ISSUE : 1120/08

HIDEN ANALYTICAL

Customer Research REVIEW

Thin Films, Plasma & Surface Engineering

Customer Contributions:

Highly selective etching with C_5HF_7 plasma

Y. Miyawaki, M. Sekine, K. Ishikawa, T. Hayashi, and M. Hori, *et al.* ¦ Nagoya University
A. Ito, H. Matsumoto, *et al.* ¦ ZEON Corporation

HIPIMS and traditional pulsed sputtering compared

John Kiwi ¦ EPFL-SB-ISIC-LPI

New ion beam implantation technique described

Dr Daniel Höche ¦ Helmholtz-Zentrum Geesthacht

Ion density study in high power magnetron system

O.V. Vozniy ¦ Centre de Recherche Public - Gabriel Lippmann

Related Products:

IG20 - for UHV Surface Analysis Applications

EQP - Plasma Sampling Mass Spectrometer

ESPion - for Measurement of Plasma Properties

MAXIM - for Static & Dynamic SIMS/SNMS

In the press:

Dedicated probe for SIMS/SNMS

A very big thank you to all who have contributed:

NAGOYA UNIVERSITY
ZEON
EPFL ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE
Helmholtz-Zentrum Geesthacht Centre for Materials and Coastal Research
Centre de Recherche Public Gabriel Lippmann

Highly selective etching of SiO_2 over Si_3N_4 and Si in capacitively coupled plasma employing C_5HF_7 gas

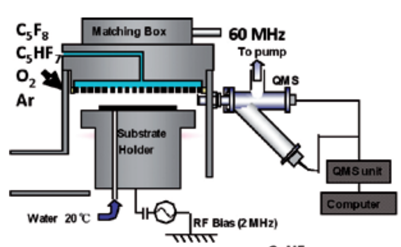
Quadrupole mass-spectroscopic analysis - in the novel $C_5HF_7/O_2/Ar$ plasma - has revealed important neutral and ionic species, such as C_xF_y (X>2), C_xF_y (Y/X<2), and C_xHF_y. Compared with conventional $C_5F_8/O_2/Ar$ plasmas, it was found that plasma etching of SiO_2 films with high selectivity against SiN films was obtained. In accordance with the analytic results, the mechanism involved the formation of thicker C-rich fluorocarbon film on SiN obtained by impinging the C-rich hydrofluorocarbon species, characterised in the novel plasma.

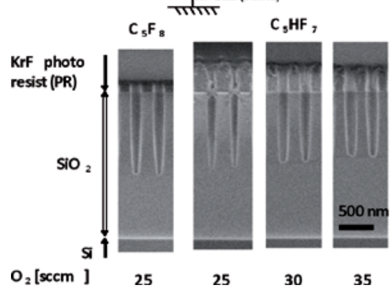
C_5F_8 and C_5HF_7 are mainly fragmented in electro-impact ionization at 70 eV into C_3F_3 and C_3HF_2, respectively. Indeed, the fragmentation pattern for C_5HF_7 clearly detected H-containing species substituting one F atom with one H atom, ie $CF_2 \rightarrow CHF$, $C_2F_2 \rightarrow C_2HF$, $CF_3 \rightarrow CHF_2$ and so on.

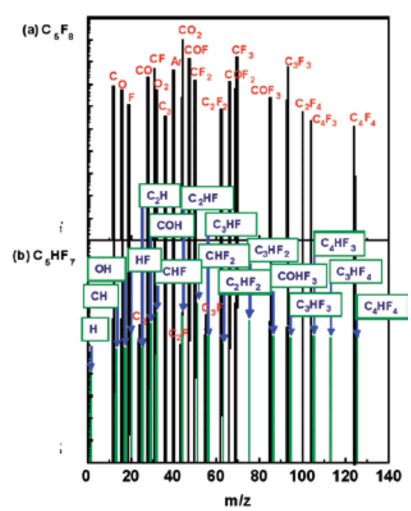
In a real plasma for dielectric etching, it is well-known that, dissociation, ionization and attachment occur by collisions with electrons, which typically have a Maxwellian energy of a few eV. Therefore, there was a large difference in gas chemistries between neutral species with and without H atoms for the actual $C_5F_8/O_2/Ar$ and $C_5HF_7/O_2/Ar$ plasma. In addition, combined with quantum chemical calculations, it was concluded that the main dissociation pathway of the cyclic C_5F_8 molecules was $C_5F_8 \rightarrow CF_2 + C_4F_6$ and through further multiple dissociations, smaller fragmentation occurred following reactions; $CF_2 \rightarrow CF + F$, or $C_4F_6 \rightarrow C_3F_3 + CF_3$. Therefore, large fraction of CF_3, CF_2, CF, C_3F_3 and each related H-substituted species, such as CHF_2, CHF, CH, and C_3HF_2 were detected.

Furthermore, the entrance of the quadrupole mass spectrometer was located at the chamber wall of the commercialized reactor, which unfortunately only provided information about the composition of positive ions at the closed chamber wall excluding the sample surface. The main positive ionic species detected were CF_3^+, CF_2^+, CF^+ in addition to Ar^+. It is also noteworthy that large molecule ions such as $C_3F_3^+$, $C_2F_4^+$ and $C_4F_4^+$ were detected. The behaviour of large molecule ions – C_xF_y or C_xHF_y coincided with selective etching of SiO_2 films, since selective formation of the C-rich fluorocarbon layer on SiN films was achieved.

The main focus of this research was the characterisation of gas molecules for improved etching. To improve the etching performances such as etch rates, material's selectivity, etched profile control, it is generally recognized that the key factors are surface reactions that obey plasma chemical properties. Hence, feedstock gases are the most important issues. The main gases of selection in the etching of SiO_2 has changed over time – for instance, CF_4, C_2F_6, C_4F_8, C_4F_6, and C_5F_8. Also, H- and O-containing species – CHF_3, CH_2F_2, C_3F_6O, $C_5F_{10}O$, etc – are helpful as controls, especially with regards to the amount of F atoms involved in the plasma chemistry. We emphasize that information on the relationship between the etching properties and the chemistry of novel gases is of significant interest for scientific and industrial purposes. Therefore, we concentrate our continuous research in the elucidation of the etching mechanism through the diagnostics of the gas phase and surface analysis.







Our Reference: **AP-EQP-0002**

PROJECT SUMMARY BY:

NAGOYA UNIVERSITY **Y. Miyawaki, M. Sekine, K. Ishikawa, T. Hayashi,** and **M. Hori,** *et al.* Nagoya University, Department of Engineering, Nagoya, Japan

ZEON **A. Ito, H. Matsumoto,** *et al.* ZEON CORPORATION, Kawasaki, Japan

PAPER REFERENCE:

Y. Miyawaki *et al* 2013 *Jpn. J. Appl. Phys.* **52** 016201 doi:10.7567/JJAP.52.016201

HIDEN PRODUCT:

EQP Mass & Energy Analyser for Plasma Diagnostics

High power impulse magnetron sputtering (HIPIMS) and traditional pulsed sputtering (DCMSP) Ag-surfaces leading to *E. coli* inactivation

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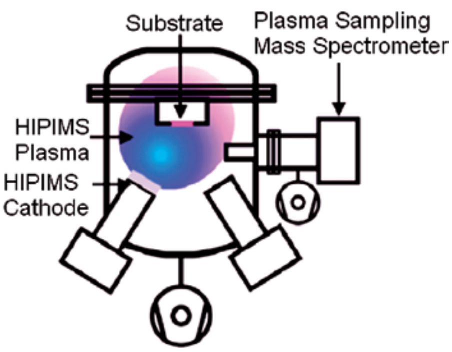
This study addresses the high power impulse magnetron sputtering (HIPIMS) deposition of Ag-nanoparticle films on polyester and the comparison with films deposited by direct current pulsed magnetron sputtering (DCMSP).



Schematic of the HIPIMS setup, the cathode used was Ag and the substrate polyester

The first evidence is presented for the *E. coli* bacterial inactivation by HIPIMS sputtered polyester compared to Ag-polyester sputtered by DCMSP. HIPIMS layers were significantly thinner than the DCMSP sputtered layers needing a much lower Ag-loading to inactivate *E. coli* within the same time scale. The Ag-nanoparticle films sputtered by DCMSP at 300 mA for 160s was observed to inactivate completely *E. coli* within 2 hours having a content of 0.205% Ag wt%/polyester wt%. HIPIMS-sputtered at 5 Amp for 75s led to complete *E. coli* bacterial inactivation also within 2 hours having a content Ag 0.031% Ag wt%/polyester wt%. The atomic rate of deposition with DCMSP is 6.2×10^{15} atoms Ag/cm^{2}s while with HPIMS this rate was 2.7×10^{15} atoms Ag/cm^{2}s. The degree of ionization of Ag^+/Ag^{2+} and Ar^+/Ar^{2+} was proportional to the target current applied during HIPIMS-sputtering as determined by mass spectroscopy. These experiments reveal significant differences at the higher end of the currents applied during HIPIMS sputtering as illustrated by the ion-flux composition. X-ray photoelectron spectroscopy (XPS) was used to determine the surface atomic concentration of O, Ag, and C on the Ag-polyester. These surface atomic concentrations were followed during the *E. coli* inactivation time providing the evidence for the *E. coli* oxidation on the Ag-polyester. X-ray diffraction shows Ag-metallic character for DCMSP sputtered samples for longer times compared to the Ag-clusters sputtered by HIPIMS leading to Ag-clusters aggregates. Ag-nanoparticle films on polyester sputtered by HIPIMS contain less Ag and are thinner compared to Ag-nanoparticle films sputtered by DCMSP.

The mass spectroscopy analysis of the ions in the chamber was carried out by way of a Hiden mass spectrometer connected with the DC-magnetron gas chamber. The Ar^+, Ar^{2+} and Ag^+ and Ag^{2+} ions were determined. With increasing current the Ar^+ decreases and the Ag^+ gas phase increases. At higher discharge currents Ag^+-ions exceeded the amount of Ar^+-ions. The most interesting result is that HIPIMS discharges at 10 A peak current produced high quantities of Ag^+-ions along a small amount of Ag^{2+}-ions.

Our Reference: **AP0319**

PROJECT SUMMARY BY:

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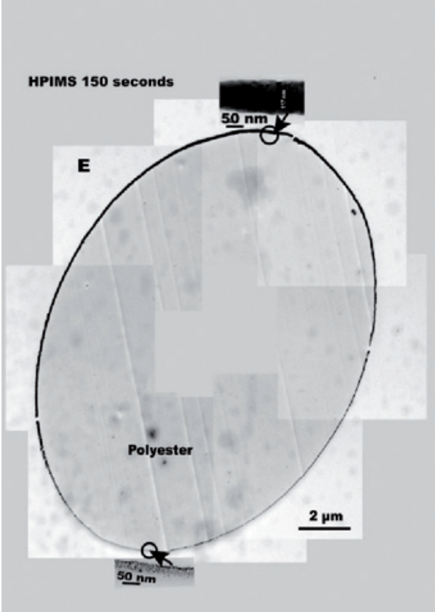
PAPER REFERENCE:

O. Baghriche *et al.,* (2012) "High power impulse magnetron sputtering (HIPIMS) and traditional pulsed sputtering (DCMSP) Ag-surfaces leading to E. coli inactivation" *Journal of Photochemistry and Photobiology A: Chemistry* **227** (1), 11-17

HIDEN PRODUCT:

EQP Mass & Energy Analyser for Plasma Diagnostics



Transmission electron microscopy of Ag-polyester fibers sputtered by HIPIMS at 5 Amps for 150s. E in stands for epoxide used during the preparation

Magnesium nitride phase formation through new ion beam implantation technique

Our Reference: **AP0128**

PROJECT SUMMARY BY:

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Centre for Materials and Coastal Research

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PAPER REFERENCE:

D. Höche, C. Blawert, M. Cavellier, D. Busardo, T. Gloriant (2011) "Magnesium nitride phase formation by means of ion beam implantation technique" *Applied Surface Science* **257** (13), 5626-5633

HIDEN PRODUCT:

MAXIM & IG20 SIMS Components

Magnesium alloys are interesting for industries where weight gain is the priority; unfortunately, their poor corrosion resistance has delayed its use in many industrial sectors. Particularly with regard to automotive applications, surface modifications become indispensable. On the other hand the mechanical properties of magnesium are close to that of human bones and it is of great importance for our body. This suggests the use of Mg alloys for implants or stents with tailored degradation properties to avoid additional surgeries.

With respect to technical issues e.g. in automotive industries, nitriding of magnesium by nitrogen ion implantation applying the Hardion+ technology has been carried out on well known compounds. The treatments have been studied for their corrosion resistance enhancement, the involved phase formation and the changes of mechanical properties on common Mg-based alloys (bare, AM50, AZ31). Nitrogen ions with an energy of approximately 100 keV were used to induce the formation of the Mg_3N_2 phase leading to improved surface properties. The results show nitride formation behaviour to a depth of about 600 nm.

Figure 1 shows the depth profiles of the three treated alloy systems measured by a Hiden SIMS system shown in Figure 2. The distribution of MgN- ions suggests the formation of stable Mg-N bonds which is quite interesting because of the instability of the phase on air exposure due to the affinity to form oxides. The depth profile verifies this strong oxidation behaviour. Aluminium as alloying elements seems to be enriched

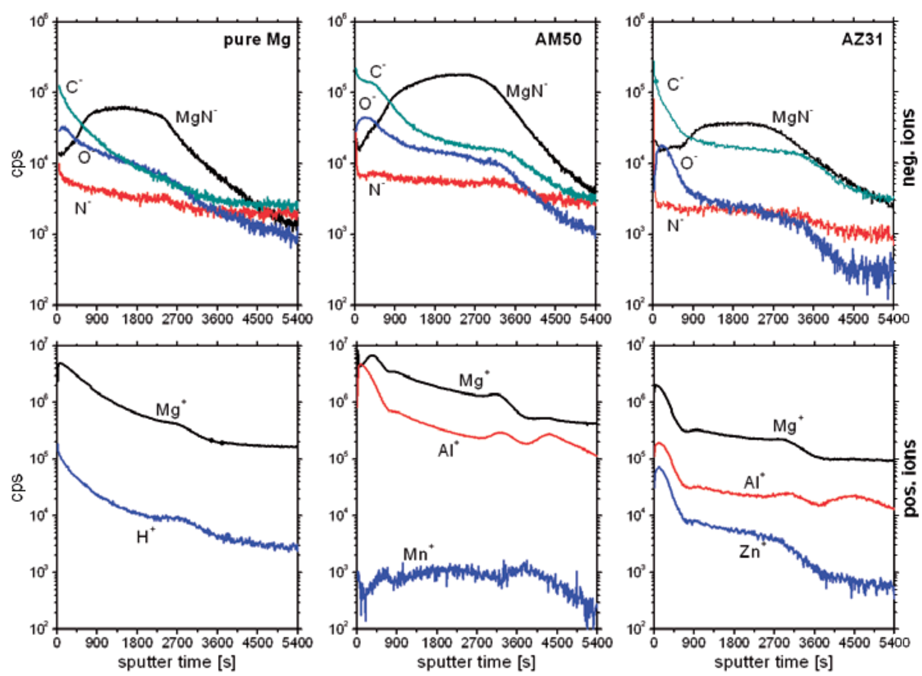

FIGURE 1: *SIMS depth profiles according the reference paper*

at the interface and at the surface due to its oxide formation ability. Comparing the results especially those of SIMS the shape of depth profiles is typical for implantation methods. Stable coatings with enhanced properties have been formed.

The project gives an insight into the possibilities of using ion implantation to modify or tailor magnesium surfaces. The hardness has been increased to a factor of four; the corrosion resistance has been modified as well due to the Mg_3N_2 formation. Upcoming studies will give further information on challenges and the possibilities applying the method.

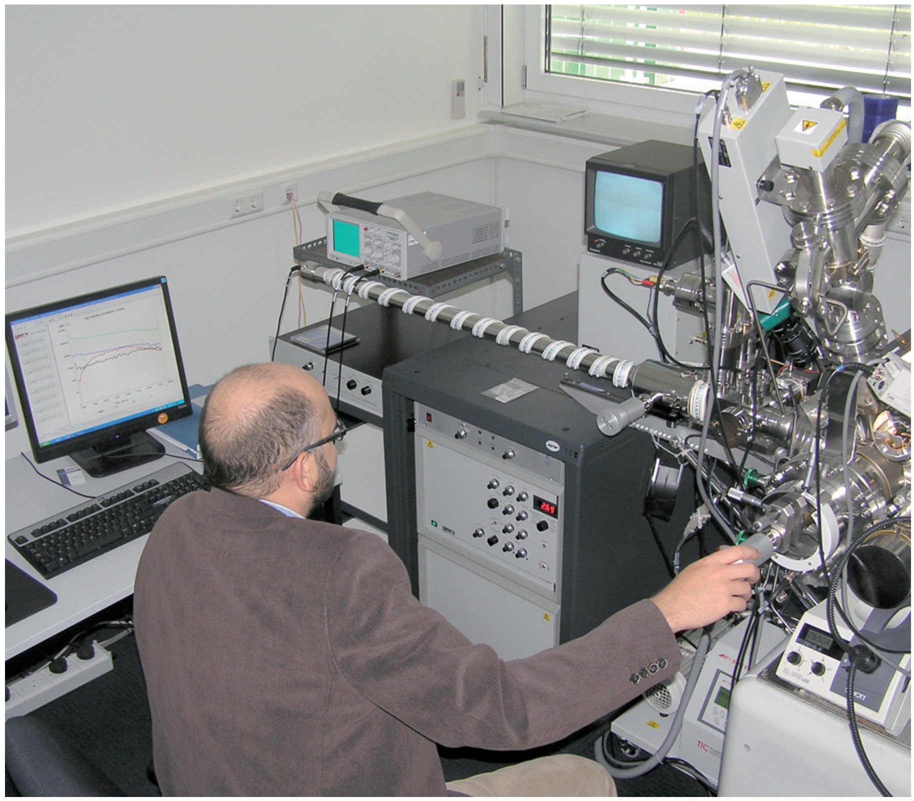

FIGURE 2: *OEM fitment of MAXIM and IG20 SIMS system to a Kratos XPS surface analysis instrument, in Helmholtz-Zentrum Geesthacht, Zentrum für Material- und Küstenforschung GmbH*

Additional activities:

Co-author: **Dr. Michael Störmer**

ANALYSIS OF PVD COATINGS:

Development of Mg based bulk metallic glass (glassy) coatings for example Mg-Gd-B with tailored properties in terms of corrosion and degradation. Hiden SIMS system has been applied to measure interface enrichments and elemental depth distributions like shown in Figure 3. This should help to optimize the deposition conditions according to stoichiometry, phase formation and thin-film growth using the HZG magnetron sputtering facility. In the future such coatings could be applied on implants, on castings or on other special devices

REFERENCE:

Patent: EP2463399 (A1) / US2012148871 (A1)

- Magnesium components with improved corrosion resistance

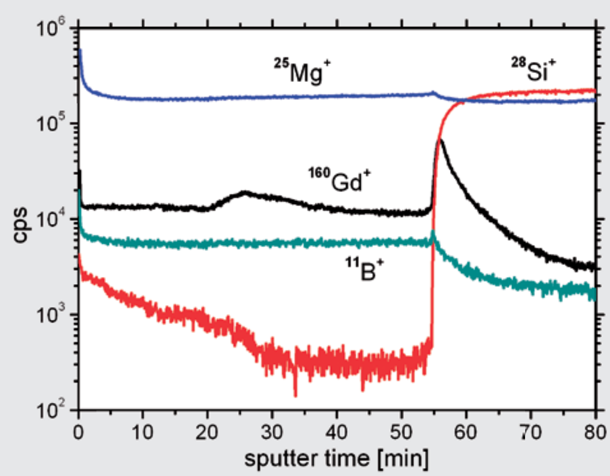

FIGURE 3: *Depth profile of pos. ions of a ternary PVD coating on a silicon substrate*

Ion density increase in high power twin-cathode magnetron system

The Optimized Wire Treatment (OWIT) project aims at developing and validating a new deposition technique allowing uniform coatings with exceptional physical properties to be obtained on wires and fibers. Conventional sputtering technique, which utilizes planar targets or point sources, suffers from serious limitations related to the impossibility to deliver a majority of sputtered species to the substrate. We propose a magnetron sputter system operating in High Power Impulse (HIPIMS) mode, which preserves a significant amount of metal ions. These ions are not lost at the chamber walls, but can be utilized repeatedly for the deposition process, maintaining high level of self-sputtering even at relatively low power inputs. New coatings with unique physical, chemical and electrical properties can be obtained with very good mechanical strength, high ageing quality, long chemical and mechanical lifetime.

Our Reference: **AP0142**

PROJECT SUMMARY BY:

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PAPER REFERENCE:

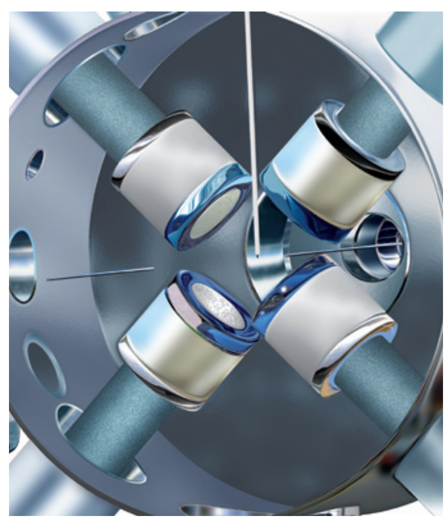
O. Z. Vozniy, D. Duday, A. Lejars, T. Wirtz (2011) "Ion density increase in high power twin-cathode magnetron system" *Vacuum* **86** (1), 78-81

HIDEN PRODUCT:

ESPion Advanced Langmuir Probe

In order to validate and evaluate the method and deposition technique, the following major objectives are considered:

- Plasma modelling with particle-in-cell (PIC) and Monte Carlo methods using experimental data obtained by means of plasma diagnostic tools. Extensive plasma modelling and calculations are performed in order to determine the optimum properties (geometry, density, field distribution, etc.) of the bulk plasma.
- New technological level in the field of smart processing of wires was achieved. The major difficulty and the originality of this project consist in concentrating high-density plasma in a small cylindrical volume having relatively large length. We aim at creating an appropriate plasma shield around wires in order to deposit and implant simultaneously the constitutive species of coatings. This new plasma configuration implies high deposition rates and thus high treatment speeds. In future, special attention will be paid to achieving perfect cylindrical plasma geometry in order to guarantee homogeneous treatment all over the wire surface.
- Plasma diagnostics by means of Hiden Analytical ESPion Advanced Langmuir Probe have been carried out. The discharge has been analyzed for different power modes during the active phase of HIPIMS plasma generation when the probe was placed in the middle of the discharge volume between four essentially balanced magnetrons. When the cycle contains more than one pulse, the triggering waveform was transformed into a single pulse using a counting device. Triggering was initiated 5 μs before the first edge level of the discharge voltage had been achieved at the beginning of each cycle. In such a configuration, the probe can offer 125 ns resolution for the main plasma parameters such as ion and electron densities, electron temperature, plasma and floating potentials.

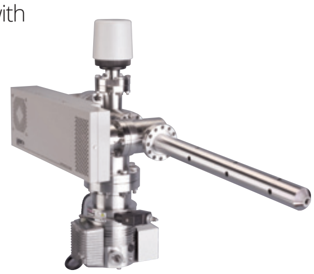


The experimental setup with four essentially balanced planar magnetrons (2" Ti targets), Langmuir probe, and the system of capillaries used to introduce wires from atmospheric pressure.

Related Products:

IG20 for UHV Surface Analysis Applications

The IG20 features a high brightness electron impact gas ion source which is designed specifically for oxygen capability but is also suitable for use with inert and other gases:



- Surface Analysis
- Thin Films & Surface Engineering
- Surface Science
- Nanotechnology
- Auger Electron Spectroscopy
- Ion Beam Sputtering
- Rastering Depth Profiling

EQP – Plasma Sampling Mass Spectrometer

The Hiden EQP is a combined mass / energy analyser for the analysis of positive AND negative ions, neutrals, and radicals from plasma processes:

- Analysis of positive ions, negative ions, neutral radicals and neutrals
- Etching / Deposition Studies
- Ion Implantation / Laser Ablation
- Residual Gas Analysis / Leak Detection
- Plasma electrode coupling - follow electrode conditions during operation
- Analysis through a viewport, grounded electrode, driven electrode

ESPion – for Measurement of Plasma Properties

The ESPion advanced Langmuir probe for rapid, reliable and accurate plasma diagnostics for industry and academia:

- Etching / Deposition / Cleaning Plasma Processes
- Pulsed plasma operation
- Ion density (Ni & Gi)
- Electron retardation (Te & EEDF)
- Electron density (Ne)
- Plasma Potential
- Debye Length, floating potential
- Ion flux

MAXIM - for Static & Dynamic SIMS/SNMS

A state of the art secondary ion mass spectrometer for static and dynamic SIMS and SNMS applications:

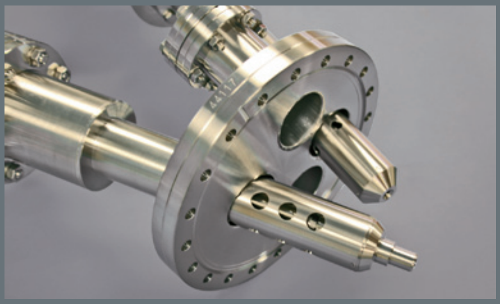
- Depth profiling with depth resolution for multiple components analysed on the nanometre scale
- Chemical 3D imaging with wide area scanning, and with spatial resolution in the low 10's of micron
- SNMS quantitative depth profiling included for analysis of nano to micron scale multilayer coatings with concentration measured in the 0.1% to 100% range
- Surface composition analysis with detection to < 5×10^{15} atoms per cubic cm (atoms/cc)
- Analysis of all elements, oxides, semiconductor compounds/dopants and clusters to 1000amu

In the press:

OUR REFERENCE: HAPR0086

Dedicated probe for SIMS/SNMS

The Hiden EQS-series of quadrupole mass spectrometer probes were introduced for measurement of external ions in a vacuum environment, specifically for application to the SIMS surface analysis technique. The systems are now even further enhanced by the addition of a new high-efficiency electron bombardment ion source mounted at the immediate entry region to the probe for direct measurement of secondary neutrals (SNMS), enabling quantification of concentration over the full abundance range from trace level to 100%.



The dual techniques are beneficial for diverse surface analyses including measurement of optical and metallurgical coatings, alloys, corrosion layers, architectural coatings. Both SIMS and SNMS can be used throughout a continuous measurement sequence to provide quantified depth profiling data through the widest concentration range.

The probes combine both mass and energy filters for optimum beam transmission efficiency together with refined mass resolution and abundance sensitivity, with mass range options selectable up to 2500amu. They are available with both gas and metal-sourced ion guns to enable SIMS/SNMS upgrade of existing surface analysis facilities, and alternatively as complete standalone SIMS/SNMS Workstations.

For further information on these or any other Hiden Analytical products please contact Hiden Analytical at **info@hiden.co.uk** or visit the main website at **www.HidenAnalytical.com**

If you would like to submit a project summary for consideration in our next Newsletter, please email a brief summary (*approx. 500 words*) and corresponding images to **marketing@hiden.co.uk**

HidenAPPLICATIONS

Hiden's quadrupole mass spectrometer systems address a broad application range in:

GAS ANALYSIS

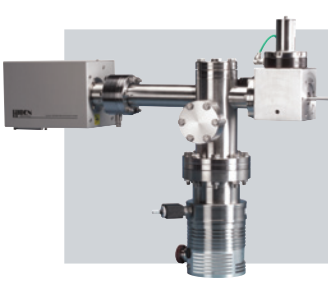
- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

SURFACE ANALYSIS

- UHV TPD
- SIMS
- end point detection in ion beam etch
- elemental imaging - surface mapping

PLASMA DIAGNOSTICS

- plasma source characterisation
- etch and deposition process reaction kinetic studies
- analysis of neutral and radical species



VACUUM ANALYSIS

- partial pressure measurement and control of process gases
- reactive sputter process control
- vacuum diagnostics
- vacuum coating process monitoring

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