to measure lifetime down to 10s of ps - dynamic understanding of semiconductor materials by analyzing the properties of molecular reactions  
 - quantum yields



TRPL measurement obtained with TCSPC (Time Correlated Single Photon Counting)



Stress distribution in Si layer