HORIBA Scientific

Technical Note

PP-TOFMS

TOF01

Plasma Profiling Time of Flight Mass Spectrometry

The Plasma Profiling-TOFMS that has been developed by HORIBA Jobin Yvon within a EU research project is a unique instrumentation. It combines the speed of the plasma sputtering process with the rapidity and the sensitivity of time of flight mass spectrometry.
The instrument is capable of bulk and depth profile analysis of thin and thick films with nanometre depth resolution. Compared to GD-OES, it offers higher sensitivity and provides isotopic and molecular depth profiling.

In contrast, commercial GD-MS instruments feature a sequential magnetic sector mass analyser and a dc source and are therefore rather dedicated to the analysis of trace impurities in bulk conductive materials. Main customers are high purity metal manufactures as well as their consumers from microelectronics, aerospace and nuclear industries. On the other hand Plasma Profiling-TOFMS differentiates itself from ToF-SIMS (IonTOF, Phi) as it can analyse thicker films due to its higher sputtering rate.

HORIBA Jobin Yvon, the University of Oviedo and EMPA (Institute of Materials Science and Technology in Thun) have collaborated with many universities, research institutes and industry on diverse applications. To name a few:

- With the University of Catania, on molecular depth profiling of polymer thin films (monolayers/Si and bilayer on PET) (publication: Tuccitto et al, Rapid communications in Mass Spectrometry, **23**, p 549-556, (2009).)
- With the University of Manchester, on depth profiling of thin oxides with tracers and markers, including isotopic labelling using O18 rich electrolytes. (more than 5 publications: A. Tempez et al, Surface and Interface Analysis, **41**, 966-973 (2009)., Molchan et al, Journal of Analytical Atomic Spectrometry, **24**, 734-741 (2009)….)
- With the Texas Center for advanced Materials, University of Houston, profiling of nitride thin films (InGaN, AlGaN, BON layers, ^{10}B implanted Si)
- With Saint Gobain, profiling analysis of very thin metallic layers on thick glasses (publication: Muniz et al, *Journal of Analytical Atomic Spectrometry* (**23**, p 1239–1246, 2008).

Other industrial applications concern mainly photovoltaics including multilayers of the Si with Ecole Polytechnique (France), CIGS, and CdTe technologies.
Among other specimens which have also been successfully measured with our PP-TOFMS: ITO/glass (InSnO), galvanized steels, paints with polymers, hard discs…

Figure 1. PP-TOFMS

Specifications

Mass Resolution:	3500 at m/z 208, High Resolution 5000 at m/z 208
Dynamic range:	10^7
Mass accuracy:	40 ppm
Acquisition rate:	33 kHz to cover elements up to U (a full spectrum every 30 µs versus 150 ms with magnetic sector MS)
Sensitivity:	10^3 cps/ppm
Depth resolution:	3 nm

Both negative and positive ion modes
Flexible blanking capability up to 4 ions
Easy and horizontal sample mounting

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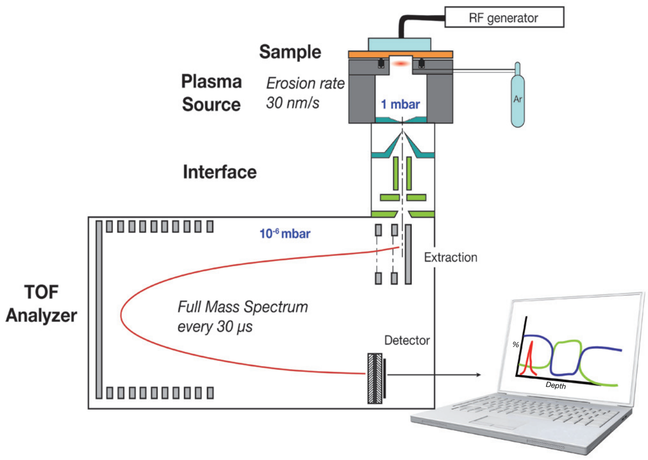

Figure 2. Schematics of PP-TOFMS applied to bulk and depth analysis of solid materials

Description

Plasma Profiling Time of Flight Mass Spectrometry (PP-TOFMS) couples a plasma source with a time of flight mass analyser. This instrument is dedicated to the depth profiling analysis of advanced materials made of conductive and/or non-conductive layers down to the nanometre scale. The plasma created in the radio frequency glow discharge source routinely operated in Ar creates Ar ions and fast neutrals that sputter away the sample. The sample sputtered neutrals are then excited and ionised in the plasma. Ions are transferred and separated in the orthogonal extraction TOFMS. Raw data are variations of ion signals as a function of sputtering time. Quantitative results can be obtained upon time to depth conversion and signal calibration, giving element/species distribution along depth (plots of element % as a function of depth).

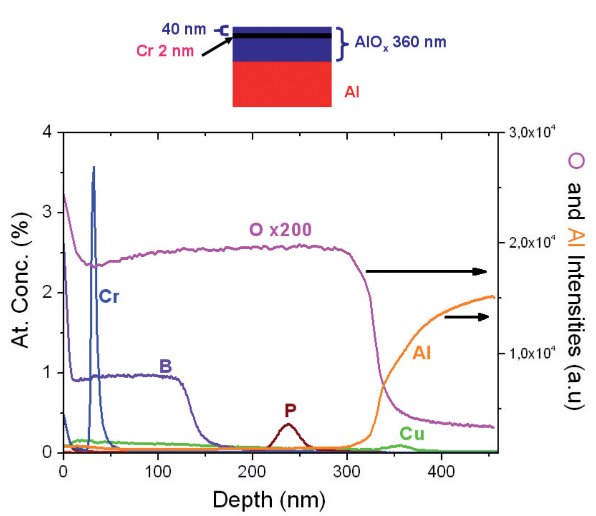

Figure 3. Typical Data obtained by PP-TOFMS from an oxide layer on aluminium with a 4 nm thick Cr delta layer at 40 nm from the surface.

Domains of applications embrace corrosion science, solar cells manufacturing and molecular electronics; the instrument should interest all labs involved in research, development, characterisation and measurement on thin/thick films.

This instrument combines the speed of analysis inherent to plasma sources to the MS sensitivity and time of flight detection capability of simultaneously measuring elements, isotopes and molecular fragments. The sputtering rate of the plasma source is in the order of µm/min and depends on the materials. The TOFMS acquires a spectrum with a mass range covering all elements of the periodic table every 30 µs. The instrument is thus capable of measuring and resolving nm thick layers.

In addition, an important feature of this reflector based spectrometer is the high mass resolving power ($m/\delta m$, δm being the full width at half maximum of Gaussian-fitted peak). In the routine conditions used in this work, the actual mass resolving power ~ 3500 at mass 208 although values as high as 5200 can be obtained.

The great advantage of orthogonal TOF extraction is to monitor fast transient ion signals. Transient ion signals are generated from the pulsed operation mode of the plasma source. This mode allows (i) to lower thermal stress on thick non conductive samples, (ii) to tune the sputtering rate. Typically, in pulsed RF operation, the source is pulsed from 100 µs to few ms over a few ms period. The synchronized and fast TOF acquisition allows to monitor all ions during the source period and to create a source pulse profile. The pulse profile shows the occurrence of Penning ionisation (soft ionisation by Ar metastables) once the RF is turned off. In this so-called afterglow region, ion signals from the sample are typically enhanced. Selecting the region of interest in the pulse profile generates the depth profile; raw data are thus three dimensional. This 3D feature has been proven useful for enhanced sensitivity, signal to noise and for separation of analyte from isobaric ions (e.g. interfering Ar adducts).

The interface includes a blanking stage and electrostatic ion optics. The blanking interface stage attenuates intense signals from Ar and matrix ions to avoid the saturation of the detector occurring for currents above 20×10^6 ions/s. The blanking interface can filter up to four different masses.
The polarity of the TOFMS can be inversed for negative ion mode. Collecting negative ions may be beneficial for higher sensitivity of electronegative elements (halogens, oxygen) and negative molecular fragments.
As shown in the schematics, the sample is simply placed horizontally on the source, which makes sample mounting quite easy.

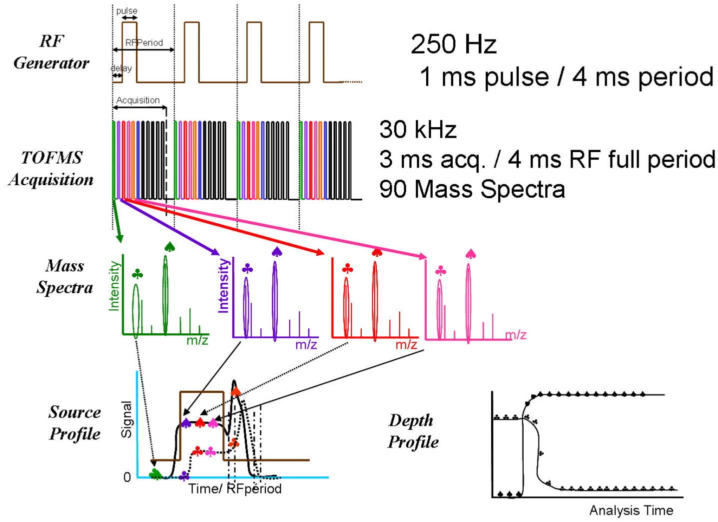

Figure 4. Timing scheme of the pulsed mode operation, with generation of the 3D data (mass spectrum, source profile and depth profile).

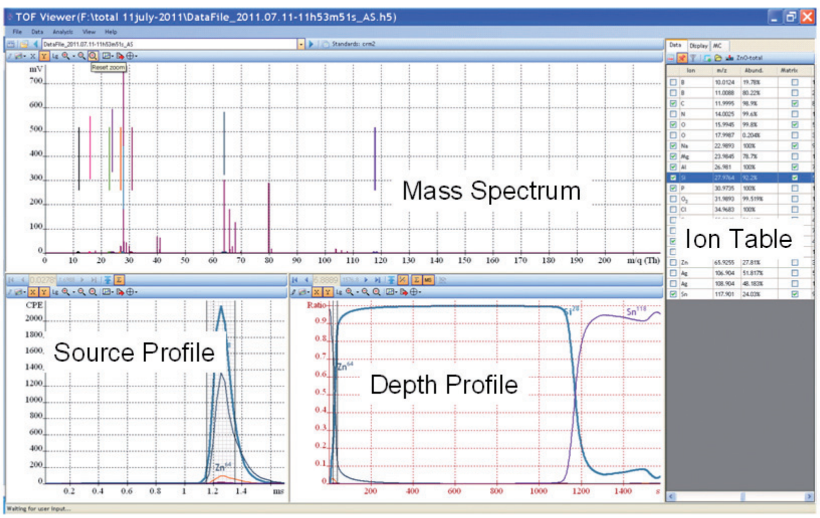

Figure 5. Screen shot of the acquisition software showing 3D data.

Main characteristics of PP-TOFMS

- Fast Depth Profiling Analysis
- High Depth Resolution AND High Sensitivity
- Analysis from Nanostructured to Micron-thick
- All types of materials (metal, glasses, polymer…)
- Full Element coverage and molecular capability
- Retrospective Analysis
- Ergonomic Instrument, Easy and Fast Operation

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