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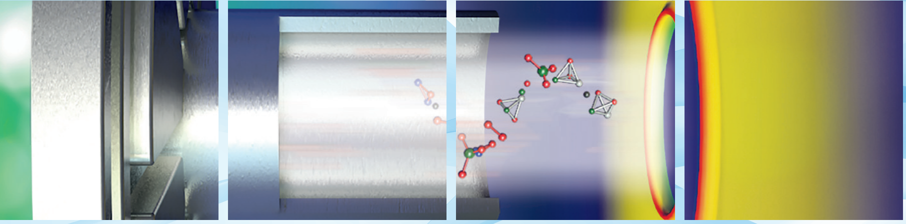
Scientific

Glow Discharge
Optical Emission Spectrometry



Focus on: Renewable Energies

From Bulk Analysis of Metals to Depth Profiling of Advanced Materials

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Introduction

First developed in the late 60's – 80's, Glow Discharge Optical Emission Spectroscopy was transformed by the developments made over the past several years. With the capability to characterize conductive and non-conductive samples, it was already able to address a large variety of samples. The most recent developments introduced in a previous paper [1] – a Pulsed Radio Frequency generator, Ultrafast Sputtering, Differential Interferometry – along with special accessories – lithium bell, indium kit – make it an even more versatile technique. Glow Discharge Optical Emission Spectrometry is now able to address multiple applications, from well-known metallurgical samples – aluminum, coated steel, to the most advanced materials, including photovoltaic materials – CIGS, perovskites – or lithium battery electrodes. Some research groups are also using it as a complementary technique to X-ray Photoelectron Spectroscopy (XPS) or Scanning Electron Microscopy (SEM).

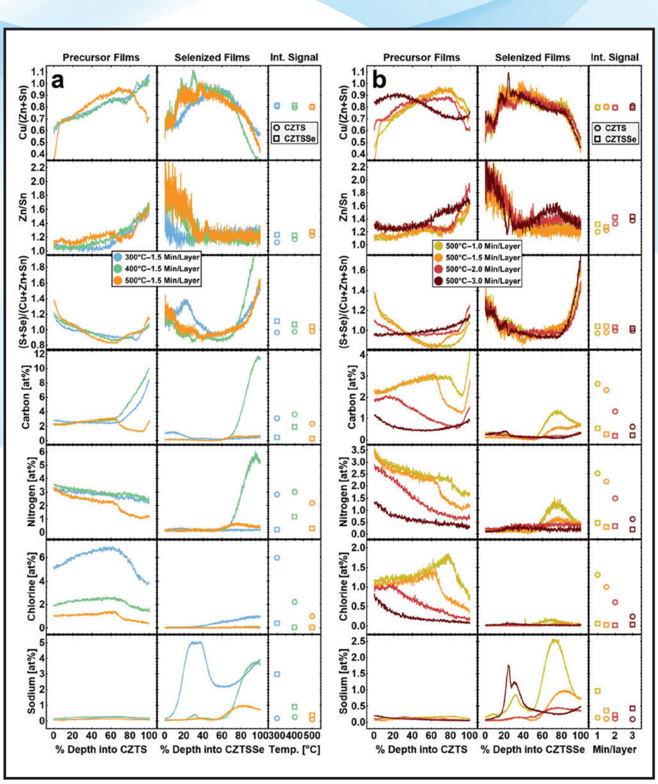


Figure 1: Depth profiles on precursor and selenized films for various annealing conditions. Reprinted with permission from Clark JA, Uhl AR, Martin TR, Hillhouse HW, Evolution of morphology and composition during annealing and selenization in solution-processed $Cu_2ZnSn(S,Se)_4$, Chem. Mater. 2017, 29, 9328–9339. Copyright 2017 American Chemical Society.

Photovoltaic

Glow Discharge Optical Emission Spectroscopy and its ability to characterize coatings and layers, and perform elemental analysis, makes it an almost obvious tool for the study of thin films photovoltaic materials that involve multiple layers and specific elements: Cd, Te, Zn, S, In, Se, to name a few.

The most recent developments also make it possible to use Glow Discharge for the characterization and the study of CdS/CdTe, CZTS, CIGS and Perovskites.

Study of CZTS cells

Clark et al. from Washington University, used Glow Discharge to perform depth profiles on CZTS cells precursors and selenized films [2]. The profiles of the various elements and their ratios help find the best annealing conditions and thus optimize the process (Figure 1).

In the same paper, they also presented results on the effect of lithium doping on sodium transport. From these results, the mechanism of sodium migration is explained as lithium displacing sodium in the soda lime glass; this displaced sodium can then diffuse in the bulk of the precursor film (Figure 2). Films doped with lithium show significant sodium enrichment of precursor films (Figure 2a). Lithium from precursor films diffuses into the soda lime glass and displaces sodium (Figure 2b). Along with results from other techniques that showed that sodium has increased grain growth after selenization, it shows that the sodium likely contributes to the formation of dense absorber layers.

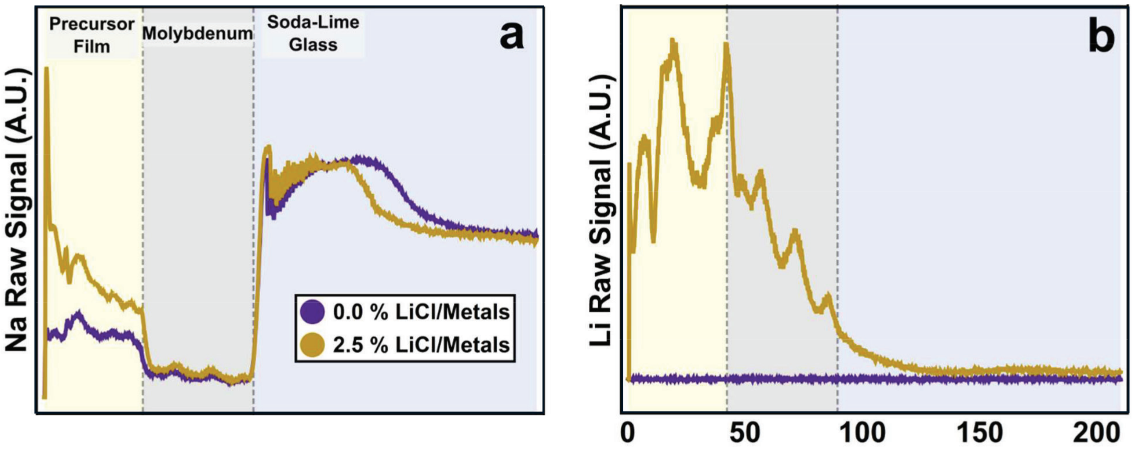


Figure 2: GD-OES depth profiles of precursor films with and without LiCl doping. (Reprinted with permission from Clark JA, Uhl AR, Martin TR, Hillhouse HW, Evolution of morphology and composition during annealing and selenization in solution-processed $Cu_2ZnSn(S,Se)_4$, Chem. Mater. 2017, 29, 9328–9339. Copyright 2017 American Chemical Society.)

Sodium diffusion at Zn(S,O)/CIGS interface

N. Naghavi used Glow Discharge for the study of the diffusion of sodium in the Zn(S,O) layer, which is known to lead to meta-stability problems [3]. Results presented during the French GD users' meeting in 2016 show diffusion of sodium during the manufacturing process. Figure 3 shows the depth profile of a CIGS solar cell exhibiting a low amount of sodium at the interface, whereas Figure 4 displays the GD-OES results obtained on a different CIGS solar cell showing a significantly higher amount of sodium.

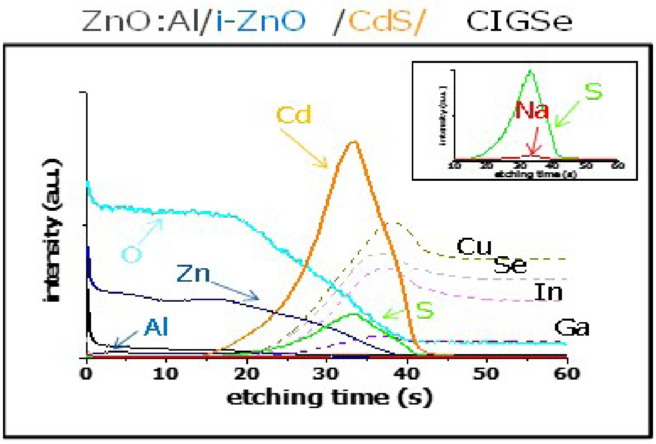


Figure 3: Depth profiles of CIGS solar cell exhibiting low amount of Sodium. Reproduced with authors' permission from Naghavi's presentation in the 2016 GD Users Meeting

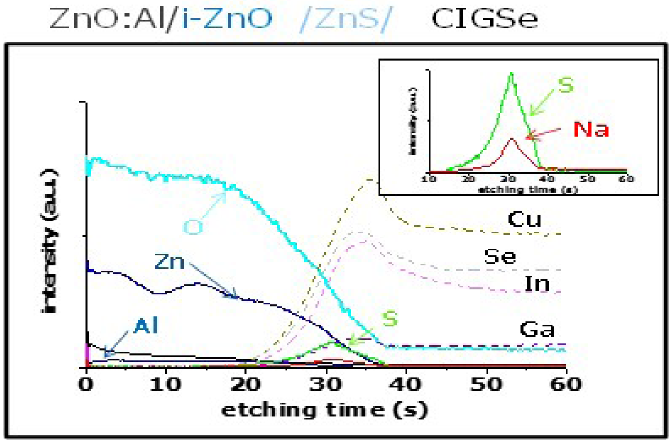


Figure 4: Depth profiles of CIGS solar cell exhibiting high amount of Sodium. Reproduced with authors' permission from Naghavi's presentation in the 2016 GD Users' Meeting

This study of sodium diffusion is possible only thanks to the pulsed source. Thanks to the pulsed mode, the thermal load in the sample during analysis is little, and there is no diffusion of light elements such as sodium induced by the analysis itself. Without the pulsed mode, diffusion of light elements will occur during analysis and it will not be possible to distinguish if it is due to the manufacturing process or to the characterization.

Thickness measurements on CIGS/Mo/Glass

DiP [1] allows layer thickness measurement on CIGS solar cells along with the elemental depth profile. CIGS samples are challenging due to their roughness, partial transparency and surface oxidation.

Results presented during the “GD Day 2016,” show depth profiles obtained on CIGS/Mo/Glass samples [4]. The samples were etched using a HBr:Br_2 solution as described in the literature [5] for 2 and 5 minutes before using GD-OES for depth profile analysis, along with layer thickness measurements (Figures 5, 6 and 7).

To validate the accuracy of the depth measurements, a profilometer was used to measure the depth of each sample, and values were compared with the data obtained using DiP. Values displayed in Table 1 show excellent agreement between the profilometer and DiP, confirming the capability of DiP to provide accurate measurements. Differences are due to roughness, as DIP typically measures a 50 µm zone over the 4 mm crater area.
Table 1: Comparison of depth measured by DiP and with a profilometer

Etching Time	Sample	DiP µm	Profilometer µm
2 minutes	A	2.30	2.15
	B	2.05	2.11
	C	2.35	2.10
5 minutes	A	1.80	1.55
	B	1.81	1.71
	C	1.70	1.61

Table 1: Comparison of depth measured by DiP and with a profilometer

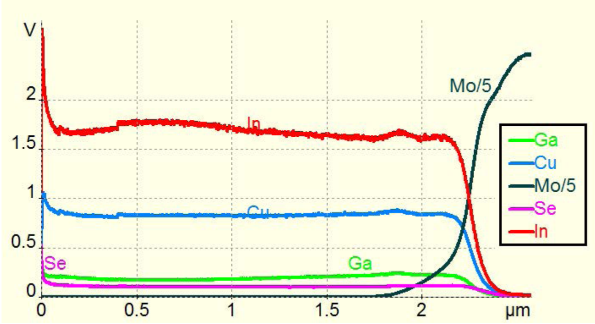


Figure 5: Elemental depth profile for CIGS/Mo/Glass solar cell before etching (RMS 277 nm). Reproduced with authors' permission from GD Day 2016 proceedings [4]

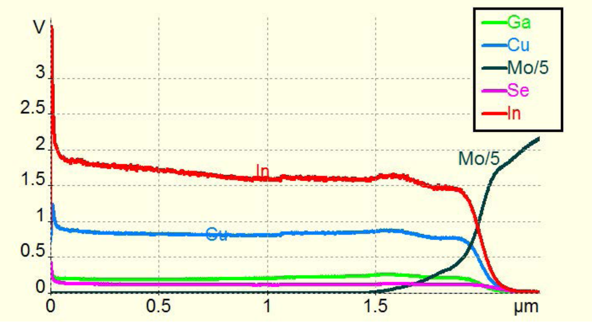


Figure 6: Elemental depth profile for CIGS/Mo/Glass solar cell after 2 minutes etching (RMS 65 nm). Reproduced with authors’ permission from GD Day 2016 proceedings [4]

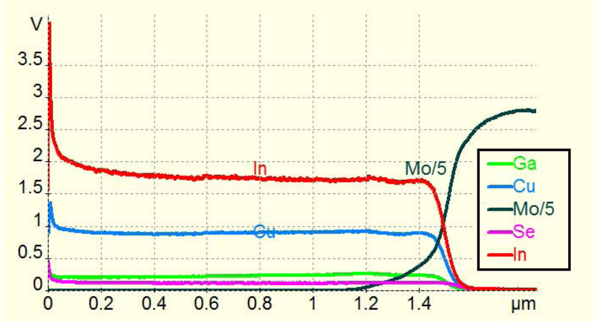


Figure 7: Elemental depth profile for CIGS/Mo/Glass solar cell after 2 minutes etching (RMS 37 nm). Reproduced with authors’ permission from GD Day 2016 proceedings [4]

Ionic migration in perovskites

There is continuous growing interest of perovskites for solar cells, and many scientific papers published over the past years are on this type of material. Perovskites are hybrid organic-inorganic material involved in a stack of layers, typically $CH_3NH_3PbI_3$/TiO_2/FTO. Thanks to the radio frequency generator and UFS mode [1], the characterization of perovskite-based solar cells with GD-OES is possible.

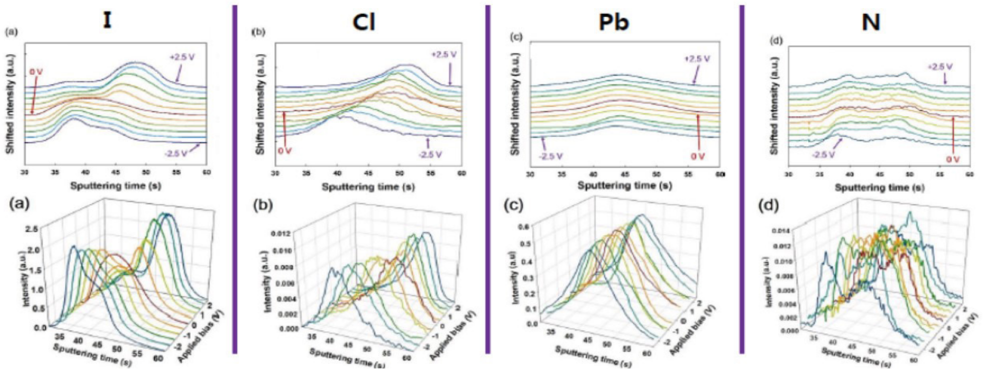


Figure 8: GD-OES depth profiles for I, Cl, Pb and N with applied voltage bias. Profiles displayed on top are shifted for better visibility. Reproduced with authors’ permission from Surface Fest 2018 proceedings (Hybrid perovskite solar cells – Some problem analysis presented by Y. Bonnassieux)

Due to its ability to perform elemental analysis and the possibility to have in-operando measurements, Lee et al. used the GD-Profiler 2 for halide migration studies [6]. Depth profiling under various voltage biases applied was performed and signals for iodine, chlorine, lead and nitrogen were studied (Figure 8).
The study shows that there is no migration for lead and nitrogen but that iodine and chlorine migrate toward the PCBM under negative bias and toward the PEDOT:PSS under positive bias.

Results obtained helped to calculate the average length of ionic migration for both positive and negative bias (Table 2).

	Negative bias	Positive bias
Iodine	120 nm	130 nm
Chlorine	120 nm	30 nm

Table 2: Average length of ionic migration

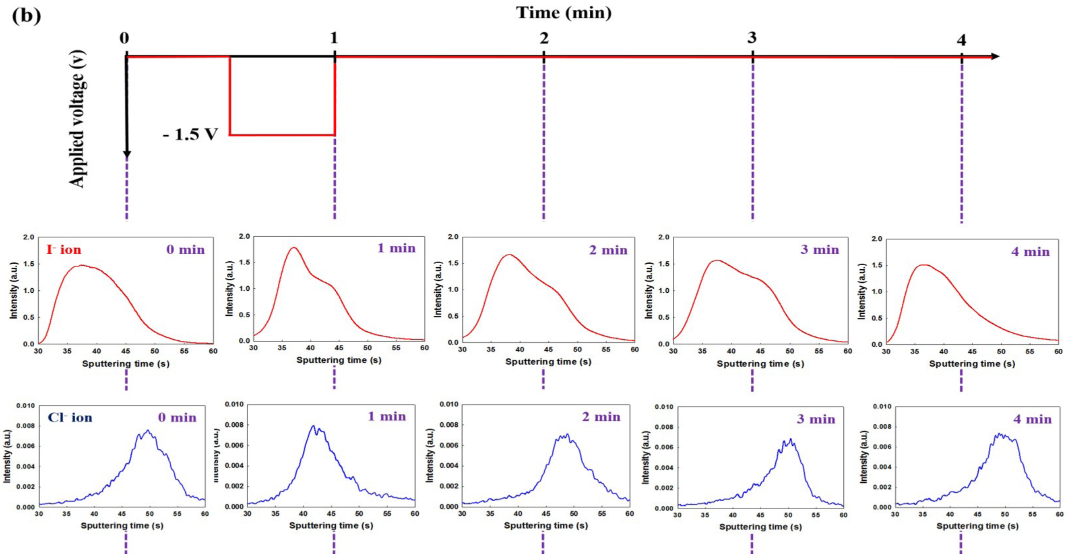


Figure 9: GD-OES profiles for iodine and chlorine under voltage bias applied and stopped. Reversibility of the migration is observed for both ions. Reproduced with authors' permission from Surface Fest 2018 proceedings (Hybrid perovskite solar cells – Some problem analysis presented by Y. Bonnassieux

Lithium battery

Lithium battery electrodes are usually fragile samples, flexible substrates and air sensitive. Therefore, their characterization requires specific features in order to get relevant results.

Characterization of lithium batteries requires the pulsed radio frequency source to reduce the average power and heat dissipation in the sample that may cause damages. Sputtering the graphite layer requires the UFS mode, so appropriate sensitivity is provided, and to maintain a short analysis time. Sputtering the layers of the graphite electrode down to the foil – about 70 µm – takes typically about 10 minutes. Without the UFS mode, only 10 µm are sputtered after 60 minutes, and sensitivity is very limited (Figure 10). Thanks to the UFS, there is no need to peel the polymer layer of the separator from the graphite to perform analysis.

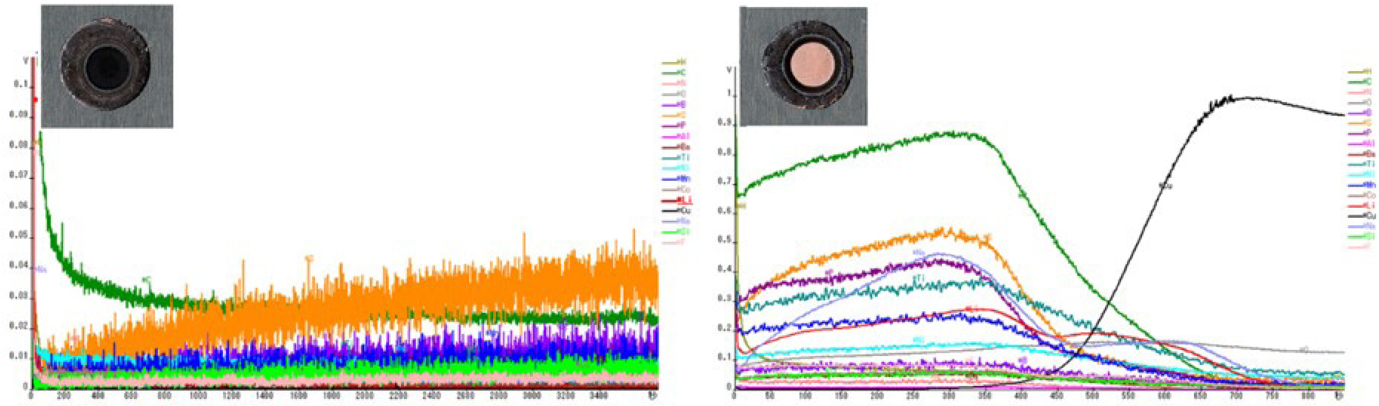


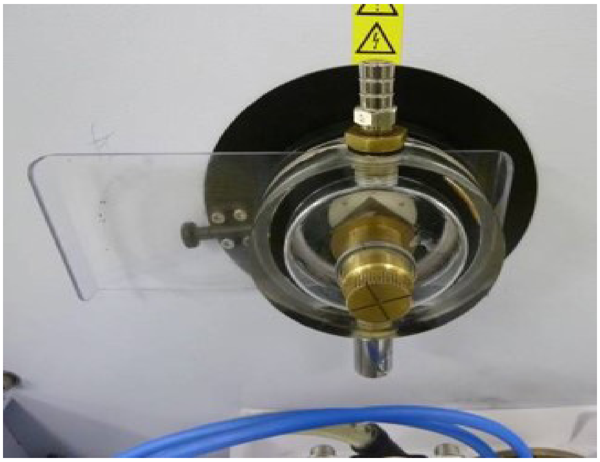
Figure 10: Depth profile of a negative electrode without UFS and picture of resulting crater after 60 minutes sputtering (left), and depth profile of the same negative electrode with UFS and picture of resulting crater showing the foil after 10 minutes sputtering (right).

To handle air sensitive samples, the lithium bell is designed to avoid exposure to air. The sample handled in a controlled atmosphere glove box can be loaded into the lithium bell (Figure 11). The lithium mounts on the anode and connects to the argon flush to protect the sample from air during the analysis. Thus, the GD-Profiler 2 provides results that are more relevant, as there is no modification of the surface of the sample due to reaction with oxygen (air).

Evaluation of electrodes after charge/discharge cycles

Depth profiles on both an anode and $LiCoO_2$ cathode are done after several charge/discharge cycles. The whole depth of analysis is about 120 µm – sputtered in 10 minutes. Even with a high sputtering rate and deep analysis, the GD-Profiler 2 is able to provide information on the extreme surface of the electrode, providing a lot of information for charge/discharge cycles studies.

The depth profiles obtained show a presence of lithium at the surface of the anode, for a depth less than 20 nm, suggesting that some lithium migrated from the Solid Electrolyte Interphase (SEI), and reacted with the surface of the electrode. The fluorine detected on the surface of the cathode can correspond to the binder component, as the concentration is higher on the surface than in the depth (Figure 12).



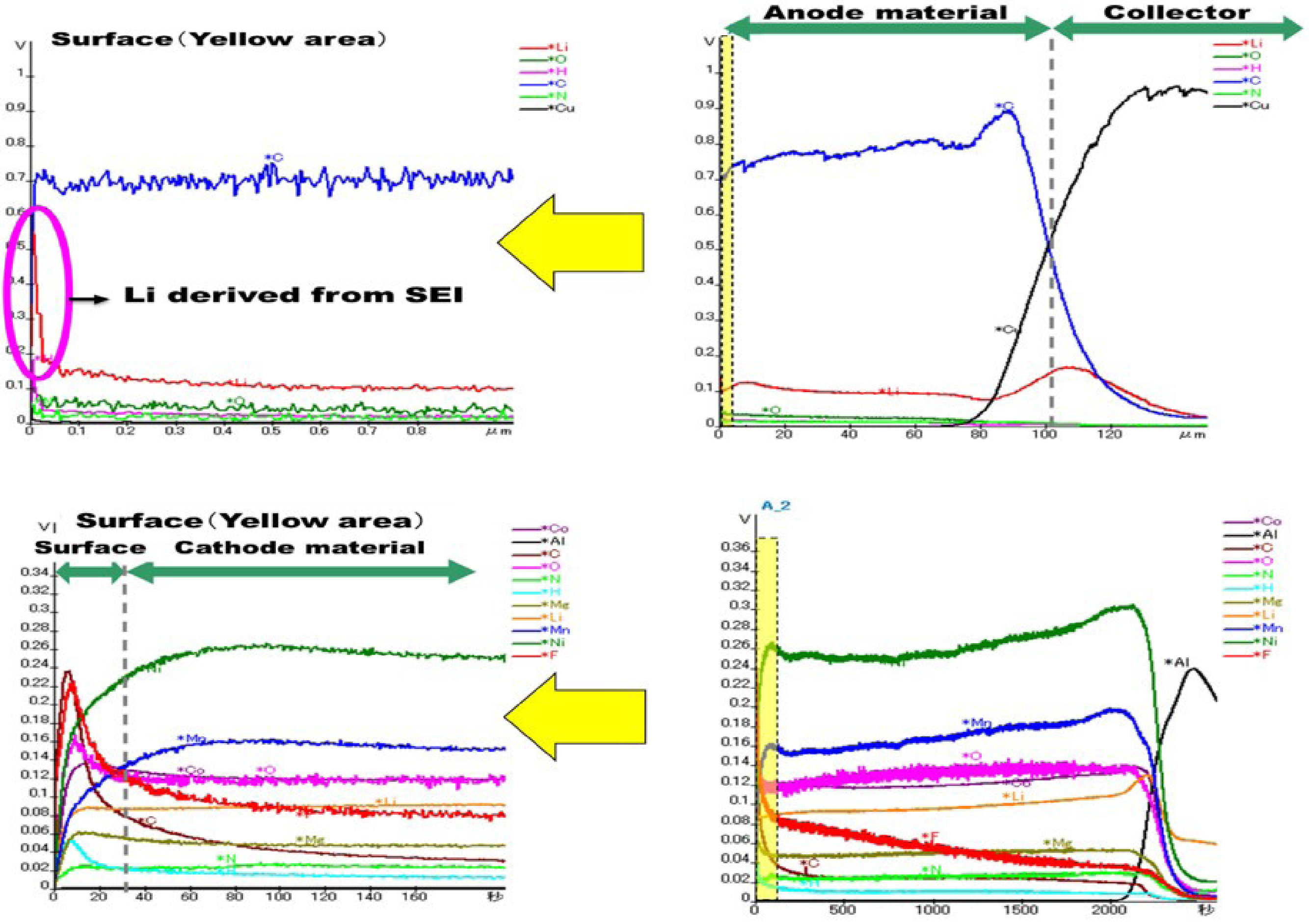


Figure 12: Depth profiles on anode (top) and $LiCoO_2$ cathode (bottom) - Full depth profile shown (right) as well as zoom on the surface defined by the yellow area (left)

Evaluation of damaged electrodes

The GD-Profiler 2 is also a tool used for battery failure analysis and root cause investigation. It can help investigate cathodes showing average and heavy damage level – causing color change on the surface and performance decrease – by comparison with a non-damaged cathode.

The comparison of depth profiles between the non-damaged and the damaged electrodes can help identify the source of degradation. As an example, if barium and aluminum increase at the surface, they may indicate damage due to the anode collector reacting with the active material of the cathode.

TiO_2 nanotubes

TiO_2 nanotubes are widely used in photo-catalysis and for dye-sensitized solar cells. This is one of the most studied compounds in materials science, and there is an interest to perform depth profiles on the synthetized nanotubes. A recent study from Mohjernia, et al. from the University of Erlangen-Nuremberg shows the interest of Glow Discharge for this application [8].

Depth profiling capable techniques – XPS, AES and TOF-SIMS – were investigated for the characterization of 1D self-aligned TiO_2 nanotubes of 25 µm length. They failed to measure layers greater than 1 µm and led to very long analysis time. SEM analysis on cross-sections involved lengthy sample preparation and led to artifacts introduced by the sample preparation.

Investigation of Glow Discharge as a possible technique for this characterization showed very good performance, fast analysis time and gentle sputtering for artifact free characterization. Pulsed radio frequency plasma is required to avoid damage of the tubular structure (Figure 13). The SEM image obtained after depth profiling using XPS shows a considerable preferential non-homogeneous sputtering which increases in severity for extended sputtering (Figure 14).

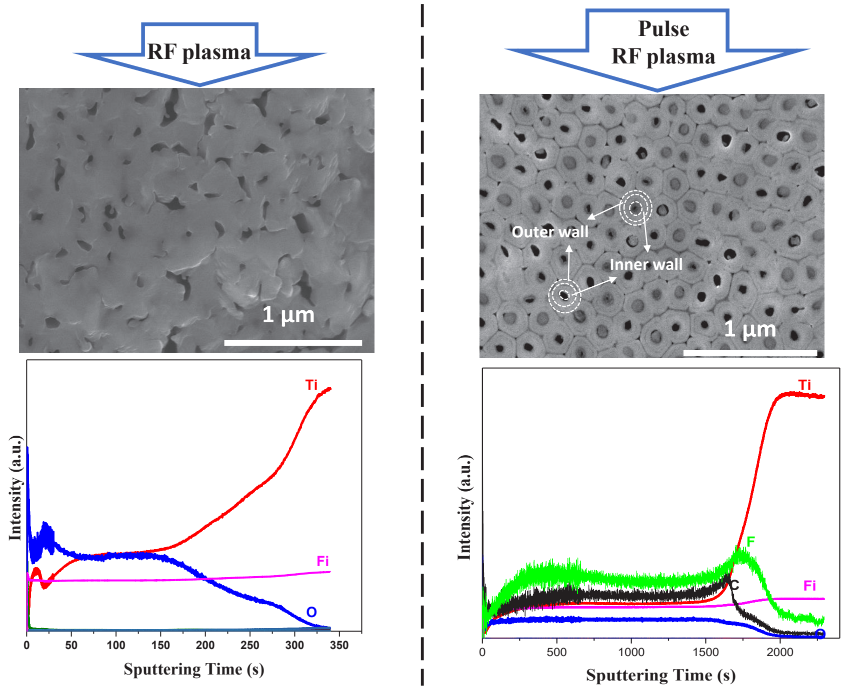


Figure 13: Depth profiling and SEM images with standard radio frequency plasma (left) and pulsed radio frequency plasma (right). Reproduced with authors' permission from Surface Fest 2018 proceedings (Depth elemental characterization of 1D self-aligned TiO_2 nanotubes, presented by S. Mohajernia)

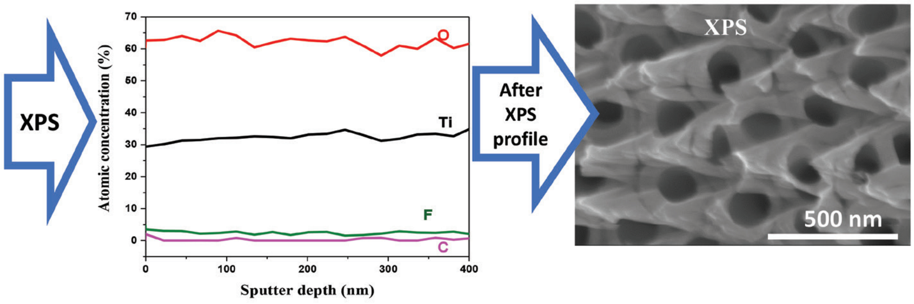


Figure 14: XPS depth profiles up to 400 nm and corresponding SEM image showing non-homogeneous sputtering and damaged surface. Reproduced with authors' permission from Surface Fest 2018 proceedings (Depth elemental characterization of 1D self-aligned TiO_2 nanotubes, presented by S. Mohajernia).

The tubular structure study using SEM images at different depths after GD-OES sputtering confirms that there is no damage induced by the sputtering process and that the structure is preserved (Figure 15).

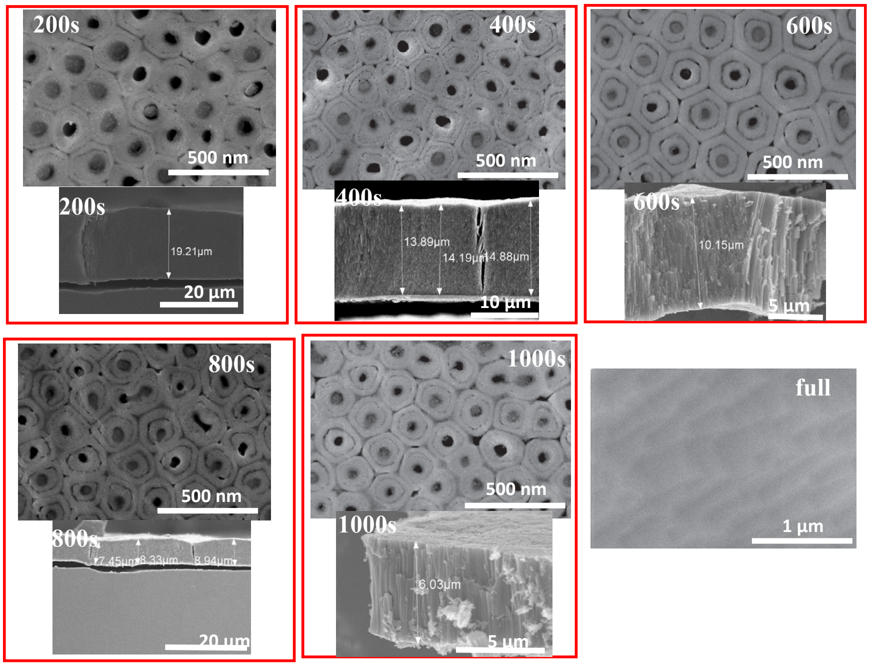


Figure 15: SEM images of the TiO_2 nanotubes at different depths after sputtering with GD-OES. Reproduced with authors' permission from Surface Fest 2018 proceedings (Depth elemental characterization of 1D self-aligned TiO_2 nanotubes, presented by S. Mohajernia).

Conclusion

All recent developments made by HORIBA Scientific opened a brand new field of application for the Glow Discharge technique. None of the applications mentioned previously are possible without the pulsed radio frequency generator, the UFS and DiP. Glow Discharge is now a very valuable tool for the research on renewable energies and more and more scientific papers published are including data from HORIBA GD-Profiler 2. The unique features of the GD-Profiler 2 make it a very complementary instrument to XPS, bringing the benefits of the ability to measure hydrogen, its fast sputtering, its ability to perform depth profiles up to 150 µm in minutes, and the possibility to sputter inorganic and organic layers. In some cases, the GD-Profiler 2 provides superior performance to XPS or other surface techniques due to the quality of the sputtering that does not induce damage on the structure of the sample or diffusion of elements.

Bibliography

[1] From Bulk Analysis of Metals to Depth Profiling of Advanced Materials: A Story of Glow Discharge Optical Emission Spectrometry, Part I – Instrumentation
[2] Clark JA, Uhl AR, Martin TR, Hillhouse HW, Evolution of morphology and composition during annealing and selenization in solution-processed $Cu_2ZnSn(S,Se)_4$, Chem. Mater. 2017, 29, 9328–9339
[3] N. Naghavi, GD Users Meeting, 2016
[4] S. Gaiaschi, A. Loubat, S. Richard, M. Bouttemy, P. Chapon, A. Etcheberry, Characterization of CIGS solar cells through Glow Discharge Optical Emission Spectrometry and Differential Interferometry Profiling, Poster GD Day 2016
[5] M. Bouttemy, P. Tran-Van, I. Gerard, T. Hildebrandt, A. Causier, J. L. Pelouard, G. Dagher, Z. Jehl, N. Naghavi, G. Voorwinden, B. Dimmler, M. Powalla, J.F. Guillemoles, D. Lincot, A. Etcheberry, Thinning of CIGS solar cells: Part I: Chemical processing in acidic bromine solutions, Thin Solid Film 2011, 519, 7207-7210
[6] Lee H, Gaiaschi S, Chapon P, Marronnier A, Lee H, Vanel JC, Tondelier D, Bourée JE, Bonnassieux Y, Geoffroy B, Direct Experimental Evidence of Halide Ionic Migration under Bias in $CH_3NH_3PbI_3$–xClx-Based Perovskite Solar Cells Using GD-OES Analysis, ACS Energy Lett. 2017, 2, 943–949
[7] Lee H, Gaiaschi S, Chapon P, Tondelier D, Bourée JE, Bonnassieux Y, Derycke V, Geffory B, Effect of Halide Ion Migration on the Electrical Properties of Methylammonium Lead Tri-Iodide Perovskite Solar Cells, J. Phys. Chem. C 2019, 123, 17728-17734
[8] Mohajernia S, Mazare A, Gaiaschi S, Chapon P, Schmuki P, Depth elemental characterization of 1D self-aligned TiO_2 nanotubes using calibrated radio frequency glow discharge optical emission spectroscopy (GD-OES), Appl. Surf. Sci. 2018, 442, 412-416