Feature Article

New Developments in GD Spectrometries for Advanced Materials Characterisation

Patrick CHAPON, Agnès TEMPEZ

Over than 70% of recent papers published with GD data refer to HORIBA Jobin Yvon instruments and several key patents give us a world leading position in the field. In this article we will illustrate the latest developments in GD Spectrometries through a survey of recently published articles. Pulsed RF Glow Discharge OES and Plasma Profiling TOFMS provide rapid depth profile composition of thin and thick layers of conductive and non conductive layers with excellent depth resolution, sensitivity and multi-element capability. Thus, they contribute to the development of new advanced materials and, being fast and easy to operate, they are changing the way people consider surface analysis.

Introduction

RF Glow Discharge Optical Emission Spectrometry (RF GD-OES) and the new Plasma Profiling Time of Flight Mass Spectrometry (PP-TOFMS™) developed within a EU project[1] coordinated by HORIBA Jobin Yvon contribute to provide fundamental and strategic information for advanced material's development. Over than 70% of recent papers published with GD data refer to our instruments and several key patents give to HJY a world leading position in the field.

GD Spectrometries rely on the controlled sputtering (Figure 1) of a representative area (2-8 mm) of the

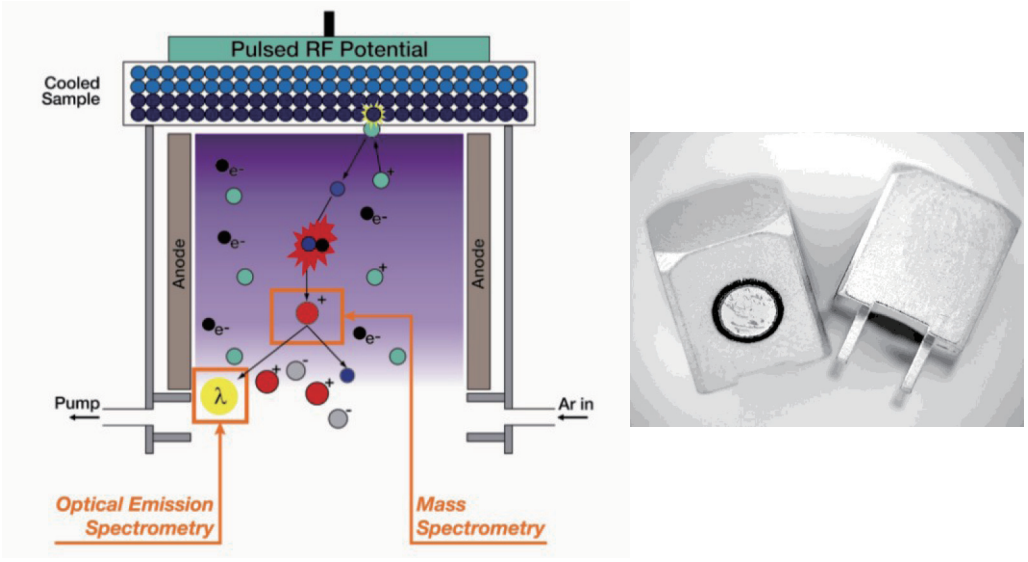

Figure 1 Principle of GD and sputtered crater

material of interest by a high density (10^{14} cm^{-3}) and low energy RF plasma and the parallel detection of the sputtered species excited or ionised in the plasma with a spectrometer. The unique characteristics of the GD plasma allow very fast erosion (2-10 nm/s, several microns per minute) with nanometre depth resolution, absence of charge effect and induced heat and with minimum surface damage (as the incident particles have an average energy of about 50 eV). The spectrometers match the speed of erosion and measure all elements simultaneously at any depth.

The latest developments in GD spectrometries (OES & TOFMS), most of them patented, will be presented through published results covering new materials or coatings applications (nano-scale and upward).

Deuterium and other Isotopes

Access to transport mechanisms within materials can be studied through isotopic depth profiles. With OES, only Deuterium (D) can be measured, with TOFMS all isotopes are readily available. D in OES is measured at the wavelength 121.534 nm and is well separated from the most intense H line at 121.567 nm. D can be accessed from H using the Polyscan™ function (patent 2 651 575A1) or measured simultaneously to H using multiple orders of the diffraction grating. The capability to detect D together with H and all other elements in a depth profile is crucial as it provides unambiguous determination not affected by residual background and is used notably for corrosion studies of fusion reactors materials. In a recent paper[2] Nakamura *et al* have studied with GD-OES the deuterium behaviour at the interface of different metals (SS304, F82H and nickel) oxidized under high temperature heavy water.

PP-TOFMS™ measures all masses at any depth in a depth profile from H (mass 1), D (mass 2) to U (238/235) and beyond (for molecular fragments) and is therefore ideal for obtaining isotopic depth profiles. Baron Wiechec *et al*[3] have looked with PP-TOFMS™ at amorphous anodic alumina permeated by linear pores using ^{18}O tracers. Another example from a paper by Tempez et al[4] is given here with thin anodic Ta_2O_5 layers, material of interest in electronics: ^{18}O enriched layers have been prepared in ^{18}O enriched H_2O. The graph in the figure 2 below is the depth profile of a sample consisting of three bilayers of ^{18}O enriched Ta_2O_5/ non-enriched Ta_2O_5, each Ta_2O_5 layer being 50 nm thick.

Lithium (Li) Batteries

Intense research is conducted on Li-ion batteries used in electric or hybrid vehicles and electric power tools. Both positive[5] and negative[6] electrodes have been studied with GD, with research notably conducted on degradation mechanisms and coatings for thermal stability and cyclic performance. Li cannot be measured with X Ray-based techniques but it is very sensitive both in OES (measured at wavelength 670.791 nm) and MS (Li has 2 stable isotopes, most abundant at mass 7).

The GD source does not require UHV and sample handling is usually straightforward as the specimen is simply placed against an O-ring sealing the discharge chamber. However this ease of use, generally an advantage, might be a drawback for some Li based materials where contact with air should be minimized or prevented. A transparent dedicated chamber has therefore been designed and patented (P 2001-197308) allowing easy sample handling to the instrument and GD analysis under Ar inert gas atmosphere.

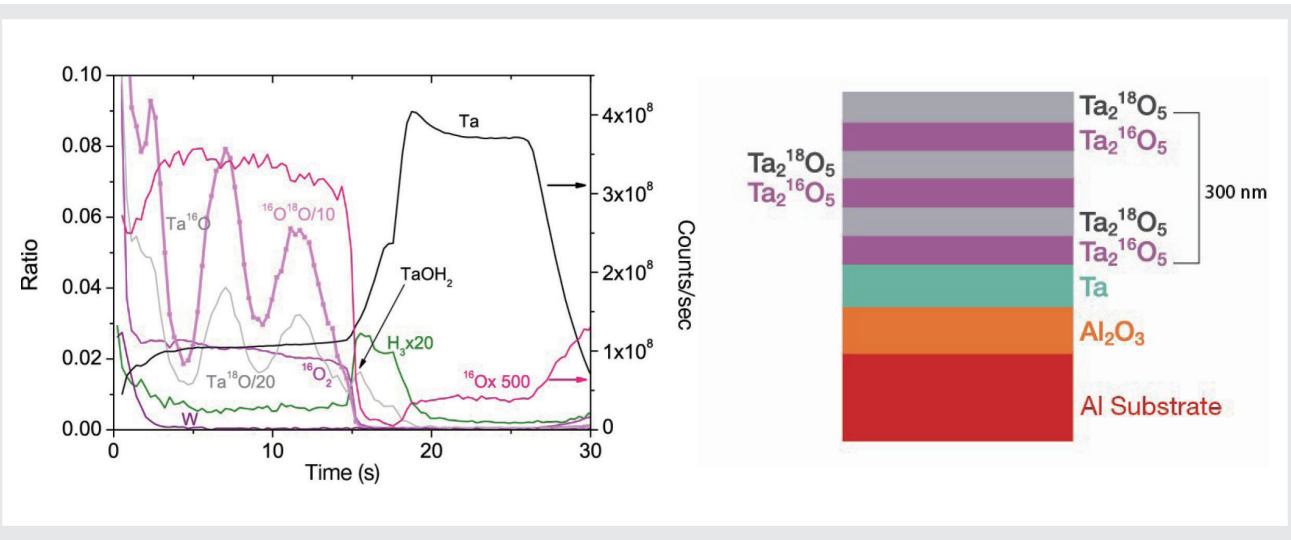

Figure 2 Isotopic Depth Profile with PP-TOFMS

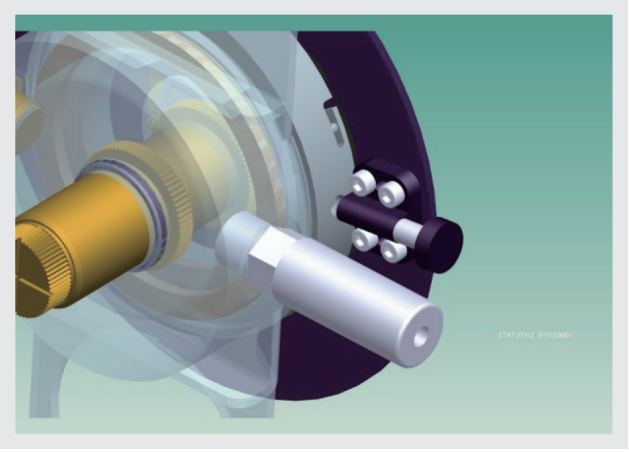

Figure 3 Patented "Li bell"

A similar concept was used by Lobo et al for PP-TOFMS[7] and shown to minimize residual air background.

Plasma Cleaning Strategies

A specific way of tuning the RF GD plasma with very soft conditions (typical power less than 3 W and pulsed mode) has been described by Molchan et al[8] and used to clean sample surfaces prior to depth profile analysis – a strong reduction of surface C notably was observed in OES and TOFMS.

With slightly stronger conditions, pulsed mode and very short erosion time, GD plasma can be used to structure surfaces at the nano-scale and upward or, as demonstrated by Shimizu et al,[9] to prepare sample surfaces for SEM observation (patent EP 1715504A2, 2006) – not only by eliminating residuals of polishing or removing a superficial oxide layer but also by revealing the grain structure or the phases within the material under investigation due to preferential sputtering over the large sputtered area. (Figure 5)

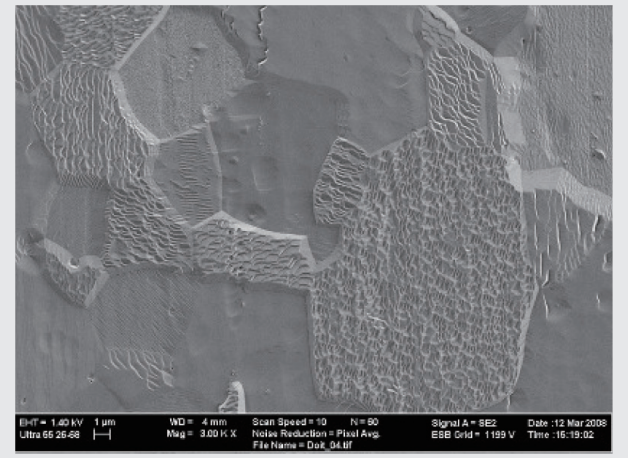

Figure 4 SEM View after GD Sputtering, Grain Structure is revealed

Pulsed Operation

The patented development of a pulsed RF source (patent 10 52883, 2010) having the speed and capability of matching impedance changes in pulsed mode has represented a major step forward for many applications. Pulsed operation allows minimizing the average power (and so the thermal constraints) while keeping high instantaneous power for sensitivity. Pulsed operation is also beneficial for the precise control of the crater shape offering enhanced depth resolution.[10]

Depth Resolution

The following example illustrates the enhanced depth resolution offered by the pulsed RF operation – here with OES detection. The sample is a mirror for X-ray and features 60 stacks each with Si/B_4C/Mo multilayers. Each layer is less than 7 nm thick. (Figure 5)

In addition, in the case of TOFMS detection and RF pulsed mode a significant enhancement of the ion signals after the pulse ends is observed linked to the ionisation mechanisms. Such effect (not observed in OES) was central to the work done within the EU project EMDPA due to its analytical benefits and for the information it provides on plasma physics and plasma surface interactions; following this work all EMDPA partners were invited to contribute to the chapter on thin/thick films in a new Handbook of Mass Spectrometry[11] where most findings are summarized.

The orthogonal configuration in the PP-TOFMS and the speed of TOFMS detection allows for monitoring the transient signals over the ms period of the pulsed RF source with a high duty cycle. So not only the full mass spectrum is obtained at each depth within a depth profile but also at each time during the pulses (the so called "source profile") offering the possibilities to select for each element optimum time region for intense signals, high signal to noise, and time separation of isobaric interferences which greatly enhances analytical results. (Figure 6)

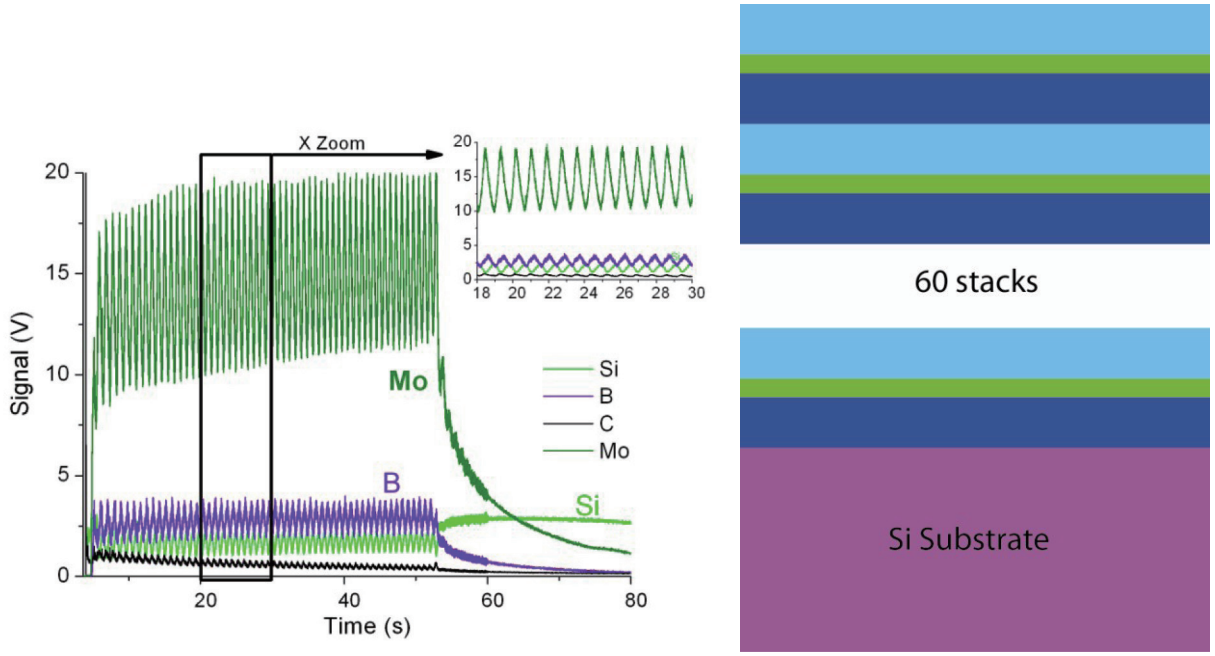

Figure 5

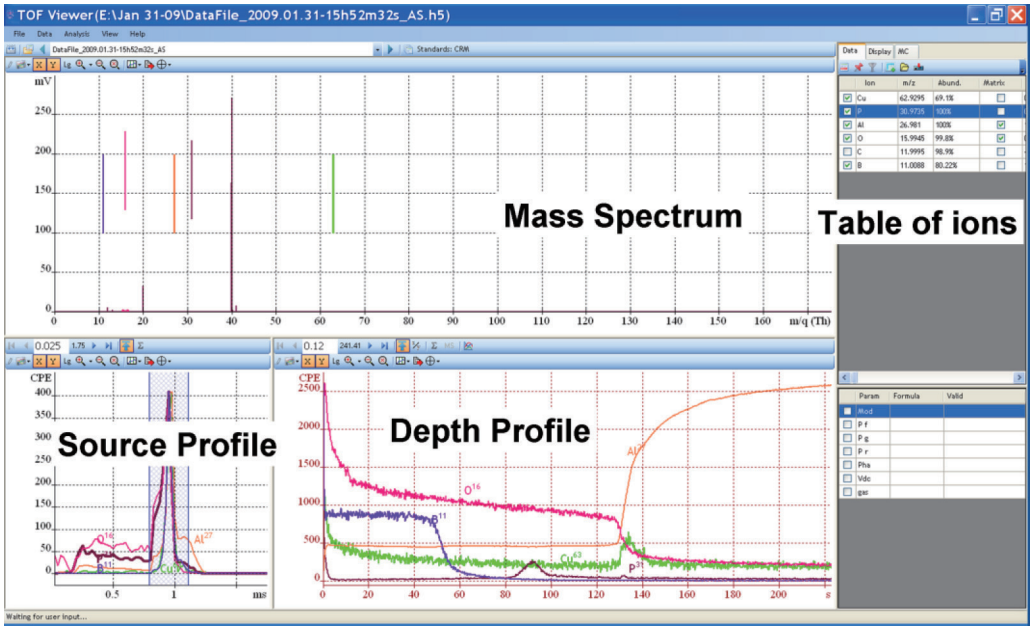

Figure 6

Polymers

Many advanced materials feature polymer layers or substrates.

GD-OES provides elemental depth profile analysis. However the emission spectrum includes some regions featuring emission bands from molecular origin that can be detected. They are often found at the surface (hydroxide OH band at 306 nm, good tracer of humidity[12]) or when polymers are to be measured. They indirectly indicate that the GD plasma may content some information of interest beyond the elemental composition. Simply the nature of the detection (OES) is not suitable to

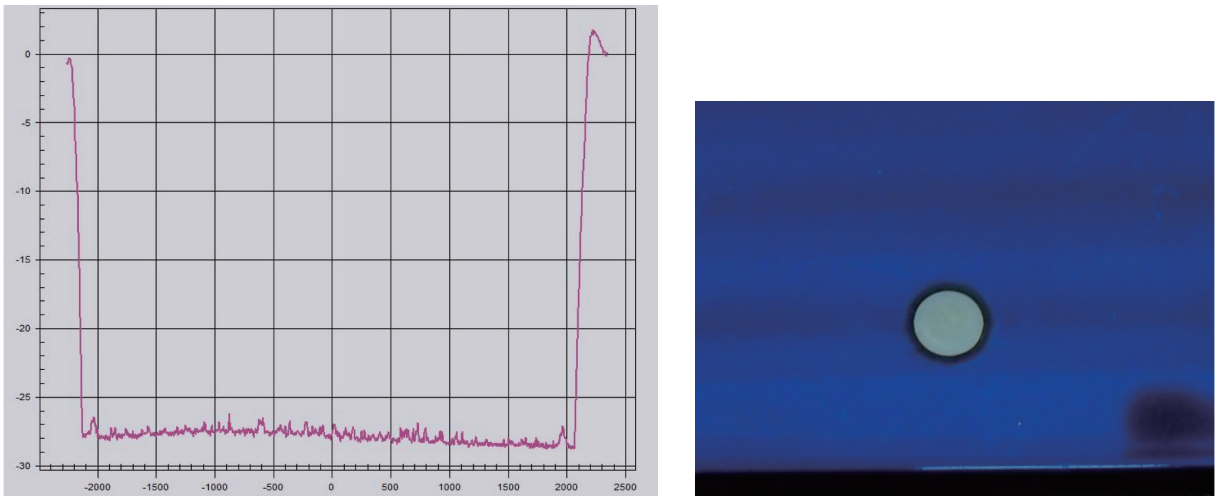

Figure 7 GD crater obtained on a car part covered with an organic layer – over 25 microns were sputtered in 3 minutes

interpret this information correctly and as such, bands do not provide any insight on the chemistry of the molecules as compared to Raman spectroscopy and they are more considered as a nuisance for the measurements of elemental lines in their vicinity.[13]

With PP-TOFMS however, when a polymer is sputtered with soft conditions some significant fragments can be detected if they are ionized in the afterglow region of the pulse. The paper written by Tuccitto *et al* on this topic within EMDPA was awarded the RCM Beynon Prize for best paper published in 2009/2010.[14]
By selecting the adequate source profile region after the RF pulse, so called "molecular depth profile" could be obtained which might allow for instances to distinguish different polymers in an organic solar cell.

However in many cases, polymer layers can be extremely thick (10-100 µm) and as the sputtering of polymers has to be done very slowly, with soft operating conditions in order to minimize unwanted sample degradation this leads to long analysis times and often poor crater shapes affecting the depth resolution and limiting the practical use of the techniques for these applications. To take an example from automotive industry, it is known that painted car bodies for instances have to be sputtered for nearly 2 hours[15] before the metallic coatings below the paint can be reached, where for comparison inorganic multilayers can be profiled in minutes. (Figure 7)

The most recent development made by both French and Japanese HORIBA GD labs (patent 1057722, 2010) completely solves this drawback and has already brought substantial benefits (orders, retrofits and invitations to participate to some R&D projects). This new method allows for ultra fast and uniform sputtering (minutes) of organic layers and is therefore ideal for observing embedded layers with nanometre depth resolution. This new invention has already been successfully applied to painted car bodies, protecting layers on cardboards used in packaging, DVDs etc.

PV Photovoltaics

HJY GD references in PV include world leading companies such as First Solar (US), Nanosolar (US), Solar Frontier (Japan) as well as major research institutes such as ZSW (Germany).
We are coordinating a new project with Ecole Polytechnique (France) for PP-TOFMS. In addition, we have been asked to participate in two national RD and one EU FP7 projects by leading laboratories in the field.
There is therefore a growing interest in the capabilities of GD for PV applications [16], [17] due to the fact that technologies for PV evolve very rapidly with a definitive trend towards thin-films – the driving force of all research is cost reduction for which thin-film technologies are promising.

PV films can be based on Si with various dopants, CdTe (as for First Solar), CIGS (quaternary CuInGaSe2 - as for Solar Frontier and others, Figure 8), or organic films.

Hybrid configurations are also subject to intense research with for instance, layers made of Si nanowires coupled to organic layers or nanoparticles deposited inside the layers. Investigations are also made on alternative substrates to bulk glass to create flexible cells. However, even if materials evolve and change rapidly needs for characterisation and control are now well identified. Thin-film technologies involve a number of operations to be performed and key parameters to be followed carefully (including time, temperature etc – any variation to the optimum conditions inducing major defects in the final product). Therefore rapid characterisation to assess efficiency and provide immediate feedback to the process by measuring depth distribution of major, traces, and contaminations and aspect ratio in thin to thick films (most cells have now a total thickness of 3-5 µm with most layers being less than 1 µm thick) are crucial.

The GD spectrometries have therefore the potential to be recognised as the metrological companion to solar cells elaboration and applied worldwide.

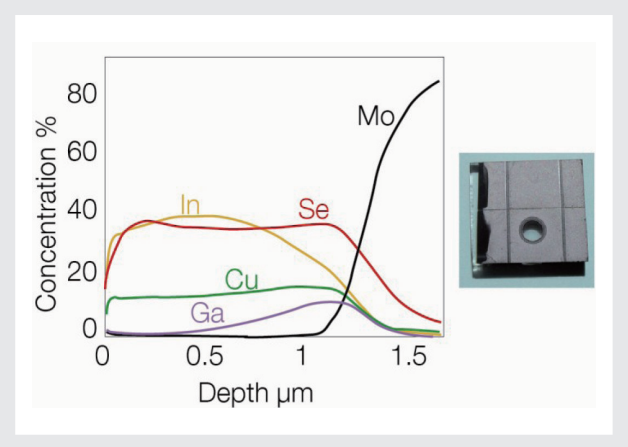

Figure 8

Conclusion

More patents have been awarded, notably some related to the use of magnetic fields in TOFMS and OES (0950848 & WO_2010_092301) and several new papers from on going researches are in preparation.
The 6th international GD day (http://www.horiba.com/fr/scientific/products/atomic-emission-spectroscopy/6th-gd-day/) will be the occasion of a review of new results and applications (e.g. bio compatible or nano-structured materials, PV, hard disks etc) and a special issue of the Journal of Analytical Methods in Chemistry will then be published associated to this GD day. Finally a GD group has just been created through LinkedIn with the ambition to gather GD' friends world wide.

References

[1] www.emdpa.eu
[2] H. Nakamura, et al, "Deuterium behavior at the interface of oxidized metal under high temperature heavy water", *Fusion Eng.* Des. (2012), doi:10.1016/j.fusengdes.2012.02.044
[3] A. Baron Wiechec et al, "18O distributions in porous anodic alumina by plasma profiling time-of-flight mass pectrometry and nuclear reaction analysis", *Surface and Interface Analysis* (2012) doi 10.1002/sia.5032
[4] A. Tempez, et al, "$^{18}O/^{16}O$ isotopic separation in anodic tantala films by glow discharge time-of-flight mass spectrometry", *Surface and Interface Analysis* (2009), 41, 966-973
[5] Y.Saito et al, "Investigation of positive electrodes after cycle testing of high-power Li-ion battery cells IV. An approach to the power fading mechanism by depth profile analysis of electrodes using glow discharge optical emission spectroscopy", *Journal of Power Sources* 174 (2007) 877–882
[6] H. Gab.Song et al, "The effects of LaPO4 coating on the electrochemical properties of Li[Ni0.5Co0.2Mn0.3]O2 cathode material" (2012) doi:10.1016/j.ssi.2011.12.014
[7] L. Lobo et al, "A purged argon pre-chamber for analytical glow discharge—time of flight mass spectrometry applications", *Journal of Analytical Atomic Spectrometry* (2011) 26, 798-803
[8] I. Molchan et al, "The concept of plasma cleaning in glow discharge spectrometry", *J. Anal. At. Spectrom*., (2009), 24, 734–741
[9] K. Shimizu, T. Mitani. "New Horizons of Applied Scanning Electron Microscopy". Springer (2010).
[10] Ph. Belenguer et al, "Pulsed glow discharge for analytical applications", *Spectrochemica Acta* B, 64, (2009), 623-641
[11] P. Le Coustumer, P. Chapon, A. Tempez et al. "Thin and thick films analysis" chapter 41 of Applied Handbook of Mass Spectrometry. Wiley (May 2012)
[12] N. Fukumuro et al, "Confirmation of hydroxide in electroless cobalt alloy films by GDOES", *Transactions of the Institute of Metal Finishing*, 2007, vol 85, N°2
[13] T. Nelis, R. Payling. "Practical Guide to Glow Discharge Optical Emission Spectrometry". RSC 2003
[14] N. Tuccitto et al, "Time-of-flight pulsed radio frequency glow discharge mass spectrometry for molecular depth profiling of polymer-based films", *Rapid Communications in Mass Spectrometry*, 23, 549–556 (2009). *Paper awarded the RCM Beynon Prize for best paper published in 2009/2010*
[15] T. Torok, J Pallosi et al, "Characterizing Coatings of Car Body Sheets by GD OES" chap 11 of High Performance Coatings for Automotive and Aerospace Industries, Nova Science Publishers (2011)
[16] J . Pisonero et al, "Quantitative depth profile analysis of boron implanted silicon by pulsed radiofrequency-Glow Discharge-Time of Flight Mass Spectrometry", Solar Energy Materials and Solar Cells, 94, 1352-1357 (2010).
[17] S.W. Schmitt et al, "Chemical and optical characterisation of atomic layer deposition aluminium doped ZnO films for photovoltaics by glow discharge optical emission spectrometry", J. *Anal. At. Spectrom* DOI: 10.1039/c0ja00158a

Feature Article New Developments in GD Spectrometries for Advanced Materials Characterisation

Patrick CHAPON

GD Product Manager
HORIBA Jobin Yvon SAS

Agnès TEMPEZ

PP-TOFMS Product Manager
HORIBA Jobin Yvon SAS
PhD