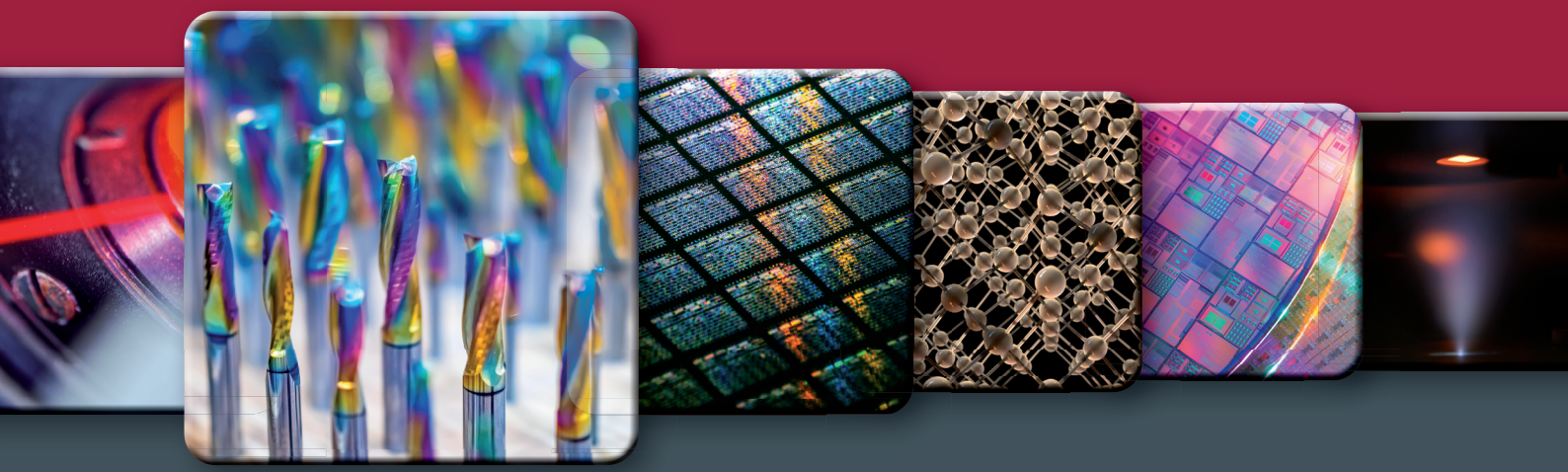
HIDEN ANALYTICAL



Low Pressure Plasma Applications

INTRODUCTION
Low Pressure Plasma Applications

Hiden Analytical have been designing and developing the highest quality quadrupole mass spectrometer based systems for over 40 years. We have built a reputation for delivering instruments with superior sensitivity, accuracy and reproducibility together with a first class global service and applications support network.

Low pressure plasma is used in a wide range of research, development and manufacturing settings for the purpose of, amongst other things: surface modification, cleaning, etching and coating. Each of these processes require careful selection and control of various plasma properties.

Our range of plasma sampling mass spectrometers and Langmuir probe systems allow real time monitoring of key plasma characteristics such as: Ion, neutral and radical concentrations, ion and electron energy distributions and plasma potentials. Signal gating further expands these capabilities to the pulsed regime.

Our products combine high performance and ease of use with unparalleled flexibility. Hiden can provide customisation for specific research needs or process monitoring requirements, ensuring optimised performance tailored to your application.

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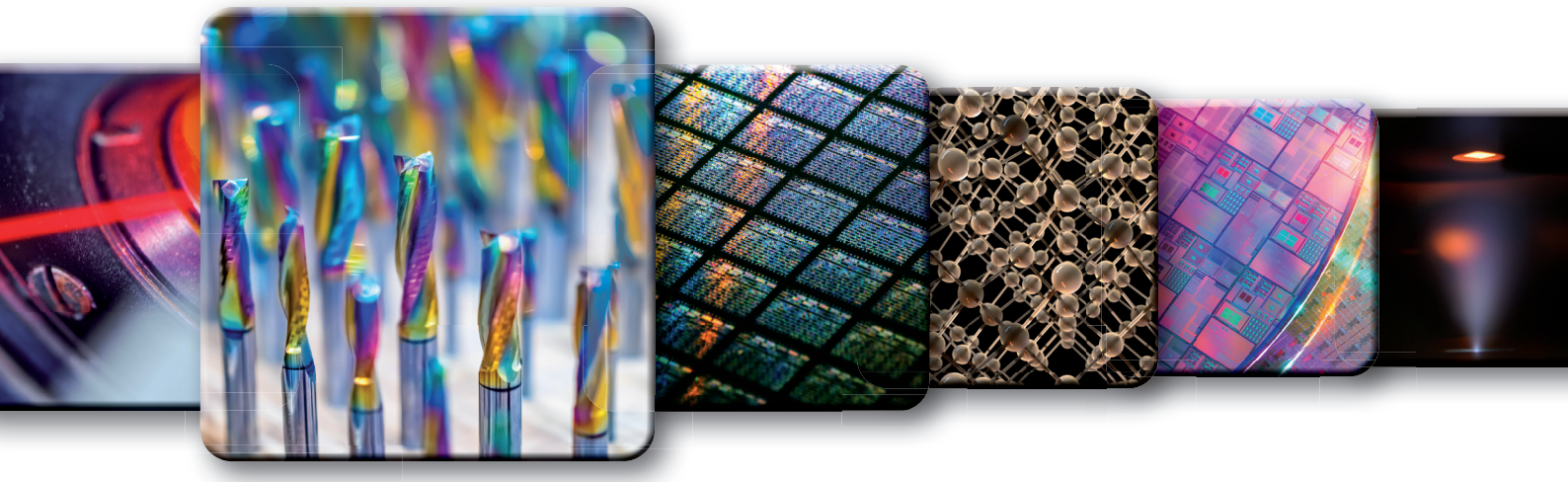
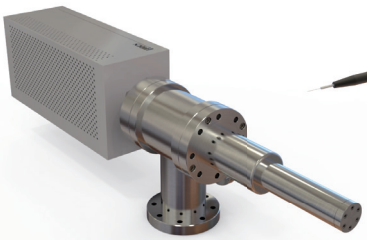
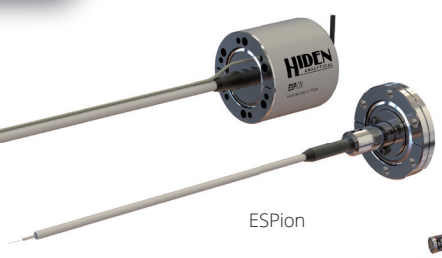
10. DC Magnetron Deposition of Silicoboron-carbonitride (SiBCN) Films for Microelectronics Applications





PSM



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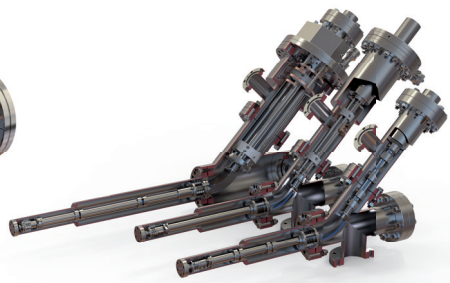


EQP Series

Titanium Nitride Deposition using High Power Impulse Magnetron Sputtering (HiPIMS)

HiPIMS is a sputtering technique that is based upon conventional magnetron sputtering. In magnetron sputtering, the increased plasma density created near the target increase the sputtering rate beyond that of traditional diode technology. The plasma density could be increased further with a higher rate of power applied to the cathode; however, the heat generated from these processes can limit any practical use.

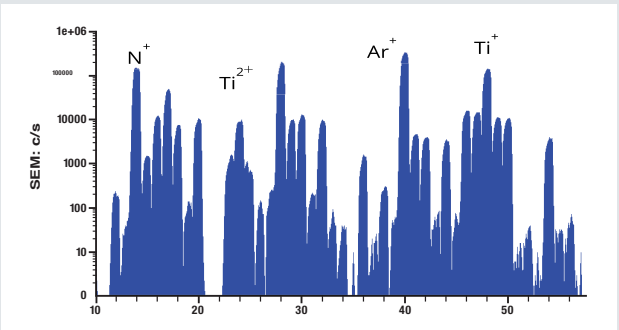
In HiPIMS, a sequence of short, intense, pulses are delivered to the cathode, with a peak power in the range of kW to MW. This creates and extremely dense plasma locally to the cathode. Pulses are applied with a low duty cycle, typically in the region of 10-100 µs, keeping heat, as well as average operating power relatively low compared to a DC process. HiPIMS plasmas are highly ionised, and the high proportion of plasma generated ions give increases in surface density, lower friction and reduce substrate temperature.

TITANIUM NITRIDE COATINGS

Ultra-hard materials such as titanium nitride, TiN, can be deposited using the HiPIMS technique, to give engineered components increased hardness, and wear resistance over the bulk material. Surface conformity is also maintained, allowing use in applications for dimensionally sensitive components such as fasteners, cutting devices and gears.

MASS RESOLVED ION SPECTRA

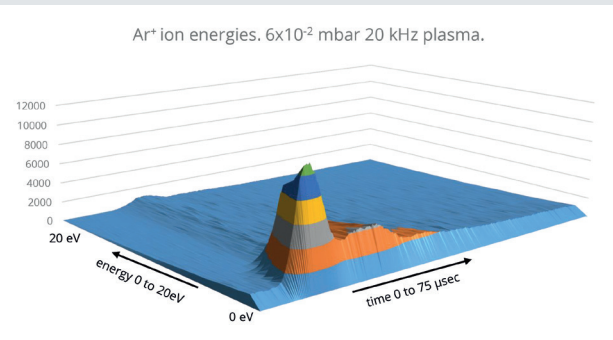
The Hiden EQP mass and energy analyser system allows for plasma species to analysed both in terms of mass and energy. In TiN deposition plasmas, direct analyses of positive and negative ions as well as neutral and radical species can be carried out. For a TiN plasma, a typical positive ion spectrum shows nitrogen, titanium and argon isotopes and compounds. Isotopic and molecular species can also be analysed, with Ti compounds showing the five characteristic isotopes of titanium. The mass spectral data allows direct monitoring of the deposition plasma, allowing the effects of changes in parameters such as pressure, gas composition, plasma power and duty cycle to be directly correlated with the resultant film properties.



Time averaged mass spectrum from a titanium nitride HiPIMS plasma.

ENERGY RESOLVED SPECTRA FROM HIPIMS DEPOSITION PLASMAS

Analysing the transient events in HiPIMS plasmas can be a challenge using conventional mass spectrometry techniques due to the speed at which these events occur. The Hiden EQP can be equipped with an integral multichannel scaler (MCS) detector, allowing mass and energy spectra to be measured with time resolution to 50 ns. The MCS detector can be synchronised with the plasma pulse, allowing plasma ignition, extinction and afterglow events to be measured. A typical dataset can be found below, where the ion energy distribution of argon ions is measured with respect to the start of the plasma pulse.



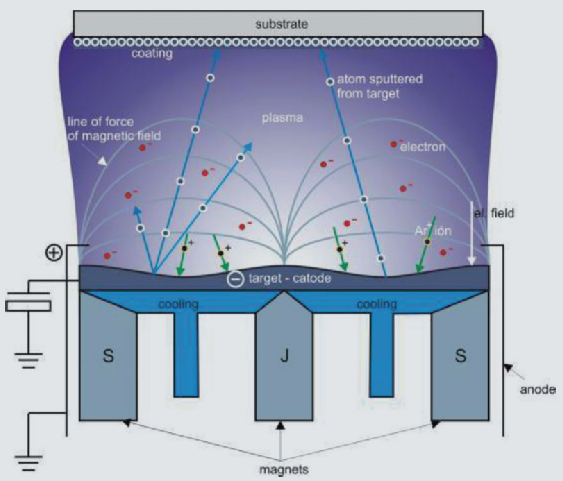
Ion energy distribution of argon ions with respect to time after the onset of a plasma pulse.

MAGNETRON SPUTTERING

Magnetron sputtering is a deposition technology involving a plasma which is generated and confined to a space containing the target material to be deposited onto the substrate. The surface of the target is eroded by high-energy ions from the plasma, and the liberated neutrals and radicals are deposited onto the substrate to form a thin film.

A magnetron sputtering source uses very strong magnets to confine the electrons in the plasma at or near the surface of the target. Confining the electrons not only leads to a higher density plasma and increased deposition rates, but also prevents damage which would be caused by direct impact of these electrons with the substrate or growing film.

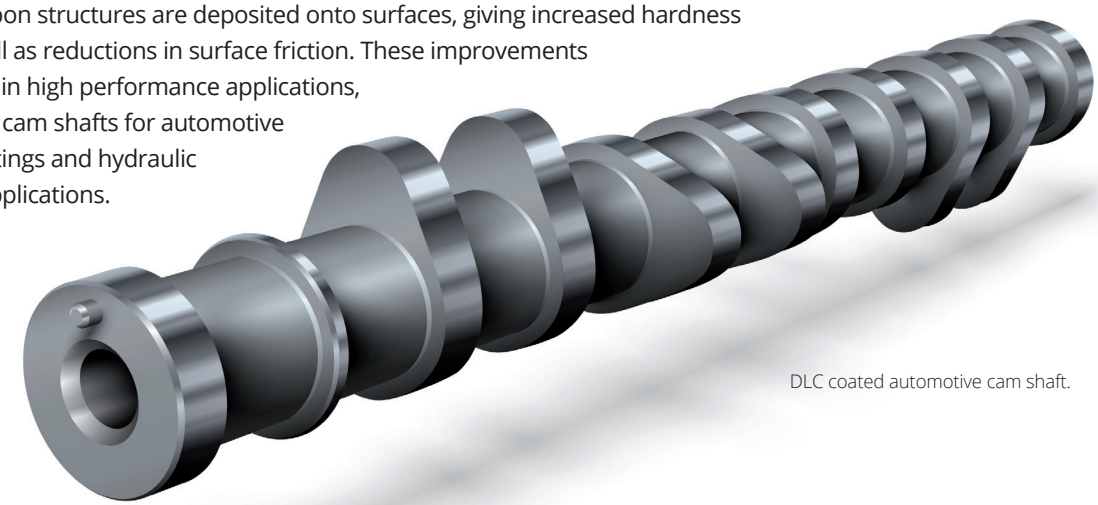
Typical applications for DC magnetron sputtering are wear resistant coatings, corrosion resistant films, dry film lubricants, optical and decorative films.



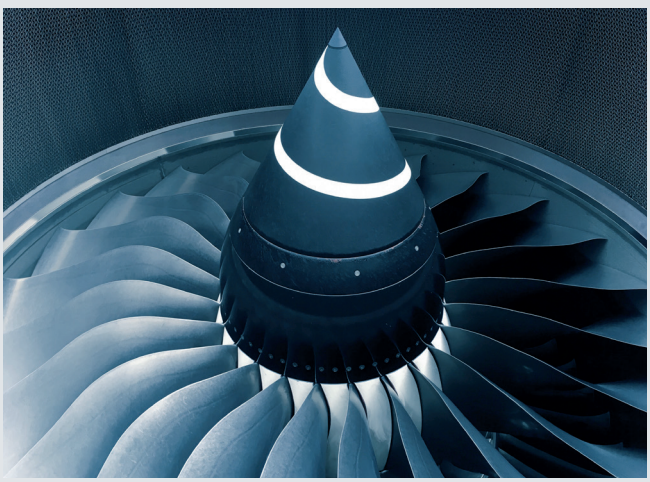
Typical magnetron sputtering arrangement.

Deposition of Diamond Like Carbon (DLC) Layers

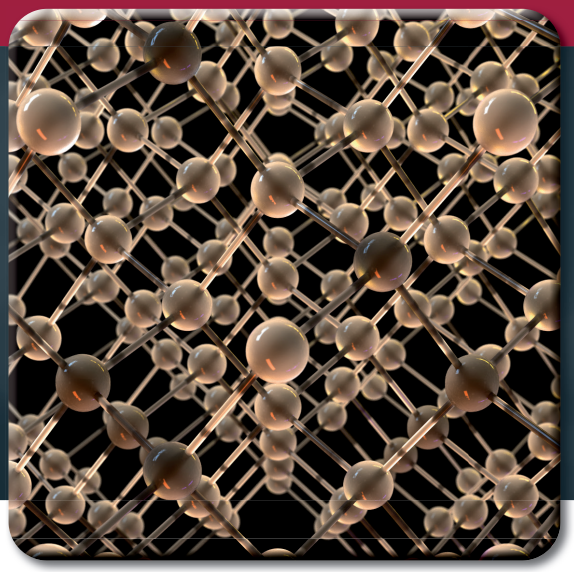
Diamond like Carbon (DLC) is a super hard material that can be applied as a coating to a variety of substrates. Spherical, amorphous carbon structures are deposited onto surfaces, giving increased hardness and wear resistance as well as reductions in surface friction. These improvements lead to more frequent use in high performance applications, such as cylinder liners and cam shafts for automotive use and turbine blade coatings and hydraulic actuators for aerospace applications.



DLC coated automotive cam shaft.



DLC layers are typically 2-4 µm thick, and applied by plasma deposition techniques, such as RF, capacitively coupled plasma (CCP), expanding thermal plasma and inductively coupled plasma (ICP). With modification to the plasma chemistry, power and pressure, the coatings properties are able to be tailored for the desired application. The Hiden EQP system allows for plasma species to be directly analysed, allowing researchers to understand the conditions required to produce DLC films optimised for specific application requirements.



DLC COATINGS FROM ACETYLENE-ARGON PLASMAS

Amorphous carbon coatings can be deposited using radio frequency (RF) capacitively coupled (CCP) plasma systems. Acetylene (C_2H_2) was used as the precursor in an argon plasma and the resulting film properties were investigated using electron microscopy, AFM and micro hardness tests. The Hiden EQP and ESPion systems were used to determine the plasma composition with variations in the gas composition and substrate bias.

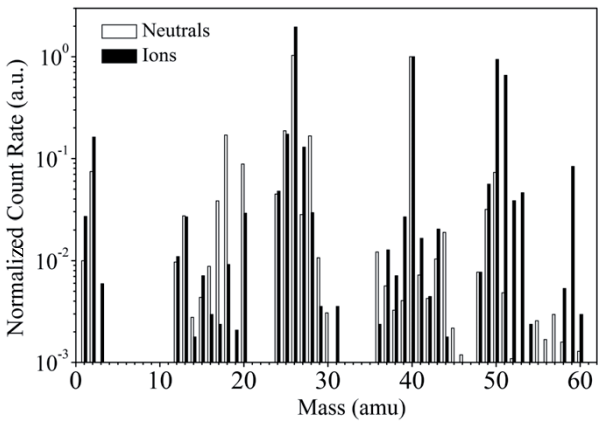
DLC deposition plasmas were found to be rich in acetylene and the C_2H radical, a number of different mechanisms were suggested for their production in the plasma, these can be found in the table below.

Reactions

$e + Ar \rightarrow Ar^+ + 2e$
$e + Ar \rightarrow Ar^m + e$
$e + Ar^m \rightarrow Ar^+ + 2e$
$e + C_2H_2 \rightarrow C_2H_2^+ + 2e$
$e + C_2H_2 \rightarrow C_2H + H + e$

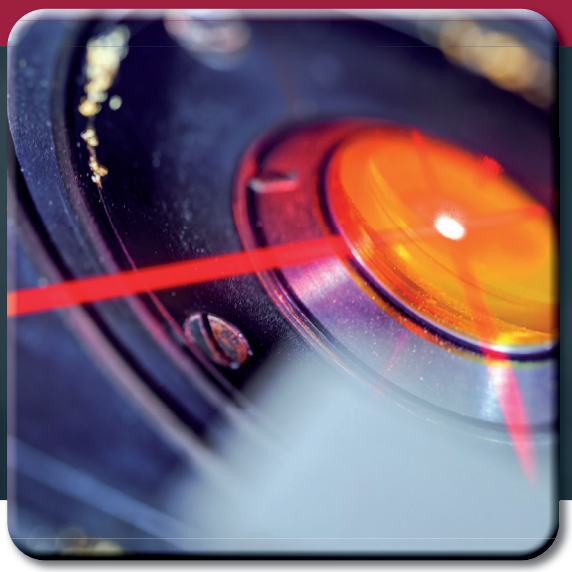
Ionisation, metastable and dissociation products in a C_2H_2:Ar^+ DLC deposition plasma

Mass spectra of the ionic and neutral species, showed the DLC plasma to be high in the desired C_2H radical as well as C_2H_2, C_3H_x, C_4H_x as well as argon species from the plasma gas. With this information, the mechanisms for the nucleation and growth of the DLC films can be postulated and interdependencies of parameters can be investigated.

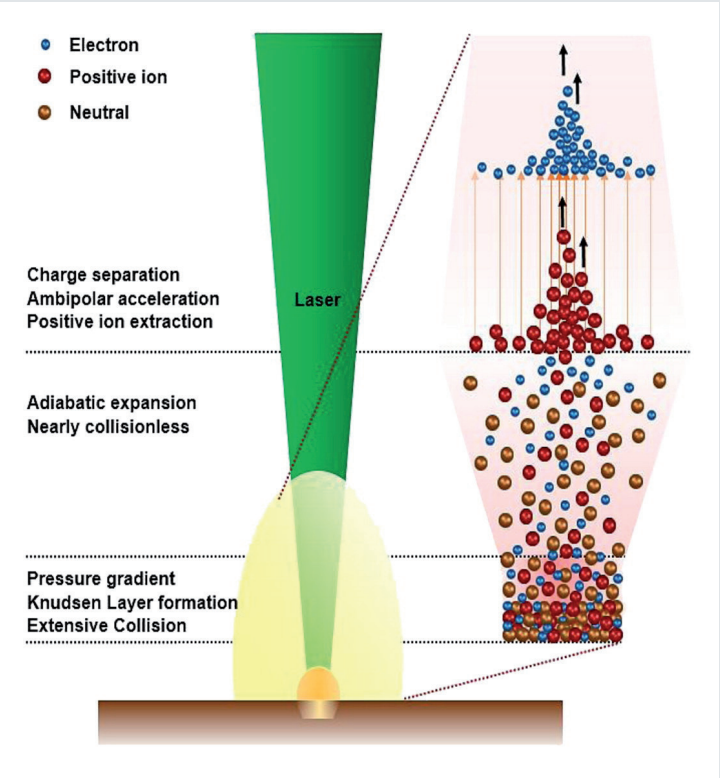


Neutral and ion mass spectra normalised with respect to argon in a CCP at 6 mTorr with 2:1 C_2H_2:Ar ratio.

Pulsed Laser Deposition (PLD) Coatings



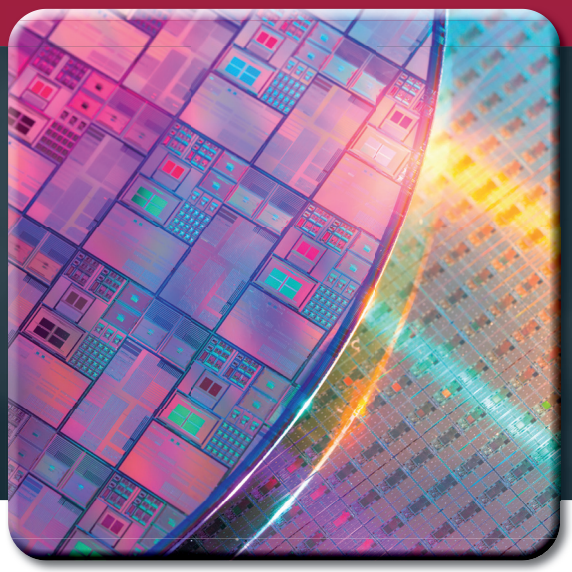
Pulsed Laser Deposition is a deposition technique that utilises a high-power pulsed laser to ionise a target material creating a plasma plume, which is used to deposit species onto the surface of a substate in close proximity to the plasma.



Schematic representation of the vital regimes for laser-surface interations in a vacuum for the ns laser case at an irradiance greater than the ablation threshold for the ion acceleration and the anisotropic distribution.

The Hiden EQP is used by many researchers in this field to provide direct monitoring of the resultant plasma plume. Ionic, neutral and radical species can be measured and the mechanisms for film nucleation and growth can be determined using the data gained.

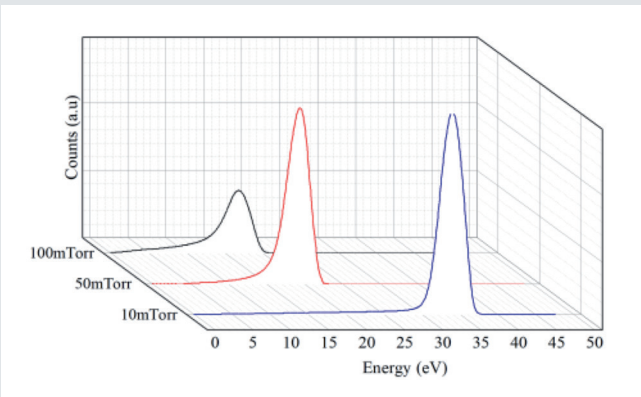
Plasma Etching and Atomic Layer Deposition



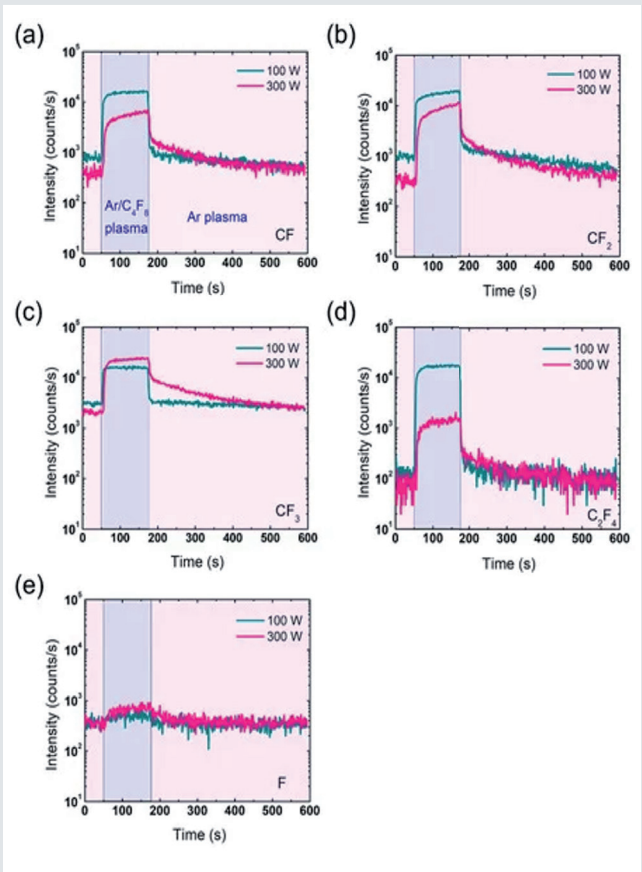
During plasma processing it is important to maintain the optimum plasma conditions for the process. Plasma diagnostics are critical in determining and maintaining this process window.

Atomic Layer Etching (ALE) is a two-step process which allows for reliable single atomic layer precision of the etch. The first step is to form a reactive layer on the substrate. The second step then removes this layer, and the underlying substrate layer, in a self-limiting manner. For the second step to be self-limited it is critical that the ion energy is higher than the sputtering threshold of the reactive layer but below that of the substrate layer.

Radical and ion fluxes are also important for the formation of the reactive layer. The Hiden PSM or EQP can be used to monitor both the fluxes of radicals and ions and their energies in real time.

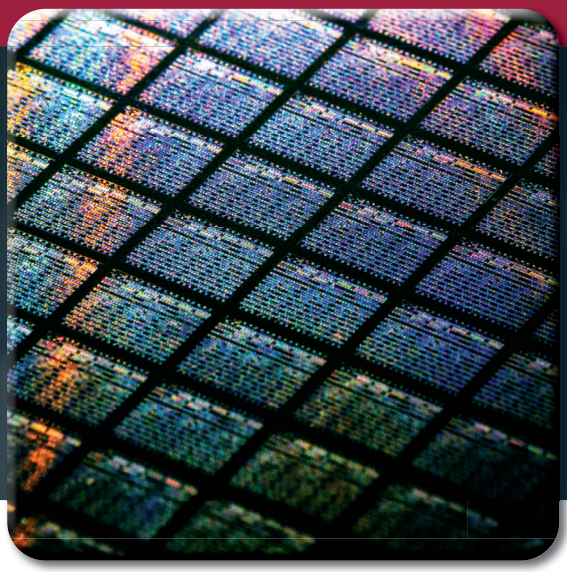


IEDs as a function of pressure in 1000 W Ar.



FC radical densities measured using a QMS during one cycle of ALE at 100 W and 300 W of (a) CF, (b) CF_2, (c) CF_3, (d) C_2F_4, and (e) F.

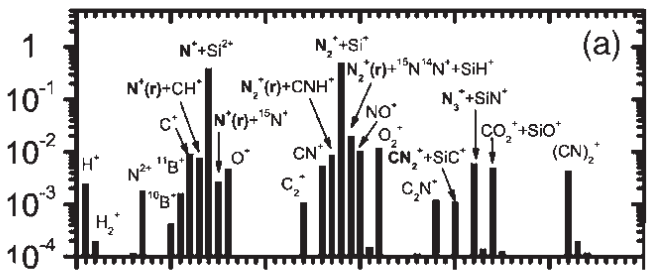
DC Magnetron Deposition of Silicoboron-carbonitride (SiBCN) Films for Microelectronics Applications



Silicoboron-carbonitride films have a unique combination of properties, such as extremely high temperature stability and oxidation resistance, low thermal coefficient of expansion, low thermal conductivity, high hardness, high creep resistance even at elevated temperatures, reduced film stresses, and good substrate adhesion. Films deposited with magnetron sputtering also offer enhanced electronic capabilities.

The Hiden EQP was used to investigate the composition of the plasma, allowing the properties of the resultant films to be correlated to plasma conditions.

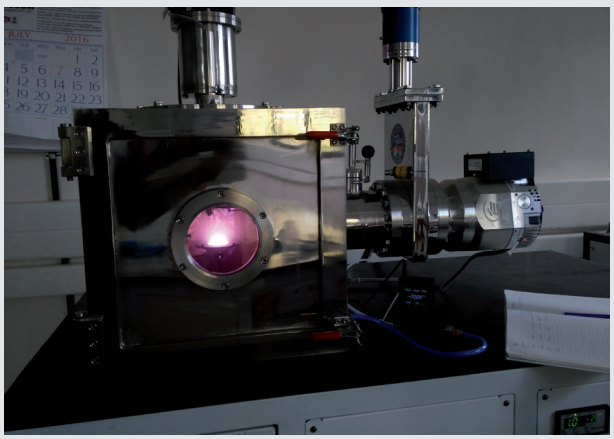
The Hiden EQP system was placed directly into the plasma plume, and the species present were directly analysed using the integrated tuneable ion optics. The affects of gas composition, power and substrate temperature were optimised. The resultant films were found to have an amorphous structure, with high hardness, low surface roughness and excellent oxidation resistance at elevated temperatures up to the substrate limit of 1350°.

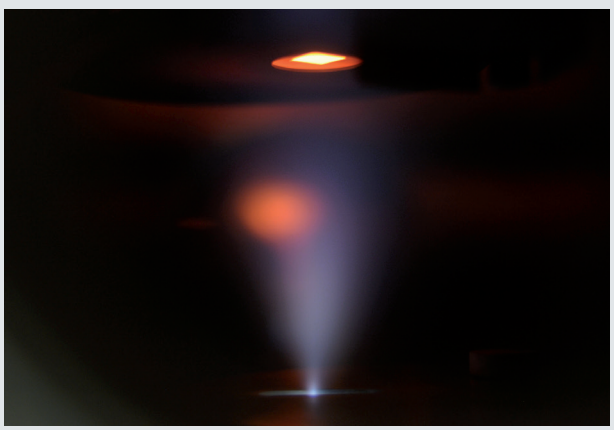


Positive ion spectrum of a silicoboron-carbonitride plasma.

PLASMA DEPOSITION

Plasma deposition is a surface technique that involves using a plasma to deposit species onto the surface of a material with the goal of enhancing specific properties of the material. Enhancements in hardness, chemical resistance, adhesion and corrosion resistance are common benefits to the bulk material.





Plasma deposition chamber

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- "Ion kinetic energy distributions in laser-induced plasma" Spectrochimica Acta Part B 99 (2014) 101–114

- "Plasma Dynamics of Very-High-Frequency (VHF) Discharges with Application to Atomic-Layer-Etching (ALE)" PhD Thesis, Doras (2021)

For more information scan the QR codes

Hiden**APPLICATIONS**

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

GAS ANALYSIS

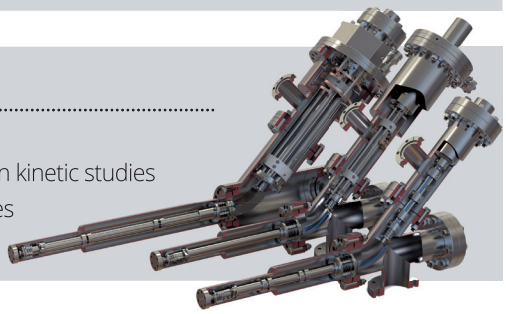
- dynamic measurement of reaction gas streams
- catalysis and thermal analysis
- molecular beam studies
- dissolved species probes
- fermentation, environmental and ecological studies

SURFACE ANALYSIS

- UHV TPD
- ToF qSIMS and SIMS analysers
- end point detection in ion beam etch
- elemental imaging – 3D 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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