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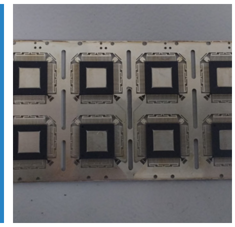
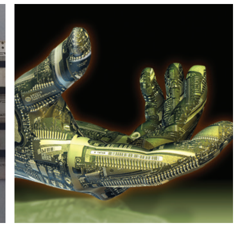
GDOES

How to analyse your electroplated coating?





Application Note

Material Science GD39

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Abstract: Pulsed Radio Frequency Glow Discharge-Optical Emission Spectrometry was used to study different electroplated samples. The flexibility of the spot size, the use of a pulsed RF source and the introduction of the differential interferometry profiling make RF GD-OES a key technique for the electroplating industry.

Key words: Electroplating, Depth Profile Analysis, Differential Interferometry Profiling, GDOES, Elemental composition, Thickness determination

Introduction

Even if alchemy does not exist, electroplating can be considered the next best thing. The idea is to coat relatively common metals (e.g. copper, steel, etc.) with a more precious one (e.g. gold, silver, etc) using electricity!
Actually electroplating has many different uses, besides making cheap metals look expensive. Indeed, it can be used to make anti-corrosion coatings, to produce a variety of alloys like brass or bronze on steel, etc...

In order to optimize the manufacturing process, it is of great importance not only to determine the thickness/composition of the electroplated coating, but also to verify the absence of contaminants in the electrolytic baths. Therefore it is crucial to have access to a reliable technique providing this information.
Glow Discharge Optical Emission Spectrometry (GD-OES), coupled with the Differential Interferometry Profiling (DiP), can be the best friend of any electroplating industry/research laboratory [Ref 1].

Instrumentation and sample preparation

The GD Profiler 2 (Figure 1) couples an advanced Radio Frequency (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

Thanks to the use of the RF as an excitation source, with the GD Profiler 2 it is possible to analyze conductive, insulating and hybrid materials. Moreover, thanks to the addition of DiP, it is now possible to have direct measurement of layers thickness, crater depth and erosion rate, during the GD-OES analysis. 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.

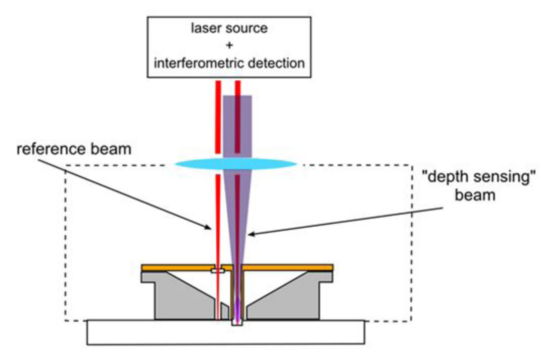

Figure 2: Schematic representation of the Differential Interferometry Profiling (DiP).

In case of non-transparent materials, like those developed in the electroplating industry, the thickness determination is straightforward, as there is always a linear relation between the phase shift ($\Delta\varphi$) 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 $\lambda/4\pi$ is a conversion factor of nearly 50.5 nm/rad.

Results

Several electroplated samples were analyzed to prove the efficiency of RF-GDOES for this specific industry.

The first analyzed sample is presented in Figure 3. The complex geometry of such sheet requires the use of a smaller GD source, with the diameter of 2 mm, and the small sample holder (Figure 4(a)). For this reason, samples were cut in order to fit the desired size (Figure 4(b)).

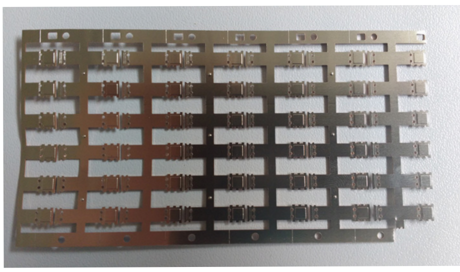

Figure 3: Example of an electroplated sample.

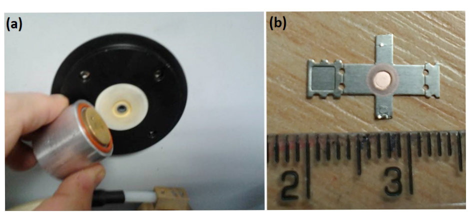

Figure 4: (a) The small sample holder and (b) a small analyzed sample, with a 2 mm GD crater in the center.

The result of the GD-OES analysis is presented in Figure 5. The sample is a NiP coating of Ni on Cu. The two electroplated layers can be clearly resolved and the analysis can be efficiently carried out, even on this peculiar geometry.

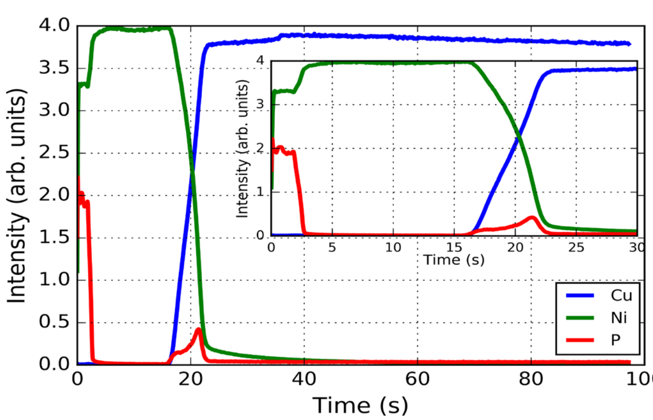

Figure 5: GD-OES analysis of the sample presented in Figure 4(b). The whole electroplated layer is analyzed in less than 1 minute. In the inset, a zoom on the first 30 seconds of the analysis is presented, clearly showing the first NiP layer, on top of the electroplated Ni coating.

However, GD-OES is a relative technique, and the direct result is an elemental intensity as a function of the sputtering time. By establishing a set of calibration curves it is possible to obtain a quantified depth profile with concentration as a function of depth (Figure 6).

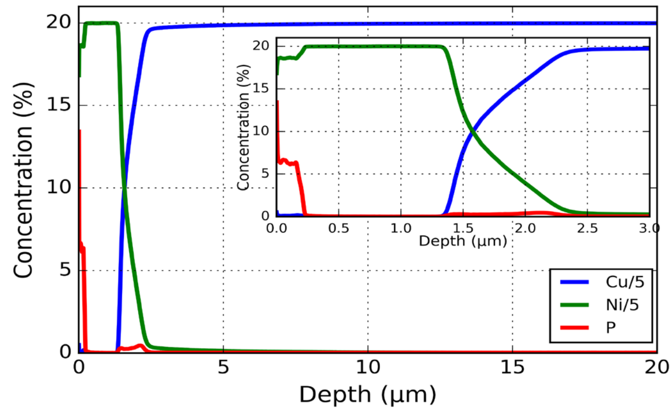

Figure 6: Quantified elemental depth profile for the sample presented in Figure 4(b). By establishing a set of calibration curves it has been possible to convert the relative GDOES analysis presented in Figure 5 in a quantitative result.

Another electroplated sample, installed on a plastic substrate (ball grid array package), was analyzed and is presented in Figure 7. Thanks to the use of a RF plasma source, even hybrid materials can be efficiently analyzed. Moreover, in this case the size of the sample allows the use of the 4 mm anode coupled with the DiP accessory (Figure 8).

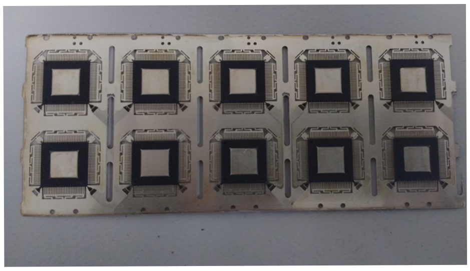

Figure 7. Example of an electroplated sample.

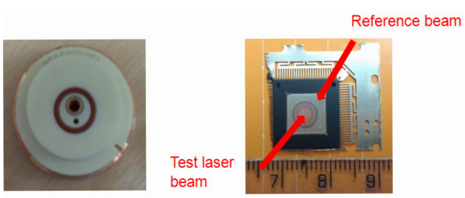

Figure 8. DiP anode and the analyzed sample, with a 4 mm GD crater. .

The results of the qualitative GD-OES analysis are presented in Figure 9. In the zoom mode, it can be seen that all layers are clearly resolved and that in less than 60 s they are completely eroded.

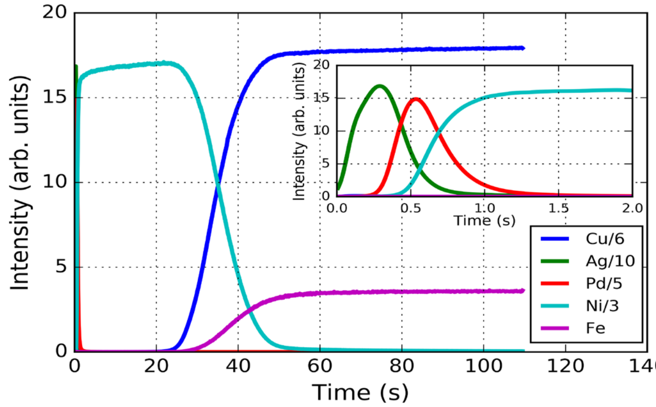

Figure 9. GD-OES analysis of the sample presented in Figure 8. The whole electroplated layer is analyzed in less than 1 minute. In the inset, a zoom on the first 2 seconds of the analysis is presented, showing clearly the Ag top layer, on the Pd layer , on the electroplated Ni coating.

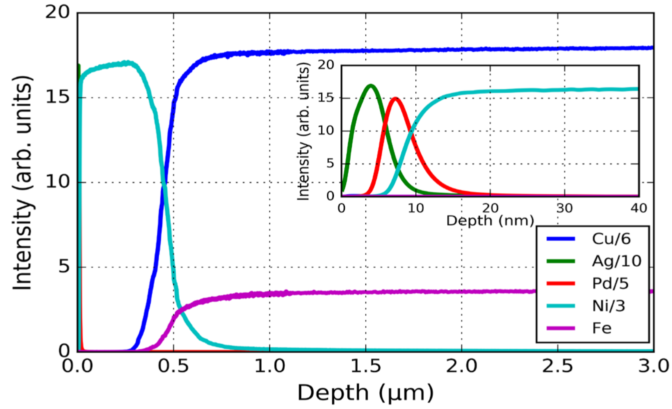

Figure 11: Semi-quantitative elemental depth profile for the sample presented in Figure 8. The time-to-depth conversion is achieved thanks to the DiP module.

Figure 10 shows the evolution of the depth as a function of the sputtering time. With DiP, it is possible to monitor in real time all variations in erosion rate due to the presence of different coatings.

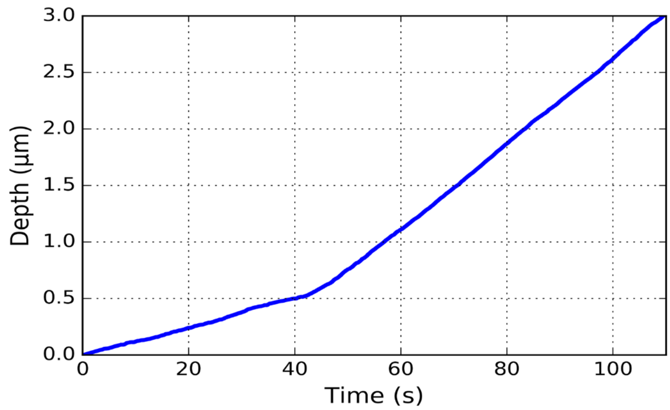

Figure 10. The depth vs. sputtering time curve, as measured by DiP. The variation of the slope of the curve highlights the different sputtering layer between all the layers.

The combination of the results presented in Figure 9 and in Figure 10 allows obtaining a semi-quantitative elemental depth profile (Figure 11). Calibration curves are still needed in order to achieve the intensity-to-concentration conversion.

Conclusion

Pulsed RF GD-OES is the perfect tool for the analysis of electroplated materials. Thanks to the flexibility of the spot size, it is possible to analyze samples with varying size and shape. The use of the RF source allows the measure of all kinds of samples, even the insulating one. The possibility to pulse the source guarantees an excellent depth resolution, for the identification of extremely thin coatings. Finally, the new differential interferometry profiling tool assures the direct measurement of the crater depth and of the sputtering rate, for an easy semi-quantitative analysis.

References

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