Customer Contributions:

- Highly selective etching with C₅HF₇ plasma
  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:

- IG2O - 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:
Highly selective etching of SiO\textsubscript{2} over Si\textsubscript{3}N\textsubscript{4} and Si in capacitively coupled plasma employing C\textsubscript{5}HF\textsubscript{7} gas

Quadrupole mass-spectroscopic analysis - in the novel C\textsubscript{5}HF\textsubscript{7}/O\textsubscript{2}/Ar plasma - has revealed important neutral and ionic species, such as C\textsubscript{x}F\textsubscript{y} (X>2), C\textsubscript{x}F\textsubscript{y} (Y/X<2), and C\textsubscript{x}H\textsubscript{y}F\textsubscript{z}. Compared with conventional C\textsubscript{5}F\textsubscript{8}/O\textsubscript{2}/Ar plasmas, it was found that plasma etching of SiO\textsubscript{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\textsubscript{5}F\textsubscript{8} and C\textsubscript{5}H\textsubscript{2}F\textsubscript{7} are mainly fragmented in electro-impact ionization at 70 eV into C\textsubscript{5}F\textsubscript{3} and C\textsubscript{5}H\textsubscript{2}F\textsubscript{7}, respectively. Indeed, the fragmentation pattern for C\textsubscript{5}H\textsubscript{2}F\textsubscript{7} clearly detected H-containing species substituting one F atom with one H atom, i.e. CF\textsubscript{2}→CHF, C\textsubscript{5}H\textsubscript{2}→C\textsubscript{5}HF, C\textsubscript{5}F\textsubscript{4}→C\textsubscript{5}H\textsubscript{2}F\textsubscript{7}, 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\textsubscript{5}F\textsubscript{8}/O\textsubscript{2}/Ar and C\textsubscript{5}H\textsubscript{2}F\textsubscript{7}/O\textsubscript{2}/Ar plasma. In addition, combined with quantum chemical calculations, it was concluded that the main dissociation pathway of the cyclic C\textsubscript{5}F\textsubscript{8} molecules was C\textsubscript{5}F\textsubscript{8}→CF\textsubscript{2}+C\textsubscript{4}F\textsubscript{6} and through further multiple dissociations, smaller fragmentation occurred following reactions; CF\textsubscript{2}→CF+F, or C\textsubscript{5}H\textsubscript{2}→C\textsubscript{5}H\textsubscript{2}F\textsubscript{7}+CF\textsubscript{3}.

Therefore, large fraction of CF\textsubscript{3}, CF\textsubscript{2}, CF\textsubscript{+} and each related H-substituted species, such as CHF\textsubscript{2}, CHF, CF\textsubscript{3}H, CHF\textsubscript{2} and C\textsubscript{5}H\textsubscript{2}F\textsubscript{7} 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\textsubscript{3}+, CF\textsubscript{2}+, CF\textsubscript{+} in addition to Ar\textsuperscript{+}. It is also noteworthy that large molecule ions such as C\textsubscript{7}F\textsubscript{7}+, C\textsubscript{7}F\textsubscript{6}+ and C\textsubscript{7}F\textsubscript{5}+ were detected. The behaviour of large molecule ions – C\textsubscript{7}F\textsubscript{7} or C\textsubscript{7}H\textsubscript{2}F\textsubscript{7} coincided with selective etching of SiO\textsubscript{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\textsubscript{2} has changed over time – for instance, CF\textsubscript{4}, C\textsubscript{2}F\textsubscript{6}, C\textsubscript{4}F\textsubscript{8}, C\textsubscript{4}F\textsubscript{6}, and C\textsubscript{5}F\textsubscript{8}. Also, H- and O-containing species – CHF\textsubscript{3}, CH\textsubscript{2}F\textsubscript{2}, C\textsubscript{3}F\textsubscript{6}O, C\textsubscript{5}F\textsubscript{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

**ZEO♥ CORPORATION,** Kawasaki, Japan

**PAPER REFERENCE:**


**HIDEN PRODUCT:**

EQP Mass & Energy Analyser for Plasma Diagnostics
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).

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^{3+}, 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.
Magnesium nitride phase formation through new ion beam implantation technique

Customer Research:

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 Mg₃N₂ 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...
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:

- Magnesium components with improved corrosion resistance
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.

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.

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

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 10s 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 $5 \times 10^{15}$ 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
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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