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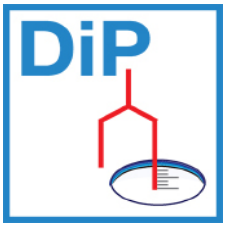
GDOES

Layer thickness and elemental composition determination of metallic coatings: the power of GD-OES & DiP and EDXRF



Technical Note

GD11

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Abstract: The modern manufacturing world is increasingly focusing its effort on a coating-based cost reduction.
In order to achieve a fruitful optimization, it is of great importance to determine the thickness/composition of the different coatings.
In this perspective HORIBA Scientific can offer, within its portfolio, three different techniques capable of satisfying this requirement and showing an excellent correlation: Glow Discharge Optical Emission Spectrometry (GDOES), coupled with the Differential Interferometry Profiling (DiP), Energy Dispersive X-Ray Fluorescence (EDXRF) and ellipsometry. While ellipsometry is the reference technique for transparent material, in this technical note we will focus on metallic coatings and therefore on the correlation between GD-OES/DiP and EDXRF.

Key words
Depth Profile Analysis, Differential Interferometry Profiling, GD OES, X-Ray Fluorescence, Thickness determination

Introduction

One of the solutions that the modern manufacturing world is considering to achieve a better product performance/costs ratio, is based on coatings. Metallic coatings can be used in a variety of applications: from electronics to anti-corrosion and wear resistance. New layer systems are usually developed in order to satisfy specific requirements and these are often multi-layer systems, which may include very thin layers (< 100 nm).

In order to optimize the manufacturing process, it is of great importance to determine the thickness and composition of the different coatings. It is therefore crucial to have access to reliable techniques providing such information within just a single measurement.

While ellipsometry is the reference technique for the analysis of transparent layers, within the HORIBA Scientific catalogue there are two other additional techniques able to efficiently quantify composition and layer thickness for metallic coatings: Glow Discharge Optical Emission Spectrometry (GDOES), coupled with the Differential Interferometry Profiling (DiP) and the Energy Dispersive X-Ray Fluorescence (EDXRF) using both the Fundamental Parameter Method (FPM) or calibration curves method.

Instrumentation

The GD Profiler 2 (Figure 1) couples an advanced RF-GD source to a high resolution, wide spectral range Optical Emission Spectrometer. This technique relies on the precise and fast (typically µm/min) sputtering of a representative area of the investigated sample. All elements of interest are simultaneously measured as a function of the sputtering time, using a spectrometer.

Figure 1: GD Profiler 2

Now, thanks to the addition of DiP (Ref 1), it is also possible to have the direct measurement of layer thickness. This solution (Figure 2) is based on an interferometric method, consisting of measuring the relative phase shift ($\Delta\varphi$) between two laser beams reflected at the surface of the sample - the reference beam - and inside the GD crater - the depth-sensing beam.

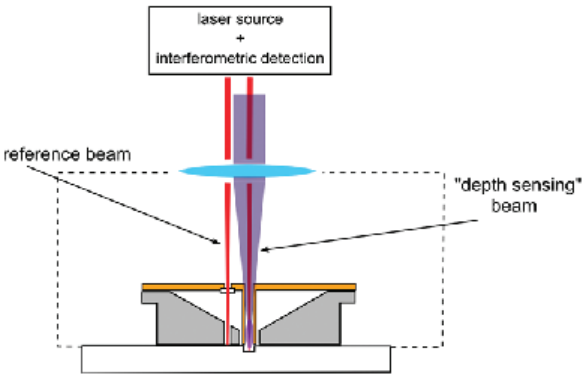


Figure 2. Schematic representation of the Differentail Interferometry Profiling (DiP).

In case of non transparent materials, the thickness determination is straightforward as there is always a linear relation between the phase shift (Δφ) of the two laser beams and the depth (d) of the crater.
Such relation is given by:

$$d = \lambda/4\pi \cdot \Delta\phi$$

where λ/4π is a conversion factor of nearly 50.5 nm/rad.

The MESA 50 (Figure 3a) is a portable, small footprint and light weight EDXRF analyzer. This is a powerful instrument as it relies on a contactless and non destructive technique. Analysis times are typically in the order of a few minutes for sensitivity to concentrations below 100 ppm (0.01%). On one hand, as for RF-GD-OES, it can be applied to both metals and insulating materials. On the other hand, one of its advantages is the fact that it allows the efficient thickness determination of both transparent and opaque materials, whereas DiP is applied straightforwardly only to non-transparent samples. EDXRF relies on a 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 are restricted to surfaces only, the relatively large penetration depth of x rays (typically from several µm to mm levels) allows multiple layers to be simultaneously interrogated. For an EDXRF analysis the order and element composition of the different layers must be known in advance. Then, 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 every 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). The parameters in question (eg, layer thickness and concentration) are then adjusted, and the results are compared with the actual x-ray intensities of the sample spectrum. Using an iterative process the thickness and concentration of each layer can be calculated.

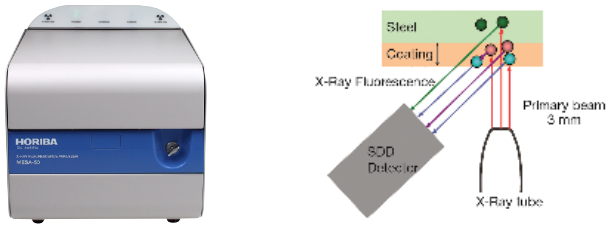


Figure 3. (a) MESA50 and (b) schematic representation of an EDXRF analysis.

Reference samples for thickness measurements were bought from KOCOUR (Figure 4). These samples consists of a Ag coating, with a varying thickness, deposited on a Ni coating on steel. The expected thicknesses are reported in Table 1.

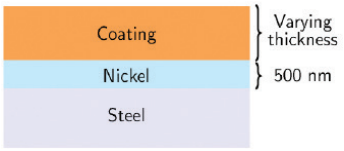


Figure 4. Schematic representation of the analyzed samples.

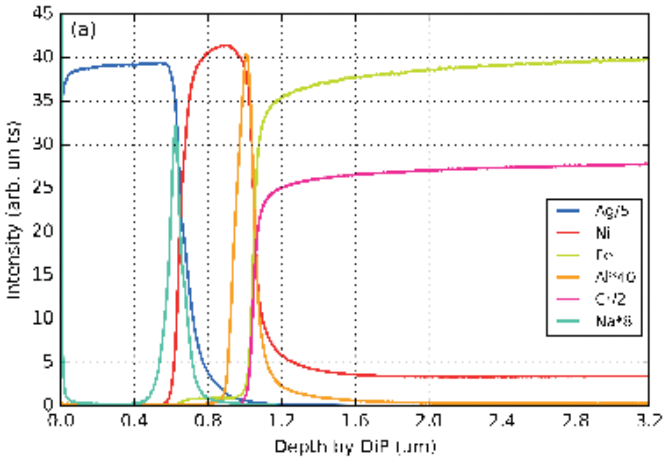
Sample name	Ag thickness (µm)
S1	0.66
S2	0.96
S3	4.94

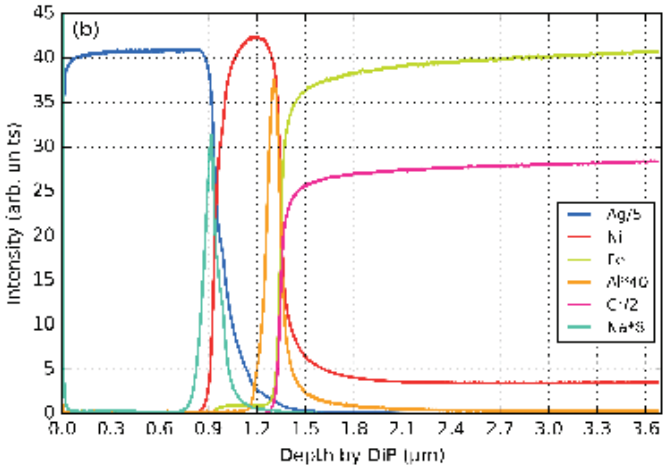
Table 1. Summary of the Ag coatings provided by KOCOUR.

Results

RF-GD-OES & DIP analyses were performed on the three reference samples provided by KOCOUR. Standard conditions were used, allowing to obtain a flat crater bottom.

The GDOES semi-quantitative depth profiles of the three samples are presented in Figure 5. (Intensity as a function of the depth measured using DiP)





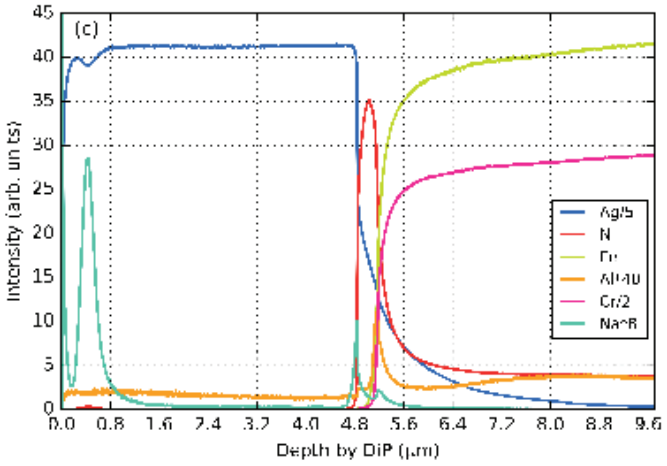


Figure 5. Qualitative depth profiles of samples (a) S1, (b) S2 and (c) S3. The profiles are presented as Intensity as a function of the depth measured by DiP.

From these profiles it is possible to determine the layer thickness and crater depth, which are reported in Table 2. The obtained values are in good agreement with what is given by the supplier and the crater depth measured using DiP is within 10 % of what is measured using a standard mechanical profilometer.

Sample	Ag (µm)	Ni (µm)	Crater depth by DiP (µm)	Crater depth by profilometer (µm)
S1	0.6	0.4	3.2	3.5
S2	0.8		3.7	3.7
S3	4.9		9.7	10

Table 2. Summary of the coating thickness and crater depth as determined by DiP.

EDXRF spectra were acquired for the three analysed samples (an example is given in Figure 6).

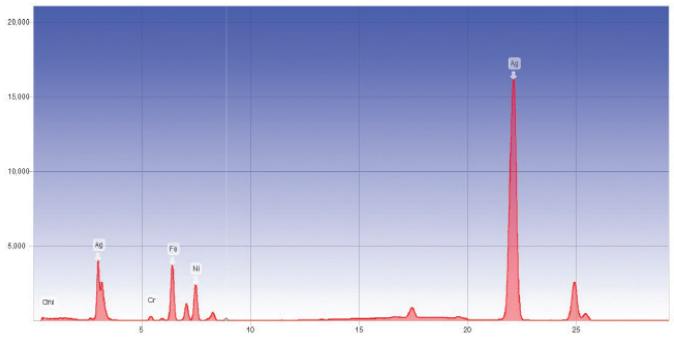


Figure 6. EDXRF spectrum of a Ag coating on Ni on steel.

Using the simulation software it is possible to calculated the coating weight. Then, by using the layer density, the linear thickness can be obtained. The results are presented in Table 3.

Sample	Coating weight (mg/cm2)	Ag Density (g/cm^3)	Linear thickness (µm)
S1	0.71	10.5	0.68
S2	0.99		0.94
S3	4.82		4.59

Table 3. Summary of the coating weight and layer thickness as determined by EDXRF.

Conclusion

HORIBA Scientific can offer, within its portfolio, two powerful instruments for the fast and efficient determination of elemental composition and layer thickness. Thanks to the introduction of DiP, RF-GD-OES can now provide the direct measurement of the crater depth, the material erosion rate and the layer thickness. EDXRF and RF-GD-OES have been proved to be complementary techniques, providing accurate results.

References

1. TN 10: A new development in GDOES: the Differential Interferometry Profiling for measuring Erosion Rate, Crater Depth and Layer Tickness

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