

Pulsed RF GDOES and XPS for Depth Profile Analysis



Application Note
Material Science
GD35

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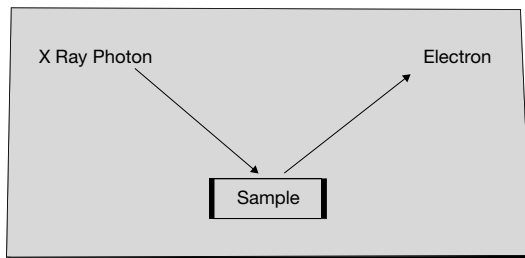
Abstract: XPS is a reference technique for surface analysis. When depth profile is the main focus, a complementary approach of XPS & GD is of interest this note tells why.

Key words

XPS, Glow Discharge, Depth Profiling

Principle of XPS

X-Ray Photoelectron Spectroscopy XPS (also named ESCA - Electron Spectroscopy for Chemical Analysis) is one of the most popular surface techniques nowadays. It is used in research and manufacturing. It provides the chemical composition of the top surface of materials (first nanometers).



Ultra-high vacuum chamber (1 X 10⁻⁹ Torr)

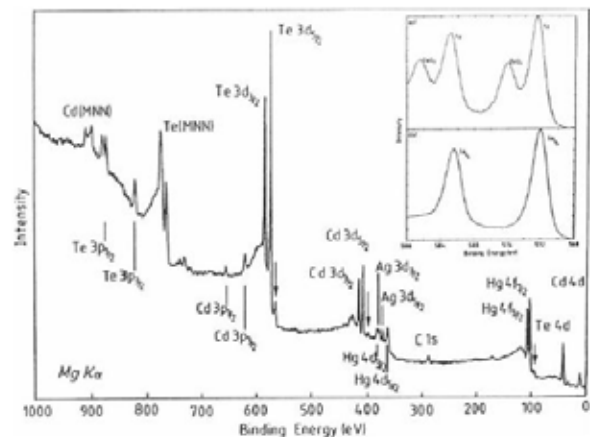
The basic process in XPS is photo emission. The sample is irradiated with X-rays of known energy $h\nu$. Electrons of binding energy (BE) E_b are ejected if $E_b < h\nu$.

These electrons have a kinetic energy (KE) E_k which is measured by the spectrometer and the main equation (once instrument function is taken into account) is $E_k = h\nu - E_b$.



A typical XPS instrument

It is of course important to note that XPS requires that the analysis be performed in an ultra-high vacuum.



Mg K α XP spectrum of Hg_{0.6}Cd_{0.4}Te grown via Metal Organic Chemical Vapour Deposition (MOCVD). Insert: (a) Te 3d region of full spectrum before cleaning, showing the presence of oxide. (b) Te 3d region after ion etching, which has removed the oxide. (From Ref 1.)

The study of the XPS spectrum tells from which atoms they were coming (and so gives **information on the composition**). XPS measures all elements from Z =2 (so it does not measure H) where GD measure all elements including H.

The measurement in XPS of the area below the peaks is directly proportional to the concentration of the element (in the observed area). The technique is therefore **quantitative**.

In addition XPS also tells what is the binding of the atoms in the material: the XPS peak of an element in metallic form and the XPS peak of the same element is oxidized form are shifted by a known value and this is the **key strength of the technique**.

On the other hand, the GD sputtering is designed to break all bindings and elemental information only is provided.

Many references books are available on XPS. Data bases and manufacturers' operating software are extremely powerful and the instruments can be operated in fully automatic mode.

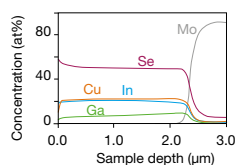
The spatial resolution of XPS is in the order of 50 microns, the typical analysis spot is in the range 100-400 microns. XPS is therefore not really a local analysis technique: for mapping, people would use other surface techniques (Auger, TOFSIMS).

Depth Profiling

The use of XPS in **depth profiling** applications, rather than surface analysis is dependent on the sampling depth of the incident and ejected particles. For XPS, this value ranges from approximately 3 monolayers (≈ 10 angstroms) to 10 nm.

Subsurface information can only be obtained beyond these levels through the removal of sample material, usually through sputtering with a high energy ion beam. This step is done with an auxiliary feature – an ion gun. One would alternate between bombardment of the sample with ions for material removal and X-rays for analysis to generate a depth profile.

Below is an example of analysis of CIGS (PV absorber) by Pulsed RF GDOES and XPS. The GD result is well known. The erosion zone is typically 4 or 2 mm. The Pulsed RF plasma **simultaneously** assures the sputtering of the material and the excitation of the sputtered species.



Analysis of CIGS absorber layer by pulsed RF GDOES

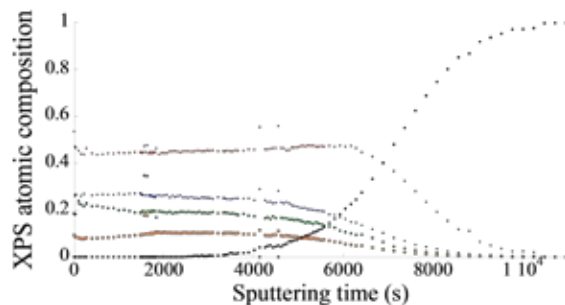
Total Analysis Time for GD: 2 minutes

If one now looks at the XPS profile, on the right, the information obtained looks similar. In this experiment the measurement was done with 121 steps of sequential sputtering with Ar⁺ ions. The X axis is the **sputtering time**. Like in GD, this time can not be linearly converted in depth as different materials have different erosion rates.

The sputtering time of XPS (or rather of the Ar ion gun within the XPS) is of course longer than in GD but one has to keep in mind that at each point the XPS measurement has to be done and each individual measurement takes about 1 hour!

So the analysis time in XPS is not the same as the sputtering time. In GD analysis time and sputtering time are identical.

One understands better with such analysis times, why it is crucial to have automatic instruments!



Total Analysis Time for XPS: 92 hours

Complementary approach

Rather than opposing Pulsed RF GDOES and XPS, it is much more sensible to use the 2 techniques in complement of each other considering their respective lateral resolution.

The approach there is similar to the one proposed by Ken Shimizu for Pulsed RF GD and SEM/EDS.

It is for instances possible to do XPS analysis within the GD craters. So when deep interfaces have to be studied by XPS, why not simply removing the top layers by GD?

A flat crater bottom can be obtained; the real time display of the GD analysis allows stopping the discharge prior the interface is reached in order to prevent any contamination from GD redeposition or contact with air affecting the buried interface. The sample could after that, be inserted in the XPS chamber for final sputtering down to the interface and analysis. Hours of lost time can therefore be saved!



In addition the XPS quantitative information could be used to calibrate the GD profiles of a reference sample at different depths – this is the idea of our Layer Mode.

Such complementary approach is the topic of the work in common between HORIBA Jobin Yvon and the ILV laboratory Versailles University and our first paper has been published (Ref 2).

References

- Ref 1: O'Connor & al. "Surface Analysis Methods in Materials Science", Springer
- Ref 2: 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". Applied Surface Science. doi:10.1016/j.apsusc.2015.04.093