Abstract: Pulsed RF Glow Discharge Optical Emission Spectrometry, coupled with the Ultra Fast Sputtering system, offers the Ultra Fast Elemental Depth Profiling of plastic thin films Polymer Mobile Screen Protection Covers. By coupling this technique with the Raman spectroscopy z-Scan analysis it is possible to acquire important information concerning the fabrication of smartphone screen protectors.

Key words
Polymers, Smartphone, Depth Profile Analysis, Ultra Fast Sputtering, GD OES, Pulsed RF source; Raman spectroscopy

Introduction
Despite the improvement in glass manufacturing, it is still annoying when a brand new mobile phone falls on the ground and its screen shatters. To avoid (or at least minimize) this scenario, a new industry has risen and is supplying mobile screen protection covers. Besides protecting mobile screens from breaking, such protection films avoid scratching of the display when carrying the phone in the pocket, and they are also dirt-repellent.

Besides real glass cover foils, which also tend to be fragile, it is possible to find in commerce efficient protecting polymer covers. As simple as such polymer foils look, the polymer technique behind is quite demanding. Controlling the production process to ensure reliable protection capability for large batches is required to guarantee consistent quality.

Analytical depth profiling methods are the means of choice by which such polymer films can be analyzed in terms of composition and layer structure. HORIBA Scientific (HSci) shows how combining its two techniques, pulsed Radio Frequency Glow Discharge Optical Emission Spectroscopy (RF-GDOES), coupled with the Ultra Fast Sputtering (UFS), and micro Raman spectroscopy, obtains a comprehensive picture of mobile screen protection covers [1,2].

Instrumentation and sample preparation
The GD Profiler 2 (Figure 1) couples an advanced Pulsed RF-GD source to a high resolution, wide spectral range Optical Emission Spectrometer. The precise and fast sputtering of a representative area of the investigated sample (usually a crater of 4 mm in diameter) is assured using an RF-pulsed source, which also allows the reduction of the thermal load on the sample, preventing any damage. All elements of interest are simultaneously measured, as a function of the sputtering time, using a spectrometer. Additionally, the use of the patented UFS mode allows the efficient (10 μm/min) GD profiling of polymeric materials.

While GDOES gives access to the elemental depth profile, Raman spectroscopy is capable of providing information about the molecular composition of the polymer layers. This technique relies on the detection of inelastic scattered photons whose energy corresponds to a specific molecular vibration. Measurements were done using a LabRAM EVO (Figure 2) with a lateral spatial resolution of 300 nm and an axial spatial resolution of 1 μm. Measurements were done using a 532 nm laser.

A common Polymer Mobile Screen Protection Cover (PMSPC) was bought to study its composition. The principle setup (Figure 3) of such foils consists of a multilayer polymer system containing the:
- Protection cover for the mobile screen (3/4/5)
- Covering foils acting as protection and carrier films for the PMSPC (1/2/6)
Such films are thin and flexible and therefore for a proper analysis with RF-GDOES, it is necessary to cut them and glue them on a rigid substrate, as shown in Figure 4 (a proprietary methodology was used to glue the film to an Al plate and the obtained GD craters are clearly visible). On the other hand, no specific preparation is necessary for the Raman analysis.

Results

Both UFS-RF-GDOES analysis and Raman investigations were carried out starting from the surface of the thin top layer 3, after the removal of the PET carrier film (Figure 5).

The results, presented in Figure 6, were detailed in ref [3], and are summarized as follows:

a) The sputtering time 0 – 10 s corresponds to the hard coating layer 3
b) After 10 s, the CH signal shows a clear peak and a high Na content, indicating that the interface between layers 3 and 4 is achieved.
c) At 20 s, a second Na peak appears, decreasing towards the bulk material.
d) After 500 s, the Si & H content increases, indicating the transition to layer 5.
e) After 600 s, the PMSPC is fully sputtered (120 μm crater, by profilometer).

By performing a Raman z-Scan analysis through the PMSPC, different polymer spectra can be obtained and are reported in Figure 7. For such analysis an oil immersion objective was used.
At the very beginning of the z-Scan, the immersion oil is detected (the red curve in Figure 7). However, for the other spectra, an additional interpretation is needed. While a spectra library search easily identifies the spectrum corresponding to layer 2(4) - the blue curve in Figure 7 - as a single component spectrum, those of layer 1(3) and 3(5) can only be explained as a mixture of several components. The identification of such components was done using BIORAD’s KnowItAll™ software.

The first layer - 1(3) - shows a complex composite spectrum consisting of oil, poly(ethylene terephthalate) (PET) spectrum originating from the layer below and above, and the spectrum of a branched poly acrylate (PA) containing an impact modifier. This 2 μm thick layer acts as a hard coating.

The second layer - 2(4) - shows a spectrum which is clearly consistent with that of PET (from Sadttler spectra library provided by BIORAD). Its thickness is estimated at nearly 100 μm and therefore it represents the main part of the PMSPC.

The third layer - 3(5) - shows the spectrum of poly (dimethyl siloxane) (PDMS). As this layer is covered by the thick PET layer, it contains a small proportion of the PET spectrum. PDMS has good adhesion properties and in this kind of PMSPC it acts as a glue for the protective film. Its thickness is estimated at around 25 μm.

Finally, in Figure 8 the total Raman z-Scan profile is presented.

Moreover, thanks to Raman spectroscopy, it is possible to have additional insights on some features of the UFS-GDOES profile. Indeed, as shown in Figure 6(b), the RF-GDOES analysis shows the presence of several Na peaks at the interface between the hard coating and the PET layer. Such Na content could be due to the presence of a lonomer of Poly (Acrylate Acid) Na salt. These polymers, typically, are «self-sealing» and are included in coatings of sensitive electrical wiring to keep moisture away from the wires, ensuring the safe transmission of electrical signals. In addition, PETs are thermoplastic, therefore they are produced by thermic molding. This could explain the interfacial segregation of Na.

**Conclusion**

The GD Profiler 2 can be a key instrument during the optimization and follow up of manufacturing processes. This is a fast technique which allows the easy comparison of different materials, the detection of defects and the presence of contaminants. Moreover, combined with the UFS system, it proves to be a flexible technique for organic and hybrid materials, providing numerous new application domains.

For the detection of thin hard coatings it is a prerequisite to have a full confocal Raman microscope with a spatial resolution at the diffraction limit otherwise it is impossible to spatially resolve and detect such thin layers.

Finally, microRaman and UFS-RF-GDOES are useful complementary techniques for depth profiling of complex multilayered polymer materials. The results given by these techniques prove to be in excellent agreement.

**References**

[2] HJY application note AN GD21
[3] HJY application note AN GD36