Feature Article

Masao Horiba Award

Development and Evaluation of an Innovative "Soft Ionization Technique" Based on Atmospheric Pressure Glow Discharge Time-of-Flight Mass Spectrometry (AP-GD-TOFMS) for the Determination of Inorganic/Organic Contaminants on Semiconductor Surfaces.

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The development of new and innovative "soft ionization techniques" coupled to fast, simple, reliable and robust mass analysers is providing powerful instrumentation able to carry out direct analysis of inorganic/organic compounds on sample surfaces with almost no surface damage. This methodology could open new "research fields" in the direct analysis of semiconductor surfaces with little or no sample pre-treatment. In this project, in particular, an Atmospheric Pressure Glow Discharge (AP-GD) is proposed. Operating with He gas, it will generate a flow of He metastable species, that will be transported outside the discharge chamber and could be directed towards a sample surface. The reactions of the metastables with ambient gas constituents lead to the production of reagent ions that leads to desorption/ionization of the sample surface constituents. Generated ions are then transported into a Time-of-Flight Mass Spectrometer (TOFMS) able to detect both positive and negative ions permitting identification and quantization of the species. AP-GD-TOFMS could provide a fast, simple, reliable and robust analytical method, able to carry out direct analysis of inorganic/organic compounds present on the surface of semiconductor samples (i.e photovoltaic silicon). The spatial resolution could be in the order of ~mm^2 allowing mapping of the sample surface, and limits of detection at femto-mol level could be achieved.

Introduction

The rapid development of new materials and, particularly, the production of thin and coated materials with different kinds of surface treatments (used to modify their properties) have given rise to the need of parallel development of new and more powerful techniques for their analytical characterization.

In the raw silicon industry, routine analysis used to determine the chemical composition (particularly minors and traces) is carried out using analytical techniques that require sample dissolution (e.g. Inductively Coupled Plasma Mass Spectrometry (ICP-MS). Dissolution is a source of contamination due to the presence of impurities in the reagents and at the surface of the silicon samples. Moreover, not all elements contained in silicon can be dissolved using one single dissolution method, making the analysis a time-consuming process that decreases sample throughput and efficiency of quality controls.

Therefore, techniques allowing direct solids analysis are usually preferred for the evaluation of both elemental and molecular composition and for the mapping of distribution of the species in the materials (which ultimately determine their properties and characteristics).

However speed and ease of use are also crucial to keep pace with new materials development and these necessary requirements are not possible with classical surface techniques (e.g. X-Ray Photoelectron Spectroscopy (XPS), Secondary Ionization Mass Spectrometry (SIMS) or Auger Electron Spectroscopy (AES)) that are rather slow, often destructive and complex to use as they require careful sample handling. Therefore, it is of special interest to develop new non-destructive techniques for fast and sensitive direct analysis of impurities on Si

surfaces.

Total reflection X-Ray Fluorescence (TXRF) (non-destructive technique) is known as the reference technique for the measurement of contaminations on semiconductor surfaces (i.e. Si samples). In particular, over the past 25 years, work with TXRF has produced an improvement in the limits of detection (LOD) of five orders of magnitude from ng to some fg.

Most of the improvements are however due to the use of synchrotron radiation (SR), which provides high photon flux, with a continuous spectral distribution (from eV to 500 keV). However, SR is not easily available for quality control or routine laboratory work. Moreover, long integration times (~ 1000 s) are required to determine trace elements. Another approach applied to improve the LOD in TXRF is to prepare the sample in a way that the impurities from the whole surface are concentrated in one spot. The disadvantage is the loss of information about the exact location of the impurity.

Glow Discharge (GD) analytical sources may be an interesting approach as their flexibility make them tuneable for a variety of applications[1].

In particular, we have used in our laboratory a low pressure GD coupled to a TOFMS for the determination of traces in solar grade silicon. This technique is based on sputtering and ionization processes and therefore is considered as a destructive technique.

The silicon industry is working on the development of new methodologies to purify metallurgical grade Si in order to obtain solar grade Si (SoG-Si) at reasonable prices. Our studies are, therefore, of high commercial and technological interest as it is crucial to evaluate with accuracy and precision the amount of elemental impurities contained in the Si samples; to investigate the threshold concentration of these impurities that could degrade the efficiency of the solar cells; and to study the spatial distribution of these impurities.

The capabilities of this approach using low pressure GD-TOFMS are shown in Figure 1, where a calibration curve used for the quantification of B mass content in Si samples is represented.

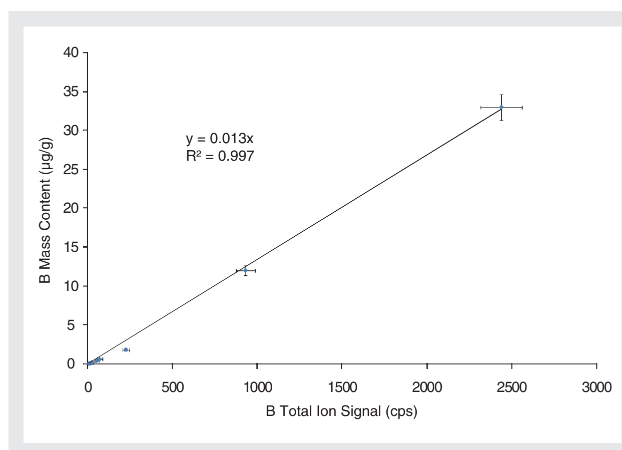


Figure 1 Calibration curve obtained plotting the total B^+ ion signal obtained using low pressure GD-TOFMS versus mass content of B in homogenous Si samples.

A different type of GD still coupled to the TOFMS for sensitivity and large measurement range could be applied in a non destructive way to determine the contaminants on the semiconductor surfaces.

In the preparation process of semiconducting industry (e.g. chips production), surface of silicon wafers may be exposed to various contaminants (e.g. oil, wax, photo resist, metal ions, and many others). These contaminants must be detected and removed; otherwise, they will negatively impact the following processes and could lead to operating failures. Moreover, surface contaminants may weaken the bonding between the chip surface and the deposition membrane, and thereby adversely affect its properties. Furthermore, they may also be converted to other harmful products, causing additional pollution on the chip surface (e.g. when a chip is heated at high temperatures in an anaerobic environment, organic contaminants are carbonized, and will react with silicon to produce silicon carbide on the device surface).

Atmospheric Pressure Ionization Techniques

The development of new ionization strategies usually opens the way to new fields of application. For instance, ground-breaking applications have followed the introduction of new ionization sources such as electrospray ionization and matrix-assisted laser desorption ionization.

Soft ionization techniques such as atmospheric pressure chemical ionization (AP-CI) are new analytical tools available for inorganic/organic mass spectrometry. The mechanisms for the generation of reagent ions and the ionization pathways are similar for most AP-CI sources. First, the buffer gas is ionized by a beam of electrons accelerated in a high electric field. Then, a series of reactions, which vary depending on the buffer gas composition, lead to the generation of reagent ions that will interact with the sample surface (desorption/ionization).

A turning point in atmospheric pressure desorption-ionization techniques, for the analysis of chemical compounds, was reached very recently with the introduction of desorption electrospray ionization (DESI) (U.S. Patent Application 20050230635; commercialized by Prosolia, Inc., IN, USA). In this approach, charged

droplets from an electrosprayed solution are directed toward a solid sample by means of a high-velocity gas stream. The charged droplets ablate the exterior of the sample, removing and ionizing the chemical compounds present on the surface. Accordingly, DESI permits the direct analysis of condensed-phase samples with minimal or no sample preparation. Another remarkable technique is DART (direct analysis in real time) (U.S. Patent Numbers 6,949,741 and 7,112,785; commercialized by JEOL, Inc., MA, USA), where a corona discharge sustained in helium or nitrogen is used to produce ions and excited species, which are then transported to a secondary compartment fitted with an additional set of electrodes. The gaseous stream that leaves this compartment is then heated and used to produce desorption and ionization of inorganic/organic substances in open air.

It is clear, that this new, active, and extremely attractive field of MS offers room for new ideas and improvements. In this sense, Glow Discharges (GDs) are known to generate a much larger number and wider variety of reagent ions than other CI techniques.

AP-GD could be used to generate ions and excited species, which will be transported outside the discharge chamber, where they react with atmospheric constituents. These reactions lead to the production of reagent ions. When impinging a surface, these ions may desorb and ionize the sample surface constituents[2]. The research group of Prof. G.M. Hieftje at Indiana University (USA) is currently working on the development of such kind of soft ionization sources. In particular, they have applied the technique for the ionization of compounds in the gas phase and for the desorption-ionization of some solid organic compounds[3].

The present project is related to the instrumental development of an emerging technique based on “atmospheric pressure (AP) glow discharge (GD) Time of Flight Mass Spectrometry (TOF MS)”, for chemical characterization (elemental and molecular) of semiconductor surfaces.

The AP-GD-TOFMS system

AP-GD is sustained in helium applying direct current or radiofrequency power to some electrodes placed inside a discharge chamber (Figure 2). The AP-GD is used in the flowing afterglow mode as a chemical ionization source: the helium metastable (He*) species generated by the AP-GD are transported outside of the GD cavity and produce reagent ions (Figure 2).

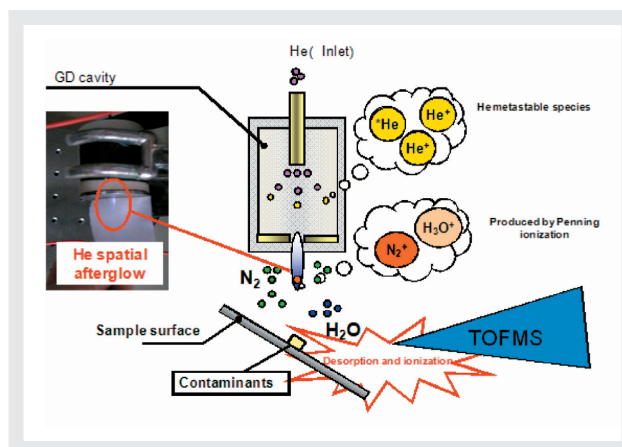
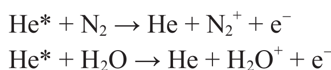


Figure 2 Schematic description of the AP-GD-TOFMS system for the direct analysis of semiconducting surfaces and picture of the AP-GD.

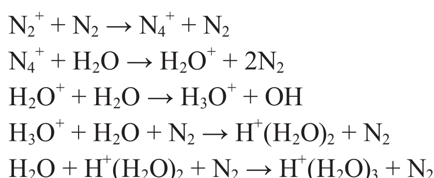
The energy of the He* is approximately 20 eV, high enough to virtually ionize any molecule; the nonradiative lifetime is on the order of several seconds. Penning ionization can subsequently occur whenever a neutral molecule collides with the He metastable species.

Two Penning processes have particularly large cross sections and are the most likely to take place:



$$He^* + N_2 \rightarrow He + N_2^+ + e^-$$
$$He^* + H_2O \rightarrow He + H_2O^+ + e^-$$

Clearly, He* will not survive long in a nitrogen-rich environment (such as open air) and will quickly generate an equivalent amount of N_2^+. The importance of these reactions is that their reaction products permit the generation of reagent ions for surface interaction[4].



$$N_2^+ + N_2 \rightarrow N_4^+ + N_2$$
$$N_4^+ + H_2O \rightarrow H_2O^+ + 2N_2$$
$$H_2O^+ + H_2O \rightarrow H_3O^+ + OH$$
$$H_3O^+ + H_2O + N_2 \rightarrow H^+(H_2O)_2 + N_2$$
$$H_2O + H^+(H_2O)_2 + N_2 \rightarrow H^+(H_2O)_3 + N_2$$

This reaction scheme is at the heart of all current APCI sources, and it is deeply linked to the qualitative and quantitative performance of the source. In such systems, proton transfer is the main ionization pathway[5]. The amount of the analyte substance that can be ionized and also the influence of other sample species on the ionization efficiency of the analyte are related to the number of reagent ions generated.

In this sense, AP-GDs should be superior as being capable to generate a much larger number and wider variety of reagent ions than other chemical ionization techniques,

such as corona discharge[6].
A soft desorption and ionization of the surface constituents is produced upon interaction of the reagent ions with the sample surface. The analyte ions are then extracted into the mass analyser.

Why a TOFMS?

The inherent scanning detection mode of magnetic field sector field and quadrupole mass analyzers is not appropriate for surface and ultra thin film analysis. This limitation has been overcome with the development of TOF-MAS that offer many interesting features: like quasi-simultaneous detection of a large mass range, from hydrogen to macro-molecules, relatively high mass resolution, low cost and the unique high spectral acquisition rate that allows the measurement of transient ion signals. In particular, in this project, we will use a commercially available orthogonal time-of-flight mass spectrometer (TOFMS) from Tofwerk (Switzerland) with a detector containing two micro channel plates for the separation and detection of the analyte ions. The nominal mass resolving power m/dm is about 3500 for the $^{63}Cu^+$ isotope. Ion extraction pulse rates are usually operated at 50 kHz (20 µs/mass spectrum). At this acquisition rate the detection of masses over charge up to 300 m/z is possible, covering the most important range of all stable elements. Moreover, this TOFMS is able to detect both positive and negative ions, which allows for instance the detection of alkalines (i.e. Na^+, K^+) and halogens (i.e. F^-, O^-)[7]. In addition, the detector configuration provides a high dynamic of 8 orders of magnitude. Thus, it is possible to simultaneously detect major, minor and trace ion signals.
A benefit of the AP-GD-TOFMS technique is that the sample to be analyzed does not need to be introduced into the discharge chamber. As a consequence, the system avoids the presence of chemical compounds that could alter the processes that sustain the He AP-GD, and the deposition of material on the electrodes or on the discharge chamber walls that could lead to short- or long-term instabilities, memory effects, and other difficulties.

Preliminary Results:

The first step to achieve the objective of our proposal consists in the optimization of the AP-GD design, its coupling to the TOFMS, and the optimization of the relative orientations between AP-GD, sample to be analysed, and MS (Figure 3).

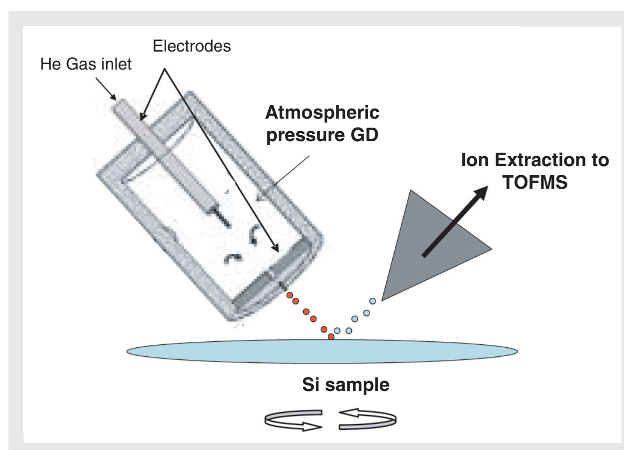


Figure 3 Relative orientations to be optimized between AP-GD, sample and MS entrance.

The analytical performance of the AP-GD is investigated applying to the electrodes dc, rf, pulsed rf and pulsed dc power. Other parameters to be optimised are: the electrode materials (such as Cu, steel or tungsten), the distance between the electrodes, the dimension of the extraction hole, the gas inlet position and flow rate, and the dimension of the GD cavity.
Preliminary studies about the evaluation of the AP-GD are now being carried out using optical emission spectroscopy (OES). Figure 4 shows a schematic view and a picture of the experimental set-up that consists of two optical lenses and an optical fiber connected to a spectrometer. Using this configuration it is possible to obtain the emission spectra from the excited species produced in the AP-GD, in order to investigate the temporal and spatial distribution of the He* and reagent ions species. This experimental set-up can be placed on-axis with the AP-GD or orthogonal to it to obtain information about the spatial distribution of metastables and reagent species.
Figure 5 shows the variations of the emission intensity (391 nm and 587 nm) at different applied voltages obtained using the AP-GD-OES system. It is observed that the emission intensity of the nitrogen band at 391 nm has a sharp increase at applied voltages above 1100 V; while for the same value of applied voltage, the emission intensity of the helium line at 587 nm decreases. This effect could be related to the production of N_2^+ through Penning collisions with He species. Further necessary studies are being carried out at different operating conditions to get more detailed information.

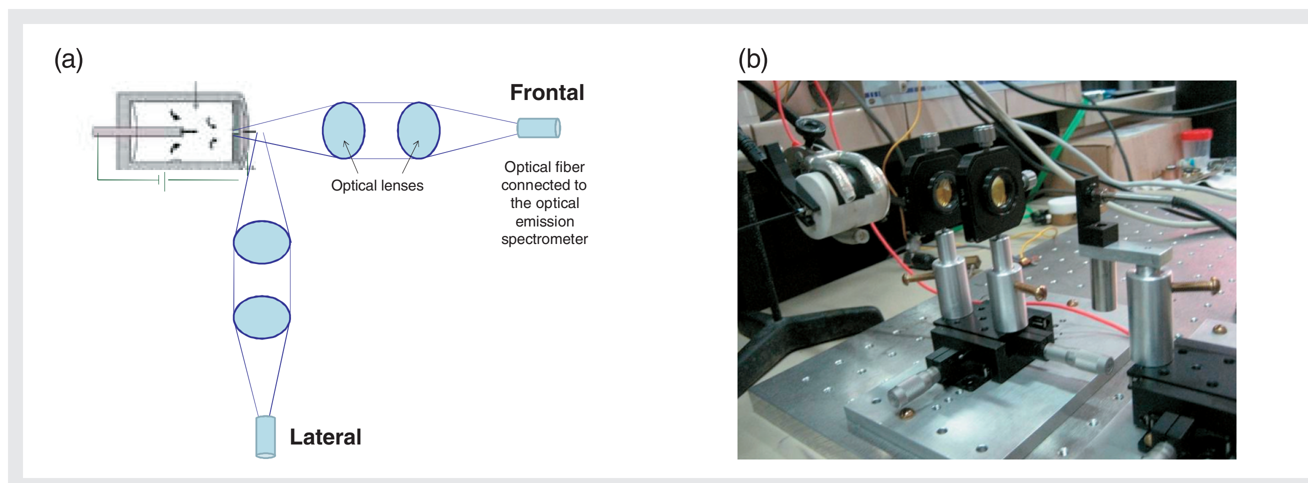


Figure 4 (a) Schematic view AP-GD-OES system showing the frontal detection mode (emission from the internal plasma) and the lateral detection mode that allows studies of the spatial distribution of excited species along the plasma afterglow region.
(b) Picture of the experimental set-up in the lateral detection mode configuration.

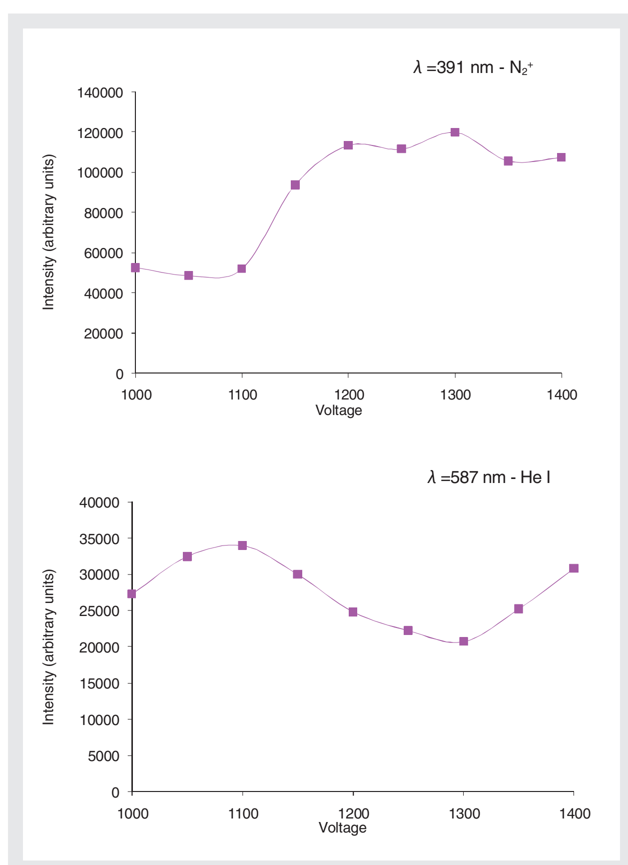


Figure 5 Variation of the emission intensity from N_2^+ (391 nm) and from He (587 nm), obtained using the AP-GD-OES system at different applied voltages (direct current) to the AP-GD electrodes.

Conclusions

AP-GD is an exciting source capable of generating a flow of He metastable species that are transported outside the discharge chamber and interact with air-ambient constituents (N_2 and H_2O) to produce reagent ions (N_2^+, H_3O^+, etc.) for surface analysis.
The AP-GD coupled to an optical emission spectrometer is now under investigation to characterize the distribution of excited species in the afterglow region and to optimize the operating conditions.
In the next step, the AP-GD will be directed towards a Si sample and coupled with a fast orthogonal TOFMS that allows fast mass acquisition rate of positive and negative ions. Reagent ions will interact with silicon surface contaminants (e.g. wax, oils, metal ions, etc) to produce a soft desorption and ionization of these contaminants. Elemental and molecular ions will then be transported into the TOFMS to be separated and detected.

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