

How pulsed operation has revolutionized Glow Discharge Optical Emission Spectrometry

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RF Glow discharge Optical Emission Spectrometry is a recognized analytical method for elemental depth profile analysis of surface and interfaces of solid layered materials. The possibility of easily pulsing the RF source has widened the application domains and enhanced the performances and for all recent applications, whether it is enhanced depth resolution, measurement of fragile materials, plasma cleaning or use of the GD source for SEM observation, pulsed operation is a key asset. In this paper we will illustrate the benefits of pulsed RF operation in Glow Discharge Optical Emission Spectrometry.

Introduction

Among the different techniques used for surface and thin films analysis, the key differentiating factor and main advantages of Glow Discharge Optical Emission Spectrometry (GD-OES) are its fast analysis time, multielement capability and easy to use operation.^[1]

Without the need for ultra-high vacuum, a radio frequency (RF) plasma is used in GD-OES to obtain the elemental depth profiles of conductive, insulating or hybrid materials, from the first atomic layers down to more than 150 μm , allowing the direct determination of major and trace elements, ranging from H (121 nm), O (130 nm) to Li (670 nm) and K (766 nm).

The key-part of a GD-OES instrument is the source, where the GD plasma is created. It may look simple but attention to details is crucial there.

As shown in **Figure 1**, the sample (right) will be placed against the ceramic, pressing the O-ring and assuring the sealing of the plasma chamber. Facing the sample is a tubular anode in which the plasma will be created when the RF- power is applied to the sample. The mechanical tolerances of the ceramic and anode are tight so that the gap between the sample when pressed and the anode is about 150 μm .

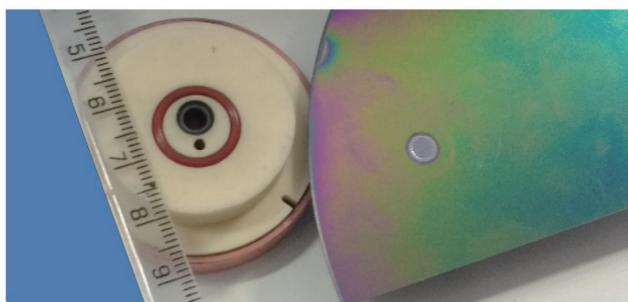


Figure 1 View of the GD source with DIP

The plasma is restricted inside the anode by the use of differential pumping with 2 pumps and so the inner dimensions of the anode define the analysed spot shape. Anode is not necessary circular but can be adapted to the sample shape as shown in **Figure 2**.

Finally when DIP (our differential interferometer) is used,^[2] the path for the 2 laser lights through the anode and ceramic is assured.

Glow Discharge is a gas discharge. Ar is the most commonly used plasma gas however other gasses or gas mixtures can be used.

The tube is not closed, the operation principle is to combine the pumping with a flow of Ar gas directed towards the sample.

When the discharge gas breaks down electrically, electrons and positively charged ions are formed. The latter are accelerated towards the sample causing the sputtering of the material to be analysed.

Then, the sputtered atoms move inside the gas phase environment of the glow discharge where they are excited through collisions with high energy electrons, metastable argon atoms and ions. The de-excitation of these excited species causes the emission of photons which are characteristic of the material.

The spatial separation of erosion (at sample surface) and excitation (in the gas phase, away from the sample surface) is characteristic of GD - at the difference of SIMS for instances where measured ions come directly from the sample surface.

A dynamic process therefore creates during GD operation with continuous sputtering/excitation/removal of sputtered particles. By measuring in real time the light emitted by the de-excitation of the excited atoms, using a fast simultaneous optical spectrometer, it is possible to obtain the elemental depth profiles of the analysed material.



Figure 2 View of non-circular craters obtained on odd shape samples

In short, we can say that the plasma has a double role in GD, firstly it sputters a representative surface of the sample corresponding to the anode inner dimensions, secondly it excites the sputtered atoms. The depth resolution depends on the material (its roughness notably) but also on the crater shape which can be optimized by adjusting the plasma conditions in order to obtain a flat crater bottom.^[1]

For analytical applications, new advantages can be obtained by pulsing the RF discharge. The possible analytical benefits of pulsing the RF GD source were described by Belenguer et al. in a 2009 paper.^[3] Firstly, it provides an additional way of controlling the plasma by choosing the pulse parameters (i.e. pulse length and period) (**Figure 3**).

Secondly, by varying the duty cycle of the applied pulse it is possible to reduce the thermal load on the sample, nearly independently from the instantaneous power which is responsible for the sputtering excitation. Finally using time resolved measurement, analytical benefits can be derived from observations made in the different phases of each pulse: the ignition, the plateau region and the afterglow.^[4]

However it is only in 2011 that we have been able to routinely implement Pulsed RF operation in all our GD spectrometers thanks to a patented development assuring auto-matching of the RF source in both pulsed and nonpulsed modes.^[5]

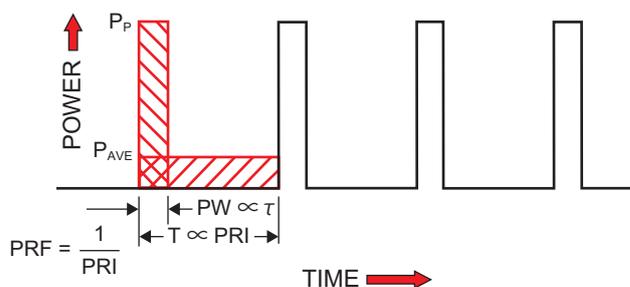


Figure 3 Pulsed operation

Analytical benefits of pulsed RF application

Increase in signal to noise ratio

The benefits in increase the signal-to-noise ratio is particularly evident for the analysis of nanometer-thick multilayer structures. Of course for such materials, short integration times (less than 0.01 s per data point) are required and the use of HDD detection (with its speed and dynamic range) is of course mandatory.

A perfect example is given in the paper from Ber et al.^[6] showing the results of a round robin test by multiple surface techniques on Mo/B₄C/Si multilayers and Mo/Si multilayers, which are of high interest in X-ray lithography.

The analyzed samples are interferential mirrors deposited on Si and made of 60 bi- or tri-layer periodic structures with a 7 nm thickness per period, so a total thickness of 420 nm (**Figure 4**).

The GD-OES results are presented in **Figure 5**. In less than a minute the complete depth profile is obtained. All layers are clearly resolved thanks to the use of the pulsed source and the fast acquisition spectrometer.

Such combination is crucial in order to guarantee the high performance of the technique when small amount of materials are present as thin layers.

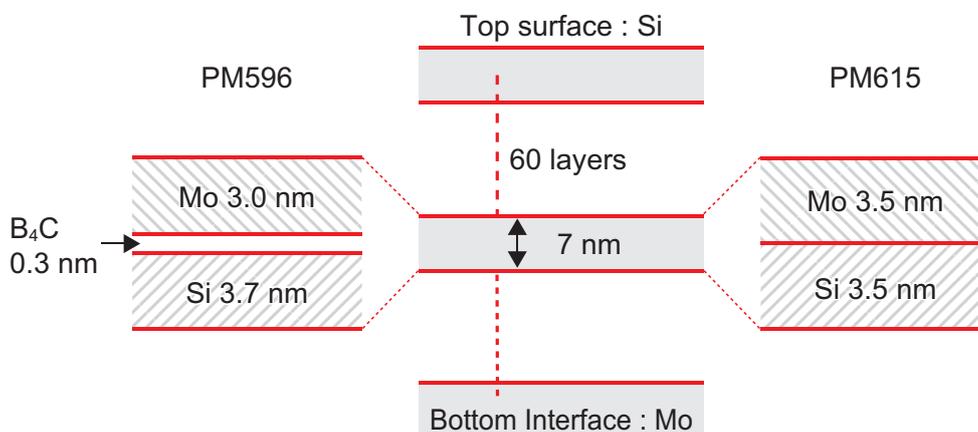


Figure 4 Structure of the multilayered sample (Reproduced with authors' permission from the Ber/Tolstoguzov presentation in the 2012 GD day proceedings.)

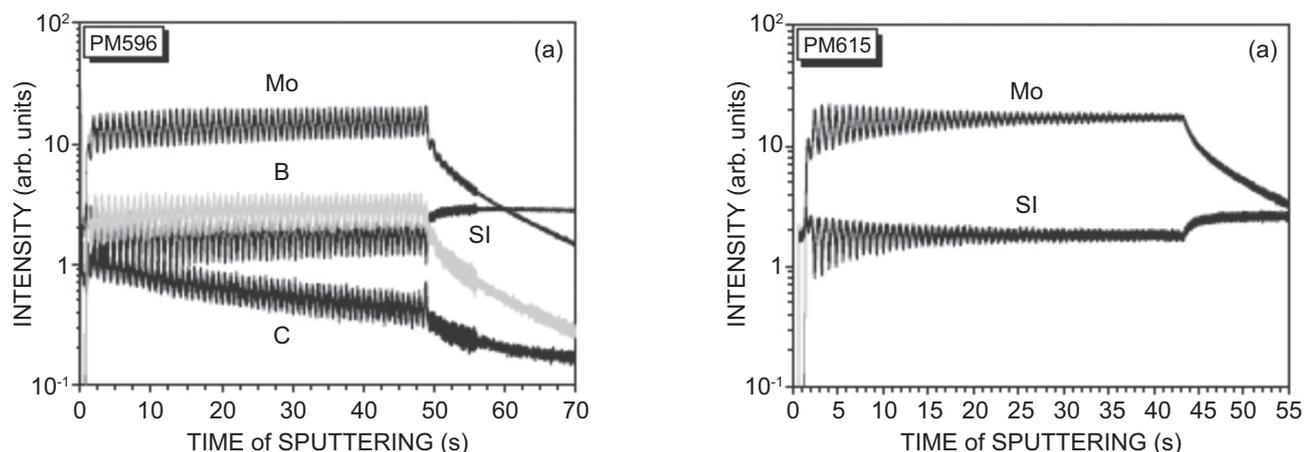


Figure 5 Mo/B₄C/Si (left) and Mo/Si (right) structure (Reproduced with authors' permission from the Ber/Tolstoguzov presentation in the 2012 GD day proceedings.)

With these samples, the depth resolution of GD is comparable to the one obtained in SIMS but of course the speed of measurement is much faster.

Enhanced depth resolution by cleaning effect

The results shown above presents an other interesting feature that has not been discussed in the paper from Ber et al. but which is important to illustrate the benefits of pulsed RF operation. With the combination Mo/Si the depth resolution degrades with the depth due to multiple factors (roughness and induced roughness of the sample, crater shape, atomic mixing etc.) which are common with sputtering techniques^[7] but with the combination Mo/B₄C/Si, the depth resolution is nearly constant - even if the B₄C layers are only 0.3 nm thick each.

There are 2 reasons to this enhancement. One is the preferential sputtering of the GD plasma which is known and used as a benefit for preparing samples for SEM.^[8]

The B₄C layer, even so thin, sputters less easily than Mo or Si. Hence anytime the plasma faces a B₄C interface it first tends to

clean the residues of previous layers that may still be in front of the anode, prior to sputtering the B₄C.

The second is linked to the cleaning effect of the sample surface by the Ar flow when the pulse is off. Even if the source is on and off during pulsed operation the Ar flow is kept constant. During the time off, the combination of the flow directed towards the sample and the pumping allows to remove sputtered materials that may have redeposited on the surface.

Modulation of the power

The operation in pulsed mode allows the independent choosing of the instantaneous and average powers. This is of particular interest for thermo-sensitive materials, e.g. glass, polymers etc.

While analysing these samples one could be lead to the conclusion that the decrease of the instantaneous power would limit the damage sustained by the material during the analysis. However, as the plasma has the double role of sputtering and excitation, the lower is the sputtering rate, the lower will be the number of atoms excited inside the plasma phase. On the other

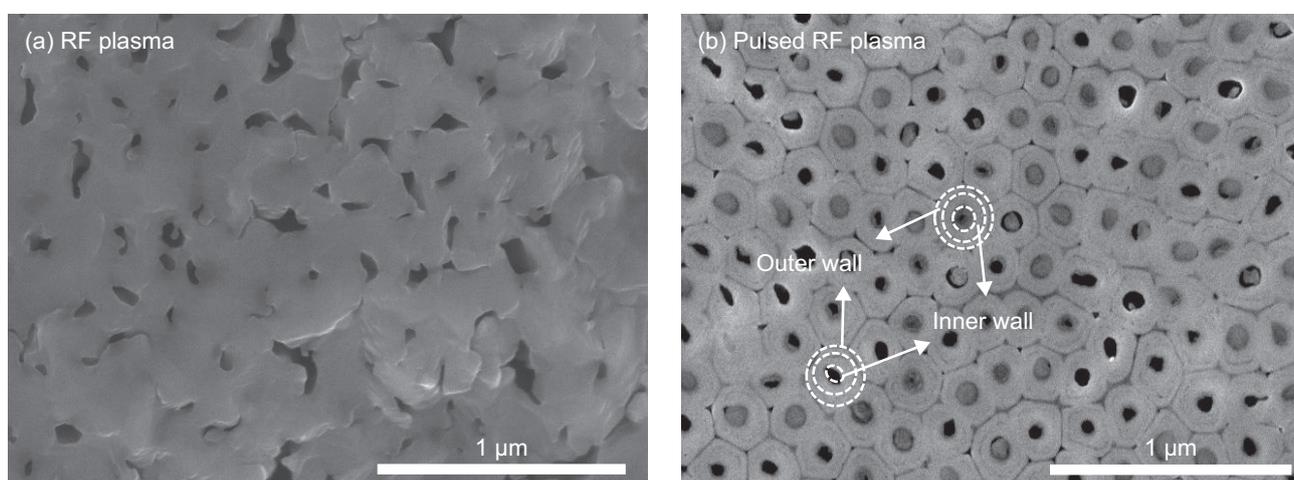


Figure 6 SEM top views of the half-length sputtered TiO₂ nanotubes with (a) standard RF plasma and (b) pulsed RF plasma. (Reproduced with authors' permission from the Mohajernia presentation in the 2018 Surface Fest proceedings.)

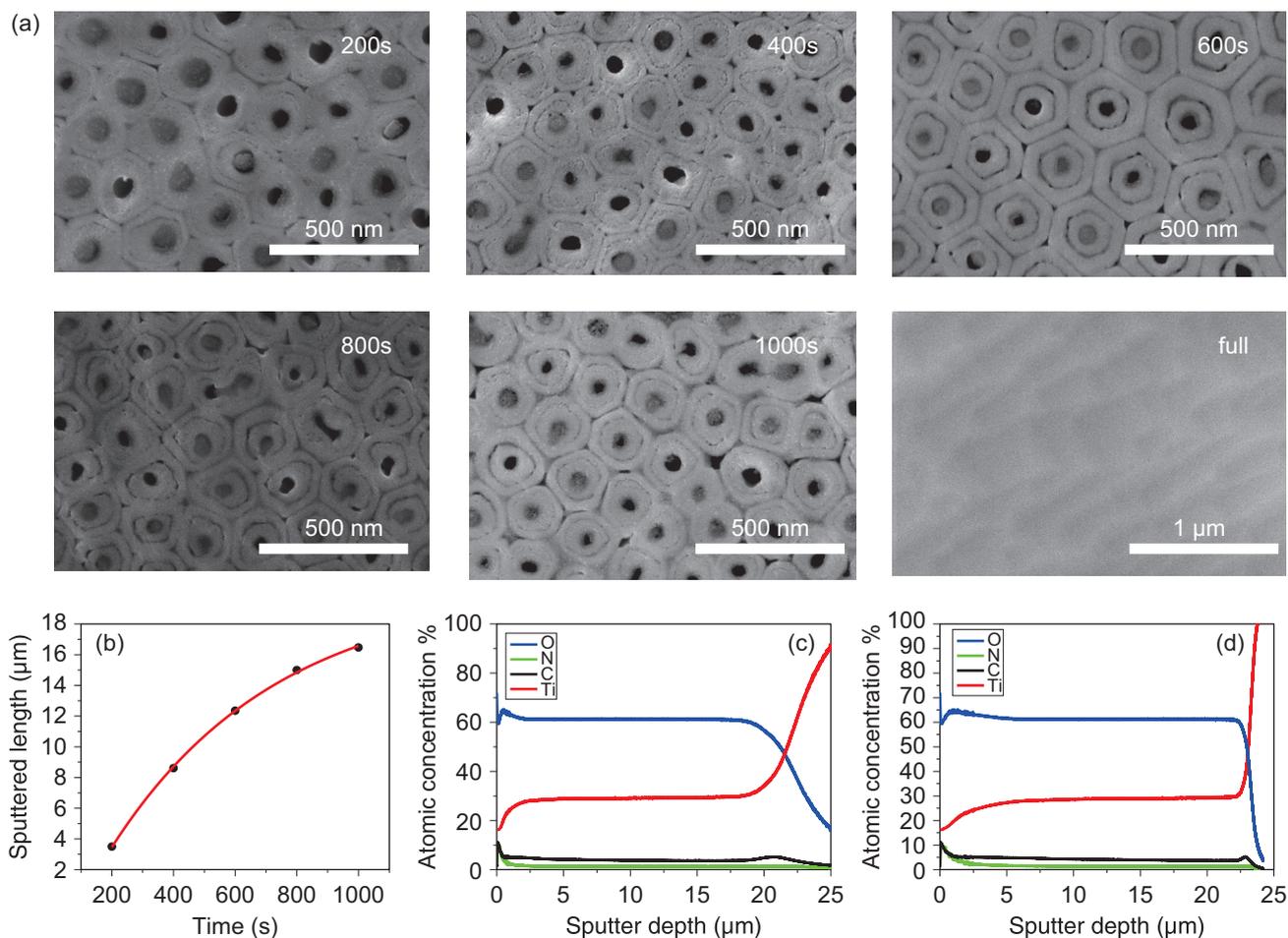


Figure 7 SEM views of the erosion at various depths and full quantitative depth profile (Reproduced with authors' permission from the Mohajernia presentation in the 2018 Surface Fest proceedings.)

hand by adjusting the duty cycle of the pulse it is possible to keep high instantaneous power and moderated average one.

A perfect illustration has been presented by Mohajernia at the 2018 Surface Fest and is described in a recent paper published^[9] for the analysis of 1D self-aligned TiO₂ nanotubes of nearly 22 µm length.

These structures are currently investigated for a variety of applications, ranging from electrochemical/photoelectrochemical to biomedical devices.

The elemental depth profiling using typical ion beam sputtering techniques (such as XPS) is generally limited to the first few hundreds of nanometers and in addition, Mohajernia shows that the depth profiling achieved using Ar⁺ during the XPS analysis leads to a considerable preferential non-homogeneous sputtering which increases in severity for extended sputtering.

On the other hand, with pulsed RF GDOES, the plasma parameters allow to obtain a reliable sputtering of the entire nanotubular structures. Therefore for such samples when

compared to the most standard surface technique, pulsed RF GDOES not only offers much faster analysis times, but also a gentler sputtering which allows avoiding artifacts.

Figure 6 presents a SEM view of the bottom of the GD crater and shows the different morphology obtained when using standard RF-GDOES (**Figure 6 (a)**) and pulsed RF-GDOES (**Figure 6 (b)**).

Thanks to the pulsed operation, no sputtering damage is induced to the tubular structure and as shown in the SEM imaging not only the individual tubes can be clearly observed, but also the presence of the inner and outer walls known to vary in thickness with the depth is confirmed and the full depth profiles are obtained as shown **Figure 7**.

Pulsed operation and DIP

DIP (Differential Interferometry Profiling) is a patented set up recently introduced in GD [2, 10]. It allows to directly measure the erosion rate and the crater depth. The main principle is the measurement of the variation of the distance between the bottom of the GD crater and a reference point at the surface of the

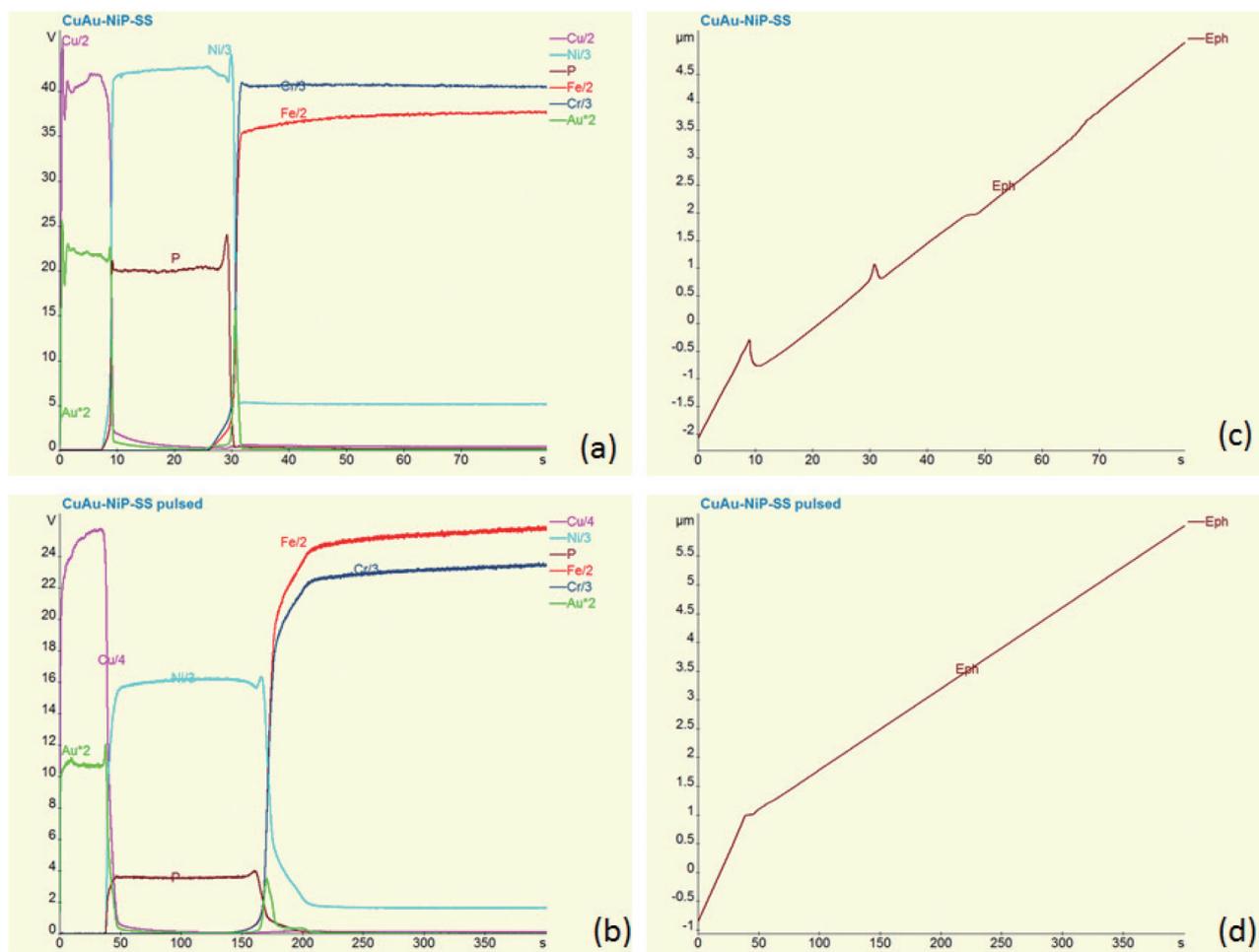


Figure 8 Analysis of an CuAu electroplated sample in (a) standard RF mode and (b) in pulsed RF mode. The depth vs sputtering time curves, obtained with DiP, are also presented.

sample. A red laser-diode ($\lambda = 635 \pm 5$ nm, $P \sim 150$ μ W, class 1 and therefore completely eye-safe) is split into two beams of orthogonal polarizations. One of the beams is focused onto the reference zone at the sample surface, the other beam is focused in the centre of the crater.

For non-transparent samples (bulk or layered), the crater depth D is directly linked to the phase and while for transparent samples the measurement of the reflectivity allows to obtain the optical depth by calculating the number of periods of the signal and to get the crater depth knowing the refractive index of the transparent layer.

Currently DIP has been efficiently implemented for both 4 mm and 2 mm diameter anodes.

In all cases, the quality of the interferometric signal (the peak-to-peak amplitude of the interference fringes) is dependent on the quality of the reflecting surfaces. Pulsed operation there can be of crucial interest even for rough industrial materials due to the better smoothing of the transition interfaces obtained by pulsed sputtering. An example is presented in **Figure 8**.

Pulsed operation and UFS

UFS is a patented mode of operation of the GD source where the Ar plasma gas is replaced by the combination of Ar with O_2 beneficial notably in the case of sputtering of organic and C based materials.^[11]

While Ar is assuring the sputtering, the addition of O makes the plasma reactive - and in some cases the erosion rate is significantly enhanced, leading not only to faster analysis but also to much better signal/noise ratios. However the studied materials being fragile, pulsed operation is mandatory to benefit from the UFS.

An illustration on Perovskite PV materials has been given by Bonnassieux at the 2018 Surface Fest and is presented in the paper of Lee et al.^[12] The structure of the material is complex - ITO glass substrate, covered with hybrid organic/inorganic layers (**Figure 9**).

For these materials the combination of pulsed operation and UFS has permitted for the first time to experimentally reveal the diffusion under bias voltage of some elements within the Perovskite layer.

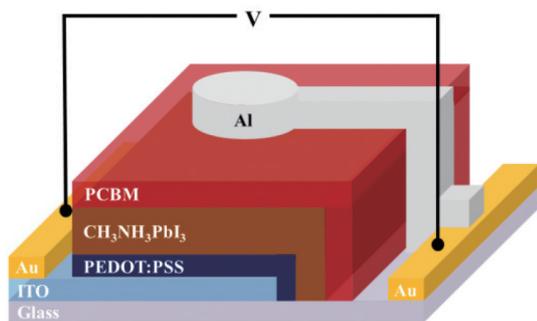


Figure 9 Structure of the Perovskite cell

Conclusion

The implementation of pulsed RF operation has opened new applications for RF GDOES making it more than ever a very powerful tool for analytical scientists and practitioners who elaborate and control layered materials.

References

- [1] T. Nelis & R. Payling, Practical Guide to Glow Discharge Optical Emission Spectrometry, RSC, 2003
- [2] S. Gaiaschi, S. Richard, P. Chapon and O. Acher, J. Anal. At. Spectrom., 2017,32, 1798-1804
- [3] P. Belenguer, M. Ganciu, P. Guillot, and T. Nelis, Spectrochimica Acta Part B, 64 (2009) 623-641
- [4] P. Le Coustumer, P. Chapon et al., chap. Thin and Thick films in Applied Handbook of Mass Spectrometry, M. Lee ed, Wiley - 2011.
- [5] HORIBA patent, Pulsed operation with automatching (US2013/200257)
- [6] B. Ber, P. Bábó, P.N. Brunkov, P. Chapon, M.N. Drozdov, R. Duda, D. Kazantsev, V.N. Polkovnikov, P. Yunin, A. Tolstogousov, Thin Solid Films 540 (2013) 96-105
- [7] S. Hofmann, S.Y. Lian, Y.S. Han, Y. Liu, J.Y. Wang, Applied Surface Science 455 (2018) 1045-1056
- [8] K. Shimizu, T. Mitani, New Horizon of Applied Scanning Electron Microscopy (2010)
- [9] S. Mohajernia, A. Mazare, I. Hwang, S. Gaiaschi, P. Chapon, H. Hildebrand, P. Schmuki, Applied Surface Science, 442 (2018) 412-416
- [10] HORIBA patent US2017/0045457
- [11] HORIBA patent; EP2434275
- [12] Heejae Lee, Sofia Gaiaschi, Patrick Chapon, Arthur Marronnier, Heeryung Lee, Jean-Charles Vanel, Denis Tondelier, Jean-Eric Bourée, Yvan Bonnassieux, and Bernard Geffroy. ACS Energy Lett. 2017, 2, 943-949



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