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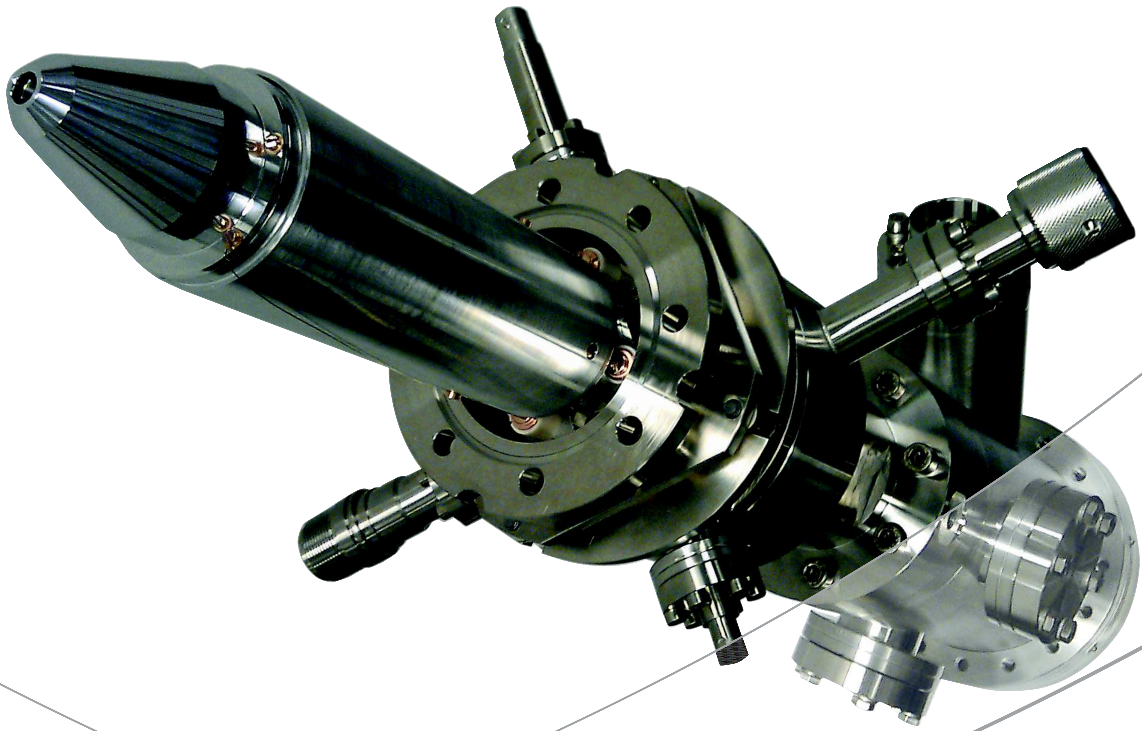
VACUUM & MATERIALS

Sputter depth profiling of polymer and inorganic materials on AXIS instrumentation

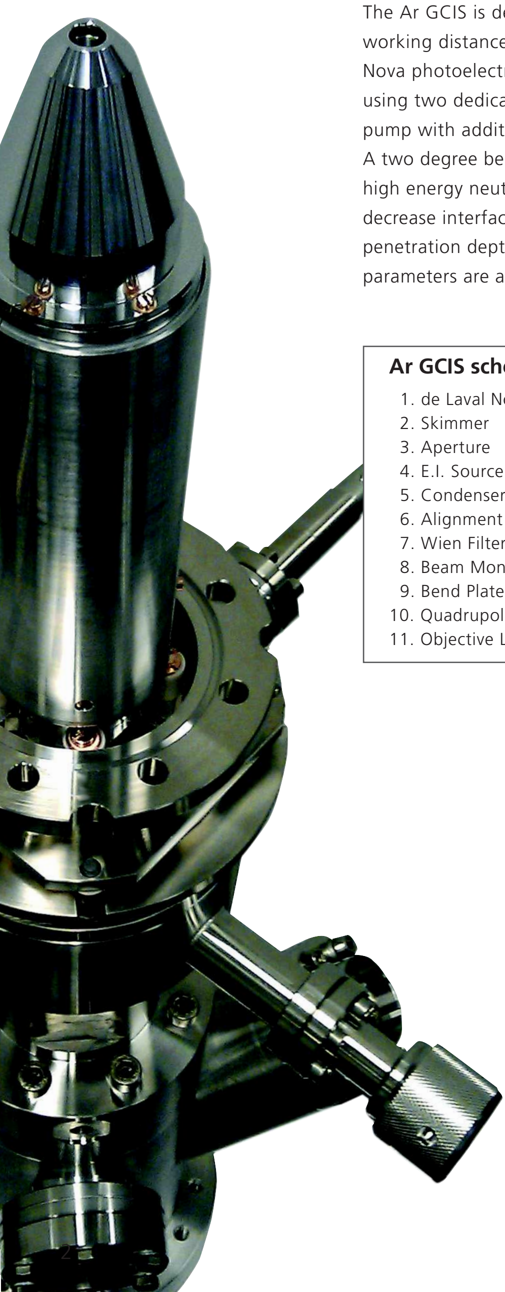
Gas Cluster Ion Source



Argon Gas Cluster Ion Source

Recent advances in depth profiling of organic materials are based on sputtering with large Ar_n^+ ion clusters consisting of hundreds or even thousands of Ar atoms. Unlike monatomic ions, large cluster ions do not penetrate deeply into the material therefore the energy of the impact is deposited within the first few nanometers of the surface. As the energy is shared by all atoms in the cluster, the energy per projectile atom, or partition energy, can be as low as a few electron volts such that the cluster ions only sputter material from the near-surface region leaving the subsurface layer undisturbed.

The Kratos Ar Gas Cluster Ion Source (GCIS) is optimised for depth profiling organic materials in Ar_n^+ cluster mode and inorganic materials in Ar^+ monomer mode, dependent on the operating parameters defined by the user and the type of material to be profiled. In Ar_n^+ ion cluster mode the ions can be accelerated up to a maximum of 20 keV. This allows the successful sputter depth profiling of the widest range of polymer materials to be undertaken. However, Ar_n^+ cluster depth profiling has been shown to give very low sputter yields for inorganic materials. In order to retain the capability of generating depth profiles from this class of materials this ion source can also be operated in the more conventional Ar monomer (Ar^+) mode.



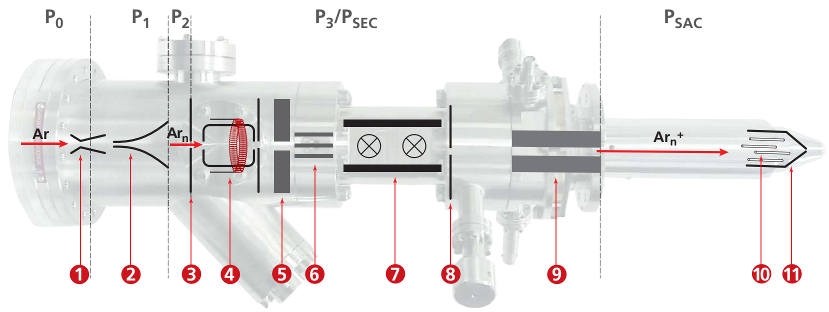
Hardware

The Ar GCIS is designed to mount on a DN64 (4.5" OD) flange with a working distance appropriate for both the AXIS Ultra DLD and AXIS Nova photoelectron spectrometers. The GCIS is differentially pumped using two dedicated turbomolecular pumps backed by an oil free scroll pump with additional pumping provided by the sample entry chamber. A two degree bend is incorporated into the ion beam column to remove high energy neutrals from the beam as these particles can significantly decrease interface resolution during depth profiling due to their greater penetration depth into the sample. Gas pressure, valves and operating parameters are all controlled through the acquisition software.

Ar GCIS mounted on the AXIS Nova (covers removed)

Ar GCIS schematics

1. de Laval Nozzle
2. Skimmer
3. Aperture
4. E.I. Source
5. Condenser Lens
6. Alignment Plates
7. Wien Filter
8. Beam Monitor
9. Bend Plates
10. Quadrupole
11. Objective Lens



Ar Gas Cluster Operating Mode

Large Ar clusters are formed by the isentropic adiabatic cooling of the gas as it expands from high pressure into the vacuum of the source region through a de Laval nozzle. The Ar clusters are ionised by electron impact and accelerated along the ion column. A Wien velocity filter is used to narrow the sampled range of cluster size. The ions are accelerated up to a maximum of 20 keV (Ar^+ cluster mode) or 5 keV (Ar^+ monomer) with a series of lenses to focus and quadrupole scan plates to raster the ion spot across the surface of the specimen.

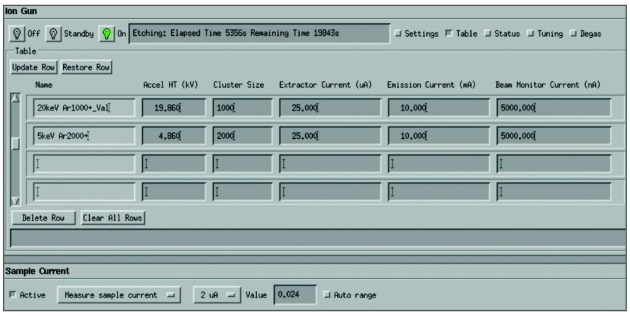
The median cluster size is determined by setting the appropriate electric field on the Wien filter. The cluster sizes used can be varied from Ar_{500}^+ to Ar_{2000}^+ such that the partition energy can be varied from 2.5 eV (eg 2.5 keV/1000 cluster etc) to 40 eV per Ar atom.

Ar Monomer Operating Mode

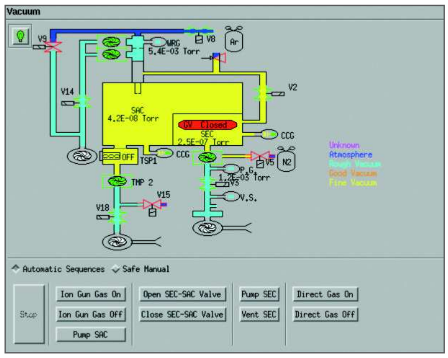
The ion source may also be operated in the more traditional monomer Ar^+ mode which is more suited to depth profiling inorganic samples. Studies have shown the sputter yield of this class of sample is very low using Ar clusters so it is important to be able to be able to sputter using Ar^+ ions. Switching to Ar monomer mode simply involves selecting the appropriate table entry in the acquisition software.

Software

Complete control of the Ar GCIS is provided by the acquisition software. Operating parameters are saved in a table that can be used to restore the optimised conditions prior to use of the source. During use the status of the GCIS may be displayed to monitor key parameters of the source. These parameters may also be saved to a log file enabling long term monitoring of the operating conditions of the GCIS.



Gas cluster ion source software interface



Vacuum mimic diagram with automated control of Ar gas and pumping of the GCIS

Control of the gas flow required for operation of the GCIS is most easily achieved using the automatic sequences in the vacuum control section of the acquisition software. Complete automation of the gas handling system means that the GCIS can be run unattended or remotely. Control of individual valves, pumps and gauges may also be undertaken using the 'safe manual' mode and the vacuum mimic diagram.

Applications

Maximum Flexibility

Published work[Matsuo] has shown that different types of polymer have variable sputter yields dependent on different cluster size and energy. To achieve maximum flexibility in terms of the range of materials which can be successfully profiled, the ion source parameters, including cluster size and primary beam energy, can be defined specifically to optimise sputter yield of the specimen under investigation. Poly (lactic-co-glycolic) PLGA acid is a well known Type II polymer[Mahoney]. Data acquired using the GCIS Ar_n^+ shown in figure 1 shows that the sputter yield of PLGA is highly dependent upon the primary beam energy. Furthermore it is evident that the capability to generate ions with 20 keV energy results in greater ion yield for PLGA.

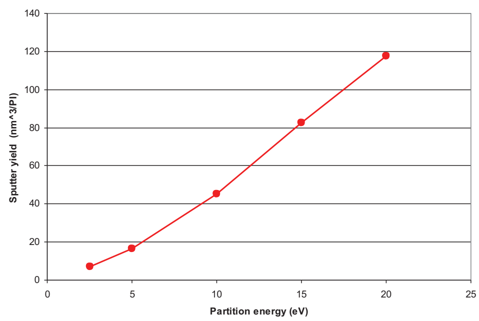


Figure 1: Sputter yields for Ar_{1000}^+ at a range of primary beam energies on 60 nm thin film PLGA polymer on Si

Organic/Organic Multilayer Depth Profile (Ar_{500}^+)

The following example is a sputter depth profile through an organic/organic multilayer sample with 10 alternating layers of a polyester with high nitrogen concentration and a methylmethacrylate with low nitrogen concentration where each polymer layer is nominally 100 nm thick. The sample is shown as a schematic diagram in figure 2.

Data were acquired from 110 µm analysis area centred in a 1.5 x 1.5 mm^2 sputter crater. The GCIS was used in cluster mode with Ar_{500}^+ accelerated to 5 keV, giving a partition energy of 10 eV per atom. The concentration depth profile is shown in figure 3 (overleaf) with the carbon chemical state plotted against sputter depth. It is immediately apparent that the sputter yeild for both polymers is very similar under the ion source parameters used giving an average etch rate of 18.5 nm/min for the bilayers. It is further noted that excellent interface resolution is maintained throughout the profile with the interface resolution between polymer layers 9 and 10 measured as 15 nm. Figure 4 shows the narrow region scans for C 1s, O 1s and N 1s as a function of sputter cycle. This demonstrates that the chemistry of both polymers is retained throughout the depth profile.

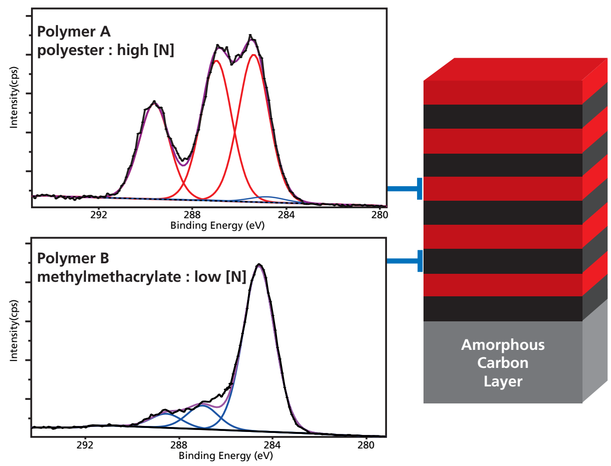


Figure 2: Schematic diagram of the polymer A / polymer B multilayer with the representative C 1s spectra from each polymer

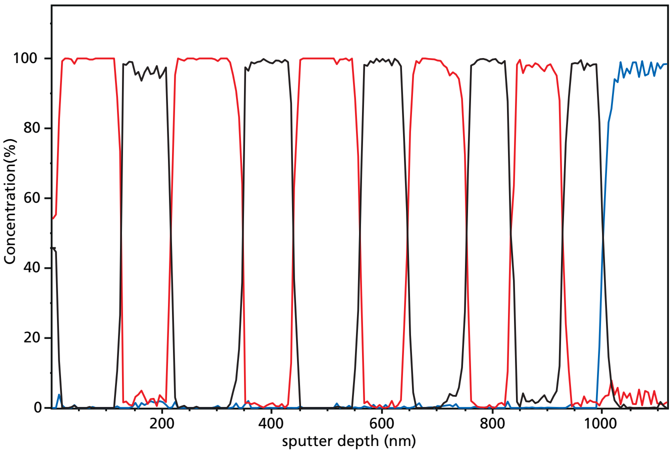


Figure 3: C 1s chemical state depth profile for polymer/polymer multilayer

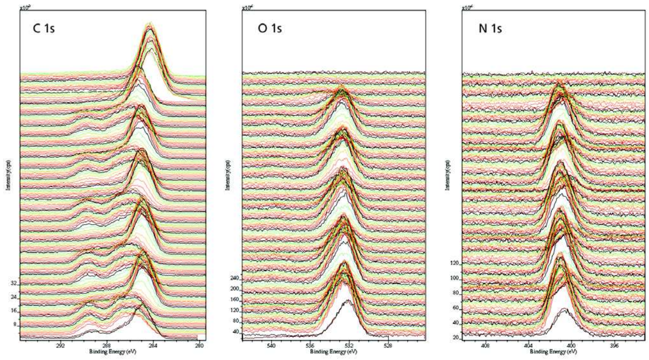


Figure 4: High resolution, narrow region scans for C 1s, O 1s and N 1s regions as a function of sputter cycle. The 'as introduced' surface is at the bottom of the figure with increasing etch time vertically to the bulk amorphous carbon substrate at the top of each plot.

Conclusions

The development of the GCIS has allowed the profiling of polymer samples with the retention of chemical state information. This has been demonstrated in the applications example above where the successful depth profile of a 10 layer polymer/polymer sample has been achieved. The chemical state of the carbon, oxygen and nitrogen was retained through the sample as well as interface resolution between each layer.

References

[Matsuo] Matsuo J, Ninomiya S, Nakata Y, Honda Y, Ichiki K, Seki T, Aoki T. 2008. What size of cluster is most appropriate for SIMS? *Appl Surf Sci* **255**(4):1235–1238.

[Mahoney] C.M. Mahoney, Cluster Secondary Ion Mass Spectrometry of Polymers and Related Materials *Mass Spectrometry Reviews* DOI 10.1002/mas.

Acknowledgements

We thank Dr M Clarke of DOW Chemical Inc. for providing the multilayer polymer/polymer sample and allowing us to use the results.

Hardware design details

Fine pumping :	2 x TMP
Backing :	oil free scroll pump
Number of filaments :	2
Flange mounting:	DN64 (4.5″ OD)

Operating Parameters

Clusters

Energy range :	0.2 – 20 keV
Beam current :	>10 nA
Cluster size :	200 – 2000
Max raster size :	1.5 mm (at 20 keV)

Monomer

Energy range :	0.1 – 8 keV
Beam current :	>200 nA
Max raster size :	6 mm (at 5 keV)

Performance

Ar_{1000}^{+} clusters at 10 keV sputter rate
> 25 nm/min on PLGA

Ar^{+} monomer ions at 5 keV sputter rate
> 4 nm/min on Ta_2O_5

Kratos Analytical Ltd, a wholly owned subsidiary of Shimadzu Corporation, has been manufacturing surface analysis instruments for over four decades. Throughout this period Kratos has continued to lead the development of new technologies relating to X-ray photoelectron spectrometers and associated accessories for surface and materials characterisation. All Kratos Analytical products are designed, assembled and supported from our headquarters in Manchester, UK.

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