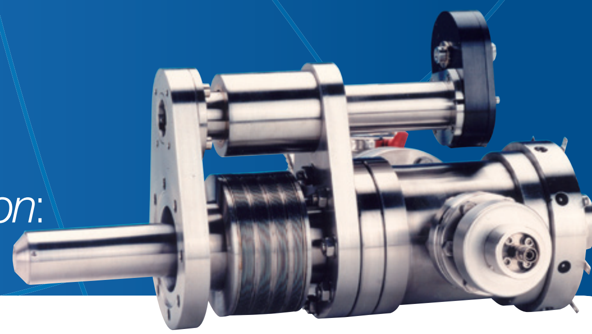
Issue Number: 1120/04

Hiden Life

A world of products connected by science & imagination

Hiden Quadrupole Mass Spectrometers *in action*:



Thin Films, Plasma and Surface Engineering

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Customer Research

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- Composition and species evolution in a laser-induced $LuMnO_3$ plasma. *Project Summary by: M. Bator, Paul Scherrer Institute, Switzerland*
- In-situ monitoring of the growth of silver thin film – the influence of sputtering gas. *Project Summary by: Michal Novotný, Institute of Physics, ASCR, vvi, Czech Republic*

Hiden Products

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- EQP
- PSM

In the Press

- Plasma Diagnostics for the Researcher

Hiden Applications

A very big thank you to all who have contributed

Hiden 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 Hiden EQP Mass & Energy Analyser, PSM Plasma Ion Analyser and HPR-60 MBMS Molecular Beam Sampling Mass Spectrometer are included.

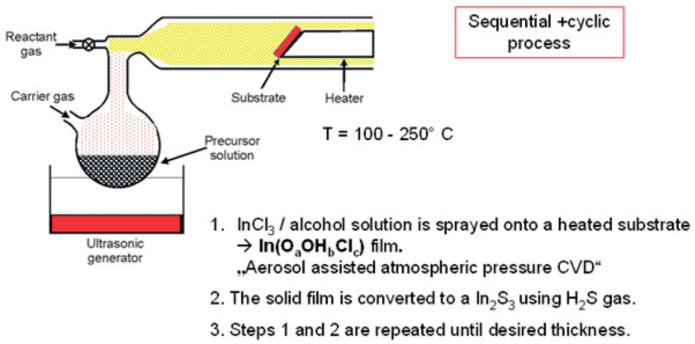
We are delighted that they have shared a brief synopsis of their research for our newsletter.

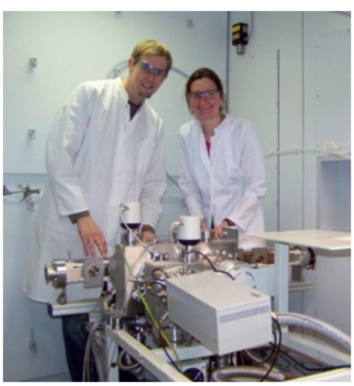
HIDEN ANALYTICAL

Customer Research:

The reaction mechanism of the spray Ion Layer Gas Reaction process to deposit In_2S_3 thin films

Ion Layer Gas Reaction 'ILGAR' is a non vacuum, thin film deposition technique characterized by economic material consumption, low cost equipment and easy control of the chemical composition and physical properties. In addition to developing the deposition techniques and extending the materials pallet that can be deposited and that include, among others, In_2S_3, ZnO and ZnS, we are active in developing prototypes for the up scaling and in-line production of materials by the ILGAR technique.





▲ Martin Krüger and Sophie Gledhill with the mass spectrometer attached to the 'specially' built ILGAR tube (manufactured by Hiden)

Above is a schematic representation of the laboratory scale Spray-ILGAR set up, used for substrate sizes up to 5 x 5 cm^2. The individual steps of the cyclic process are also indicated. These include the deposition of the precursor solution via aerosol assisted CVD (at atmospheric pressure), and the conversion of the deposited $In(O_aOH_bCl_c)$ film into In_2S_3 by H_2S.

To investigate the deposition process the ILGAR spray chamber fitted with a mass spectrometer which was custom built by Hiden Analytical. The system, provided by Hiden, is a HPR-60 Molecular Beam Sampling System with an integrated multi-stage pumping system and HAL quadrupole mass spectrometer. This allowed us to track the intermediate and side gases produced in the process. This gave us a deeper understanding of our reaction and better process control.

By the ILGAR process, In_2S_3 buffer layers have been developed on $Cu(In,Ga)(Se,S)_2$ in solar cells with equal efficiencies and damp-heat stabilities as the standard toxic CdS buffer layer . So far, best efficiencies of 16.1% certified by ISE Freiburg [2005], and very recently a 16.8 % efficiency-cell have been achieved [2011]. Equally important for the implementation are the very large processing windows in terms of layer thickness and process temperature and the robustness of the method, as well as its potential for rapid in-line processing and its reproducibility. In parallel we are working on the up-scaling of the ILGAR technique to larger sizes, which are more relevant to the industry.

Our Reference: AP0192

Project Summary by:

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14109 F, Germany

Paper Reference:

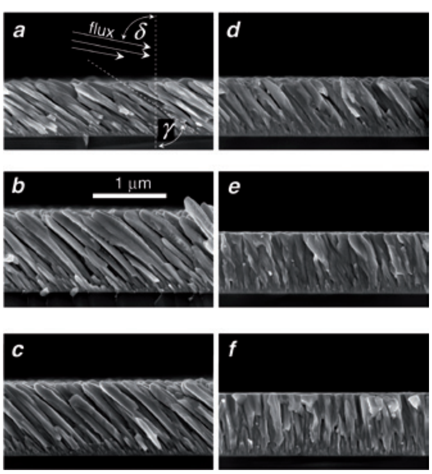
S. Gledhill, R. Allison, N. Allsop, Y. Fu, E. Kanaki, R. Sáez-Araoz, M. Lux-Steiner, C. H. Fischer (2011) *"The reaction mechanism of the spray Ion Layer Gas Reaction process to deposit In_2S_3 thin films"* Thin Solid Films **519** (19), 6413-6419.

Hiden Product:

HPR-60 MBMS - Molecular Beam Sampling Mass Spectrometer

Overcoming the geometrical limitations of conventional sputtering by controlling the ion-to-neutral ratio during high power pulsed magnetron sputtering

Thin films prepared by magnetron sputtering on substrates not facing the sputtering target often exhibit pronounced column tilt in the direction of incoming flux (see Fig.1(a)). The column tilt angle γ (relative to the surface normal) is smaller than the angle defined by the direction of incoming flux (δ). For $0° \leq \delta \leq 60°$ the so-called tangent rule applies and both angles are related by $2\tan\gamma = \tan\delta$. The effect of column tilt, commonly observed for films grown on obliquely-mounted substrates by direct current magnetron sputtering (DCMS), is believed to result from the conservation of the momentum component parallel to the film surface. Surface diffusion also plays a role such that columns tend to tilt back towards the vapor incident direction. As clearly demonstrated in Fig.1(a) resulting films exhibit open microstructure with numerous voids between the columns. In addition, surface roughness is high. All of these are serious drawbacks if the deposited film should serve as the protective coating on 3D multi-shaped objects. In such case all surfaces that are not facing the target during deposition, (*e.g.*, the rake face of the cutting tool) will exhibit the microstructure as the one shown in Fig.1(a).



▲ Figure 1

The line-of-sight nature of the conventional DCMS processing manifested by, e.g., pronounced column tilt on obliquely-mounted substrates, could be potentially avoided if film-forming species were to arrive at the growing film surface along the surface normal (as it is the case for films facing the target during deposition). This cannot be easily achieved with DCMS, as the material flux sputtered from the target is dominated by neutrals that are not affected by the application of electric or magnetic fields. However, during the high-power pulsed magnetron sputtering (HIPIMS or HPPMS), where the power is applied to the target in short ($\sim$100 μs) high-amplitude (several kW/cm2) pulses, the metal ion content in the plasma can be very high.

Therefore we use HIPIMS to grow thin chromium layers on substrates facing and orthogonal to the sputtering target. We apply the negative substrate bias with the amplitude of 150 V to effectively steer the ions along the surface normal by increasing the momentum component perpendicular to the film surface. By using a PSM003 Mass Spectrometer from Hiden Analytical, UK to monitor ion fluxes during the high-power pulses we are able to show that upon increasing the peak target current density, j_T from 0.1 to 1.7 A/cm^2 the Cr ion-to-neutral ratio in the flux to the substrate increases several times. This has dramatic consequences for the microstructure of the thin Cr layers grown on the substrates orthogonal to the target, as illustrated by the scanning electron microscopy images shown in Fig.1(b)-(f). The large column tilt characteristic for the growth at low j_T (DCMS-like conditions) decreases with increasing the relative metal ion content in the flux and almost completely disappears at the highest value of j_T (see Fig.1(f)) The latter indicates that the material flux to the substrate is highly ionized so that all film-forming species arrive close the substrate normal, despite the high nominal inclination angle (δ is fixed for all experiments). Thus, in the limit of high j_T the artifacts of conventional DCMS, resulting from the line-of-sight deposition, are effectively eliminated and the film growth proceeds more or less unaffected by the substrate orientation. In consequence, samples mounted orthogonally possess a similar texture, morphology, and topography as those facing the target.

Our Reference: AP0193

Project Summary by:

Linköping University

G. Greczynski, J. Jensen and L. Hultman
Department of Physics (IFM)
Thin Film Physics Division, Linköping University, 581 83 Linköping, Sweden

Paper Reference:

G. Greczynski, J. Jensen and L. Hultman (2011) *"Mitigating the geometrical limitations of conventional sputtering by controlling the ion-to-neutral ratio during high power pulsed magnetron sputtering"* Thin Solid Films **519** (19), 6354-6361.

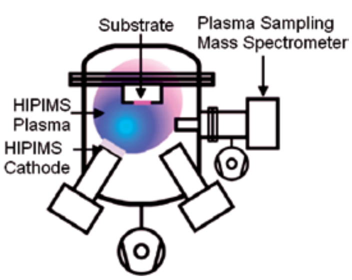
Hiden Product:

PSM Plasma Ion Analyser

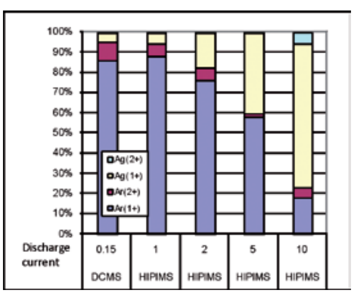
Customer Research:

Advantages of highly ionized pulse plasma magnetron sputtering (HIPIMS) of silver for improved E. coli inactivation

This study addresses the DC-magnetron sputtering (DCMS) of Ag-films on polyester and compares the results found for the E. coli inactivation with the inactivation obtained when applying highly ionized pulse plasma power magnetron sputtering (HIPIMS).



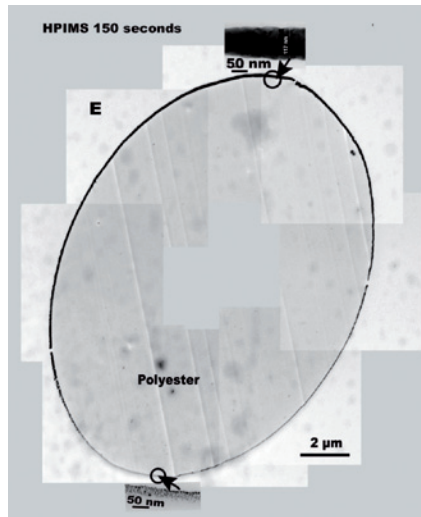
▲ Schematic of the HIPIMS setup, the cathode used was Ag and the substrate polyester



▲ Plasma ion-composition analysis of HIPIMS and DCMS sputtering in Argon, derived from mass spectroscopy analysis. HIPIMS is applied at the currents indicated in the Figure.

The amounts of Ag needed to inactivate *E. coli* by HIPIMS sputtering were an order of magnitude lower than with DCMS indicating a significant saving of noble metal and concomitantly a faster E. coli inactivation was observed compared to samples sputtered with DCMS. Higher current densities applied with DCMS led to shorter *E. coli* inactivation times and this trend was observed also for HIPIMS sputtered samples. By DCMS the thicker layers needed to inactivate *E. coli* comprised slightly larger Ag-aggregates compared to the thinner Ag-layers sputtered by HIPIMS to inactivate *E. coli* within short times. Longer sputtering times by DCMS and HIPIMS lead to optically darker Ag-deposits reaching the absorption edge of silver absorption of ~1000 nm. Mass spectroscopic analyses indicated that HIPIMS produced a much higher amount of Ag^{1+} and Ag^{2+} compared to DCMS due to the higher peak discharge current employed in the former case.

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



▲ TEM of an Ag-polyester fiber sputtered by DCMS for a) 160 s at 300 mA at 5 A for 150 s and b) HIPIMS at 5 A for 150 s.

Ag^{+}-ions along a small amount of Ag^{2+}-ions.

Our Reference: AP0280

Project Summary by:

ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE
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Laboratory of Photonics and Interfaces,
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CH-1015 Lausanne, Switzerland

Paper Reference:

O. Baghriche, A. P. Ehiasarian, E. Kusiak-Nejman, A. W. Morawski, C. Pulgarin, R. Sanjines, J. Kiwi (2012) *"Advantages of highly ionized pulse plasma magnetron sputtering (HIPIMS) of silver for improved E. coli inactivation"* Thin Solid Films **520** (9), 3567-3573.

Hiden Product:

EQP Mass and Energy Analyser for Plasma Diagnostics

Composition and species evolution in a laser-induced $LuMnO_3$ plasma

Multiferroics, materials comprising two or more ferroic properties, such as ferromagnetism, ferroelectricity or ferroelasticity in the same phase, are very promising systems for future applications in computing or sensing. These materials would allow the design of new digital storage devices thereby combining the advantages of long lived magnetic storage with easy accessibility and robustness of electronic storage technology. Still, materials combining both properties useful for applications are scarce. To better adapt multiferroicity, thin film growth introduces new parameters such as strain, allowing the tuning of the respective materials properties. For a targeted growth control mass spectrometry as well as emission spectroscopy is utilized to investigate the plasma during the growth by pulsed laser deposition.

Rare-earth manganates (*Re*MnO_3) with an orthorhombic structure are very interesting multiferroics since the electrical polarization is induced by changes of the crystalline structure and magnetic ordering. As a result, the coupling between magnetism and electrical polarization is strong. Orthorhombic $LuMnO_3$ (LMO) thin films were grown from a sintered, ceramic LMO target by pulsed laser deposition. To correlate ablation conditions like fluence, background pressure or substrate-target distance to the film growth, the composition of the laser induced plasma was investigated by mass spectrometry using a Hiden Analytical EQP Quadrupole Mass Spectrometer complemented by optical emission spectroscopy (see Fig. 1).

The plasma composition was investigated for three different background conditions, vacuum, 1 x 10^{-2} mbar O_2 and 1 x 10^{-2} mbar N_2O. In particular, the amount of metal species (Lu, Mn) and their oxides (O_x, LuO_x, MnO_x) and how the relative intensities change under varying background conditions was of interest. The mass spectrometer was used in different modes to observe positively ionized species as well as neutrals using the integrated ionizer. In Fig. 2 the neutral and positive species for the three background conditions are shown in the top and bottom rows, respectively. A clear increase of oxidized species is observed for both oxidizing backgrounds, compared to vacuum LuO^+/Lu^+ changes from 1:200 to 4:1 in O_2 and 9:1 in N_2O.

In order to observe the expansion of the plasma species spatially and time resolved, optical emission spectroscopy was utilized as a complementary method simultaneously with mass spectrometry. The emitted plasma radiation was measured as a function of time, space and wavelength. Changes in relative intensities between Lu and LuO lines over time show a distinct behaviour when comparing vacuum conditions with an oxidizing background gas. While the initial expansion of plasma species for all background conditions is similar, the behaviour changes at later times when the interactions between species from the target and the background become dominant. In oxidizing backgrounds, the relative intensities increase towards metal-oxide species agreeing well with observations from mass spectrometry.

The combined spectroscopic and spectrometry results show the importance of a background gas for the ablation of oxides. There are clear indications from these measurements that the oxidation of metals to *Me*O_x species in the background is the dominating factor to incorporate oxygen directly into the growing thin film.

Our Reference: AP0322

Project Summary by:

M. Bator, Paul Scherrer Institute, General Energy Research Department, 5232 Villigen-PSI, Switzerland

Paper Reference:

M. Bator, Y. Hu, M. Esposito, C. W. Schneider, T. Lippert, A. Wokaun (2012) *"Composition and species evolution in a laser-induced $LuMnO_3$ plasma"* Applied Surface Science **258** (23), 9355-9358

Hiden Product:

EQP Mass and Energy Analyser

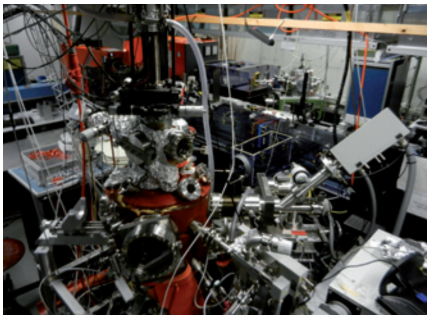


Fig. 1: Photo of the UHV chamber.

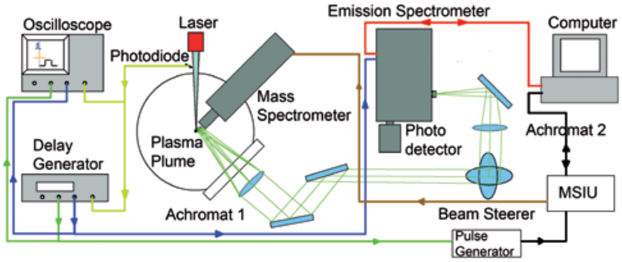


Fig. 2: Setup of the UHV chamber showing the analytical stages for mass spectrometry and emission spectroscopy.

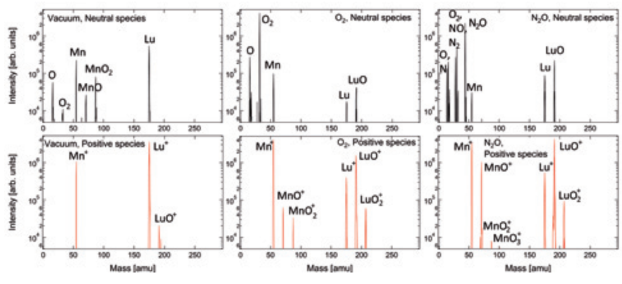
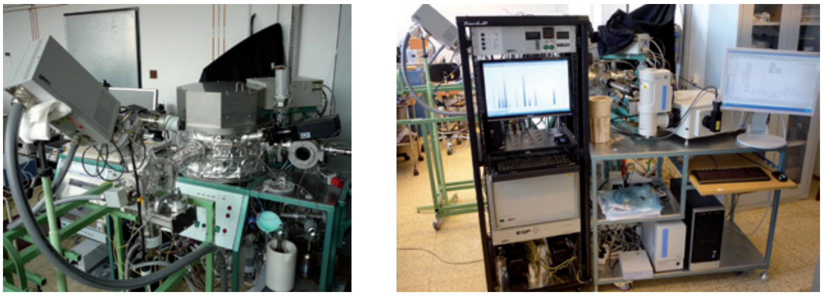


Fig. 3: Distribution of masses as taken from mass spectrometry for different background conditions: from left to right: vacuum, 1x10^{-2} mbar O_2, 1x10^{-2} mbar N_2O. The top row shows neutral species, the bottom row positive ions.

Customer Research:

In-situ monitoring of the growth of silver thin film – the influence of sputtering gas

We have been carrying out a systematic study of nucleation and growth of silver thin film prepared by magnetron sputtering in the Department of Analysis of Functional Materials of the Institute of Physics ASCR for several years. We have applied a combination of several in-situ techniques, ie. spectral ellipsometry and electrical conductivity measurements to analyse properties of the growing film, optical emission spectroscopy (OES) and mass spectrometry (Hiden EQP 500) to investigate magnetron plasma properties. The experimental setup is shown in Fig. 1 and Fig. 2. The aim is to be able to control silver growth mode on dielectric substrates – on the one hand fabrication of ultrathin smooth silver film and on the other hand preparation of nanostructured silver film.



▲ Fig.1 & 2: Experimental setup with a Hiden EQP 500 plasma analyser

We have demonstrated that silver film growth can be effectively influenced by the choice of sputtering gas, ie. Ne, Ar and Kr. We studied the influence of RF magnetron power and working gas pressure on plasma composition and properties. The magnetron power was varied from 25 to 100 W. The ambient pressure was changed from 0.5 Pa to 3 Pa. Both mass and OES spectra revealed presence of highly excited plasma in the substrate vicinity for all sputtering gases. The increasing OES signal intensities of Ag and Ag^+ with increasing RF power and gas pressure were observed. However, in Ar discharge there was no Ag^+ signal detected by OES at lower pressures of 0.5 Pa and 1 Pa. Formation of Ag_2^+, $AgNe^+$, $AgAr^+$ and $AgKr^+$ radicals was observed in the mass spectra. A maximum around 19 eV in the ion energy distribution was obtained in Ar and Kr discharges, while the maximum at 28 eV was measured in Ne discharge at pressure of 3 Pa and magnetron power of 50 W. We attribute this effect to higher plasma potential in Ne discharge. Silver thin film deposited in Ne gas revealed roughness of 2.9 nm while the roughness of the films deposited in Ar and Kr gases was 3.9 nm. This can be attributed to higher energy of the atoms and ions impinging the substrate in Ne gas discharge.

Our Reference: AP0371

Project Summary by:

FZÚ

Michal Novotný,
Institute of Physics,
Academy of Sciences of the Czech Republic,
Na Slovance 2,
182 21 Prague, Czech Republic

Paper Reference:

M. Novotný, J. Bulíř, P. Pokorný, J. Lančok, L. Fekete, J. Musil, M. Čekada (2012) *"RF magnetron sputtering of silver thin film in Ne, Ar and Kr discharges—plasma characterisation and surface morphology"* Surface and Coatings Technology, [online], Available at: http://dx.doi.org/10.1016/j.surfcoat.2012.05.024

Hiden Product:

EQP Mass and Energy Analyser

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**

In the Press:

Hiden Products referenced in our Customer Stories in this issue:

HPR-60 MBMS

The Hiden HPR-60 Molecular Beam Sampling Mass Spectrometer is a compact gas analysis system for analysis of neutrals, radicals and ions:

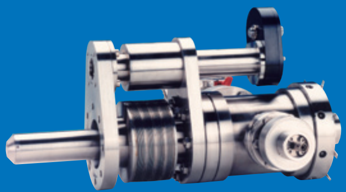
- Reaction Kinetics
- Plasma Diagnostics
- Combustion Studies – Flame Ionisation Analysis
- Catalysis Studies
- CVD / MOCVD – Diamond Growth Studies
- Flash Desorption Studies
- Atmospheric Glow Discharge Analysis
- Cluster Analysis

EQP

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

PSM

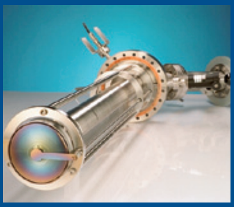


The Hiden PSM is a differentially pumped mass spectrometer for the analysis of secondary ions and neutrals from plasma process:

- Reactive Ion Etching – End Point Detection
- Plasma Deposition Studies
- Ion Implantation / Laser Ablation
- Residual Gas Analysis
- Leak Detection

Plasma Diagnostics for the Researcher

(Our Reference: HAPR0058)



Hiden Analytical mass spectrometers provide direct real time plasma monitoring for analysis of both process ion and process neutral species, addressing a pressure range from $10E^{-3}$ mbar to atmosphere and all featuring our latest, fastest Series 8 PC interface. All systems are fully compatible with Windows 7 and XP operating systems, and Windows 8 ready.

The EQ/PS Series offer optional positive/negative ion or positive ion-only measurement of process ion intensity, mass and ion energy, the pulse ion counting detector giving a continuous dynamic range of a full seven decades. Atomic mass range is up to 1000 amu with energy ranges of +/-100 eV and +/-1000 eV. The advanced low-diameter ion transfer optic enables deep penetration of the sampling orifice up to 750 mm within the process chamber. Multiple scan modes provides scanning of all key parameters for system setup optimisation, including scanning of mass range, process ion energy, electron multiplier voltage against ion intensity. An internal electron bombardment ion source enables ionisation of neutral species.

Pressure reduction stages with turbo molecular pumping are used to maintain mass spectrometer operation in a UHV environment – single stage, double stage or triple stage dependent on the process pressure. System options include magnetic screening, integrated driven electrodes, electron attachment mode for electro-negative species, linear motion drives and water cooling for high-power applications.

Applications include diverse areas of plasma etching, deposition, coating and process development including atmospheric plasma needle performance quantification.

Hiden Applications

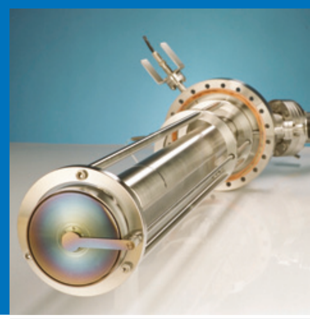
Hiden's quadrupole mass spectrometer systems address a broad application range in:

Gas Analysis

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

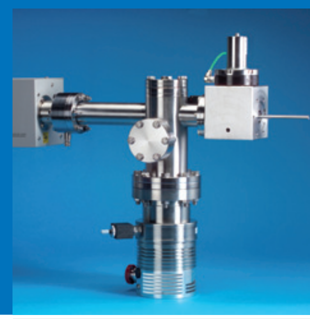
Surface Science

- 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:

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HIDEN ANALYTICAL

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