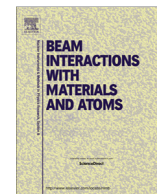




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Depth profile analysis by plasma profiling time of flight mass spectrometry

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ABSTRACT

Plasma profiling time of flight mass spectrometry (PP-TOFMS) provides direct measurement of the chemical composition of materials as a function of depth, with nanometre resolution and the capability to measure both thin and thick layers. It consists in a pulsed radio frequency (RF) glow discharge plasma source fed with pure Ar and created under a pulsed RF potential coupled to a time of flight mass spectrometer (TOFMS). There is a perfect fit between the fast erosion rate of the high density and low energy plasma and the ultra-fast detection and quasi-simultaneous acquisition of all mass ions of the TOFMS. Furthermore the separation between sputtering and ionisation processes makes this technique much less matrix dependent compared to SIMS. The orthogonal TOFMS configuration allows extraction of temporal plasma source characterisation. This is all the more important as signals are largely enhanced in the plasma extinction phase (once RF is turned off) in the so called afterglow region. Sample ion signals are then created through ionisation by Ar metastables called Penning Ionisation ($\text{Ar}^m + \text{M} \rightarrow \text{M}^+ + \text{e}^- + \text{Ar}^0$).

Various applications will be presented ranging from thin film analysis for composition, contamination detection, surface area measurements and doping level to characterisation of diffusion mechanisms. Aspects of analytical performance with regards to sensitivity, quantification, repeatability and sample throughput will be discussed.

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1. Introduction

There is an increasing demand for fast and direct analysis of multilayered solid samples. Materials scientists are looking for “close to process” tools to quickly optimise their growth sequence and to control the lateral uniformity. Regarding elemental composition distribution as a function of depth, conventional surface techniques (XPS, AES, SIMS) offer high surface sensitivity but are usually limited to thickness of few microns. For thicker or embedded layers, SEM EDX or TEM characterisation may be used but require cross section preparation. A radio frequency (RF) glow discharge (GD) plasma is a good erosion source alternative to ion bombardment. As schematically illustrated in Fig. 1, such plasma ensures uniform material removal from the surface to the bulk and parallel excitation/ionisation of the sputtered species. The attractive features of such plasma source for depth profiling are the high density of projectiles and their low energy (as they have an average energy of about 50 eV) providing very fast erosion

(2–10 nm/s) with minimum surface damage. Coupling an orthogonal extraction time of flight mass analyser which ensures simultaneous detection of elements meets the speed requirement of the sputtering source and allows for dynamic depth profiling analysis. This combination called plasma profiling TOFMS technique (PP-TOFMS) provides a direct measurement of the chemical composition as a function of depth, with a nanometre resolution and the capability to measure both thin and thick layers [1]. In addition the high TOF acquisition rate (typically 30 kHz) and the TOFMS orthogonal geometry allows for monitoring the transient signals generated in RF pulsed mode. The afterglow phenomenon observed in the RF off time, or signal enhancement from penning ionisation can be taken advantage of for higher sensitivity [2,3]. Pulsed RF mode has also been proven to be crucial to achieve high depth resolution for thin layers and nano-structured samples of conductive and non conductive materials [4–10] as it allows to reduce thermal stress induced by plasma heating. The benefit of the separation between the sputtering and the excitation/ionisation processes is major for quantification: low matrix effects. In addition, it is important to point out that the sample remains at atmospheric pressure and does not need UHV environment.

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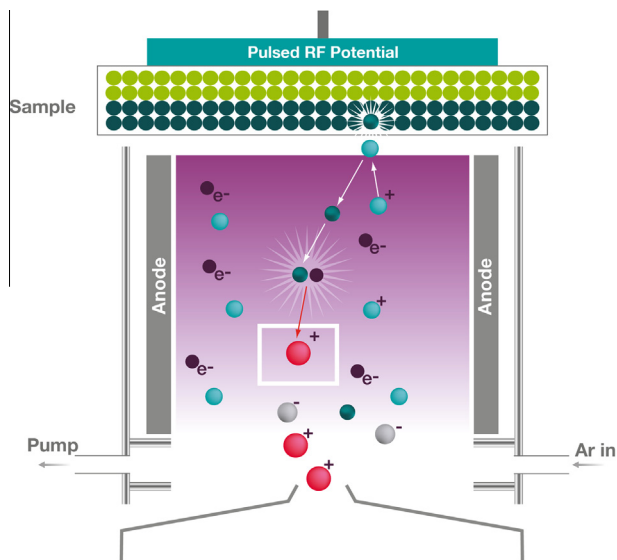


Fig. 1. Schematic diagram of a glow discharge plasma applied to depth profiling analysis.

For all these features, PP-TOFMS is definitely an appropriate tool to characterise elemental depth distribution of various thin films with nanometer depth resolution and high sensitivity over a range going from ppm level to 100%. The high sputtering makes PP-TOFMS quite interesting for reaching embedded layers or deep interfaces. Here we will present few examples of applications to show how useful PP-TOFMS is for determining dopant distribution and detecting presence of contaminants at interfaces.

2. Instrumentation

The plasma source consists in a cylindrical electrode (typically 4 mm diameter) at ground potential and the sample powered with a radio frequency (RF) voltage. The sample placed on an O-ring is actually “closing” the plasma chamber. With this geometry, no sample preparation is needed and starting analysis is almost immediate upon pumping the vessel to primary vacuum and introducing ultra high purity argon at a constant pressure of few mbars. RF excitation is brought from the back of the sample by means of a

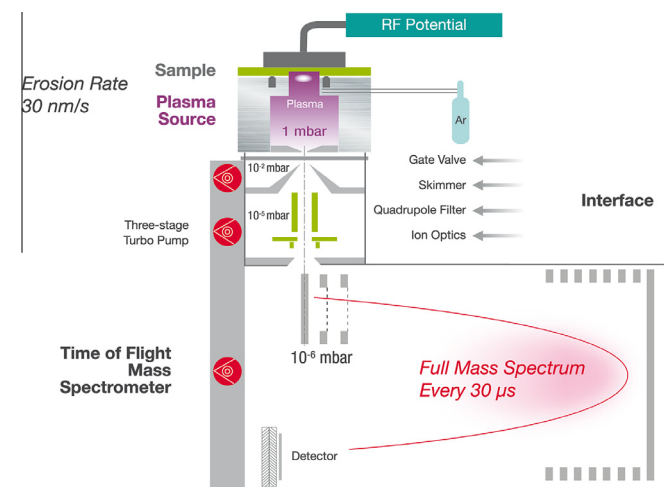


Fig. 2. Schematic diagram of the PP-TOFMS instrument.

cooled applicator pressing down the sample against the O-ring. The RF power is supplied by a 13.56 MHz generator equipped with an automatic matching network. Sputtered species induced from Ar ions and fast neutrals bombarding mainly the sample surface are then excited or ionised. As shown in Fig. 2, ions are then transferred to an orthogonal extraction TOFMS through several interface stages. First ions are extracted through a 0.5 mm diameter sampler and then through a 1 mm skimmer. These two orifices are used for differential pumping. In addition a split flow turbomolecular pump allows for optimum pumping of the different pressure stages. The interface region following the skimmer includes a notch filter used to filter out the most intense ions that would lead to the micro-channel plate detector saturation as well as electrostatic focusing and deflecting components. A gate valve between sampler and skimmer prevents mass analyser exposure to atmospheric pressure when a new sample is being positioned. An important feature of this reflector based TOFMS is the high mass resolving power defined as $m/\Delta m$ (Δm being the half width at half maximum of Gaussian peak). In usual experimental conditions, the mass resolving power is ~ 2500 at mass m/z 208. The TOFMS can also be tuned for higher resolution, 4500 at mass m/z 208.

Operating the TOFMS at a high extraction frequency, together with fast data acquisition software, allows monitoring of the temporal ion response from the plasma during and after the period of the RF pulse. In other words TOF spectra are recorded at virtually any point during the RF period. The timing diagram is shown in Fig. 3. Within a RF period, a series of successive TOF extractions (TOF extraction period of 33 μs) is recorded covering both the “RF on” time and the “RF off” time. For better statistics, TOF spectra are averaged over several RF periods. Temporal windows in the RF period of the ion signals for the pre-peak, plateau and/or afterglow region can be integrated to generate depth profile. This unique time resolved information is highly valuable as it allows for selecting the higher intensity time window (“RF-off” time also called afterglow), which permits to gain in sensitivity by a factor of up to 1000 [2]. All parameters, namely RF period, RF pulse width, number of averaged RF periods may be adjusted to achieve optimum sampling time and signal to noise ratio.

Raw data are ion signals (counts per second) as a function of time. Time to depth conversion requires an external determination of the crater depth, usually profilometry (interferometry or stylus). In addition, for multilayers, a reference sample with known thicknesses determined for example by ellipsometry may be used to determine erosion rates. Then precise conversion of signals to atomic or weight concentration also requires reference samples. But a calibration free semi-quantitative analysis is possible for most elements by calculating the ion beam ratio (signal of a peak corrected for its natural isotopic abundance divided by sum of abundance corrected signals of matrix peaks) [11] thanks to low matrix effects and ionisation cross-sections varying over a limited range.

3. Results

PP-TOFMS has been used to characterise the depth composition of the ultra thin layers deposited on a NiP substrate constituting a hard disc. Fig. 4 shows an example of full depth profile featuring raw signals of all major elements (C, Ti, Cr, Co, Fe, Ni, Ru, Pt, Ta...) as well as minor element such as B. The analysis of this 100 nm thick stack was performed in less than 30 s. In addition to speed, high dynamic range, high depth resolution, and high sensitivity make PP-TOFMS an ideal process control tool. With FIB/TEM, PP-TOFMS makes a very powerful combination for film structure, thickness and composition. The full mass coverage capability is bound to be appreciated in such application as the nature of the layers evolves quickly and nearly covers the full periodic table.

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