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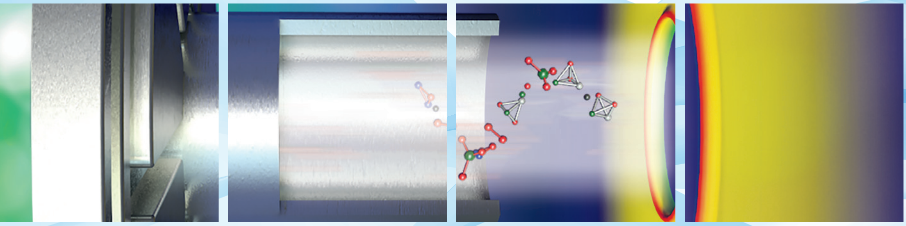
Glow Discharge Optical Emission Spectrometry



Focus on:
GD-OES, SEM and XPS

From Bulk Analysis of Metals to Depth Profiling of Advanced Materials

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Introduction

With all the major developments made over the past years [1], Glow Discharge is used for a much larger field of applications than was intended when developed in the late 60's – 80's. Used for research purposes on materials, scientist use results obtained on Glow Discharge Optical Emission Spectroscopy, along with results from other surface techniques such as Scanning Electron Microscopy (SEM) or X-ray Photoelectron Spectroscopy (XPS) to fully characterize their materials. With more scientists exposed to Glow Discharge and more results produced, we start to see more synergies between SEM, XPS and GD-OES than expected initially. Glow Discharge is no longer a technique providing results beside the results of SEM and XPS; it becomes a complementary technique to SEM and XPS.

GD-OES and SEM

Scanning Electron Microscopes are widely used in materials characterization laboratories. Coupled with an X-ray detector, wavelength or energy dispersive, they can perform elemental analysis. To perform depth profiles using SEM + X-ray detector, a sample is cross-sectioned and analyzed. Glow Discharge Optical Emission Spectrometry has some key advantages when compared to SEM-EDX (or WDX):

- No sample preparation: Cross-section is a tedious step and can induce modification of the samples or artifacts during measurements
- Ability to measure light elements: X-ray spectroscopy is very limited for the measurement of light elements when GD-OES can easily detect Li, H, O, C, N …
- Sensitivity: GD-OES is more sensitive than EDX for elemental analysis

However, we should see more use of GD-OES as a complementary technique to SEM. GD-OES can prepare samples prior SEM and EBSD.

Shimizu showed an application of GD-OES as a sample preparation tool for SEM during the 6th International GD Day on SUS304 stainless steel.

He then published a book by Springer illustrating a variety of applications on the benefits of the pulsed RF GD preparation to take full advantage of the capabilities of advanced SEM instruments [2].

During the 7th International GD Day, Kawano showed more results on MG WE43 and showed examples of the use of GD-OES for surface cleaning. After polishing until mirror finish of SUS304 stainless steel, contamination and scratches remain on the surface (Figure 1). GD-OES treatment removes contamination and reveal grain structure on the surface (Figure 2).

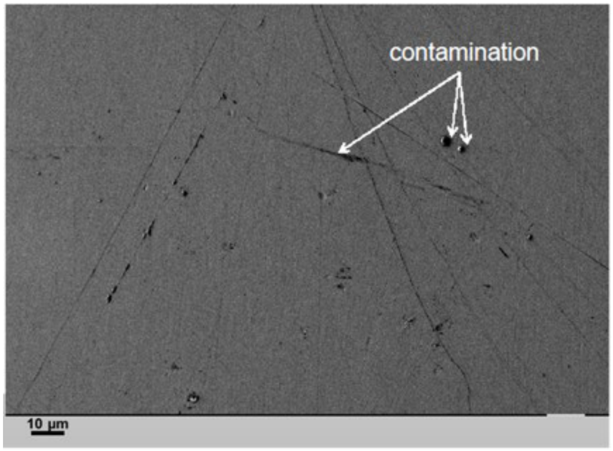


Figure 1: SEM image after mirror finish polishing of SUS304. Reproduced with authorization of the authors from the proceedings of the 7th International GD Day 2014 (Kawano et al., a unique application of GD-OES for improving SEM imaging)

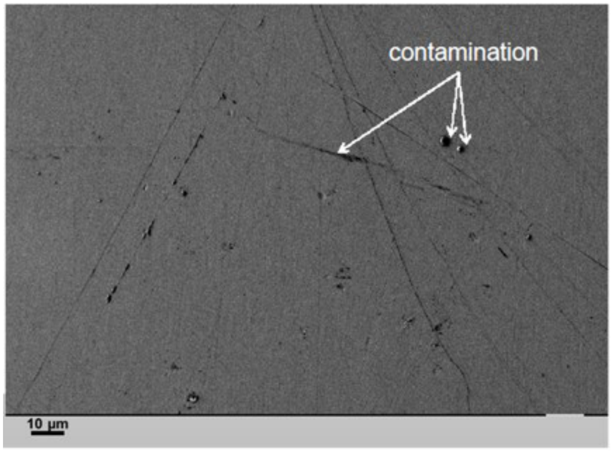


Figure 2: SEM image after mirror finish polishing and GD-OES treatment. Reproduced with authorization of the authors from the proceedings of the 7th International GD Day 2014 (Kawano et al., a unique application of GD-OES for improving SEM imaging)

For conductive materials, Kawano polished and treated with GD a MG WE43 alloy. The image obtained by SEM shows extremely fine details of the microstructure of the magnesium matrix, revealing MG14ND2Y, MG12ND, ND-rich precipitates and Y-rich particles (Figure 3).

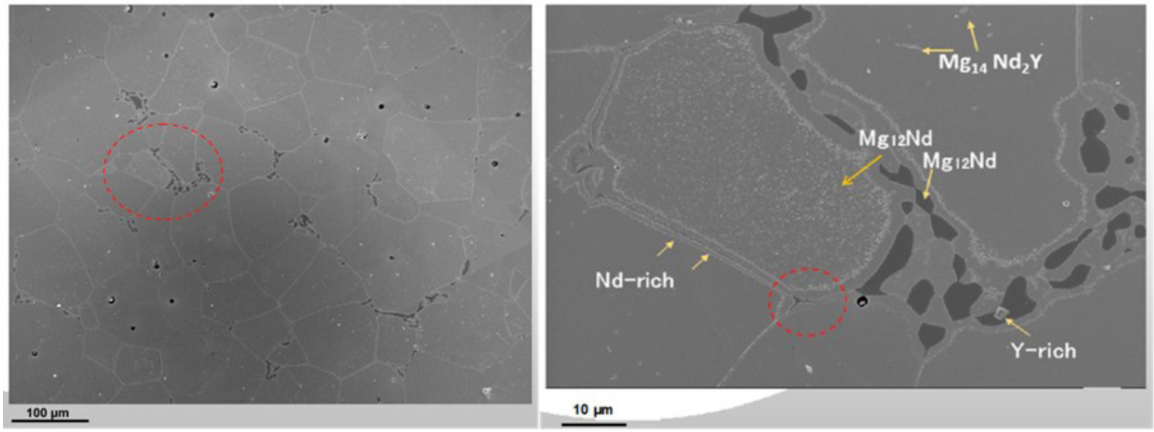


Figure 3: SEM images of MG WE43 alloy after mirror finish polishing and GD-OES treatment. Area in red-dashed circle in left picture is zoomed-in on the right picture. Reproduced with authorization of the authors from the proceedings of the 7th International GD Day 2014 (Kawano et al., a unique application of GD-OES for improving SEM imaging)

Image obtained with backscattered electrons gives more information on the presence of the ND-rich precipitates (Figure 4).

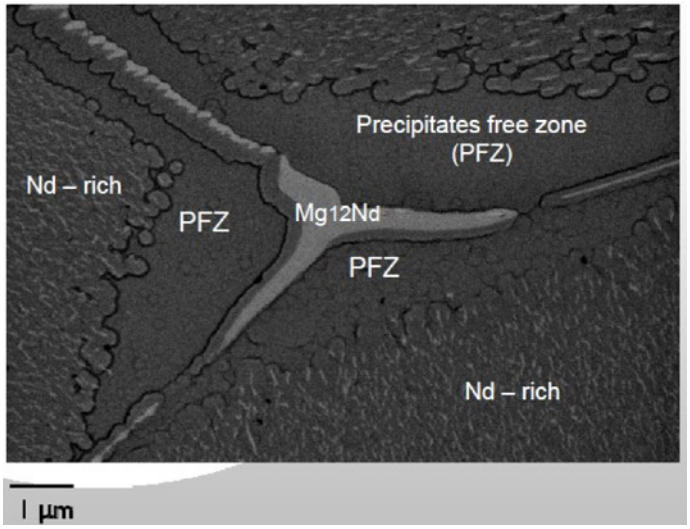


Figure 4: BSE image of red-dashed circle on the right image of Figure 3. Reproduced with authorization of the authors from the proceedings of the 7th International GD Day 2014 (Kawano et al., a unique application of GD-OES for improving SEM imaging).

GD-OES is a perfect tool for surface cleaning prior to SEM imaging. Cross-sectional image obtained after SEM observation can show hydrocarbon deposition because of beam irradiation. GD-OES can clean the surface and eliminate the hydrocarbon without damaging the surface of the sample (Figure 5).

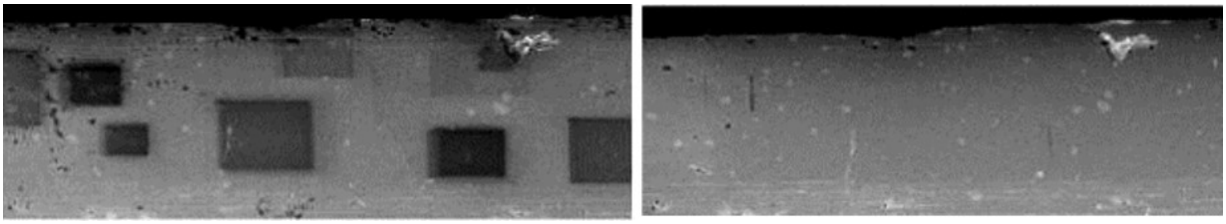
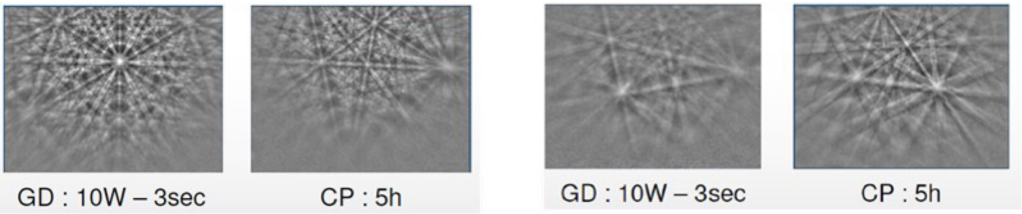


Figure 5: Cross sectional image after SEM observation without GD-OES surface cleaning (left) and after GD-OES surface cleaning (right). Reproduced with authorization of the authors from the proceedings of the 7th International GD Day 2014 (Kawano et al., a unique application of GD-OES for improving SEM imaging).

Penoy et al., presented a poster during the 6th International GD Day on the use of GD-OES as a preparation tool for the surface of cemented carbide samples (WC-Co) for EBSD observations. They compared results obtained with cross-section polishing (CP) and GD sputtering after mechanical polishing, showing that GD-OES is a faster alternative to cross section polishing for EBSD analysis, providing similar results in 3 seconds vs. 5 hours (Figure 6).



GD : 10W – 3sec

CP : 5h

GD : 10W – 3sec

CP : 5h

Figure 6: EBSD maps for WC phase (left) and Co phase (right) after 5 hours cross section polishing (CP) and 3 seconds GD sputtering (GD). Reproduced with authorization of the authors from the proceedings of the 6th International GD Day 2014 (Penoy et al., GD preparation for EBSD observation of tungsten carbide samples).

GD-OES and XPS

XPS, also known as ESCA, is one of the most popular surface techniques that is able to analyze all elements from atomic number 2. Its major strength is the ability to provide chemical state information, thanks to the shift observed according to the chemical bonding of the element. XPS by itself is not a depth profiling technique, and to perform such depth profiles, one should alternate XPS measurements with ion beam sputtering. XPS is a slow technique for depth profiling and can take hours. Depth profile of a CIGS absorber layer can take up to 92 hours, compared with 2 minutes for Glow Discharge. If only surface analysis is required, XPS is surely the technique of choice. For depth profiles, Glow Discharge can provide better performance.

Again, rather than opposing the two techniques, there is much more interest in combining them to provide better results in a similar way than for GD and SEM. For instance, it is possible to perform XPS analysis within the GD craters. The lateral resolution of a typical XPS measurement is in the range of 100 nm and allows for easy analysis within a GD crater.

For the characterization of deep interfaces, GD-OES provides fast sputtering to access the layer of interest, and XPS can perform the final sputtering down to the interface. Such a strategy saves hours of analysis on the XPS instrument.

Mercier et al., studied the complementarity of GD-OES and XPS for the chemical profiling of photovoltaic absorbers using CIGS materials [3]. The authors evaluated the chemical modifications of the crater after GD-OES sputtering and proposed different ways to limit or eliminate this effect, involving an intermediate wet chemical etching or weak sputtering to obtain the CIGS phase in the crater. They also demonstrated the ability to restart GD-OES analysis of materials after the XPS quantification, without modification of the profile shape.

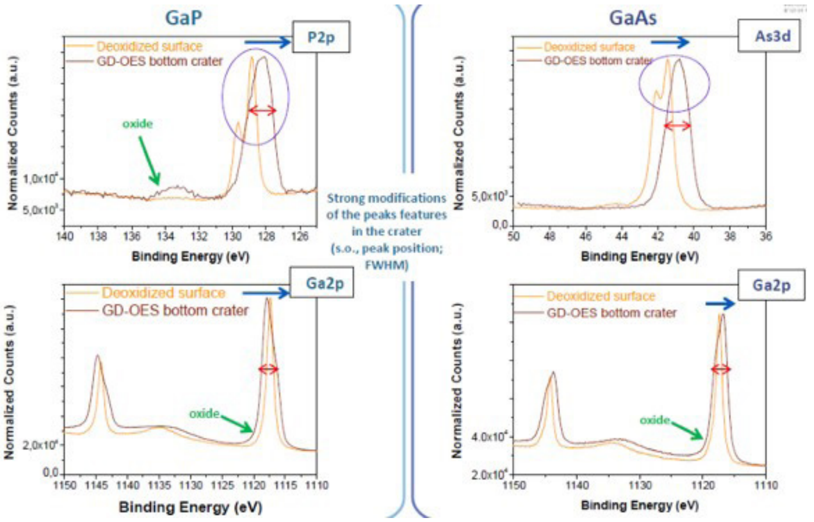


Figure 7: XPS analysis comparing deoxidized surface and GD-OES bottom crater. Reproduced with authorization of the authors from the proceedings of the Surface Fest 2018 (Bouttemy et al., Coupling GD-OES and XPS profiling to perform advanced physico-chemical characterizations of III-V layers for photovoltaic applications).

The same research group presented more work on GD-OES and XPS for the characterization of III-V layers for photovoltaic applications [4]. The modification induced by GD-OES shows on the XPS characterization as a shift of the Si2p binding energies, FWHM broadening of the Si2p peaks and n-type or p-type Si have similar behaviors.

The authors studied physical and chemical regeneration to remove this damaged layer: Ar+ sputtering, acidic treatment using HCl and basic treatment using KOH.

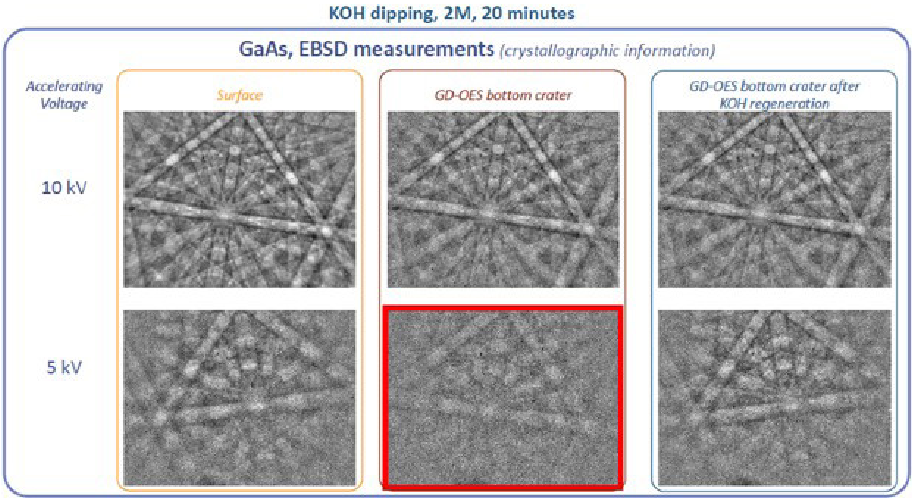


Figure 8: GaAs EBSD measurements of the surface (left), GD-OES bottom crater after sputtering (center) and GD-OES bottom crater after KOH regeneration (right). Reproduced with authorization of the authors from the proceedings of the Surface Fest 2018 (Bouttemy et al., Coupling GD-OES and XPS profiling to perform advanced physico-chemical characterizations of III-V layers for photovoltaic applications).

In-situ treatment via Ar+ sputtering eliminates the surface oxide layer in the crater but XPS signatures still differ from the deoxidized surface ones; thus, this method is then not appropriate to regenerate the GD-OES crater. Acidic treatment (HCl 1M dipping for 5 minutes) doesn’t look efficient enough to fully regenerate the GD-OES bottom crater, as improvement of the chemical XPS signature via deoxidation of the surface is observed, but the modified top layer still remains. The basic treatment using KOH 2 M dipping for 20 minutes shows the possibility to achieve a full chemical regeneration of the crater surface according to XPS analysis. EBSD microstructural characterization confirms this, showing the regenerated surface of the bottom of the crater after treatment (Figure 8).

This is an on-going study, which will include the evaluation of physical regeneration using smoother Ar+ sputtering, the optimization of dipping time and concentration of reagents for chemical regeneration and the evaluation of electrochemical regeneration.

Similarly, different groups conduct Raman microscopy and local electrochemistry studies within GD craters.

Conclusion

Glow Discharge Optical Emission Spectroscopy went through multiple important steps over the past years with the development of several hardware capabilities and accessories – pulsed radio frequency generator, UFS, DiP, Lithium bell – that opened the way to the characterization of advanced materials. GD-OES is now used along with other techniques, such as SEM and XPS, and some groups are exploring the potential to better use all these techniques together by leveraging the advantages of each. Glow Discharge is a complementary tool to SEM and XPS, providing additional information, but also being able to interact directly with these techniques to improve their ease-of-use.

We understand how Glow Discharge can interact with, and help SEM characterization. We are still in an exploratory period for Glow Discharge and XPS. Studies are targeting specific materials currently, but there is great potential to combine both techniques, and more time should reveal the full potential of the technique, and the overall benefit for the scientists.

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] New Horizons of Applied Scanning Electron Microscopy, K. Shimizu and T. Mitani, Springer (ISBN 978-3-642-03159-5 – e-ISBN 978-3-642-03160-1)
[3] D Mercier, M Bouttemy, J Vigneron, P Chapon, A Etcheberry, GD-OES and XPS coupling: A new way for the chemical profiling of photovoltaic absorbers, Appl. Surf. Sci. 347 (2015) 799-807
[4] A Loubat, S Béchu, M Bouttemy, M Frégnaux, D Aureau, J Vigneron, N Simon, AM Gonçalves, A Etcheberry, C Eypert, S Gaiaschi, P Chapon, Coupling GD-OES and XPS profiling to perform advanced physico-chemical characterizations of III-V layers for photovoltaic applications, Oral presentation, Surface Fest 2018.

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