

Hidden Applications



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



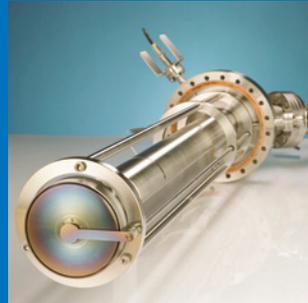
Gas Analysis

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



Surface Science

- 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

Sales Offices:

We have sales offices situated around the globe. Visit our website for further information.



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Issue Number: 1120/05

Hidden Life

A world of products connected by science & imagination



Hidden Quadrupole Mass Spectrometers *in action:*

In this issue:

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- Negative-ion surface production in hydrogen plasmas: modelling of negative-ion energy distribution functions and comparison with experiments
- Protonated nitrosamide and its potential role in the release of HONO from snow and ice in the dark
- Mass spectrometer study in time-multiplex $\text{SF}_6 + \text{CH}_4$ plasma etching of silicon

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Thin Films, Plasma and Surface Engineering

Hidden Quadrupole Mass Spectrometers are used for process, environmental and research applications throughout the world.

This newsletter includes a selection of the most recent application stories from referenced published sources.

Our contributors to this newsletter caught our eye with published articles of the highest quality.

Key data from the Hidden EQS 1000 Series SIMS Analyser, EPIC UHV Analyser, EQP Mass & Energy Analyser and HPR-30 Vacuum Process Gas Analyser are included.

We are delighted that they have shared a brief synopsis of their research for our newsletter.

A very big thank you to all who have contributed



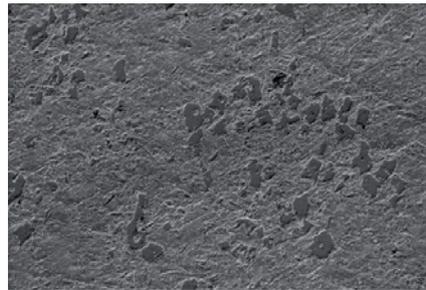
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ANALYTICAL

Customer Research:

Using FIB-SIMS to understand tribological changes in an Al-Si automotive alloy subject to transient start-stop velocities

Worldwide vehicle ownership is predicted to exceed 2 billion vehicles by 2030, with cars and vans responsible for around 45% of global CO₂ emissions from the transport sector. This has resulted in a significant drive within the automotive sector to mitigate the environmental impact from our vehicles of the future. New technologies such as innovative light-weight materials, hybrid and electrical vehicles have all progressed from advanced concept to mainstream consumer models. There has also been a greater emphasis on drive efficiency – the need to reduce mechanical and frictional losses to obtain the maximum amount of mileage whilst minimising fuel consumption.

Whilst individually these technologies all aim to reduce the environmental impact of our vehicles, when combined, the synergistic result is perhaps less well understood. Take for example the surface interactions of the piston ring against the cylinder wall. For effective hydrodynamic lubrication in the mid-stroke region, the ring must be in continuous motion. However with the introduction of a hybrid start-stop

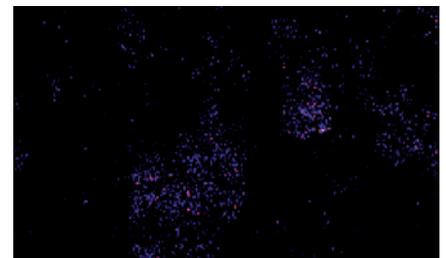
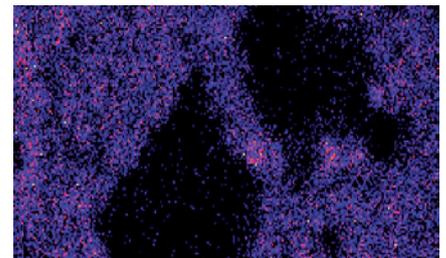
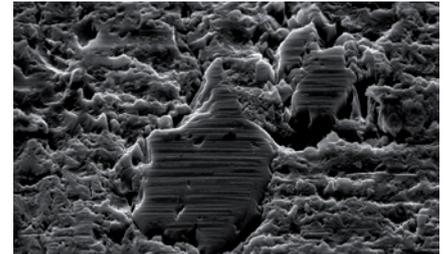


▲ Figure 1. Honed Al-Si surface showing aluminium matrix and silicon particles

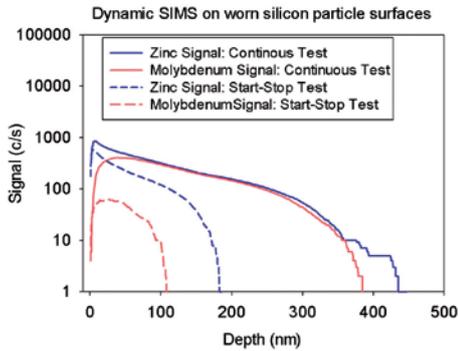
cycle, velocity interruptions are much more frequent and as a consequence boundary lubrication and surface contact much more prevalent. This could potentially be a problem in engines that use aluminium-silicon as the cylinder wall material, as aluminium is poor tribologically and prone to scuffing and adhesive wear. In order to investigate if this was the case, a series of laboratory tests were conducted on a hyper-eutectic Al-Si alloy, as shown in Figure 1. A segment from a cast iron piston ring was oscillated against a honed Al-Si surface under lubricated conditions, similar to that experienced in a real engine. One set of tests was conducted under continuous reciprocation whilst a second set was repeatedly interrupted at one minute intervals.

Each test surface was investigated using a Zeiss NVision40 dual beam focused ion beam – scanning electron microscopy (FIB-SEM). The equipment, based at the University of Southampton's Nanofabrication Centre is equipped with a Hiden Analytical EQS quadrupole secondary ion mass spectrometer (SIMS). This allowed chemical mapping of ions sputtered from the surface of the Al-Si as well as dynamic SIMS depth profiles.

For Al-Si alloys to be effective tribologically, the Si particles are engineered to stand proud of the aluminium and bear the load. It can be seen from the images in Figure 2 that formation of friction modifying additives containing Molybdenum (e.g. MoS₂) from the lubricating oil had formed a low friction layer on the aluminium matrix. Chemical analysis from the SIMS mapping showed how Zinc based anti-wear additives were forming preferentially on the silicon particles, as expected.



▲ Figure 2. Secondary electron image from worn Al-Si surface and SIMS chemical maps of Molybdenum and Zinc, respectively



▲ Figure 3. Dynamic SIMS depth profiles on silicon particle surfaces subject to continuous and start-stop sliding

Dynamic SIMS depth profiles of the zinc and molybdenum signals from the surface of the silicon particles, Figure 3, indicated that the surface tribo-films, so critical to the frictional and wear performance of the cylinder wall, appeared to be thinner as a result of the interrupted start-stop sliding.

Although the films had not been compromised, this work was good evidence for the need to maintain a good chemically functional lubricant supply throughout the lifecycle of start-stop hybrid vehicles.

Dr John C Walker is a Research Fellow at the National Centre for Advanced Tribology at Southampton University and collaborates with Dr Harold Chong at the Southampton Nano-Fabrication Centre with the FIB-SIMS system.

Our Reference: AP0459

Project Summary by:

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Paper Reference:

J. C. Walker, T. J. Kamps, R. J. K. Wood (2012) "The influence of start-stop transient velocity on the friction and wear behaviour of a hyper-eutectic Al-Si automotive alloy" *Wear* [online] Available at: <http://dx.doi.org/10.1016/j.wear.2012.11.007>

Hidden Product:

EQS 1000 Series SIMS Analyser

Negative-ion surface production in hydrogen plasmas: modelling of negative-ion energy distribution functions and comparison with experiments

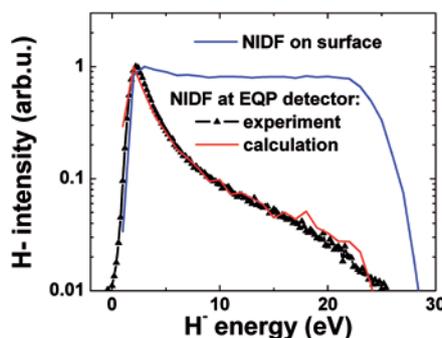
Negative ions in low-pressure plasma sources are created either in the plasma volume by dissociative attachment or, at the plasma surface interaction due to surface ionization of backscattered or sputtered particles. Negative-ions formed on surfaces are accelerated towards the plasma by the sheath. They can influence the plasma kinetics through collisions with plasma species, or are self-extracted from the plasma thanks to the energy acquired in the sheath. Self-extraction of negative-ions can affect processes like sputtering, where the negative-ions formed on the cathode bombard the layer being deposited. In applications such as negative-ion sources for accelerator or fusion devices, it is taken advantage of negative-ion surface production. A low work-function material (usually caesium-covered metals) is in contact with the plasma and greatly enhances negative-ion production because of the low energy required to extract an electron from the surface. However, caesium free negative-ion sources would be greatly valuable for fusion applications because of the strong maintenance constraints induced by caesium injection.



▲ Figure 1. The sample holder facing the EQP 300 mass spectrometer nozzle

The present project deals with negative-ion surface production in caesium free H_2/D_2 plasma for fusion applications. It is conducted under strong collaboration between Aix-Marseille University and CEA Cadarache. The goal is to understand and optimize negative-ion surface production. To this aim, a carbon sample (graphite, diamond...) is negatively

biased in a capacitively coupled plasma. Negative-ions formed upon positive ion bombardment are accelerated towards the plasma. Under the low pressure condition considered in this work (0.2 – 2 Pa) they reach without collision the Hidden EQP 300 mass spectrometer which is facing the sample (see Figure 1). H^- negative-ion distribution functions (NIDFs) are measured by means of the energy filter of the EQP mass spectrometer. In order to get insight into surface ionization mechanisms, surface-produced NIDFs have to be determined from the measured NIDFs. The first step is to choose a priori the solution, i.e. a reasonable function for the NIDFs on the surface $f(E, \theta)$. Based on this distribution, negative ion trajectories in the sheaths and in the plasma are computed to get the negative-ion arrival energies and angles at the EQP mass spectrometer entrance. The ion transmission probabilities inside the spectrometer are then calculated based on arrival energies and angles by using a full 3D modelling of the EQP mass spectrometer developed with the SIMION software. Finally the negative-ion distribution function of the ions reaching the mass spectrometer detector is calculated and compared to the experiments (see Figure 2).



▲ Figure 2. Comparison between measured and calculated NIDFs

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Customer Research:

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Using this method it has been possible to obtain the angular and energy distribution function of negative-ions leaving the surface $f(E, \theta)$ (see $f(E)$ on Figure 2). This NIDF strongly differ from the measured one (see Figure 2) because of the modifications of the trajectories induced by the sheaths. From the study of $f(E, \theta)$ it is shown that the collected negative-ions come from the centre of the sample and not from surrounding surfaces (clamp, sample holder...). Most of the negative-ions created at the surface originate from the backscattering of positive-ions (with electron capture), the rest coming from sputtering of adsorbed hydrogen atoms (with electron capture). Due to the broad distribution of emission-angle and emission-energy, only a few percent of the emitted negative-ions are collected. Finally, comparative studies of NIDFs obtained on different carbon materials sheds light on the main surface parameters influencing surface ionization. For instance, diamond material can strongly enhance negative-ion surface production when heated up to 400°C. This enhancement has been correlated with an increased hydrogenation of the surface and a reduction of surface defects.

Our Reference: AP-EQP-0001

Project summary by:

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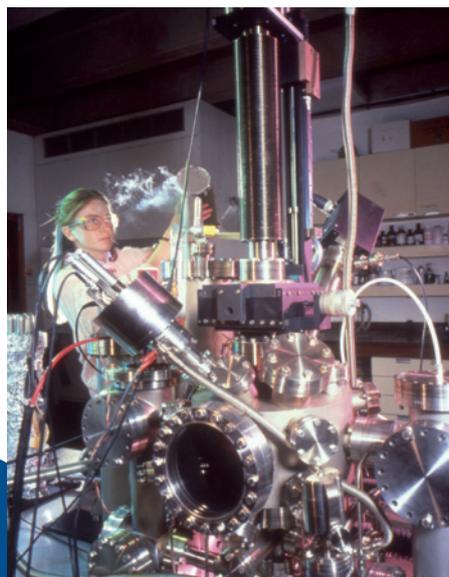


Paper Reference:

A. Ahmad, J. Dubois, T. Pasquet, M. Carrère, J. M. Layet, J. B. Faure, G. Cartry, P. Kumar, T. Minéa, S. Mochalskyd and A. Simonin (2013) "Negative-ion surface production in hydrogen plasmas: modeling of negative-ion energy distribution functions and comparison with experiments" *Plasma Sources Sci. Technol.* **22** 025006 doi:10.1088/0963-0252/22/2/025006

Hidden Product:

EQP Mass & Energy Analyser



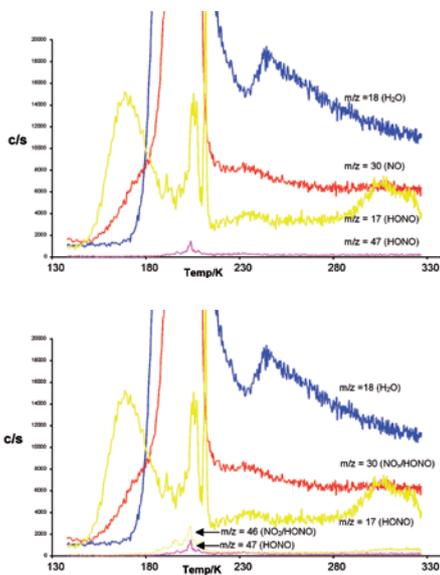
▲ The RAIRS apparatus in action.

Protonated nitrosamide and its potential role in the release of HONO from snow and ice in the dark

The effects of photolysis on frozen, thin films of water-ice containing nitrogen dioxide (as its dimer dinitrogen tetroxide) have been investigated using a combination of FT-Reflection Absorption IR spectroscopy (RAIRS) and a Hidden mass spectrometer. The observed release of HONO observed using the crucial combination of these techniques was ascribed to a mechanism in which nitrosonium nitrate (NO^+NO_3^-) is formed. Subsequent solvation of the cation leads to the nitroacidium ion, H_2ONO^+ , *i.e.* protonated nitrous acid. How are such results relevant to studies of chemistry that take place in Earth's Cryosphere (Polar Stratospheric Clouds or PSCs, cirrus clouds, frost flowers, freezing fogs, snowflakes, permafrost and hailstones)?

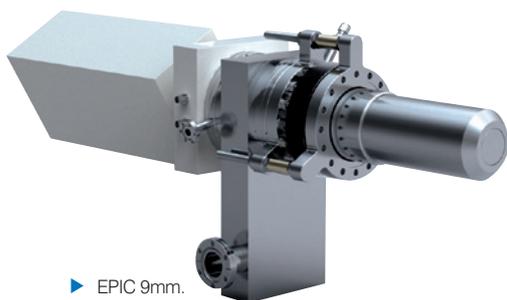
The global impact of chemistry and physics that occurs in the polar troposphere is only just being raised due to recent advances in satellite

observation, field measurement and climate change concerns. Two phenomena of chemical origin noted for both the Arctic and Antarctic



▲ Thermal Desorption Profiles obtained on the Hiden Mass Spectrometer of NO_x and H_2O subsequent to photolysis of $\text{D}_{2n}\text{-N}_2\text{O}_4$ in water ice. The mass spectral signal $m/z=17$ has been corrected for the contribution from water using the water fragmentation pattern 74% $m/z=18$, 17% $m/z=17$.

regions, have been identified as being of particular importance: (i) halogen-promoted, ozone and mercury depletion events accelerated by the effects of cooling and freezing; (ii) photochemical release mechanisms of NO_x and oxygenated volatile organic compounds (OVOC) from snow/ice surfaces.



► EPIC 9mm.

The possibility that a range of “cryo-reactions” (chemistry in/on ice) could play important roles in atmospheric chemistry began to be explored in the 1980s. Subsequently a variety of cold/frozen materials dispersed throughout the “Earth System” such as snowpack, have been put forward as potential surfaces for heterogeneous chemistry to take place on. Perhaps the most famous example is provided by the so-called Antarctic ozone “hole” driven by PSCs.

Monitoring studies at Summit, Greenland, performed in the late 1990s have shown significant enhancement in the concentrations of several trace gases in the snowpack pore (also known as firn) air relative to the atmosphere. Analytical measurements have been reported for organic compounds such as formaldehyde, alkenes, halocarbons, and alkyl nitrates that are typically a factor of 2-10 higher in concentration within the firn air than in the ambient air 1-10 m above the snow. Firn air also contains elevated levels of nitrogen dioxide and mechanisms involving nitrate ion photolysis are thought likely to be important. And that is where the study described at the start of this article is relevant. In the overall process, NO^+ produced on the ice surface by photolysis of the nitrogen dioxide dimer was shown to become solvated with water and is then hydrolysed to HONO, which is efficiently released to the gas-phase. In contrast the nitrate component is retained on the surface as Nitric Acid Trihydrate.

The mechanism proposed in the paper goes some way to explain why the field measurement of HONO at different snow-pack polar sites is often contradictory.....at some locations nothing at all is detected. But if organic

compounds (like humic acids or formaldehyde) are present, the solvated NO^+ may, in preference to becoming solvated, act as a nitrosating agent leading to little or no HONO release.

Our Reference: AP-EPIC-0004

Project Summary by:



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Paper Reference:

S. Hellebust, T. Roddis & J. R. Sodeau (2010) “Protonated Nitrosamide and Its Potential Role in the Release of HONO from Snow and Ice in the Dark” *Journal of Physical Chemistry A* **114** (43) 11632-11637.

For more information on Cryochemistry, a recent review has been published: “The effect of freezing on reactions with environmental impact”. R. O’Concubhair and JR Sodeau. *Accounts of Chemical Research*. DOI 10.1021/ar400114e. (2013)

Hidden Product:

EPIC Systems for UHV Science Applications.

Mass spectrometer study in time-multiplex $\text{SF}_6 + \text{CH}_4$ plasma etching of silicon

The chemical study of radiofrequency (RF) sulphur hexafluoride (SF_6) plasma, either pure or mixed with other gases such as oxygen (O_2), methane (CH_4) and argon (Ar), is growing everyday due to different applications in the semiconductor industry. Plasma etching of materials such as silicon (Si), silicon dioxide (SiO_2) and others, allows one to integrate the sensor structures with electronics making possible the formation of trench structures for construction of basic electronics

components such as capacitors, resistors, etc in micro/nano scale. However, in this field of application, processes involved in the formation of the plasma and the interaction between the plasma particles and etched surface are not fully understood, therefore the study of SF_6 plasma chemistry (pure or mixed with other gases) is essential to better control the generation of reactive species in the plasma and consequently the process outcome. In this work, a HPR-30 Vacuum Process Gas Analyser is used for temporal monitoring of neutral atoms and molecules as can be seen in figure 1.

Basically, the Si etch can be performed in two different ways: single-step or multi-step. In single-step the gas is inserted

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Customer Research:

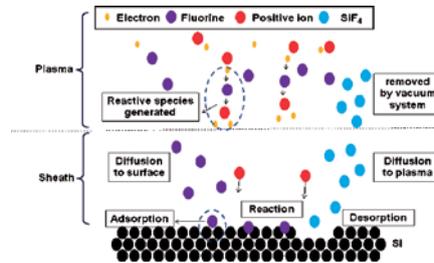
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continuously during whole Si etching process. For multi-step, also known as the Bosch method, a cyclic gas injection routine that results in alternating etching and deposition steps, is performed. A multiple-step deep Si etch process is performed which involves separate etch and polymerization steps. In multiple-step processes, a sidewall passivation film (usually a polymer) is first deposited, and the film plus Si surface are etched from the bottom of the trench in the subsequent step. These cyclic etching and deposition steps are repeated to obtain features as deep as desired.

Several steps are usually involved in the process of fluorinated plasma etching. Initially reactive particles are generated in plasma by dissociation of neutral gas



▲ Figure 1. HPR-30 Vacuum Process Gas Analyser coupled to RIE plasma etch.



▲ Figure 2. Schematic diagram of the Si fluorinated plasma etch process.

molecules by electron impact, and then these particles are directed to the material surface by diffusion where they are adsorbed. Subsequently, volatile products are formed through chemical reactions and are desorbed from the surface before

being removed by the vacuum system as can be seen in figure 2. If the reaction product is not volatile, a passivated film is formed. In the case of SF_6 molecules, these are dissociated ($SF_6 + e \rightarrow S_xF_y$ or $(S_xF_y^+) + F_n + e$, where $x = 1-2$, $y = 1-5$ and $n = 1-5$) to generate atomic fluorine (F) which is the main agent in the silicon etch due to its high affinity. Initial results indicate a cyclic behavior for the gas feed pattern in the RIE reactor (SF_5^+ and CH_4^+) as well for the formation of SiF_3^+ products (figure 3).

Our Reference:
AP-HPR-30-0002

Project summary by:



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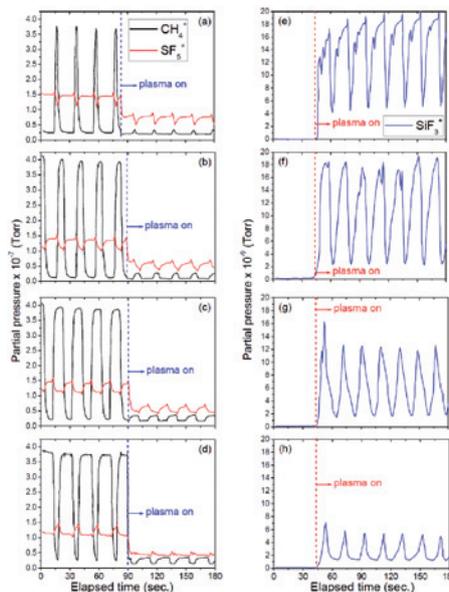


Paper Reference:

L. L. Tezani, R. S. Pessoa, G. Petraconi Filho (2012) "Automation of a Mass Flow Controller for Application in Time-Multiplex $SF_6 + CH_4$ Plasma Etching of Silicon" *Contributions to Plasma Physics* **52** (9) 735-743

Hidden Product:

HPR-30 Vacuum Process Gas Analyser



▲ Figure 3. Partial pressure time evolution of SF_5^+ and CH_4^+ species for SF_6 gas in continuous mode and CH_4 as in intermittent mode for various duty cycle values: (a) 20%, (b) 40%, (c) 60% and (d) 80% and also, the SiF_3^+ specie behavior for the same duty cycles: (e) 20%, (f) 40%, (g) 60% and (h) 80%. Here, the process time evolution is used to investigate the effect of plasma on and off, as well as the duty cycle effect.

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

Hidden Products referenced in our Customer Stories in this issue:

EPIC Systems for UHV Science Applications

Hidden EPIC mass spectrometers for high precision scientific, process applications and UHV analysis of neutrals, radicals, and ions:



- Neutrals, Radicals, Positive & Negative ions
- Electron Attachment Studies
- Surface Science, Molecular Beam Studies
- UHV Temperature Programmed Desorption
- High Performance RGA
- Desorption / Outgassing Studies / Bakeout Cycles
- Chamber / Process Gas Contaminants

EQS 1000 Series SIMS Analyser

The EQS is a secondary ion mass spectrometer bolt on SIMS analyser for the analysis of secondary positive and negative ions from solid samples:



- Static / Dynamic SIMS with Energy Analysis
- Integral Front End Ioniser for RGA
- Composition / Contamination Analysis
- Depth Profiling
- Leak Detection & Desorbed Gas Analysis
- Compatible with Hidden SIMS Workstation
- Suitable for FIB-SIMS Integration

EQP Mass & Energy Analyser

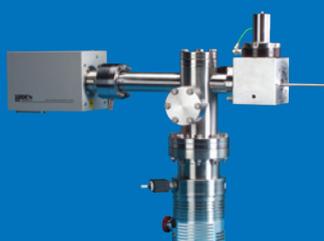
The Hidden EQP is a combined mass / energy analyser for the analysis of positive AND negative ions, neutrals, and radicals from plasma processes:



- 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

HPR-30 Vacuum Process Gas Analyser

The HPR-30 process gas analysis system is a compact gas analysis system for monitoring residual gases and vacuum processes:



- CVD / PECVD / RIE / LPCVD / MOCVD
- Vacuum Coating / Plasma Etching
- Sputter Deposition
- Contamination Studies
- Base Pressure Fingerprint
- Leak Detection / Virtual Leaks / Desorption
- Outgassing / Bakeout / Pump Performance
- Chamber / Process Gas Contaminants

In the Press:

Gas Composition in Vacua

(Our Reference: HAPR0082)

Hidden Analytical offer an extensive range of quadrupole residual gas analysers for diverse vacuum applications through the pressure range from millibar through to extreme high vacuum (XHV). The catalogue items are supplemented by a custom-engineering design service for experiment-specific requirements including in-vacuum cooling and heating, probe insertion distance and remote in-vacuum mounting.



Typical mass ranges of 1:50amu to 1:300amu accommodate most gaseous and vapour species, with alternative mass ranges to 1000amu offered for specialised applications. Analogue and pulse ion counting detectors are selectable to optimise performance for widest dynamic range of 10 decades, fastest measurement rate to 500 samples per second and highest sensitivity to 5×10^{-16} millibar. Ion source options are configured for general analysis, for molecular beam applications or for minimal degas rates for UHV/XHV applications.

The single-stage mass filters are used for many general applications, with the 3F-series triple-stage mass filter being used for the most demanding applications requiring maximum performance in terms of both mass resolution and abundance sensitivity.