Spectroscopy Focus

ULTRA FAST ELEMENTAL BULK AND DEPTH PROFILE ANALYSER FOR MATERIAL DEVELOPMENT AND CHARACTERISATION

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For many metallic applications, changes in performance are expected through applications of advanced coatings, e.g. hard coatings (diamond and nitride thin films), atmospheric corrosion protective layers (coated steels, environment-friendly anodising procedures on Aluminium, paints on cars, etc) and high temperature protective layers.

Emerging areas of interest also require surface and depth profiling chemical analysis to provide the fundamental and strategic information for material's development. In these domains, including organic thin films (diodes, polymer light emitting devices), MEMS thin films, smart thin films (PZT etc), opto-electronic thin films, optical memories (glasses doped with rare earths), solar cells manufacturing, self assembled nano-films, the speed and ease of use of control tools are of crucial importance.

Radio Frequency Glow Discharge Optical Emission Spectrometry (RF-GD-OES) is an Ultra Fast Elemental Depth Profile Analysis Technique that can provide both the surface, the layers and the bulk composition quickly, cheaply, and with high sensitivity to all elements (including the gaseous elements), for almost all solid materials, including metals, metal alloy coatings, semiconductors, polymer coatings, glass, etc.

Examples of use of RF-GD-OES for bulk and depth profile analysis of diverse materials are presented in this article and the most recent updates of the technique are described emphasising its value for materials development and characterisation.

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INTRODUCTION

Radio Frequency Glow Discharge Optical Emission Spectrometry (RF-GD-OES) is a technique that relies on a double mechanism: first the controlled sputtering by argon ions of atoms from a sample surface over an area of some mm (typically 4mm) and secondly the excitation of these sputtered atoms in the gas phase into an RF powered electric argon plasma generating light that is averaged, collected and measured with an Optical Emission Spectrometer, thereby providing compositional information that corresponds to the material that has been sputtered [1].
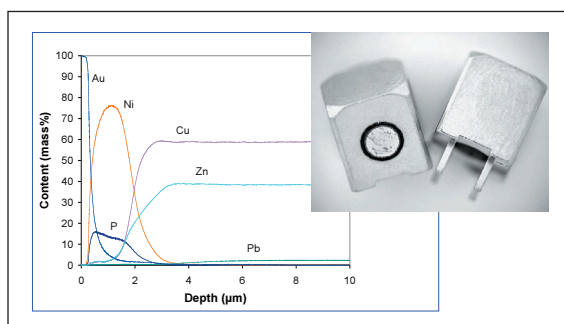

Figure 1. Sample is a brass coated with NiP and a gold top coat. The GD spot results in a 4mm diameter crater on the sample and the GD result obtained in less than 3 minutes is the composition as a function of the depth. (Courtesy of EMPA Switzerland).

RF-GD-OES is a comparative technique, i.e. calibration against known reference materials, is required for quantitative analysis (to get composition versus depth), but it is relatively matrix independent. Conductor and isolating samples could be mixed within single calibration curves, as long as a simple correction on sputtering rate is applied.

Operating RF-GD-OES is simple. The "lamp" design has not much changed since its first use by Grimm in 1967 [2] for bulk analysis and its application to surface with the study of stains on steel sheets in the 70s [3].

In RF GD-OES the specimen is usually mounted externally over the lamp and pressed against an `O' ring to seal the chamber where a primary vacuum is applied. Special holders are available for tubes or rods. No Ultra High Vacuum is required for the analysis which significantly helps with the speed and ease of use (GD operation is undertaken via a flow of ultra high purity gas, usually Argon kept at a modest pressure of about 5 Torr).

Electrically speaking, the specimen to be analysed is the driving electrode on which the RF power is applied, while the Cu face facing it is the ground electrode. The RF plasma is located within the Cu tube and is observed with an optical spectrometer. The technique has no lateral resolution as it averages the signals coming from the entire surface facing the anode, but it achieves an excellent depth resolution as shown later.

The RF plasma [4] is dense (10^{14}) but the incident particles that hit the sample surface have a low energy (about 50eV) and they bombard the surface with a wide incident angle, ensuring generally uniform and extremely fast sputtering (in the range on 10 nm/s – several microns/minute) without major alteration of the surface layers, a key feature for multi-dimensional analysis.
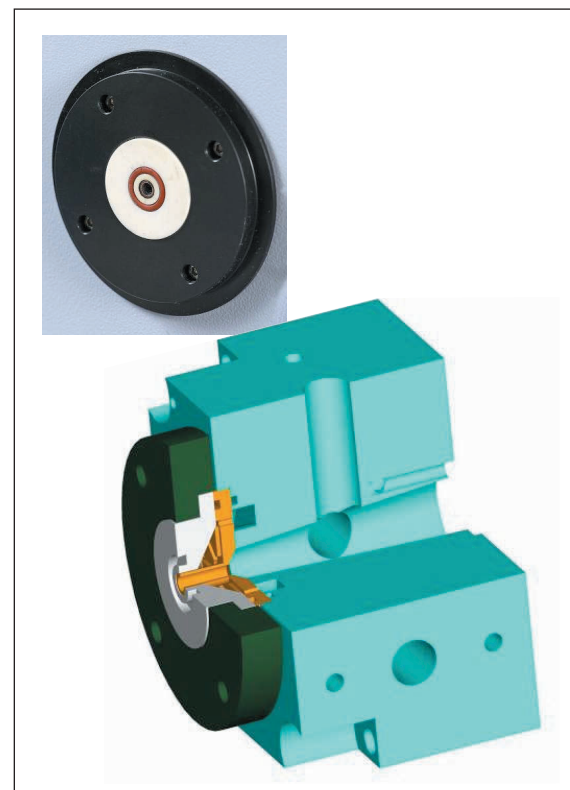

Figure 2. Photo and schematic diagram of the RF-GD lamp

Since optical signals can be collected very rapidly the technique is ideally suited to the analysis of thin and thick films from the first nanometre down to more than 150 microns.

The use of a radio frequency source allowing sampling of non-conductive coatings and that could be pulsed to minimise the induced heat on very sensitive materials (polymers etc), has done much for the development of the technique [5].

The instrumentation is now equally found in the academic field, as in industry, where its capability of measuring all elements simultaneously including: O, C, N, H, S, Cl makes it ideal for both mechanisms understanding and problem solving.

BULK ANALYSIS

For bulk analysis the success of Glow Discharge as a spectrochemical source is strongly dependant on competing methods. For direct solid analysis GDS is competing with X-ray techniques and mainly with Spark Emission, that is dominant for conductive materials.

Most users select GD for its capability to do depth profiling as well as bulk. However, in some cases GD could be better because of less matrix effects and lower detection limits. GD curves are also essentially linear, this allows extrapolation of results far beyond the calibration curves, an important point to consider when calibration samples are scarce.

Examples of the first case are the analysis of Mg alloys or the GD capablility to directly analyse grey cast irons that spark cannot do well. The analysis of precious metals [6] illustrates the second aspect, at least when the RF GD source is coupled to a very high resolution optical system providing the solution to the most demanding applications.

Matrix: Platinium

RSD = 1%

	Wavelength (nm)	BEC (ppm)	DL (3s) (ppm)
Au	268	111,46	3,34
Ag	338	13,55	0,41
Pd	340	18,58	0,56
Ir	322	86,00	2,58
Rh	366	390,02	11,70
Ru	373	37,40	1,12
Os	291	56,28	1,69
Re	346	37,07	1,11
Al	394	13,36	0,40
As	197	50,00	1,50
B	209	28,19	0,85
Be	313	8,21	0,25
Bi	307	50,87	1,53
Cd	361	90,80	2,72
Co	387	18,28	0,55
Cr	358	5,70	0,17
Cu	327	7,94	0,24
Fe	372	11,70	0,35
Mg	384	34,41	1,03
Mn	403	130,90	3,93
Mo	380	5,88	0,18
Ni	352	10,64	0,32
Pb	406	18,36	0,55
Sb	231	151,66	4,46
Se	196	20,01	0,60
Si	288	6,32	0,19
Sn	326	215,86	6,48
Te	226	24,07	0,72
Ti	369	68,03	2,04
W	401	31,29	0,94
Zn	214	8,64	0,26
Zr	339	20,85	0,63

Figure 3. Figures of merit in Pt and Au matrices obtained on a GD-Profiler HR (1m focal length polychromator). The detection limits of most elements are in the range 100ppb to 1ppm

Matrix: Au

RSD = 1%

	Wavelength (nm)	BEC (ppm)	DL (3s) (ppm)
Ag	338	5,03	0,12
Pt	266	198,88	4,55
Pd	340	6,59	0,10
Ir	322	18,00	0,29
Rh	366	124,95	3,65
Ru	373	7,17	0,17
Al	394	6,78	0,15
As	189	103,14	3,04
As	197	67,02	1,77
B	209	6,30	0,08
Bi	307	65,99	1,72
Ca	397	81,42	0,35
Cd	229	11,69	0,09
Co	387	22,23	0,55
Cr	358	10,47	0,28
Cu	327	8,07	0,12
Fe	372	7,42	0,16
Ga	294	9,82	0,24
Ge	275	44,05	0,87
In	304	24,36	0,49
Mg	384	21,51	0,51
Mn	403	57,03	1,67
Mo	380	11,18	0,33
Ni	352	3,90	0,08
Pb	406	47,72	1,14
Sb	231	54,83	0,37
Se	204	31,78	0,32
Si	212	37,68	0,28
Si	288	14,90	0,22
Sn	326	27,49	0,44
Te	226	24,11	0,21
Ti	369	7,90	0,20
W	401	23,91	0,57
Zn	214	23,21	0,35
Zr	339	11,21	0,25

Figure 5. Example of rapid analysis of a thick (>60μm) anodised Al

Figure 6. 107 layers of 20nm CrN/TiN deposited by magnetron coating. Overlay of 2 quantitative measurements. Courtesy of AIN Spain

THICK LAYERS

All coatings are not thin, painted car bodies for instance feature successive layers of more than 100 microns. Many thermal treatments (nitruration, carbonitruration, carburation etc) are done in controlled atmospheres to improve the mechanical properties of steels are also rather thick.
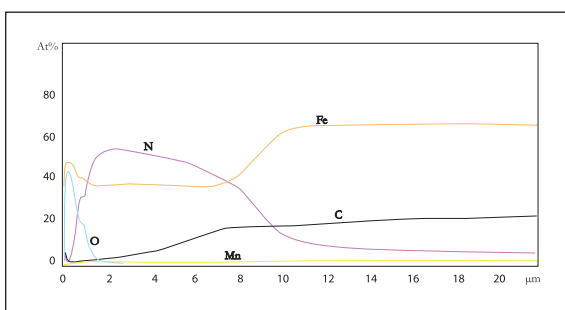

Figure 4: Thermal treatment on steel. Courtesy of Colmegna SA, Italy

To control such a process, the follow on of the segregation of elements and diffusion from the gases is to be done over several tens of microns. This task is easily achieved with the RF GD lamp that uses a double pumping system (the inside part of the anode and the outside are pumped differentially with 2 pumps) to minimise the re-deposition on the edges of the crater and allows deep craters of more than 150 microns to be obtained.

Figure 5 shows a thick non conductive anodised layer. The basic process in anodising is the transformation of the aluminium surface to anodic oxide.

The reasons for anodising are numerous and include increased corrosion resistance, paint adhesion, decorative appearance, electrical insulation (indicating why RF is required to study these layers) and coatings for subsequent plating etc.

The oxide layer thickness here was of about 60 μm and has been sputtered in 20 minutes. The first graph provides qualitative information (intensities in arbitrary units with sputtering time, whereas the second graph reveals the quantified information (atomic concentrations with depth).

This figure illustrates the capability of rapid sputtering of the technique that assures that such layers are analysed in a reasonable time. The most relevant information that RF-GD-OES can provide for such materials is the bulk composition of the substrate, the depth profile distribution of the species within the coatings and possible contamination at the interfaces.

THIN LAYERS

A special edition of Surface and Interface Analysis [7] dedicated to RF GD-OES has illustrated the interest in the technique for analyses of thin films (<100nm). Since then, the number of applications has increased as more researchers have successfully embraced the approach.
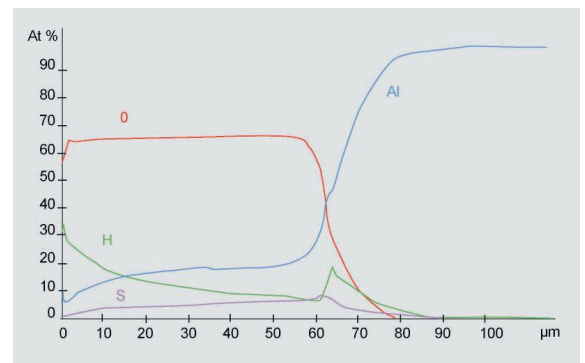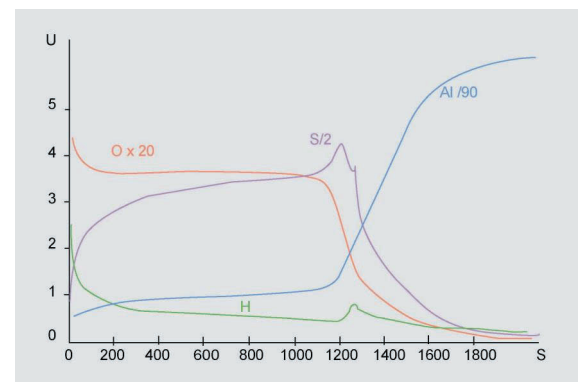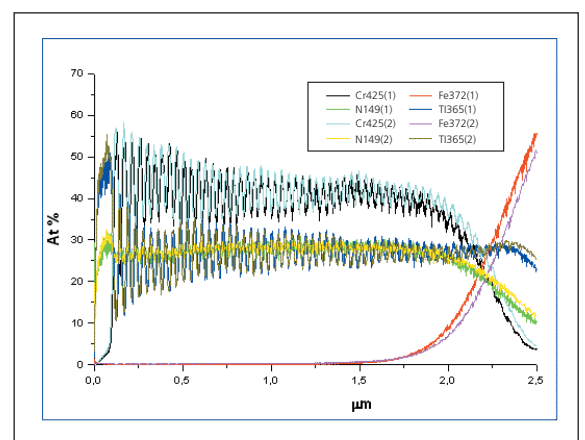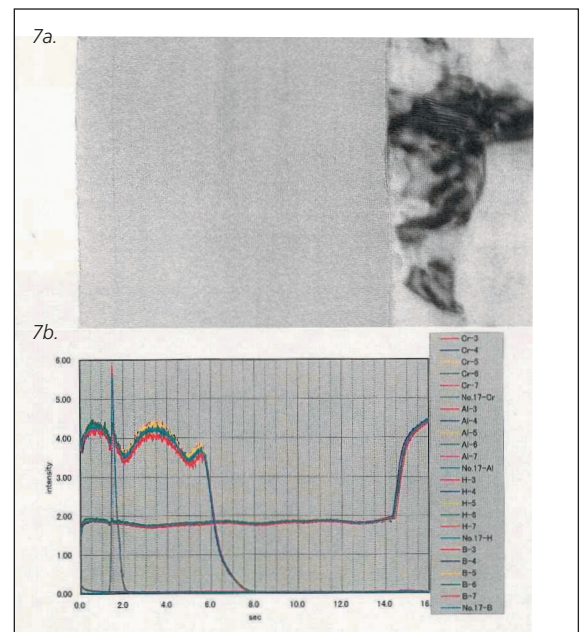
Figure 6 illustrates the benefits of RF GD for PVD coatings. The sample has 107 layers of 20nm each. Though the depth resolution degrades as we penetrate into the material due to re-deposition and atomic mixing, it remains however excellent.

7a.

7b.

Figures 7a and b. Illustration of the reproducibility of analyses (overlapping of 5 results and correlation with TEM)

The other example shown in *Figure 7* is a electropolished Al anodised in an acid solution with a Cr delta layer on a few nm deposited at the bottom of the pores. RF GD analysis was compared to SIMS on this type of sample and found to provide equivalent results but in seconds compared to hours for SIMS [8].

The reproducibility of the instrumentation is a key factor to obtain credible and valuable results. *Figure 7a* presents the transmission electron micrograph of a section of the sample (the chromium delta layer appears dark) and 7b gives the result of 5 overlapped GD measurements.

PULSED OPERATION

The RF source may be operated in the pulse mode. Pulsed operation offers the possibility to supply high instantaneous powers during short periods of time (typically around 1ms). This mode of operation has proved to be useful for fragile and heat sensitive materials such as PZT –(Lead Zirconate Titanate) [9]. It is also a method to reduce the sputtering rate, while keeping sufficient sensitivity.
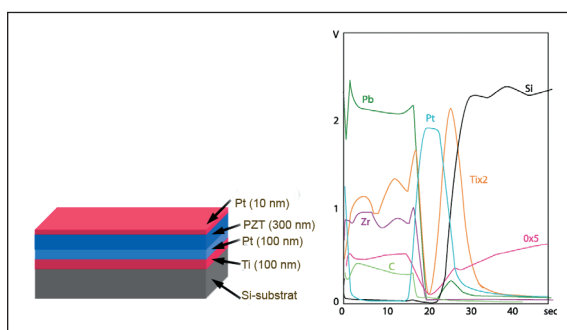

Figure 8. Multi-layered sample with heat sensitive PZT coating analysed with the pulsed mode

COMBINATION OF GD TO OTHER TECHNIQUES

RF GD could be used as a sputtering technique to gently remove a layer and access to the interface below with minimal damage. The large spot provides a large observation zone for further Scanning Electron Microscope (SEM) investigation or micro Raman analysis.

Applied during a very short time period (a couple of seconds) or with soft conditions, it helps to remove surface contamination. The photo below shows a stainless steel sample mirror polished and then sputtered for 1 second. The preferential sputtering, usually a drawback, reveals the structure without the use of any chemical so that preferential sputtering is turned into an advantage.
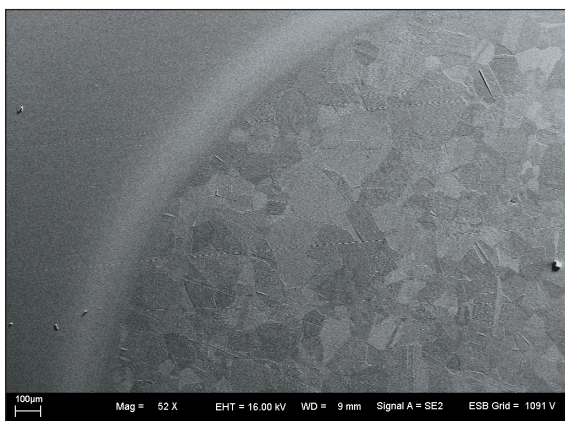

Figure 9. mirror polished stainless steel with a 1s RF GD spot. Courtesy of K. Shimizu, Keio University.

ULTRA THIN FILMS

The first result of RF-GD-OES analysis of a mono-layer was obtained by Shimizu and Payling and presented at the 2003 ECASIA conference (unpublished result). A single atomic layer of zinc was deposited on high purity electro-polished nickel using an under potential deposition method. Since then, the work on ultra-thin films has been extended to adsorbed layers and the analysis of a monolayer of thiourea on copper, revealing atomic scale depth resolution [10] at least at the surface of the samples.

Figure 10 presents an analog result from Shimizu with a specimen featuring silane deposited on aluminium.
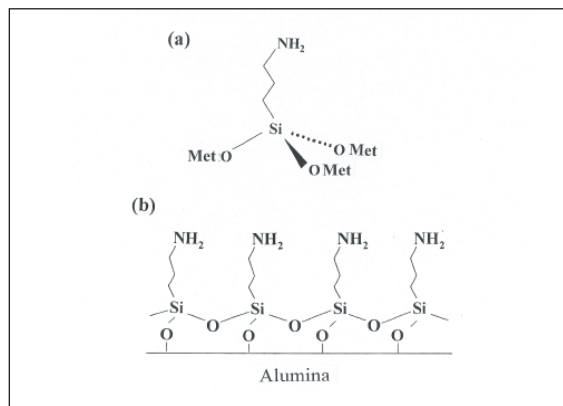

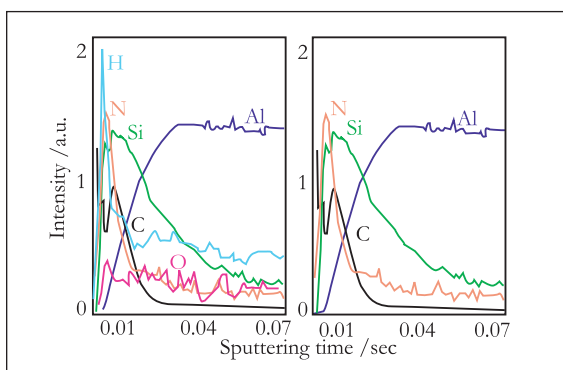*Figure 10a. Structure and orientation of the deposited monolayer of Silane*

Figure 10b. RF-GD-OES analysis of the deposited silane layer revealing peaks distribution well correlated with the structure of the specimen

DATA TREATMENT

The ability of collecting optical signals at high frequency allows doing useful data treatments on the results. A recent development concerns the introduction of a smoothing by wavelets of depth profile results.

Wavelets are relatively new mathematical tools used for instances in the jpeg2 data compression format. Compared to classical smoothing procedures they are capable of keeping unaffected the ultra shallow depth profiles (which is necessary for GD when applied to nm scale layers), while efficiently decreasing various noises.

The example above shows the depth profile of C from a Zn specimen polished and treated with ethanol. The first graph focuses on the surface C peak. The wavelet graph is in dark blue and adequately follows the raw data in light blue.

The second graph is taken from the same sample and shows the residual signal of C in the Zn. The dark blue curve features a reduced noise compared to the raw data and other smoothing procedures.
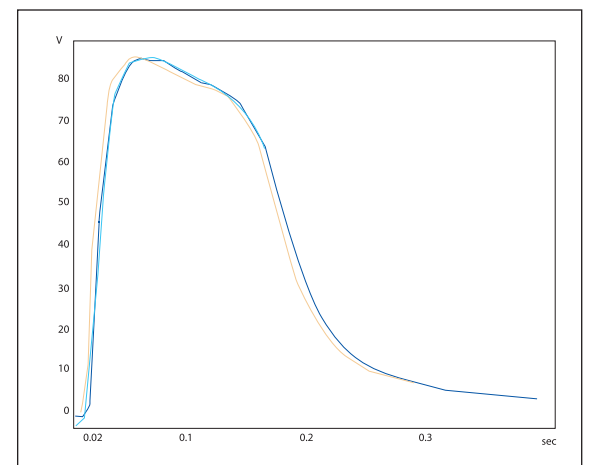

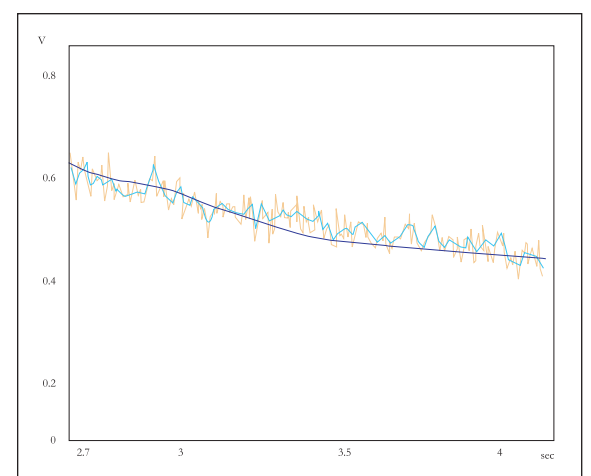*Figure 11a. Surface peak smoothed by wavelet compared to other smoothing modes*

Figure 11b. Residual signal smoothed by wavelet compared to other smoothing modes

CONCLUSION

The simplicity and versatility of RF-GD-OES and its performance in terms of depth resolution, reproducibility and sensitivity makes it a very useful technique for material characterisation. It adequately complements other instrumentation and is an efficient tool for process control and quick defect identification.

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