

New developments in RF-GD-OES extend the range of applications

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Glow Discharge Source



External mounting of the sample

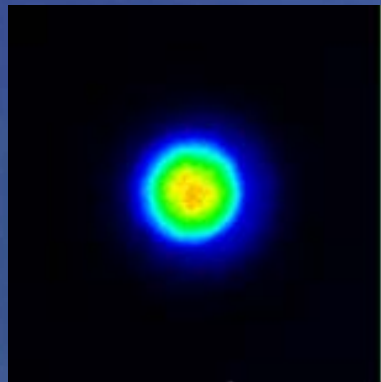
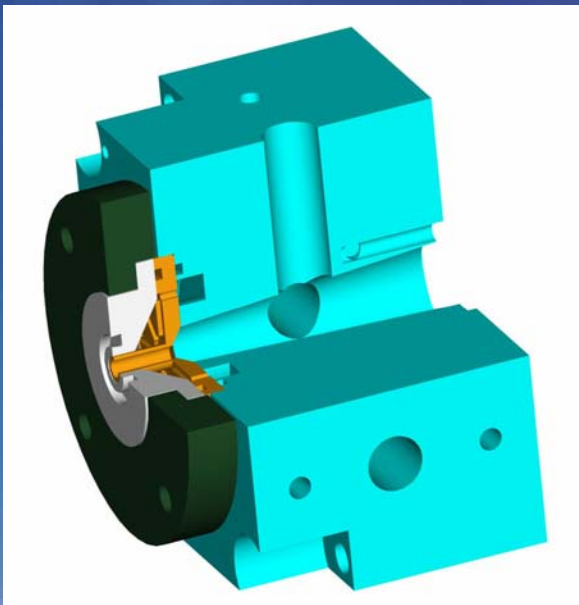
Primary vacuum (double pumping)

Fast sputtering rate
(1-5 $\mu\text{m}/\text{mn}$)

Measure all elements
(including H, O, N, Cl, C and F)

Conductive and non
conductive layer

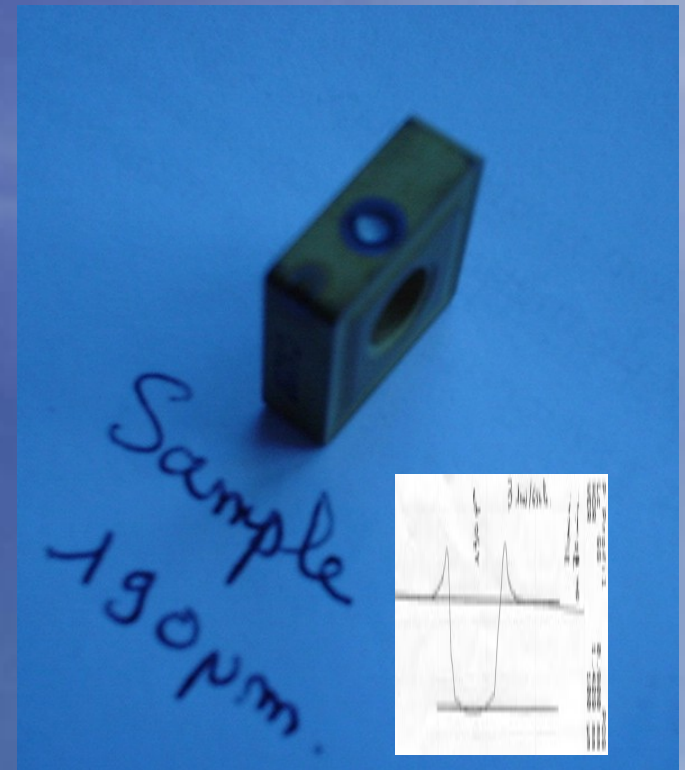
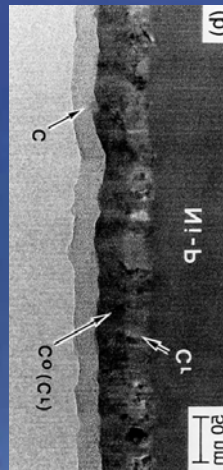
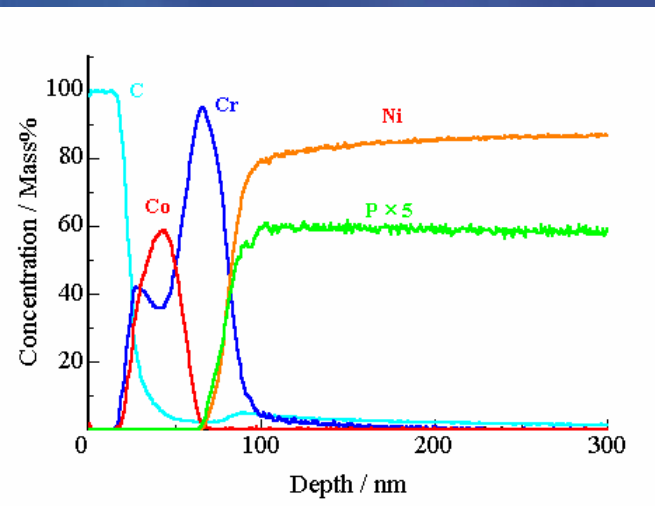
Ease of use



Range of applications

Cutting tool. 2mm Anode, deep crater

Surface layers of a hard disk
(X scale in nm)



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Practical benefits of recent advances in theory and practice

- Understanding the GD RF plasma.
 - >> Running efficiently large samples.
- Development of a pulse RF source.
 - >> Applications to fragile materials.
- Emphasis on accessories
 - >> Application to small and/or odd samples (tubes etc)
- New ideas and approaches in Quantification.
 - >> Improvements of CDP for ultra thin layers



1) Understanding the GD RF plasma

The screenshot shows an Acrobat Reader window with the following content:

Modelling the RF source in GDOES

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First published as an Advance Article on the web 4th April 2003

An equivalent model of an asymmetric radiofrequency (RF) powered glow discharge (GD) plasma is combined with an equivalent circuit of the stray cell capacitance, coaxial cable connection, matching box and power generator needed to drive it, to provide an electrical model of the impedance-matched RF source commonly used in GDOES. Component values in the matching circuit are determined *in situ* using procedures provided. The resulting model is then used to calculate plasma resistances based on the matching box settings. As a test of the model, these plasma resistances are then used as emission yield corrections in a multi-matrix calibration, and compared with the more familiar V_{DC} corrections.

1 Introduction

Emission yield plays a key role in quantification schemes in glow discharge optical emission spectroscopy (GDOES). For the determination of the length of the element...

the matching circuit. How this could be achieved is illustrated in Fig. 1. An RF generator is normally designed to deliver power into a 50 Ω load, but the RF source impedance varies with the carrier gas pressure, the nature of the sample surface

JAAS FULL PAPER
www.rsc.org/jaas

- Extensive work done in cooperation with other researchers
- Recent paper published (JAAS 2003 – special edition on GD)



Achievements and practical benefits of the work

- The RF circuitry is fully described
- Changes in impedance are understood and can be either monitored and/or minimized
- This approach is validated by the characterisation of the RF plasma
- Benefits are the improvement of the lamp design and of the quantification.



GD-Profiler design



- Large sample compartment
 - Centrelite for precise positioning
- Samples over 50cm in diameter
- Large wafers



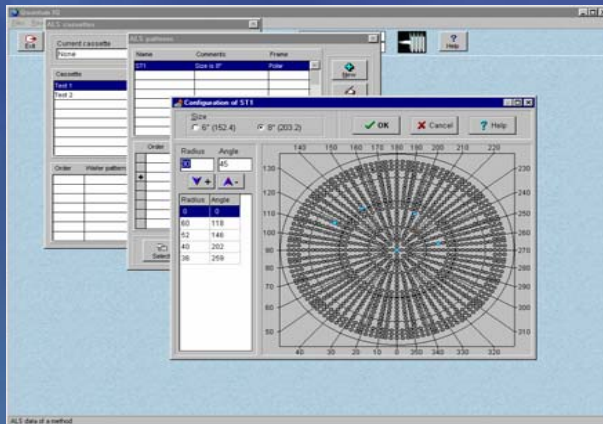
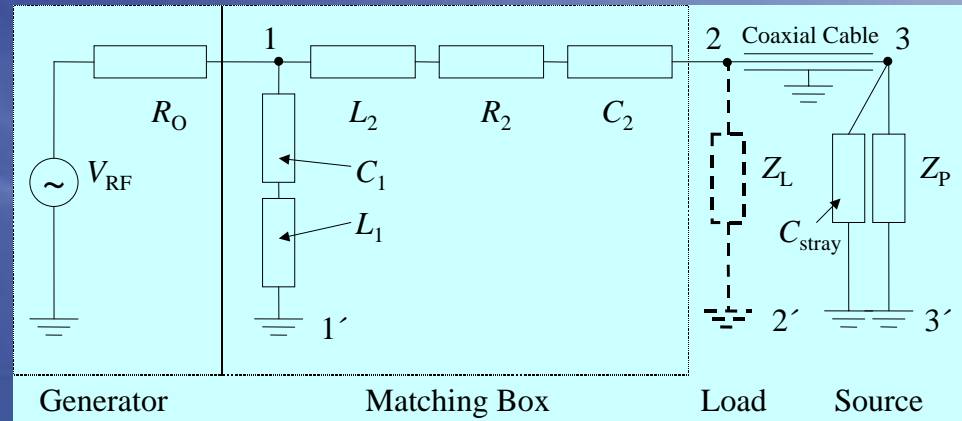
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Large samples : handling and analysis

Modelisation of the lamp



Software screen for the analysis of wafers

JY Horiba patent for large wafers analysis

No signal variation due to sample positioning



B deposited on wafers

Document1 - Microsoft Word

Normal Times New Roman 12

Fichier Edition Affichage Insertion Format Outils Tableau Fenêtre ?

Final avec balises Afficher

150%

Table 1 rf-GDOES results for B in BSG

Slot	TMB	GDOES Center			Edge			Average		Ratio Center/Edge
		Mean	SD	RSD	Mean	SD	RSD	Mean	SD	
1	85	12.67	0.15	1.17	11.85	0.24	2.05	12.26	0.20	1.07
2	85	12.13	0.09	0.75	11.92	0.11	0.96	12.02	0.10	1.02
3	135	18.27	0.31	1.67	17.40	0.45	2.61	17.83	0.39	1.05
4	135	17.85	0.26	1.46	17.28	0.04	0.26	17.57	0.19	1.03
5	100	15.40	0.07	0.43	15.24	0.30	1.98	15.32	0.22	1.01
6	100	15.27	0.22	1.44	14.27	0.22	1.57	14.77	0.22	1.07
			mean=	1.15			1.57			1.04

Page 1 Sec 1 1/1 À 9.2 cm Li 15 Col 1 ENR REV EXT RFP Anglais (Aus)

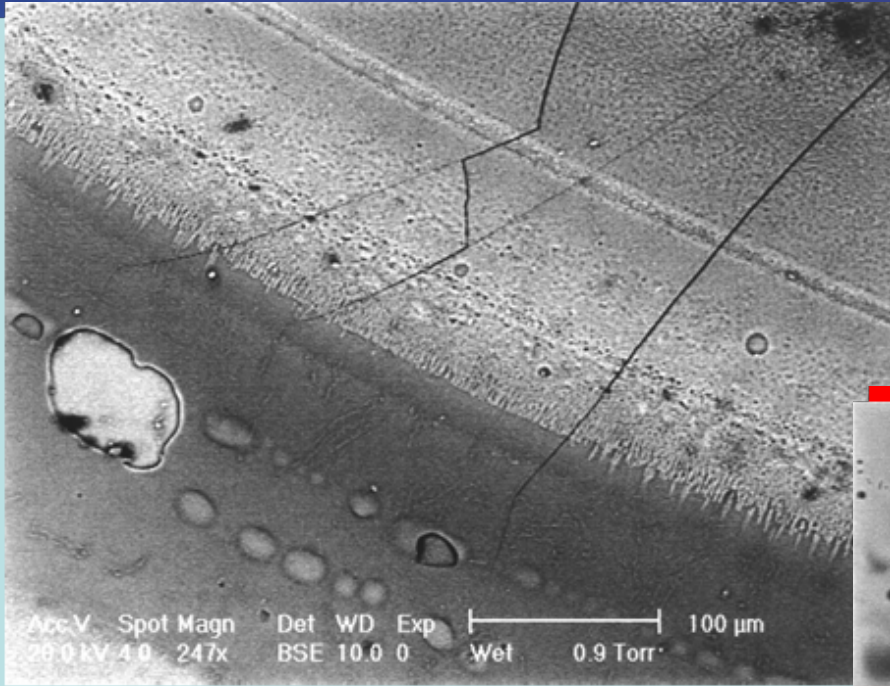


2) *Development of a pulse RF source*

- RF can analyze conductors and non conductors
- Non conductors have a poor thermal dissipation
- Risks of overheating and cracks of some materials when RF is continuously applied
- Pulsed RF extends the range of applications to thermal sensitive materials

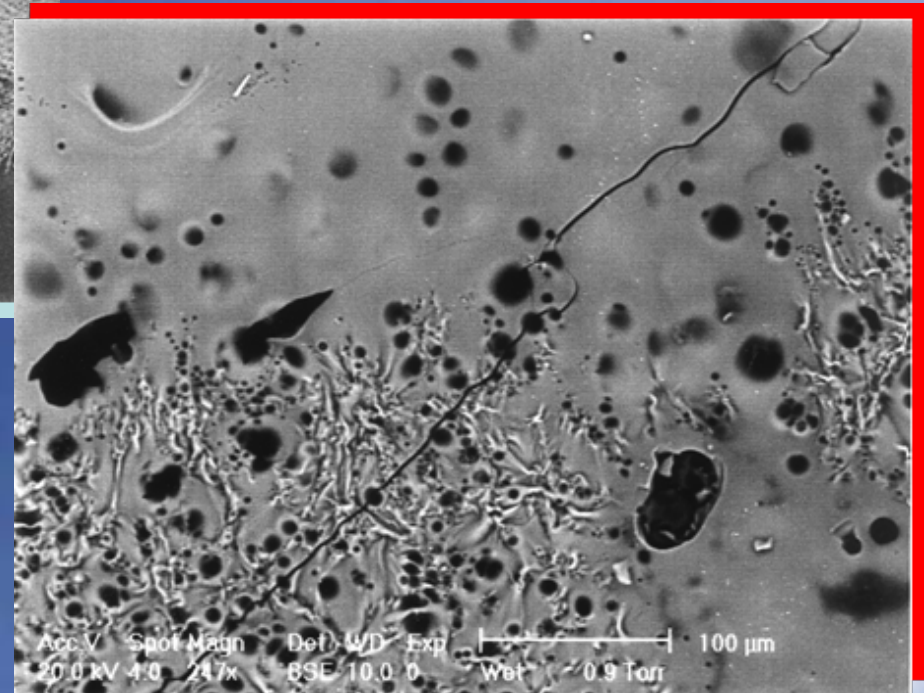


Effect of the thermal constraint on thin glasses



Outer

Inner



JY new RF source

- Can operate in normal mode and in pulsed mode.
- All modes are computer controlled
- Simple method parameters to select
- Benefits : extended ranges of applications



Operation in pulse mode : software

The screenshot displays the Quantum XP software interface. The main window shows the 'Method: Glasses - 0' configuration. A 'Generator Parameter' dialog box is open, showing the following settings:

Parameter	Value
Druck	620 Pa
Leistung	30 W
Modul (geladen)	7.40
Phase	5.00
<input checked="" type="checkbox"/> Puls	
Frequenz	5000 Hz
Arbeitszyklus	0.125
Resultierende Leistung	3.750 W

The background window shows the 'Analysenparameter' section with the following settings:

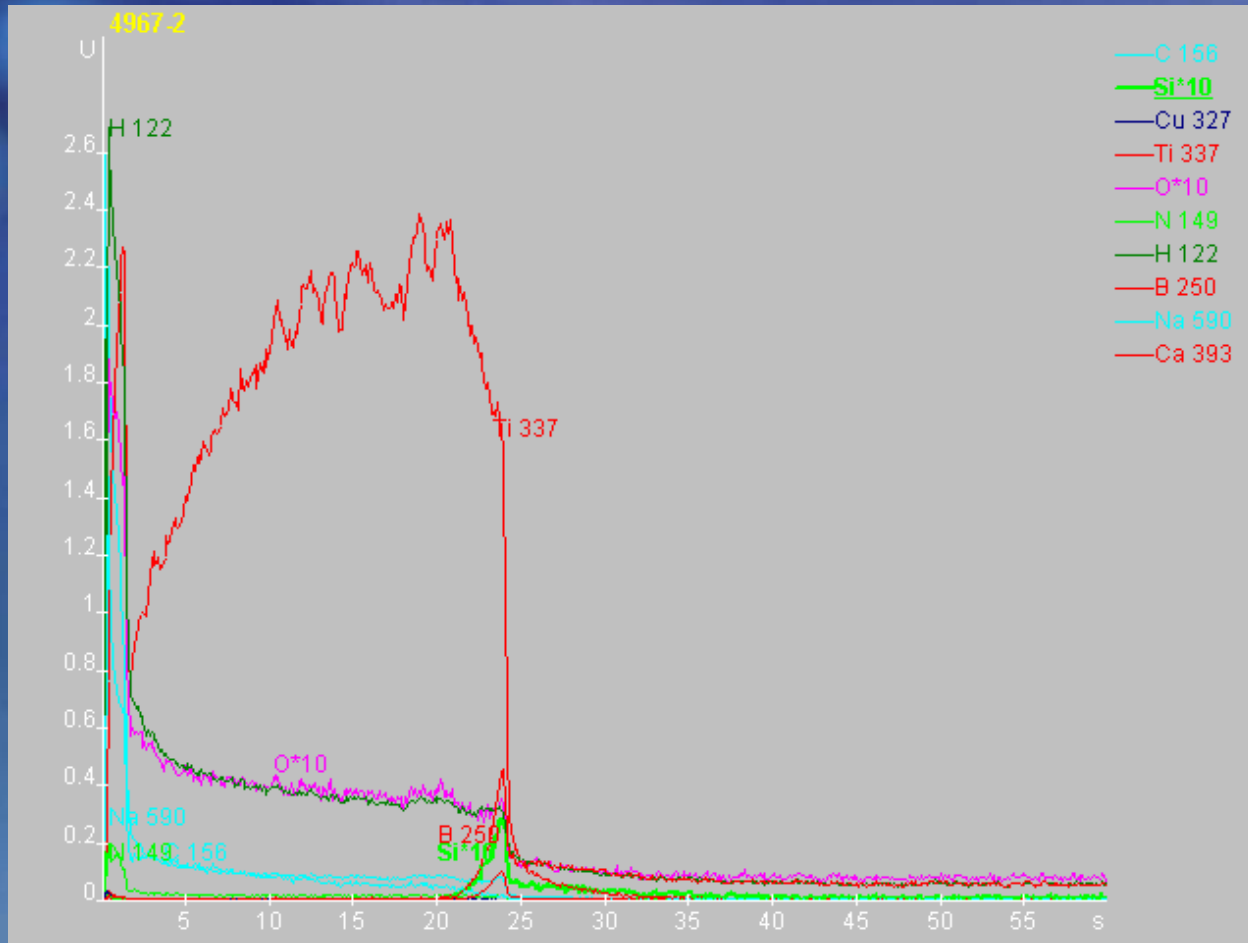
Parameter	Value
Spülzeit	50 s
Untergrundmessung	5 s
Preintegration Zeit	10 s
Bulk Aufnahme	15 s
Anregungsmodus	RF (Normal)
Anodengröße	4 mm
Pressure	620 Pa
Power	30 W
Pulse	Yes
Frequency	5000 Hz
Duty cycle	0.125
Efficient power	3.75 W
Module	7.4 V
Phase	5 V

Max power
300W in
pulse mode

Pulse
frequency and
duty cycle are
computer
controlled



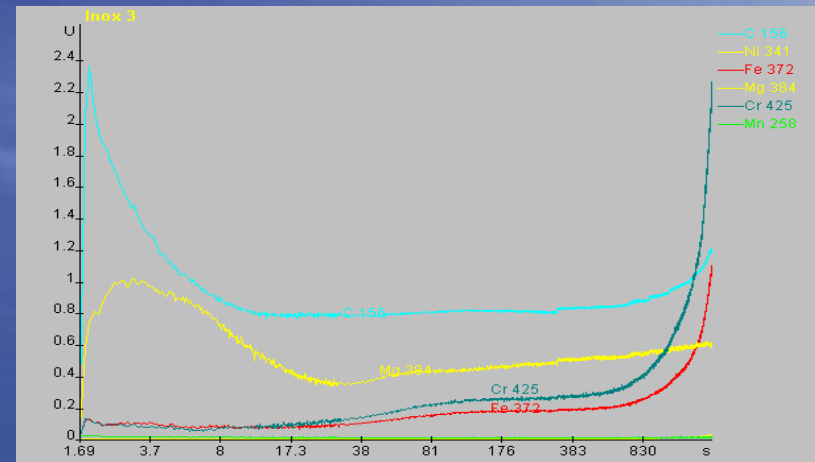
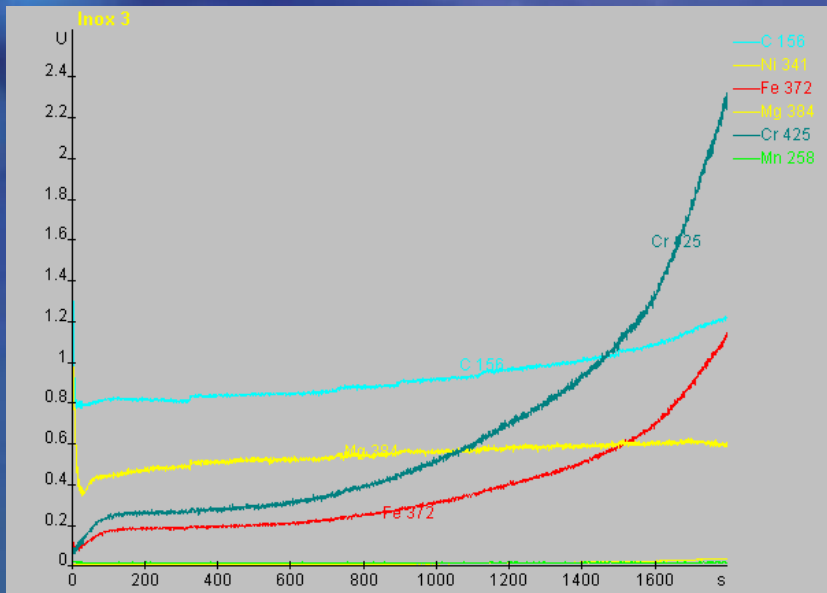
Pulsing: Coated glass



This example shows the result done on a spectacle glass lens, slightly curved with a Ti₂O₃ based, anti-reflection coating. The sample immediately melts when using non pulsed GD.



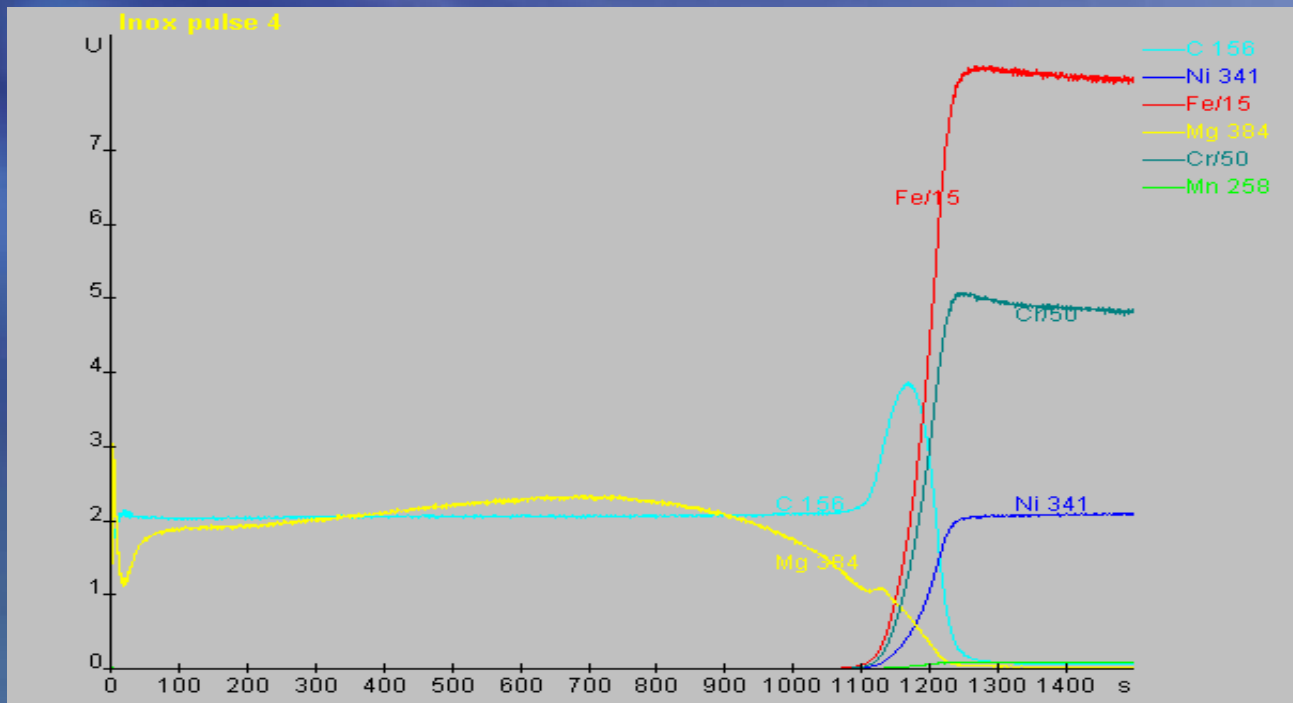
Sample : rubber on stainless steel. Normal RF



Fe and Cr signals are recorded from the beginning indicating that the outer layers are melted



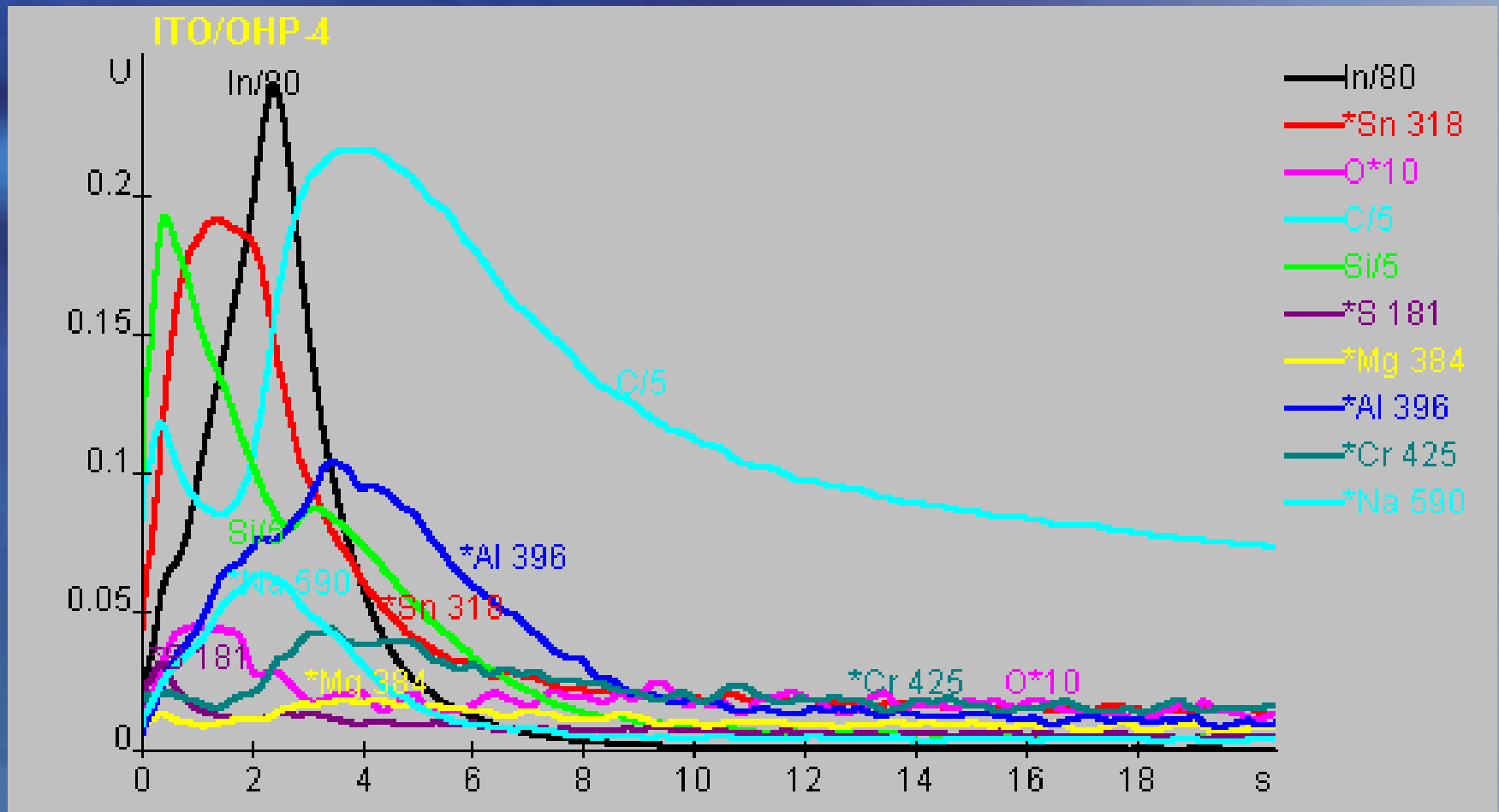
Same Sample : rubber on stainless steel. Pulsed RF



Correct analysis of the sample



Low melting point layers

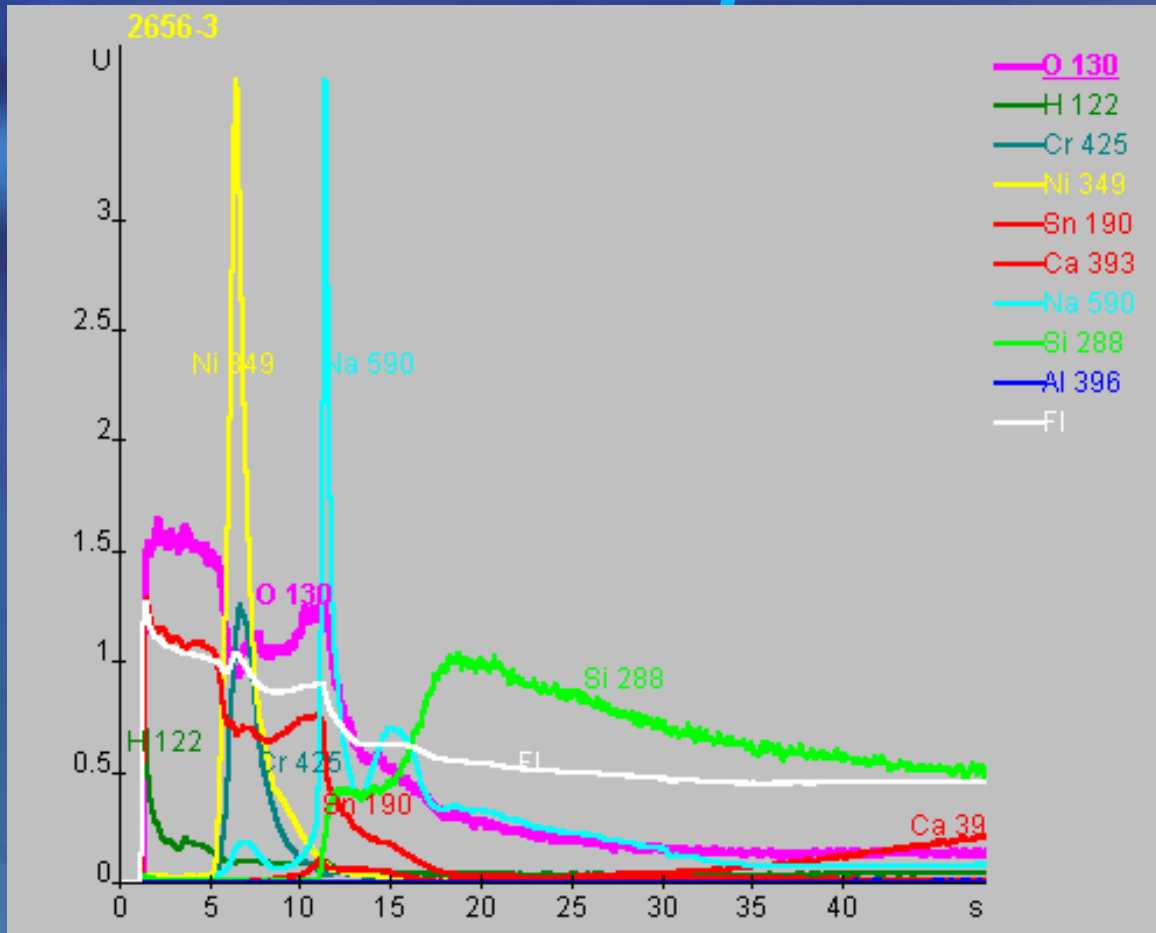


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Thin coatings on fragile glasses with pulsed RF



SnO₂/Ni-
Cr/SnO₂ on
glass

Original sample

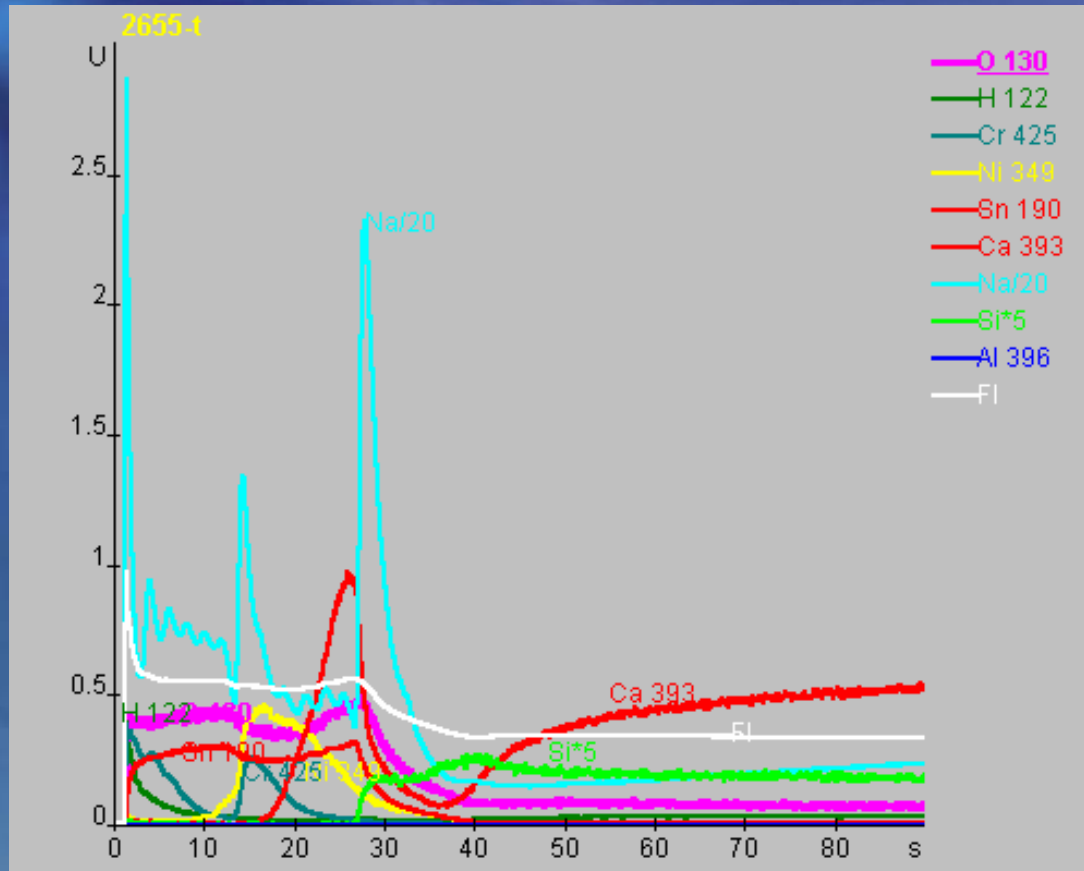
Recent application done at ITU. Paper will be presented



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Thin coatings on fragile glasses



Heat treated
sample

Migration of
Na

Migration of
Cr

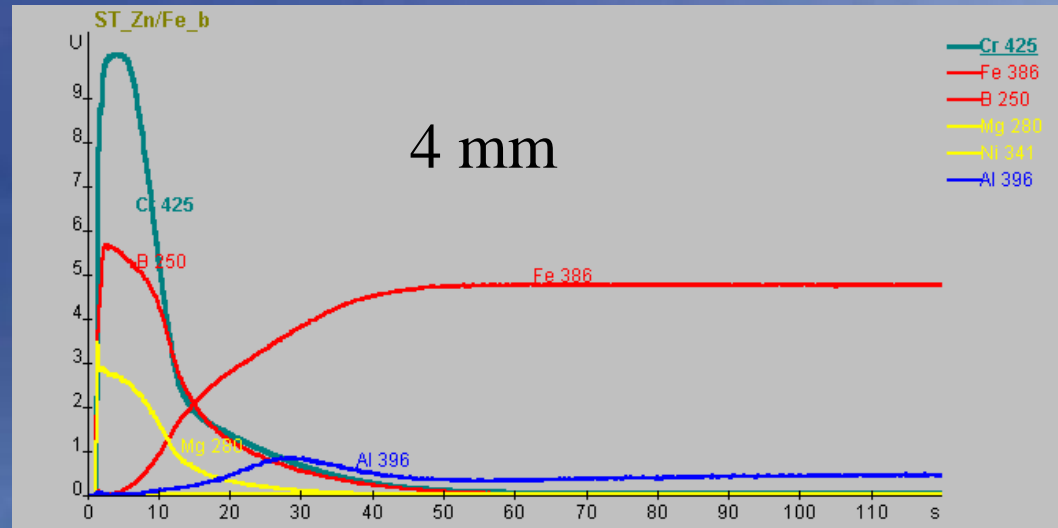
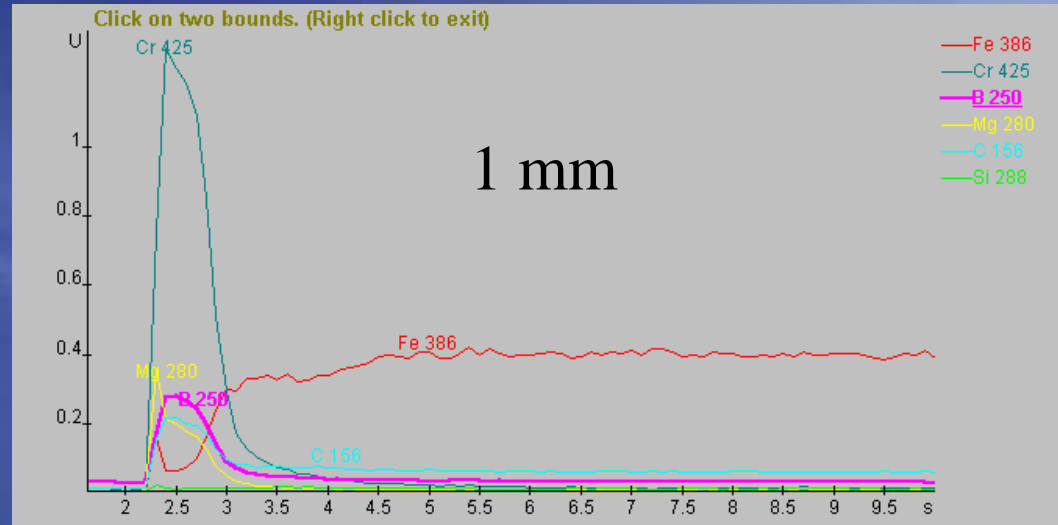
Diffusion of Sn



3) Small samples



1mm anode



Odd shape samples

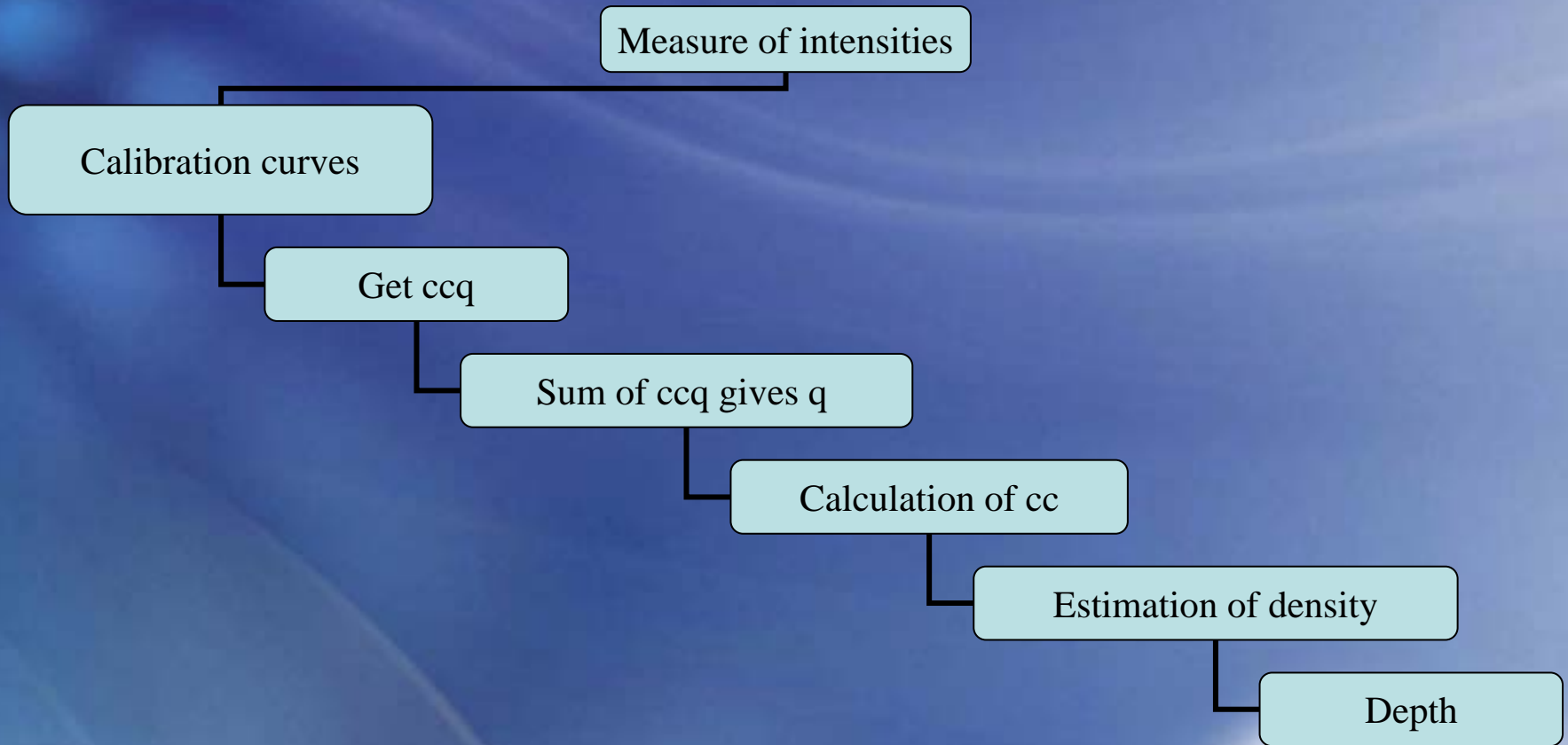


2 mm spots

Special sample holder



CDP : the quantification chain



4) Layer mode : entering known information into the model

The screenshot displays the Quantum IQ software interface. A dialog box titled "Editing of multi-layer model" is open, showing a table of layer properties. The table has columns for Layer, Rel. rate, Density, and Depth (μm). The layers listed are: AlTa anodised, Intermediate zone, AlTa, Intermediate zone, Al anodised, and Intermediate zone. Below the table, there is a section for "AI Concentration" with a table showing "Al" at 99.99001. The "Depth" is set to 31.56 μm and "Density" is 2.698. There are buttons for "Calculate", "Save", "Close", "Show Image", and "Help". The main window shows "Date/Time" as 2002/09/05 12:51:59 and "Operator name" as JY. A "Validate" button is also visible in the main window.

Layer	Rel. rate	Density	Depth (μm)
AlTa anodised	0.00000	7.7930	0.140
Intermediate zone	0.00000	0.0000	0.020
AlTa	0.00000	7.4230	0.500
Intermediate zone	0.00000	0.0000	0.500
Al anodised	0.00000	3.9770	0.360
Intermediate zone	0.00000	0.0000	0.040

El	Concentration
Al	99.99001



Layer mode 3D display of the sample

Quantum IQ

Files Results Control Analysis Calibration Image Tools ?

Date/Time 2002/09/05 12:54:39
Operator name JY

Help

Exit

Editing of multi-layer model

Layer	Rel. rate	Density	Depth (µm)
Intermediate zone	0.00000	0.0000	0.020
AlTa	0.00000	7.4230	0.500
Intermediate zone	0.00000	0.0000	0.500
Al anodised	0.00000	3.9770	0.360
Intermediate zone	0.00000	0.0000	0.040
Al	0.00000	2.6980	

Al Concentration

El	Concentration
Al	99.99001

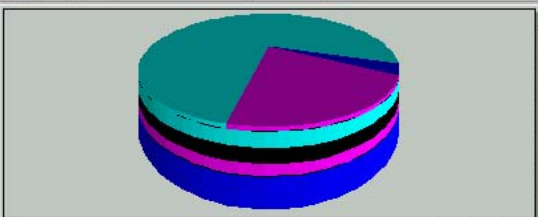
Depth 2.4
Density 2.6
Calculate

Cc = 99.99

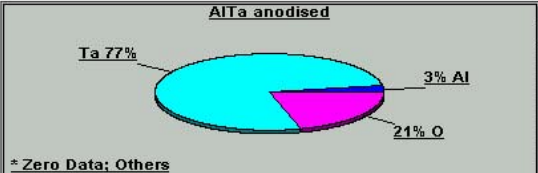
Close Show Imag

Layers description

3D image of a sample



AlTa anodised



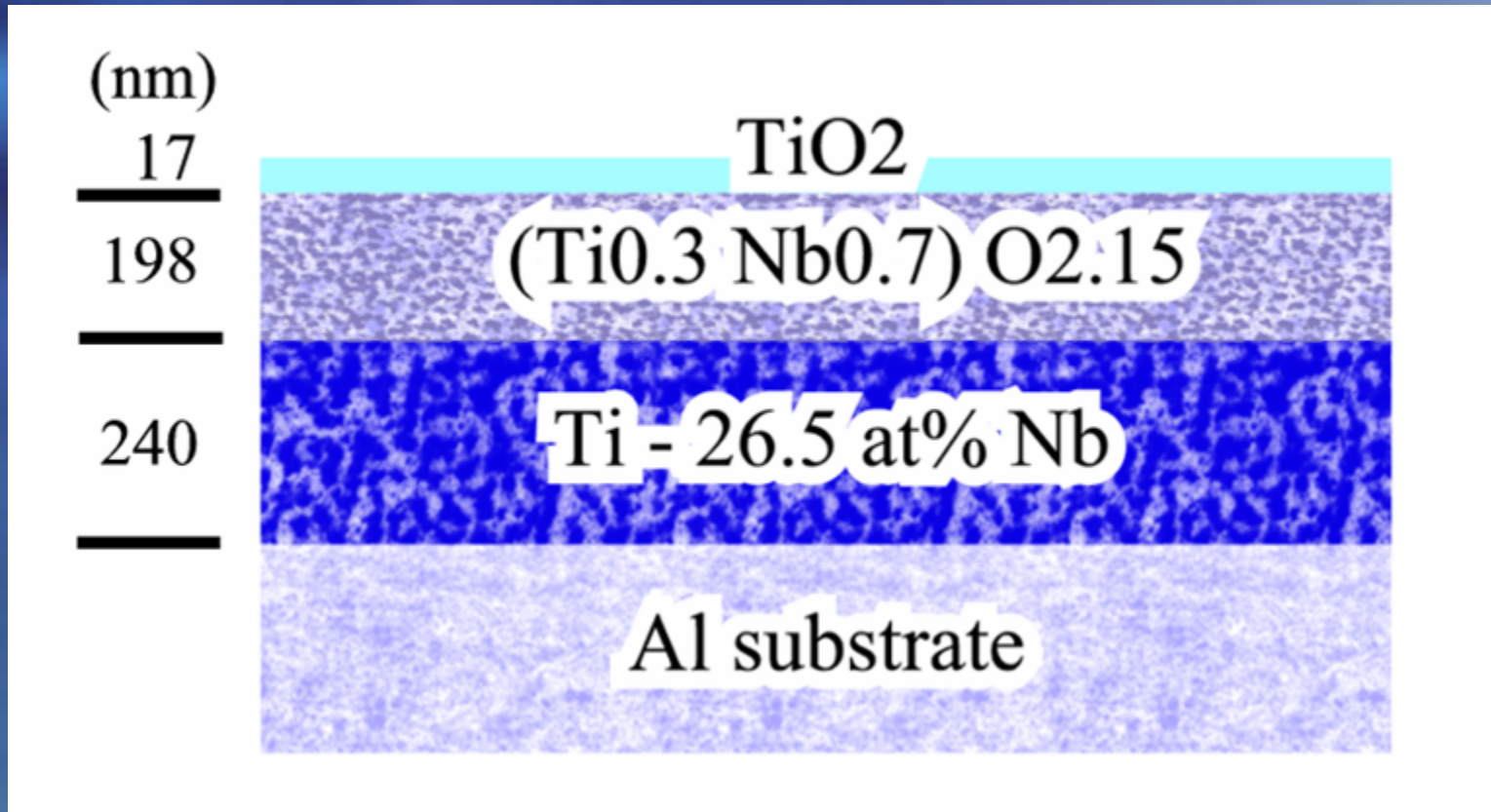
Ta 77%
Al 3%
O 21%

* Zero Data; Others

Help



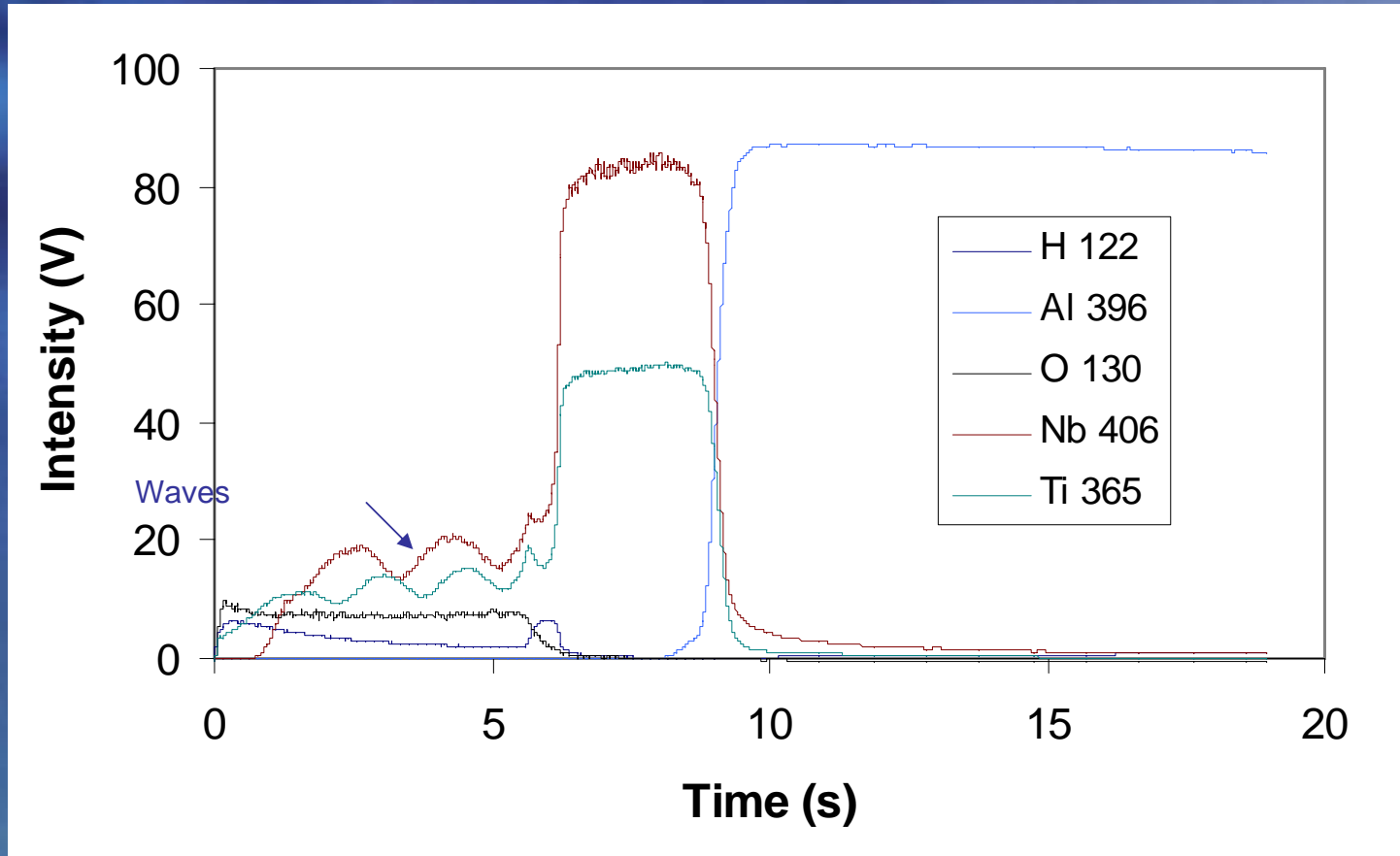
Example : Ti-Nb Layers on Al



Determined by Rutherford Backscattering



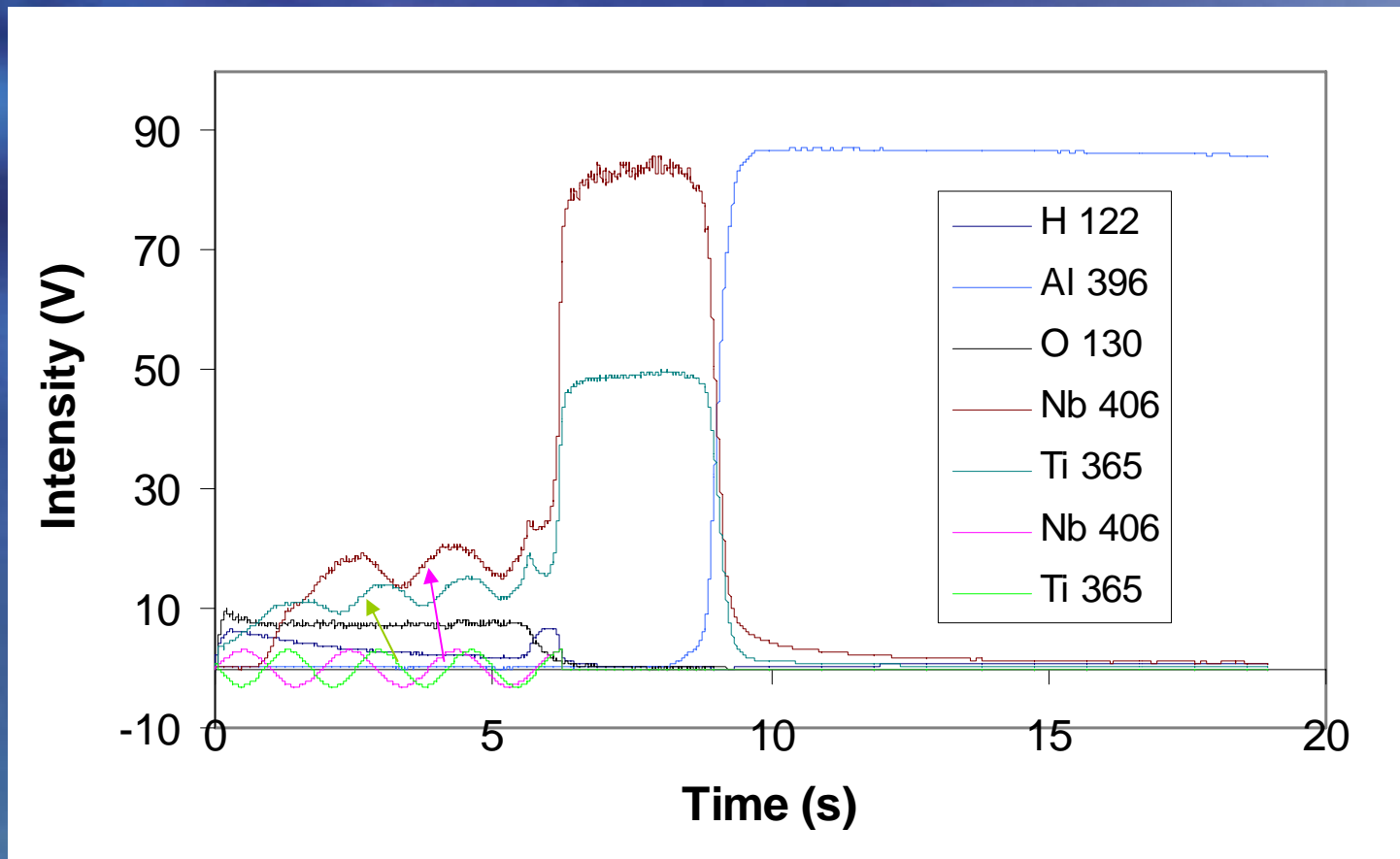
Qualitative Depth Profile



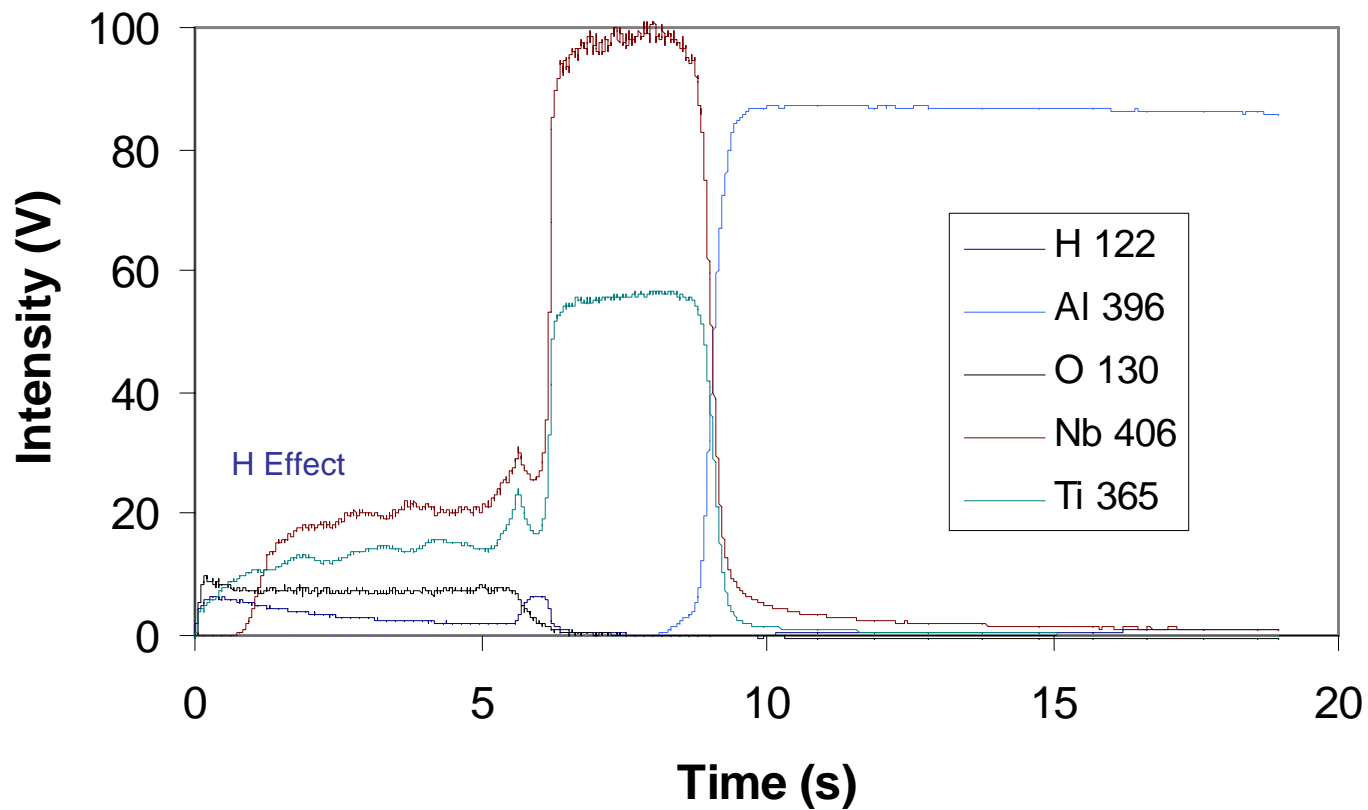
Note: 455 nm in 9 s is about 50 nm s⁻¹



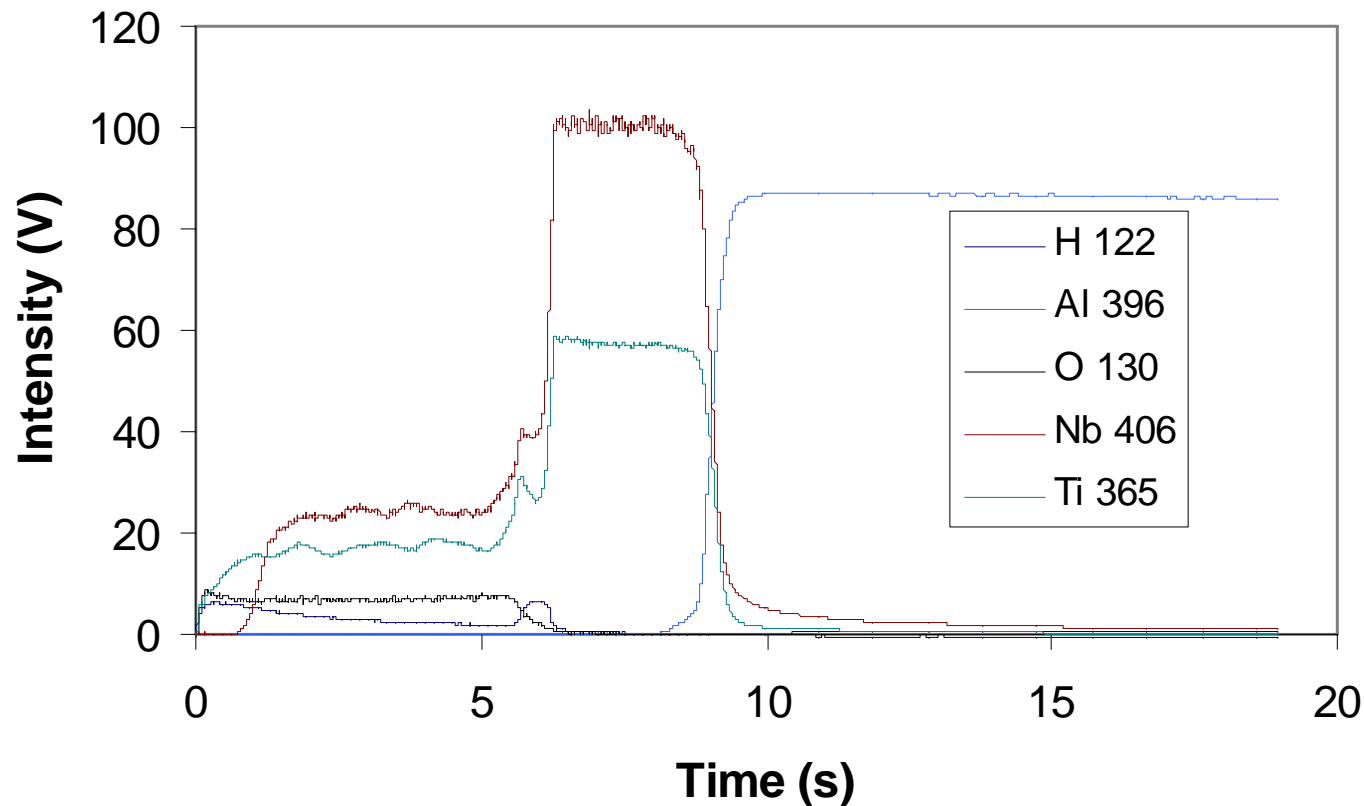
Wave Corrected Depth Profile



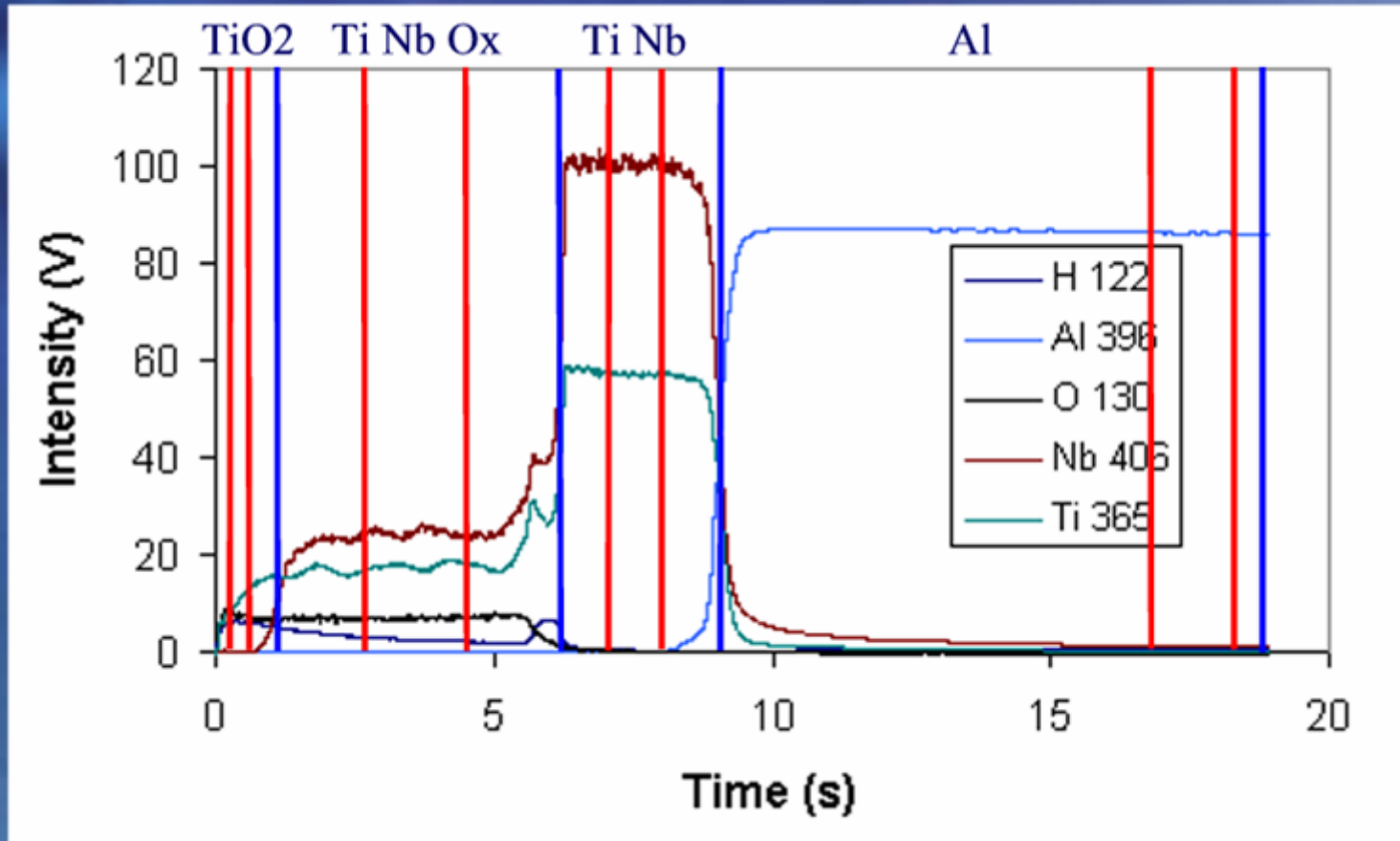
Wave Corrected Depth Profile



H Corrected Depth Profile



Qualitative Depth Profile



Blue: erosion rate

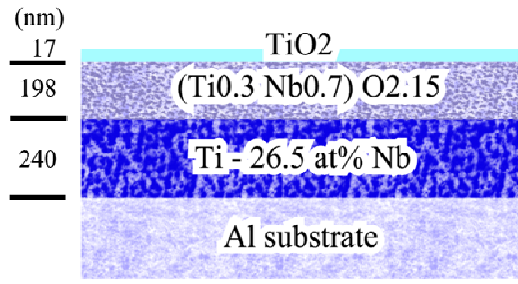
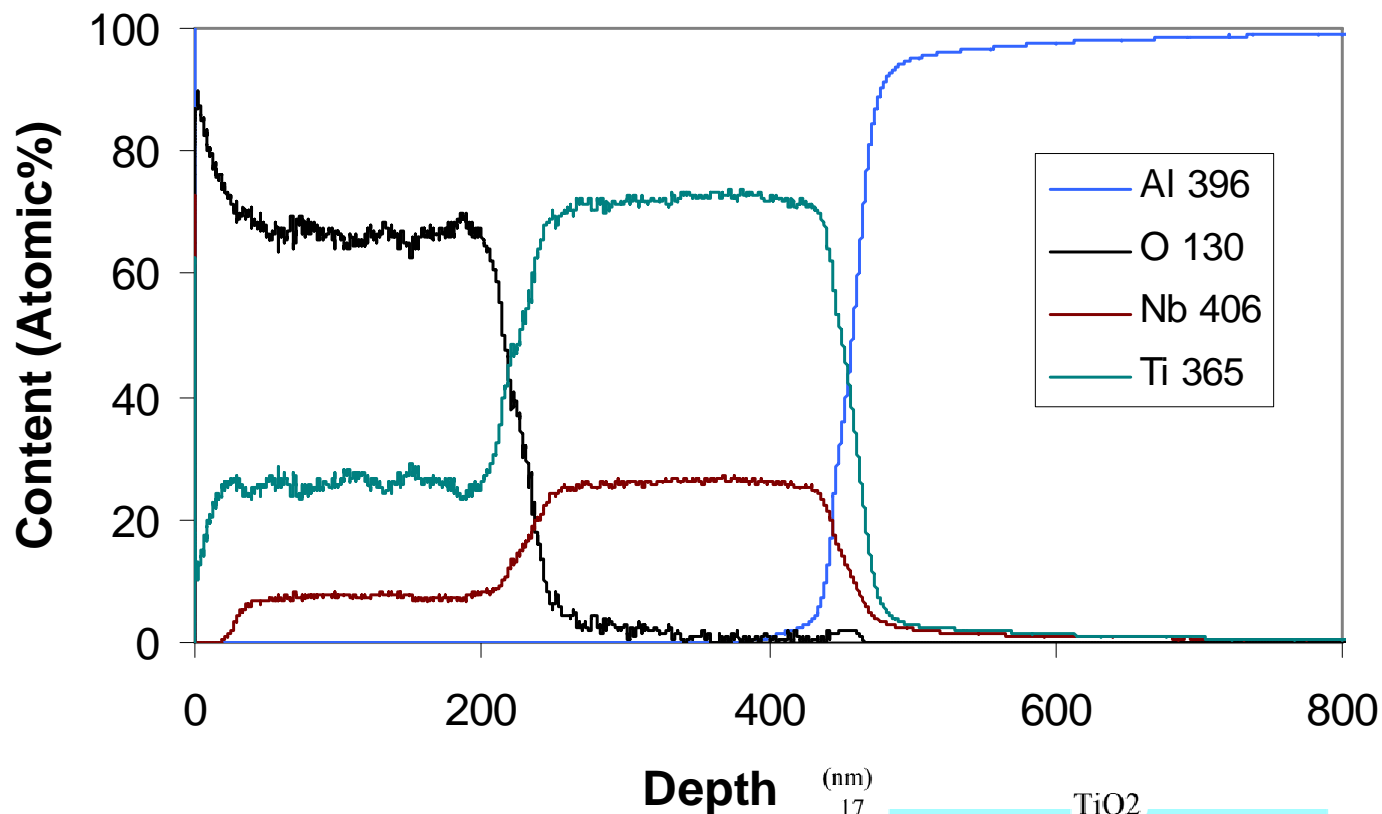
Red: mean intensity



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Compositional Depth Profile



More on thin layers

- ISO TC201 SC8.

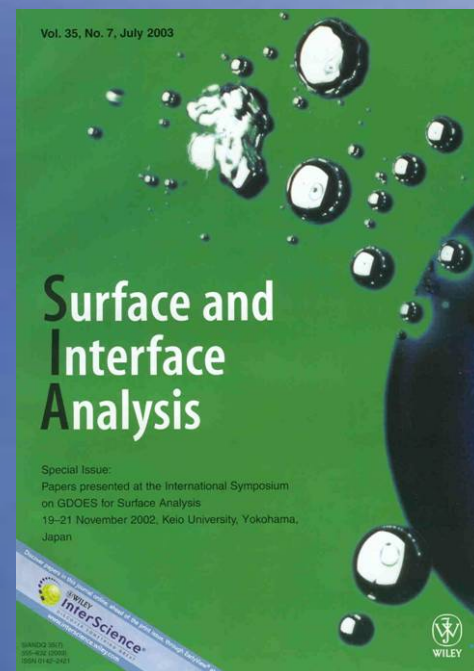


- First norm published : Introduction to use

- Second norm finished : Zn coatings

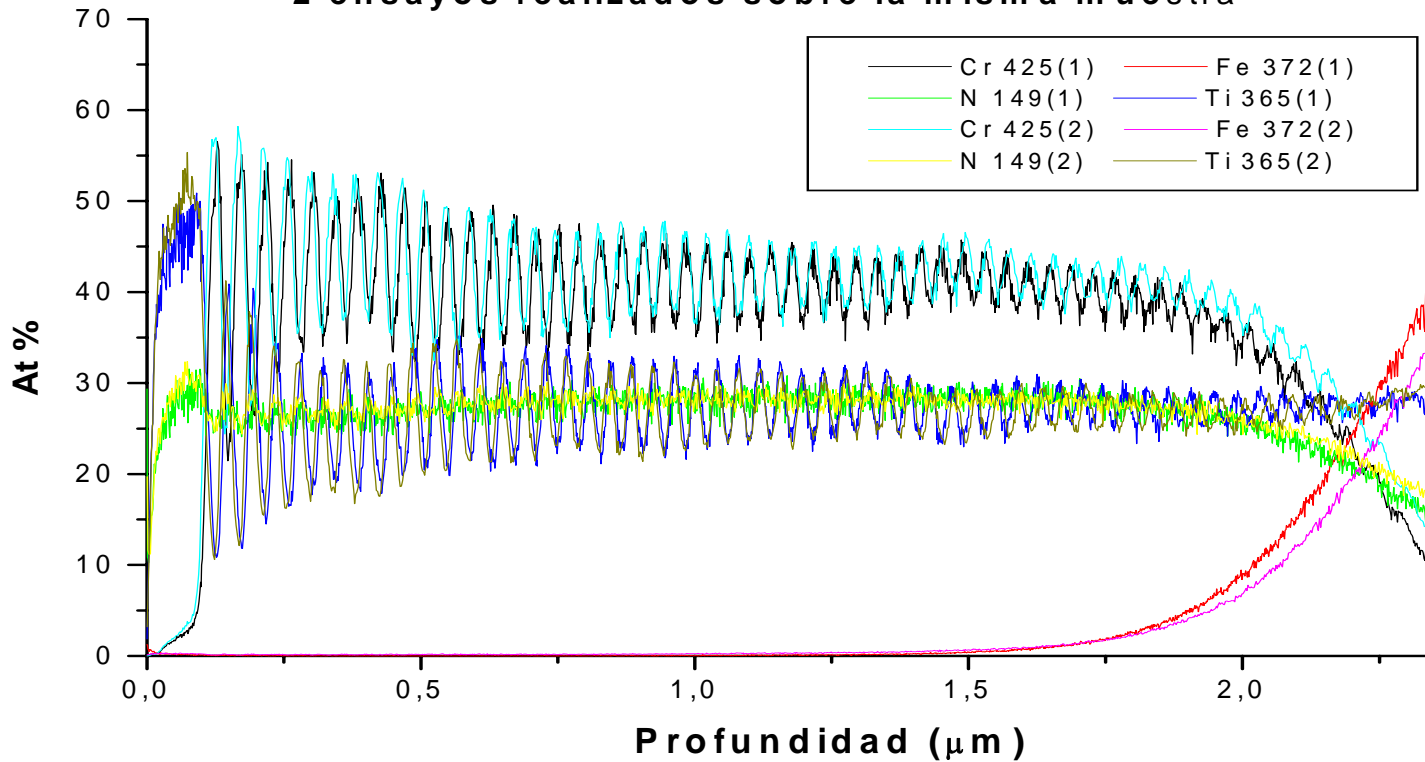
- Start of a new work on thin oxides on metals

- Special edition of Surface and Interface Analysis (Vol 45, 7) based on papers presented at the first international symposium on GD-OES for Surface Analysis

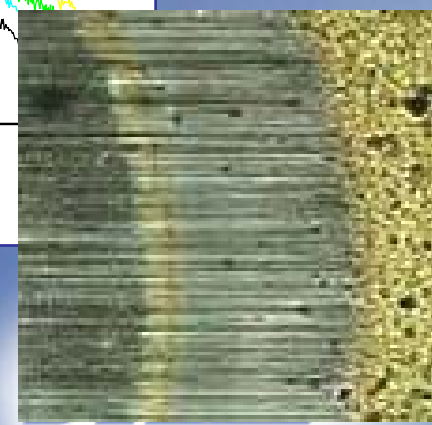
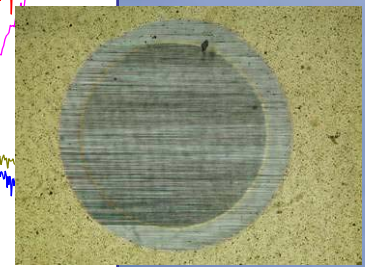


Repeatability of the JY GD

2 ensayos realizados sobre la misma muestra



107 layers

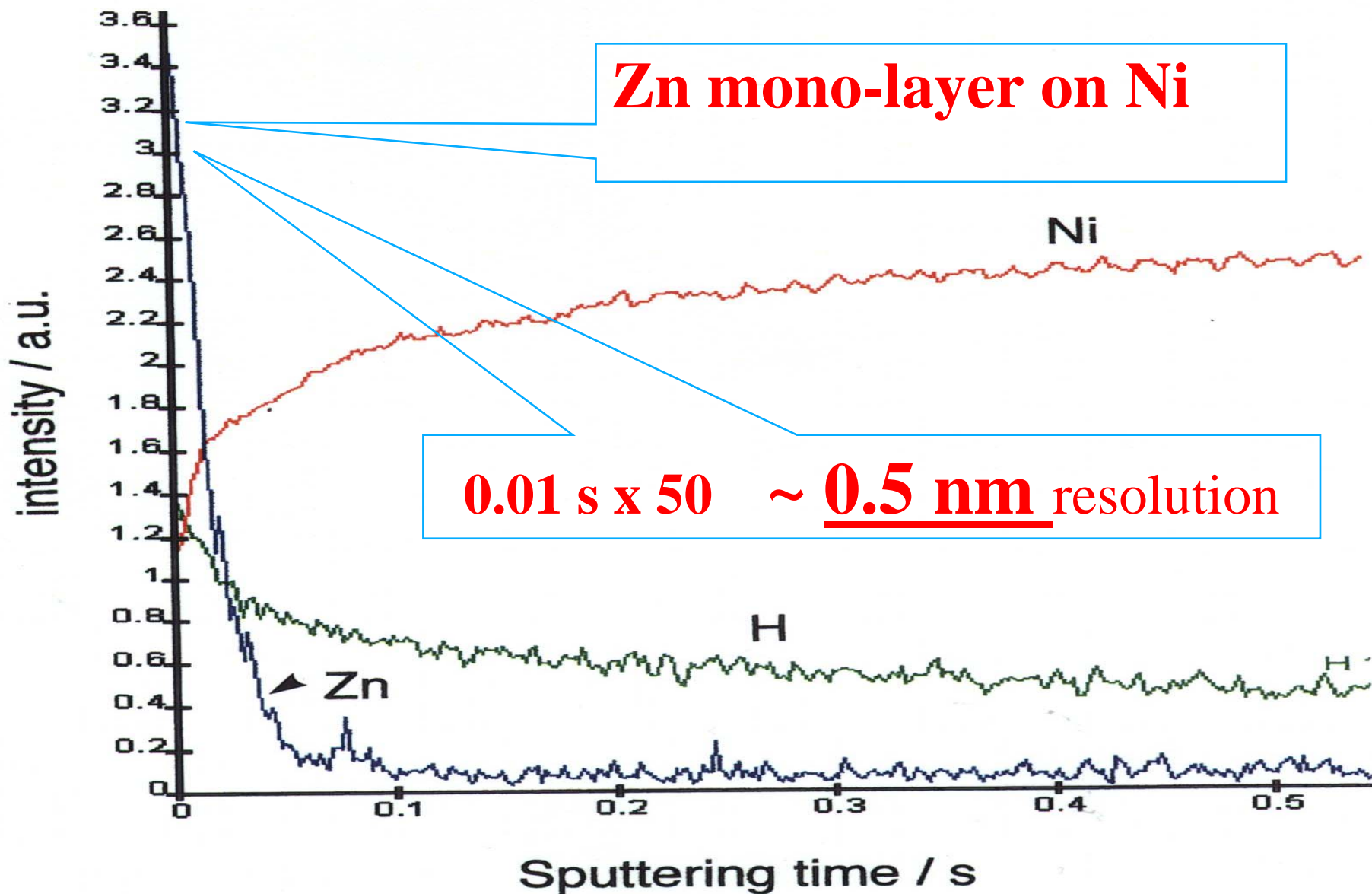


Zn Monolayer on Ni

- Ni: substrate, electropolished, high purity
- Zn: single atomic layer
 - deposited electrochemically
 - under potential deposition (UPD) method



Surface analysis – by GDS



Zn mono-layer on Ni

0.01 s x 50 ~ 0.5 nm resolution

intensity / a.u.

Sputtering time / s

Conclusions

- Recent advances in theory and practice extend the range of RF GD-OES applications :
- **Analysis of large samples**
- **Fragile samples in pulse mode**
- **Odd shape samples**
- **Layer mode offers simplified accurate CDP**



GD-PROFILER



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