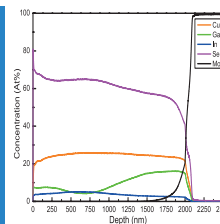


How to quantify GDOES depth profile data using XRF



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Abstract: In Glow Discharge Optical Emission Spectrometry (GDOES) analysis the quantification of layered samples historically relies on multi-matrix calibration curves. However, in many cases such as layers on glass, polymeric materials or semiconductors, or layers with key elements which can be difficult to be found in bulk certified materials, the usage of bulk samples is not sufficient to achieve the desired quantification goal (usually because they cannot cover the full elemental range). When a priori information is available, quantification becomes straightforward.

X-ray fluorescence (XRF) is often well suited for such specific samples, as for instance CuGaInSe/Mo/Glass, providing the global composition and possibly also the layer depth.

A new method to quantify GDOES data using XRF information is presented here.

Keywords: Multilayer, Depth Profile Analysis, GDOES, XRF, Quantification

Introduction

Pulsed Radio Frequency Glow Discharge Optical Emission Spectrometry (RF GDOES) provides ultra-fast elemental depth profile of solid materials, relying on a high-density plasma to sputter a representative area of the sample and to excite the sputtered species. By collecting in real time the light emitted by the de-excitation of the excited elements, the chemical composition of the analyzed sample can be achieved.

The direct result from a GDOES analysis is a qualitative depth profile, with light intensity as a function of sputtering time. In order to achieve the qualitative-to-quantitative conversion (light intensity into elemental concentration and sputtering time into depth), a set of calibration curves must be built. However, when equipped with the Differential Interferometry Profiling (DiP) module, depth can be measured in real time, simplifying the quantification [1].

Calibration curves are not universal and are adapted to the targeted application using specific certified reference materials (CRMs) for which certificates of composition are

provided. In the case of bulk materials, samples belong to the same matrix and the calibration is straightforward. However, when dealing with layered samples (e.g. TiN on stainless steel, NiP on low alloyed steel, etc...) by using the appropriate correction, different “families” (e.g. stainless steel, cast iron, Al alloys, Pb alloys etc...) can be easily mixed to extend the calibration ranges. As CRMs are usually bulk metals, this method works very well when samples are conductive or feature simple oxides or nitrides. However, what can be done when samples are polymeric or made of layers deposited on insulating substrates like glass? Is it always compulsory to build calibration curves to achieve quantification?

Energy Dispersive X-ray Fluorescence (EDXRF), a contactless and non-destructive technique, has proved to be a good partner for GDOES analysis, providing the total concentration and the thickness of each layer. A complementary quantification method, relying on XRF data, and now included in Quantum software, is presented in this note indicating when it could be used beneficially.



Instrumentation

The GD Profiler 2 (Figure 1) couples an advanced Pulsed RF Glow Discharge Source to a high resolution, wide spectral range Optical Emission Spectrometer.

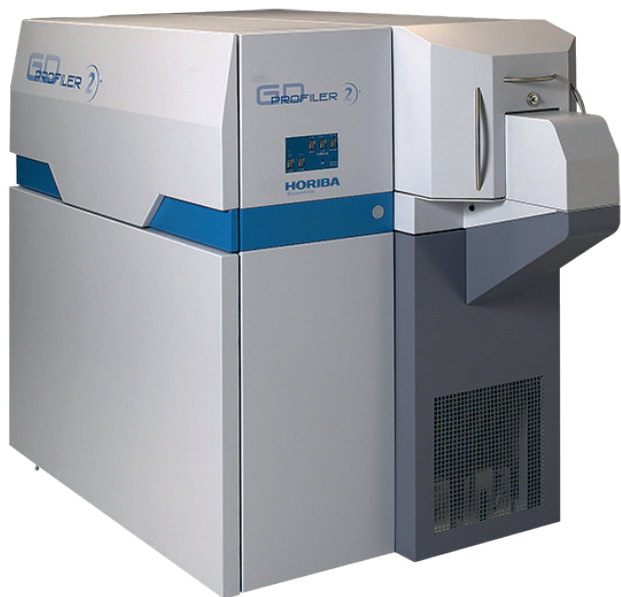


Figure 1: GD Profiler 2

This technique relies on the precise and fast (typically $\mu\text{m}/\text{min}$) sputtering of a representative area of the investigated sample by Ar^+ ions and accelerated neutrals with very low kinetic energies. The sputtered atoms are then excited by the plasma and their de-excitation leads to the emission of photons with characteristic wavelengths, enabling their elemental identification. All elements of interest are simultaneously measured, as a function of the sputtering time, using a spectrometer.

Thanks to our pulsed RF source, a high depth resolution can be achieved, avoiding unwanted diffusion of the elements during the measurements. Moreover, this type of excitation source makes the GD Profiler 2 an excellent instrument for the analysis of conductive, insulating and hybrid materials.

The MESA 50 (Figure 2) is a portable, small footprint and light weight EDXRF analyzer. It relies on an X-ray source to excite all the elements in the sample, and on an energy dispersive detector for the simultaneous collection of the emitted fluorescence radiation. Unlike SEM/EDX elemental analysis on electron microscopes, which is restricted to surfaces only, the relatively large penetration depth of X rays (typically from several μm to mm levels, depending on the analyzed matrix) allows multiple layers to be simultaneously analyzed.



Figure 2: MESA 50

For an EDXRF analysis some a priori information (i.e. the order and element composition of the different layers) must be known in advance. Once the XRF spectrum is acquired, thanks to a suitable simulation software, equations can be set up containing expressions for primary and secondary x-ray excitations for each element in each layer. These complex equations also include many physical and hardware fundamental parameters (eg, x-ray absorption, incident beam energy and intensity, etc). Using an iterative process, the parameters in question (eg, layer thickness and concentration) are adjusted, and the results are compared with the measured x-ray intensities of the sample spectrum until convergence is achieved.

Using XRF for quantification

For this technical note we have focused on CuInGaSe (CIGS) solar cells. These devices are usually deposited on a Mo layer, deposited on soda lime glass. The nature of the material demands an alternative solution to the calibration using bulk samples for quantification of the GDOES profiles, as explained in the introduction.

The synergy between GDOES and XRF has been validated by developing a quantification methodology which is now included in the Quantum software. The idea behind this algorithm is that the concentration provided via EDXRF analysis is linked to the integral of the measured GDOES profiles. This method is an easy and fast alternative to the classical quantification via calibration curves, providing additional flexibility.

Let's consider a GDOES profile (in Log scale) of a CIGS layer on Mo on glass (Figure 3).

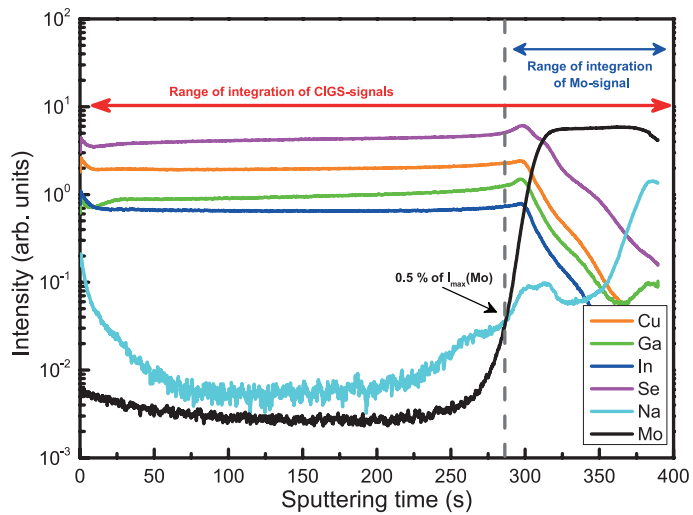


Figure 3: Qualitative depth profile of a CIGS layer deposited on Mo on Glass. The ranges of integration for the CIGS elements and the Mo are shown.

In a GDOES analysis, it is always critical to define the beginning or the end of a single layer. This is due to the broadening of the interfaces, linked to several phenomena, such as the impact of surface roughness, the diffusion of the elements or the crater shape. Therefore, the first step is to clearly define the boundaries of the CIGS layer, which are necessary to calculate the integral of the elemental profile. After several iterations, it was found that a good approximation is given by integrating the CIGS elements between the surface (or the 0.5% of the maximal Cu-signal height) and the Mo/glass interface, whereas the integration for the Mo contact should be considered between the 0.5% of the maximum Mo height and the Mo/glass interface, as shown in Figure 3. Then, considering the concentrations obtained via XRF analysis, a “sensitivity factor” $f(x_1)$ can be defined as

$$f(x_1) = \frac{Cc^{XRF}(x_1)}{\int I(x_1,t)dt}$$

where $Cc^{XRF}(x_1)$ is the measured concentration by XRF for the element x_1 and $\int I(x_1,t)dt$ is the integrated signal for the element x_1 . Values for the sample presented in Figure 3 are given in Table I.

	Cu	In	Ga	Se	Mo
$Cc^{XRF}(x)$ At%	23.04	16.42	10.59	49.94	100
$\int I(x,t)dt$	640	213	317	1427	457
$f(x)$	0.036	0.077	0.033	0.035	0.219

Table I. Example of sensitivity factors.

Having obtained the sensitivity factors for each element, the calculation of the concentration is straightforward. For each point of the elemental profile, the concentration $Cc(x_1,t_1)$

of the element x_1 at the time t_1 is calculated as

$$Cc(x_1,t_1) = f(x_1) \times I(x_1,t_1)$$

Where $I(x_1,t_1)$ is the GDOES intensity of the element x_1 at the time t_1 . Finally, the normalized concentration to 100% $Cc^{100}(x_1,t_1)$ is obtained as

$$Cc^{100}(x_1,t_1) = \frac{Cc(x_1,t_1)}{\sum Cc(x_i,t_1)}$$

Where $Cc(x_1,t_1)$ is the concentration of the element x_1 at the time t_1 and $\sum Cc(x_i,t_1)$ is the sum of all the concentrations at the time t_1 .

These simple steps lead to a semi-quantitative profile, with concentration as a function of sputtering time (Figure 4).

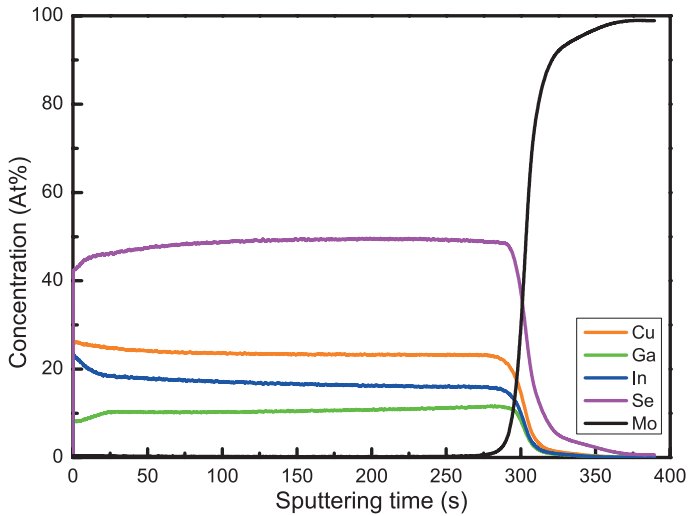


Figure 4: Semi-quantitative depth profile of a CIGS layer on Mo.

The last crucial step is the time-to-depth conversion. For this, it is necessary to determine the layer limits and therefore the sputtering rate. Considering the impact of interface broadening that was previously pointed out, it was found that for this kind of application the layer limits are well represented by the position at which the sum of Cu, Ga and In is equal to 25%. Sputtering rate $r(A)$ for layer A is then calculated as

$$r(A) = \frac{d(A)^{XRF}}{t_{end}(A) - t_{start}(A)}$$

Where $d(A)^{XRF}$ is the thickness of layer A as measured by XRF, $t_{start}(A)$ is the sputtering time at which layer A starts and $t_{end}(A)$ is the sputtering time at which layer A ends. Sputtering rate values for the sample presented in Figure 4 are shown in Table II.

	d^{XRF} (nm)	t_{start} (s)	t_{end} (s)	r (nm/s)
CIGS	1800	0	303	5.95
Mo	300	303	390	3.46

Table II. Sputtering rate values for the CIGS sample presented in Figure 4.

Having calculated the sputtering rate, the time to depth conversion is easily achieved as the depth $D(t)$ is calculated as

$$D(t) = (t - t_{start}(CIGS)) \times r(CIGS)$$

For $t_{start}(CIGS) < t < t_{end}(CIGS)$, and

$$D(t) = D(CIGS) + \Delta t \times r(Mo)$$

For $t_{start}(Mo) < t < t_{end}(Mo)$, with $\Delta t = t_n - t_{n-1}$.
The fully quantified result is presented in Figure 5.

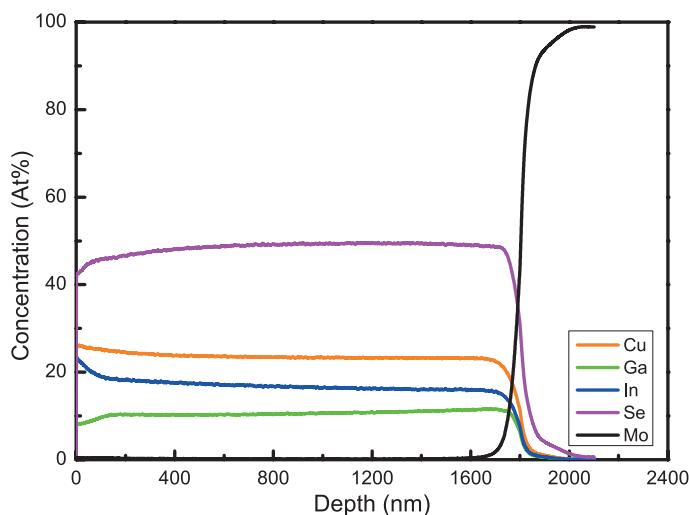


Figure 5: Quantitative depth profile of a CIGS layer on Mo.

As this method relies on the calculation of the full integral of the elemental GDOES profile, it can be easily applied to all kind of samples, those that are characterized by a simple flat elemental composition, such as the one presented in the sample, but also the more challenging ones that present concentration variations within the layer

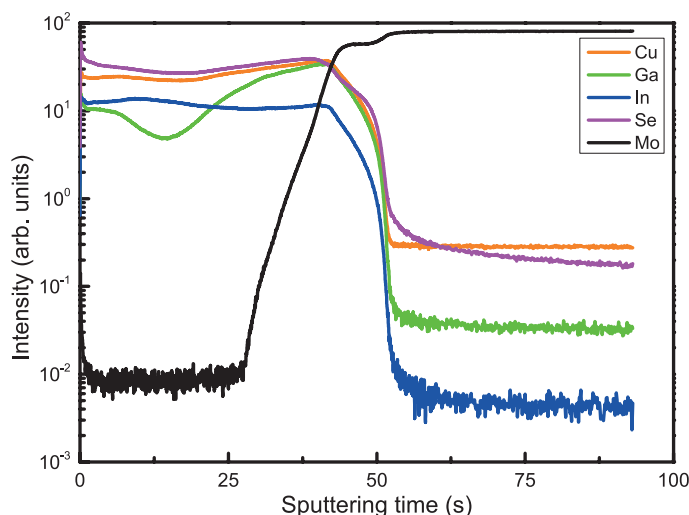


Figure 6: Qualitative depth profile of a CIGS layer on Mo, characterized by a Ga gradient

thickness. For instance, in the development of CIGS solar cells, a variation of the band gap and therefore of the band diagram, can be obtained by modulating the Ga content in the layer (Figure 6).

With this method, these variations in the elemental profile can be correctly quantified as the full integral of the GDOES signals is linked to the XRF concentration (Figure 7).

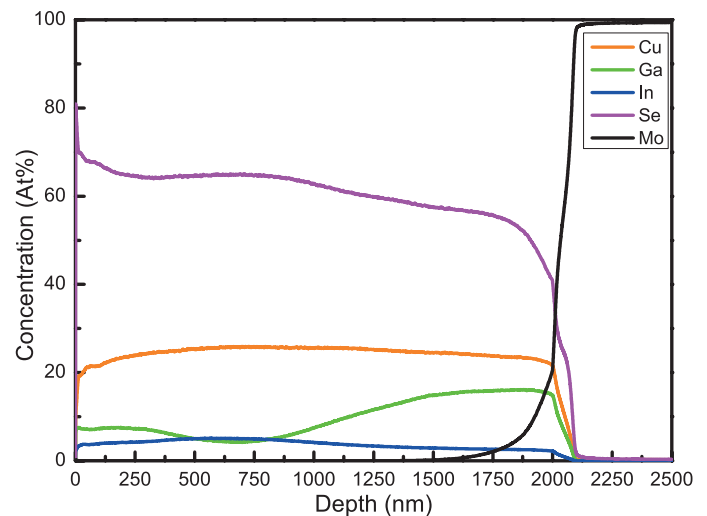


Figure 7: Quantitative depth profile of a CIGS layer with Ga gradient on Mo.

Conclusion

Within the HORIBA Scientific portfolio we can find two powerful instruments that, when combined, lead to the fast and efficient determination of elemental composition and layer thickness. The synergy between EDXRF and RF-GD-OES has proved to provide accurate quantification alternatives, when standard calibration curves based on bulk CRMs fail.

References

[1] TN10 - A new development in GDOES: Differential Interferometry Profiling for Measuring Erosion Rate, Crater Depth and Layer Thickness

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