

# GLOW DISCHARGE SPECTROMETRIES FOR ULTRA FAST DEPTH PROFILE CHARACTERIZATION OF MATERIALS

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## ABSTRACT

Glow Discharge Spectrometries provide direct measurement of the chemical composition of solid materials as a function of depth, with nanometre resolution and the capability to measure both thin and thick layers.

These techniques rely on the fast sputtering of a representative area of the material of interest by a high density ( $10^{14}/\text{cm}^3$ ) and low energy GD plasma. The same GD plasma assures the excitation/ionisation of the sputtered species that are detected in real time by the spectrometer proving compositional depth profile analysis.

When a high resolution optical system is used, the resulting technique is called Pulsed RF GDOES, when the plasma is coupled to ToF MS detection, it is named Plasma Profiling Time of Flight Ion Mass Spectrometry.

Various applications are presented and aspects of analytical performance with regards to sensitivity, depth resolution, quantification, repeatability and sample throughput are discussed.

## 1. INTRODUCTION

The first illustrative example is taken from the Photo-Voltaic domain and shows a typical GD result on a CIGS layer. The crater diameter is 4mm, the total analysis time is 3 minutes.

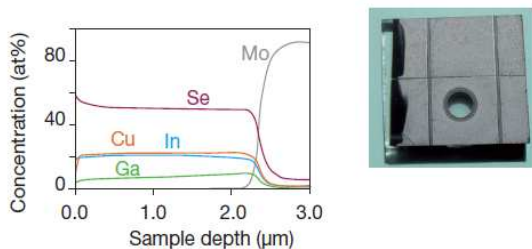


Figure 1: GD OES analysis of a PV solar cell

All elements can be simultaneously measured (including H, C, O, Na, Li etc). Deuterium can be measured with OES, all isotopes being possible with TOFMS.

The speed of analysis is a key characteristic of the GD techniques.

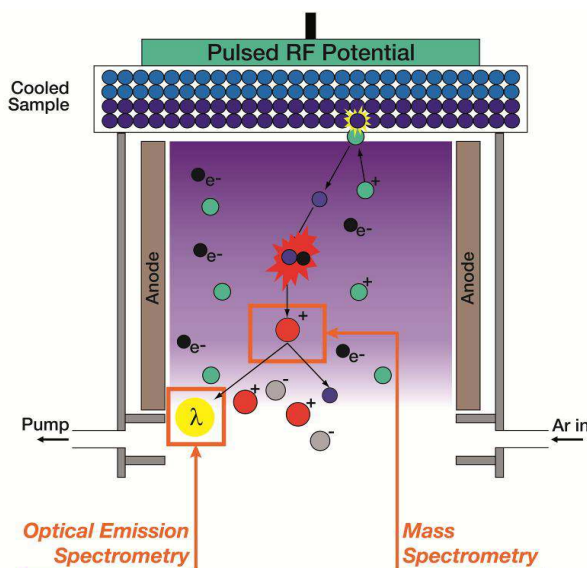


Figure 2: Schematic view of the GD plasma source

The GD plasma source consists in a cylindrical electrode (typically 4 mm diameter) at ground potential and the sample powered with a radio frequency (RF) voltage. The sample placed on an O-ring is actually “closing” the plasma chamber. With this geometry, no sample preparation is needed and starting analysis is almost immediate upon pumping the vessel to primary vacuum and letting ultra high purity argon in at a constant pressure of few mbars. RF excitation is brought from the back of the sample by means of a cooled applicator pressing down the sample against the O-ring. The RF power is supplied by a 13.56 MHz generator equipped with an automatic matching network. Sputtered species

induced from Ar ions and fast neutrals bombarding the sample surface are then excited or ionised.

The unique characteristics of this plasma allow very fast erosion (2-10nm/s) with minimum surface damage (as the incident particles have an average energy of about 50eV) and it has been shown that it can be used advantageously for sample preparation in SEM (patent JP20080241569 and Ref [1]).

The following example was shown by K. Shimizu at the 6<sup>th</sup> International GD day. Sample is a stainless steel with small inclusions embedded. The GD plasma allows sputtering the material down to the inclusions for further SEM observation and topographic information is obtained depending on the various nature of the different components.

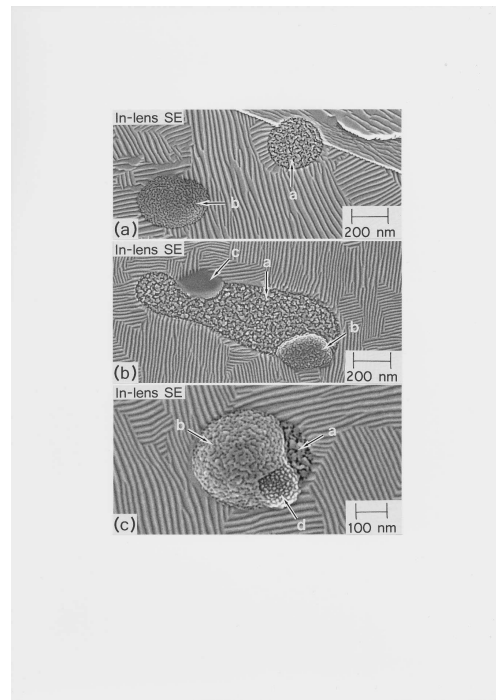
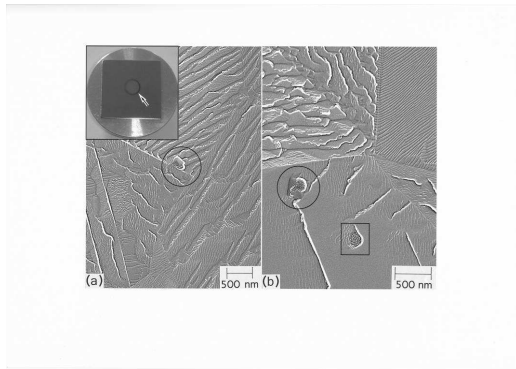


Figure 3 (a&b): Sputtering of a stainless steel revealing the grain structure. Zoom on an embedded inclusion: the GD plasma is revealing topographic information linked to compositional changes in the different parts of the inclusion.

## 2. PULSED RF

A recent development has been the introduction of Pulsed RF sources offering the capability of automatic matching in pulsed mode (patent FR 49787197).

Pulsed RF operation is crucial to avoid unwanted diffusion of the elements during the measurements, such as Na in glasses or PV cells.

Enhanced depth resolution is also possible with pulsed RF.

The following example with sub-nanometre depth resolution is taken from [Ref 2] and shows the Pulsed RF GD OES depth profile of a mirror for X ray featuring 60 multilayers [3nmMo/0.3nmB4C/3.7nmSi].

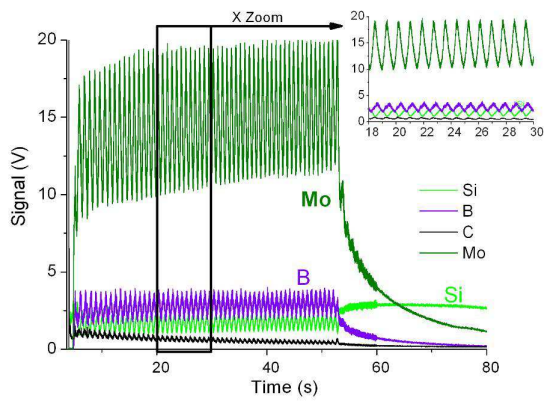


Figure 4: Depth profile analysis of a multilayered material

The depth resolution is however material dependant and issues on roughness notably are crucial,

Pulsed RF has been crucial also for the measurement of fragile materials such as electrodes for Li batteries.

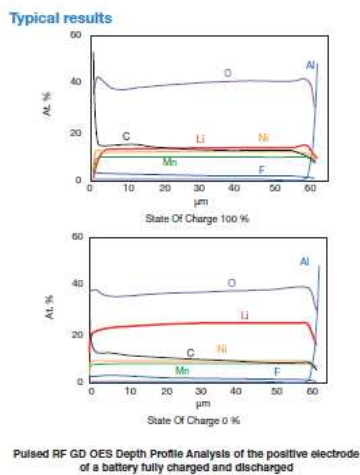


Figure 5: Depth profile analysis of an electrode of Li battery with SOC 0% and 100%

When TOFMS detection is used in orthogonal configuration (cf Figure 6) and at a high extraction frequency the monitoring of the temporal ion response from the plasma during and after the period of the RF pulse is observed. Details on the different ionisation mechanisms taking place at the different time domains (shown in Figure 7) are discussed in [Ref 3].

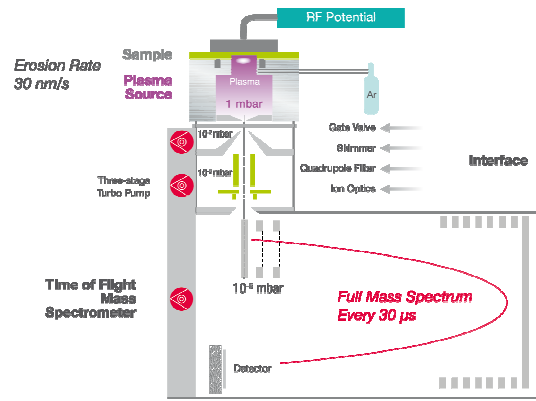


Figure 6: Schematic diagram of the TOFMS instrument (the extraction of the ions is orthogonal to their direction from the GD source)

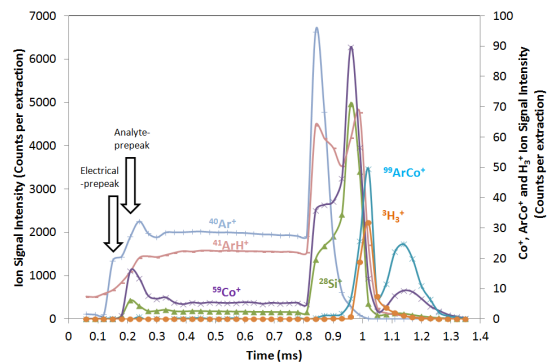


Figure 7: Temporal response of the ion signals within a GD pulse

Temporal windows in the RF period of the ion signals for the pre-peak, plateau and/or afterglow region can be integrated to generate depth profiles. This unique time resolved information is highly valuable as it allows for selecting the higher intensity time window which permits to gain in sensitivity but also to perform dedicated studies of plasma/surface interactions.

In other words entire TOF spectra are recorded at any depth but also virtually at any point during the RF period.

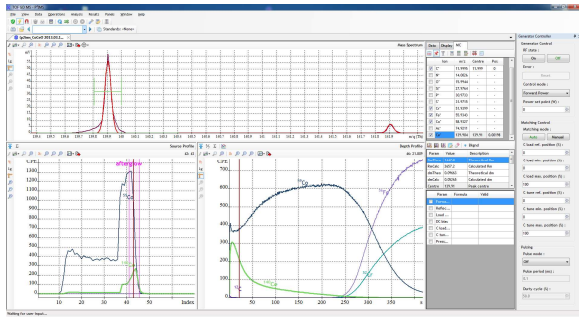


Figure 8: TOF analytical screen featuring a depth profile (bottom right), the pulse profile (bottom left) and the full mass spectrum at selected depth and time domain in the pulse period.

### 3. UFS

Plasma gas mixings are commonly used in plasma deposition but more rarely in analytical GD.

The addition of Oxygen to the plasma gas was reported to have an adverse effect in GD because only metallic layers were tried but when polymeric layers are investigated the use of a plasma with ArO gas mixing induces chemical reactions on the surface that complement the sputtering by the Ar ions and help to dissociate the chemical bonds of the organic layer.

This new development (patented, FR 50829322) has opened multiple applications. The following example is a plastic DVD where nanometre resolution is obtained on embedded layers below 70 microns of polymer!

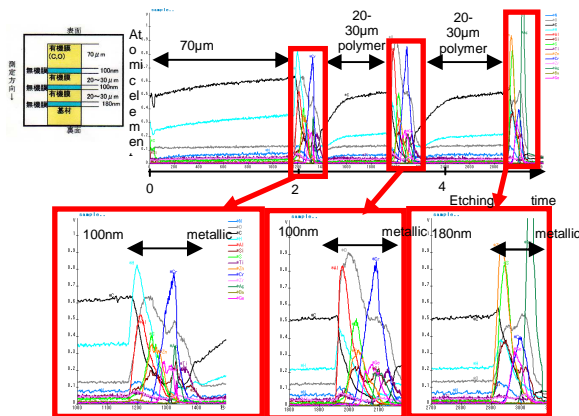


Figure 9: Depth profile measurement of a DVD

### REFERENCES

- [1] Shimizu K., Mitani T. New Horizons of Applied Scanning Electron Microscopy, Springer 2010
- [2] Ber B., Bátor P., Brunkov P. N., Chapon P., Drozdov M.N., Duda R., Kazantsev D. Polkovnikov V.N., Yunin P., Tolstogouzov A., Thin Solid Films 540 (2013) 96–105
- [3] Mass Spectrometry Handbook, Chapter 41, Analysis of Thin and Thick Films Wiley, M.S Lee editor, 2012