

Sputter depth profiling of polymer and inorganic materials on AXIS spectrometers.

GAS CLUSTER **ION SOURCE**



MULTI-MODE ION SOURCE

FOR ORGANIC AND INORGANIC SPUTTER DEPTH PROFILING

The multi-mode gas cluster ion source (GCIS) is designed to operate in both Ar_n^+ cluster and Ar^+ monatomic modes making it suitable for sputter cleaning and depth profiling organic, inorganic and metallic thin films. In addition it may also be used to generate low energy He^+ ions for use with ion scattering spectroscopy.

The use of large argon clusters for sputter depth profiling of organic materials is now widely accepted and their use is being extended to inorganic depth profiling.

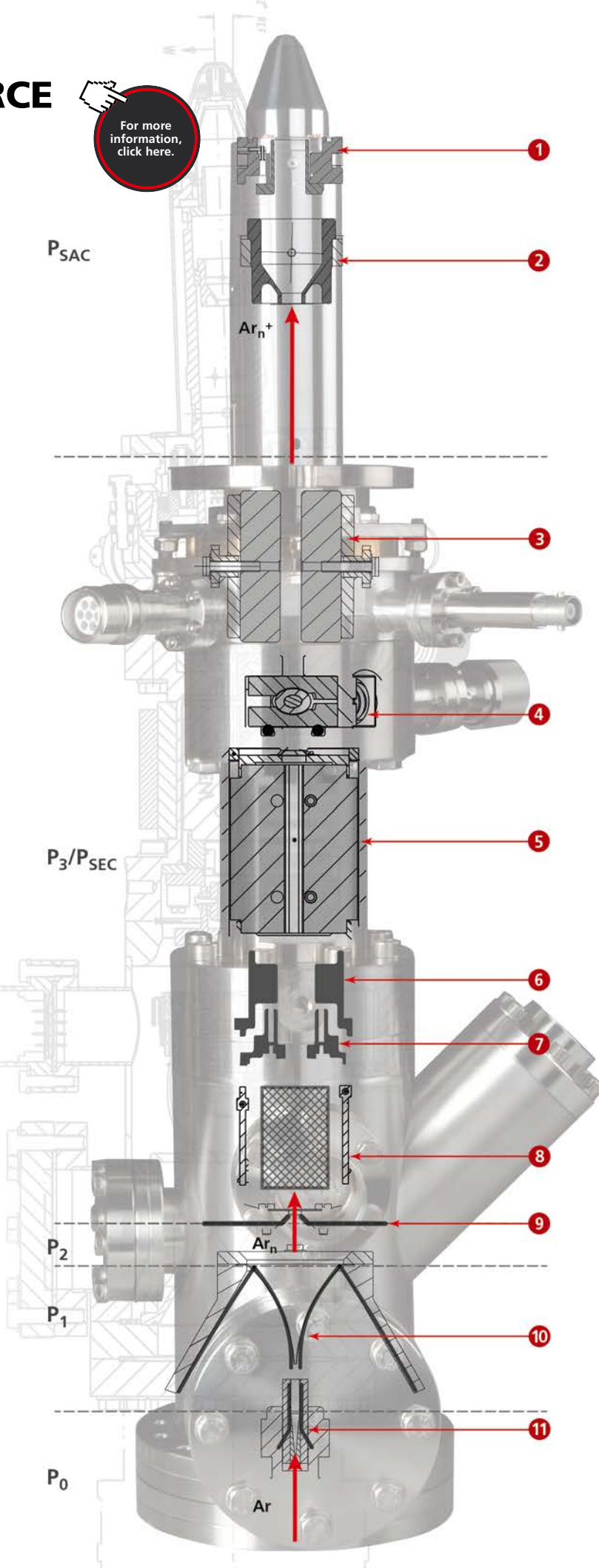
Through a combination of cluster size and acceleration voltage a wide range of materials may be sputter cleaned or depth profiled without chemical damage of the surface. The ion source can be used in monatomic mode for thin metal layers, small clusters at high beam energies may be used for metal oxides and large clusters at low or medium energy for a wide range of organic materials.

Ar_n^+ GAS CLUSTER OPERATING MODE

Large Ar clusters are formed by isentropic adiabatic cooling of the gas as it expands from high pressure (P_0) through a nozzle into the vacuum of the source region (P_1 / P_2). The Ar_n clusters are ionised by electron impact, extracted from the source region and accelerated along the ion column where a Wien velocity filter is used to select a median cluster size between 500 and 3000. These cluster ions may be accelerated up to a maximum of 20 keV such that the energy per atom, or partition energy, can be varied from <2 eV (5 keV, Ar_{3000}^+) to 40 eV (20 keV, Ar_{500}^+). A subsequent ion channelling bend in the focusing column removes energetic neutrals. The beam is then focused to a minimum spot size of 250 μm on the sample. Scan plates allow the beam to be rastered across the sample surface to create an even sputter crater.

The ability to generate Ar_n^+ ions with different cluster sizes and acceleration energies means successful depth profiles can be generated from the greatest range of materials. Large clusters, where $n > 2000$, are useful for depth profiling organic layer systems whilst smaller clusters of $n=500$ accelerated to high energies have been shown to be necessary in retaining chemistry of inorganic materials during depth profiling and sample cleaning.

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



Ar⁺ MONATOMIC OPERATING MODE

The ion source can be operated in monatomic Ar⁺ ion mode for conventional depth profiling inorganic and metallic samples. The sputter yield for this class of materials is known to be much higher for monatomic than cluster ions making Ar⁺ monatomic mode important for depth profiling in realistic experimental times. Ion acceleration voltage can be varied between 500 eV and 8 keV.

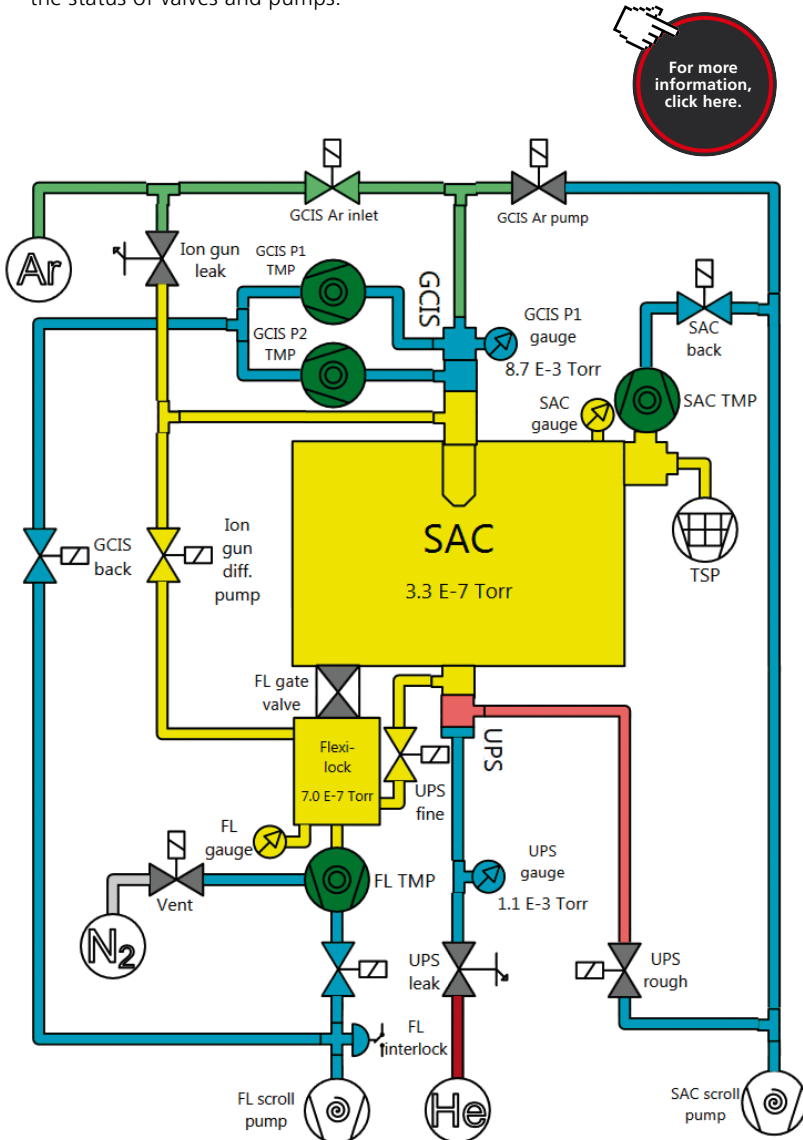
HARDWARE & SOFTWARE

The standard configuration provides differential pumping of the ion source by two dedicated turbo molecular pumps with additional pumping provided by the sample entry chamber. An automated gas handling manifold is provided to supply both high and low pressure Ar for cluster and monatomic modes respectively.

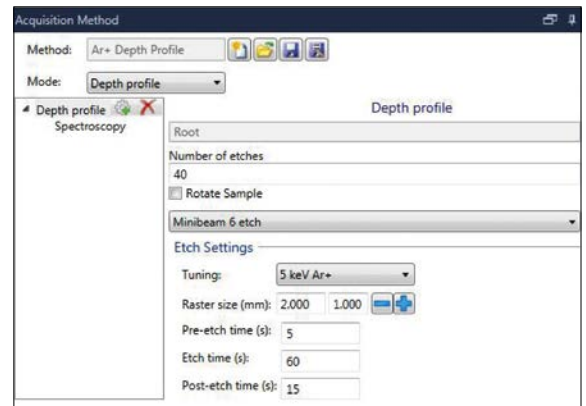
The ion source control unit is computer controlled through the ESCAPE software allowing unattended operation of and switching between Ar_n⁺ cluster and Ar⁺ or He⁺ monatomic modes. For routine operation the User interface allows simple recall of standard operating methods for sample cleaning and depth profiling in cluster and monatomic modes. Operating parameters of the ion source are continuously displayed allowing key parameters to be monitored along with a vacuum mimic diagram showing the status of valves and pumps.



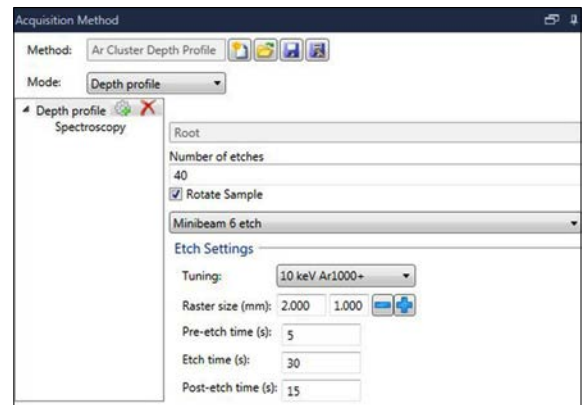
Ar GCIS mounted on the AXIS Supra



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



5keV Ar⁺ method software interface



10keVAr₁₀₀₀⁺ method software interface

■	Unknown	
■	Argon	
■	Helium	
■	Nitrogen	
■	Fine	< 5E-6 Torr
■	Good	< 5E-5 Torr
■	Rough	< 2 Torr
■	Atmosphere	> 2 Torr

APPLICATIONS

INORGANIC DEPTH PROFILING SMALL CLUSTER, HIGH ENERGY DEPTH PROFILING

It is known that the sputter yields from inorganic materials are low when using gas clusters. This challenge can be mitigated by using small clusters with high beam energy. Here we contrast the use of 5 keV monatomic Ar^+ with 20 keV Ar_{1000}^+ ions for sputter depth profiling a Lithium phosphorous oxynitride ALD thin film where the Li distribution through the film is of interest. The high acceleration voltage in cluster mode ensures that the depth profile was completed in a practical time scale.

There is a distinct difference between the two profiles. Under monatomic bombardment there is an initial increase in Li concentration after the first etch cycle – a consequence of removing surface contamination – then a subsequent decrease in Li into the bulk of the film reaching a steady-state, shown in figure 1(a). Near the LiPON interface with Si substrate the Li concentration increases. By contrast when profiled 20 keV Ar_{1000}^+ ions the profile shows a different distribution of Li, figure 1(b).

An initial increase in Li concentration is shown after the first etch however there is no subsequent decrease. Interestingly no accumulation of Li was seen at the interface with the Si substrate.

A comparison of the Li concentrations profiled using two different ions is shown in figure 1(c).

The different results are attributed to positive charge build-up in the near surface region from implanted monatomic Ar^+ ions. Charge build-up repels the small, mobile positive Li ions in the surface further into the bulk resulting in an underestimation in surface quantification.

Repulsive bulk migration also accounts for the increase in Li concentration at the interface with the Si substrate. The light ions are unable to penetrate into the Si metal and native oxide and instead accumulate at the interface.

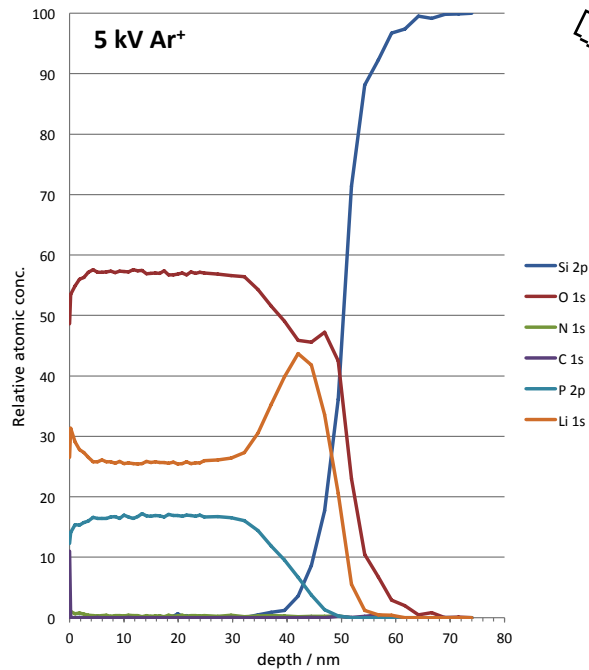


Figure 1(a) Sputter depth profile through ALD LiPON thin film using 5 keV Ar^+

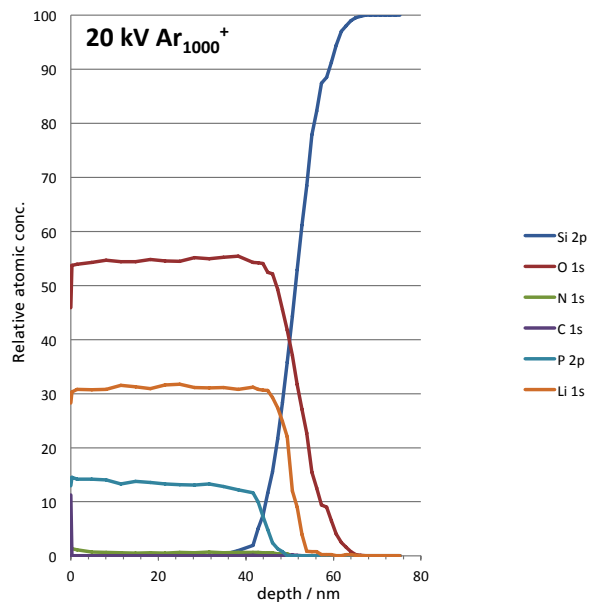


Figure 1(b) Sputter depth profile through ALD LiPON thin film using 20 keV Ar_{1000}^+

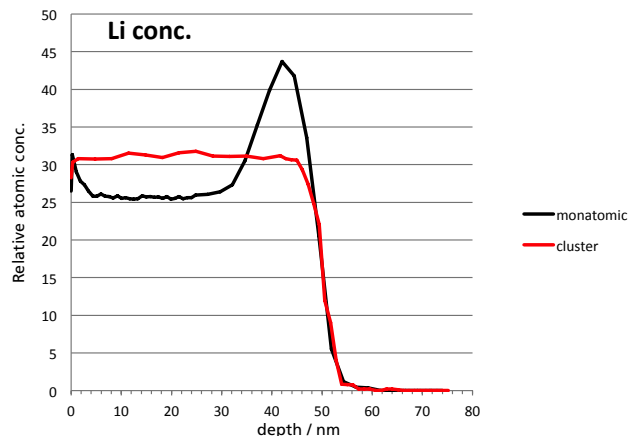


Figure 1(c) comparison of the Li concentration through the same sample generated using monatomic and cluster ion projectiles.



NANOSTRUCTURED MULTILAYER MATERIALS

LARGE CLUSTER, HIGH ENERGY DEPTH PROFILING

Nanostructured multilayer materials have emerged recently as a distinct class of super-hard materials which have found use as coatings for cutting tools and turbine coatings. They consist of nanometer repeating layers assembled via physical vapour deposition to form superlattices. An example of such a material is TiN (7nm)/CrN (3nm) multilayer with 100 repeat units which has been shown to have high resistance to oxidation and superior mechanical properties.

The conventional approach to depth profiling this sample would be to use 500 eV monatomic Ar⁺ ions. The profile is shown in figure 2(a). It is immediately apparent that there is a loss of interface resolution after 6 repeat units (12 layers) due to penetration of the monatomic Ar⁺ ions into the material resulting in mixing of the layers. This was supported by the observation of Ar in the photoemission survey spectrum during the depth profile.

The same sample was profiled using high energy, large clusters (20 keV, Ar₂₀₀₀⁺). The use of the high ion acceleration voltage ensured that the yield volume per incident ion was as high as possible so that the depth profile was completed in an overnight experiment. Figure 2(b) shows the successful depth profile with retention of the layer structure throughout the 100 layer coating. In contrast to the monatomic profile Ar incorporation into the sample was not observed for this Ar₂₀₀₀⁺ cluster profile.

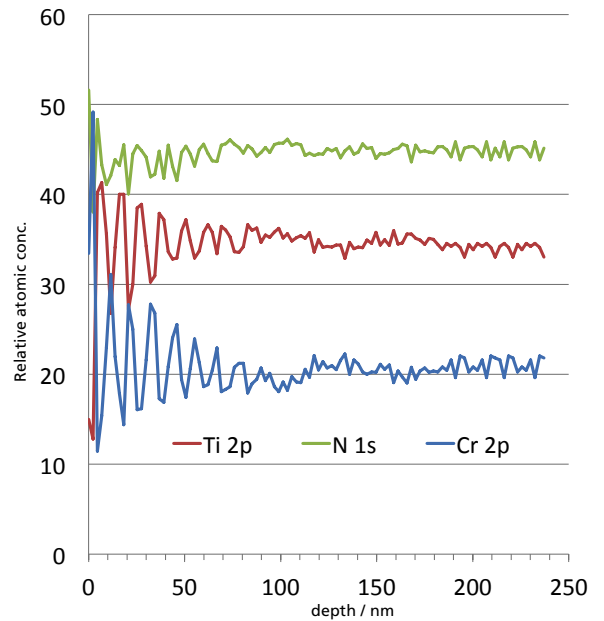


Figure 2(a) Sputter depth profile through TiN/CrN sample using monatomic 500 eV Ar⁺ ions.

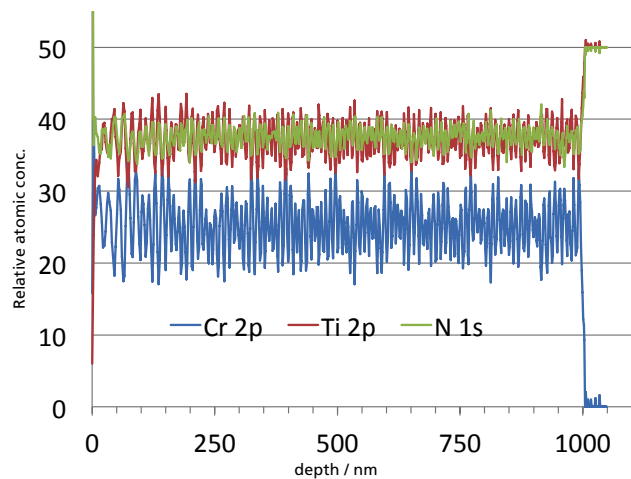


Figure 2(b) Successful sputter depth profile through TiN/CrN sample using 20 keV, Ar₂₀₀₀⁺ ions.

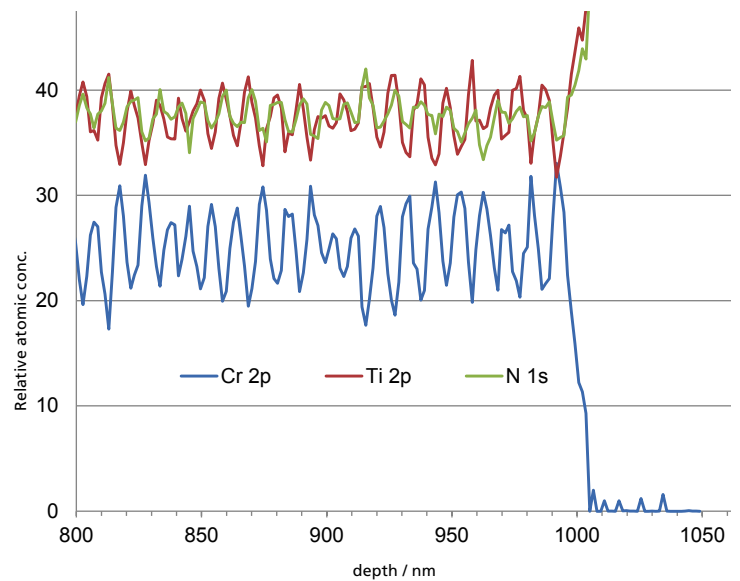


Figure 2(c) Expanded region of depth profile shown in figure 2(b) showing retention of layer resolution at the interface with bulk CrN substrate.

ORGANIC MULTILAYER DEPTH PROFILE

SMALL CLUSTER, MEDIUM ENERGY DEPTH PROFILING

Thin film polymer structures are finding an increasing number of applications including optical filters and reflectors, organic electronics and drug delivery systems. The use of gas clusters has allowed the sputter depth profiling of this class of materials, where the chemistry of the polymer is retained throughout the profile. Here, 10 keV Ar₁₀₀₀⁺ ions were used to depth profile through a 50 layer multilayer Bragg reflector comprising spin-coated polystyrene (PS) and polyvinylpyrrolidone (PVP).

The PS & PVP layers were 328nm and 288nm respectively such that the complete structure was >15µm thick. Figure 3(a) shows the sputter depth profile through the entire structure to the glass substrate. The layer structure is retained throughout the depth profile and it is evident that the fabrication of the structure resulted in uniform layer thickness for each respective polymer layer. Figures 3(b) and (c) show the C 1s spectrum for layers 35 and 36 respectively, demonstrating that the chemistry of the polymer is retained during the sputtering process.

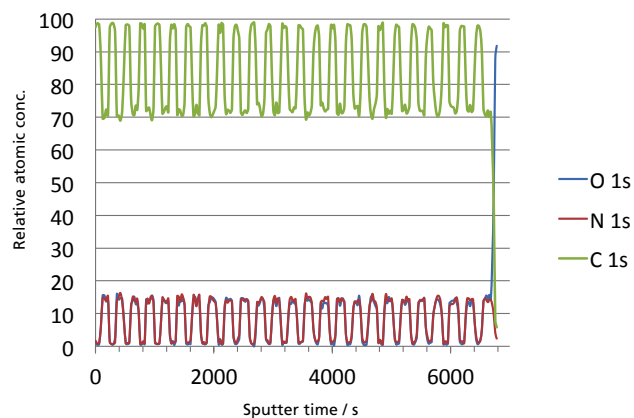


Figure 3(a) 10 keV Ar₁₀₀₀⁺ cluster depth profile through PS / PVP multilayer Bragg reflector.

CONCLUSIONS

The multimode gas cluster ion source provides the capability to depth profile polymer, inorganic and metallic samples through a choice of giant gas cluster or monatomic argon ions. Easy control of both the cluster size and ion energy allows the appropriate partition energy to be used for the application whilst maintaining suitable sputter yields per incident ion. Small clusters at high energy (20 keV, Ar₁₀₀₀⁺) are useful for depth profiling inorganic materials and demonstrate significantly improved retention of stoichiometry when compared to monatomic Ar⁺ profiles. Large, lower energy clusters (5 keV, Ar₃₀₀₀⁺) are employed for removal of surface contamination of polymer materials whilst medium energy, large clusters (10 keV, Ar₃₀₀₀⁺) are suitable for extremely deep profiling of organic materials.

Kratos Analytical Ltd, a wholly owned subsidiary of Shimadzu Corporation, has been manufacturing surface analysis instruments since 1969. 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 characterization.

All Kratos products are designed, assembled and supported from our headquarters in Manchester, UK.

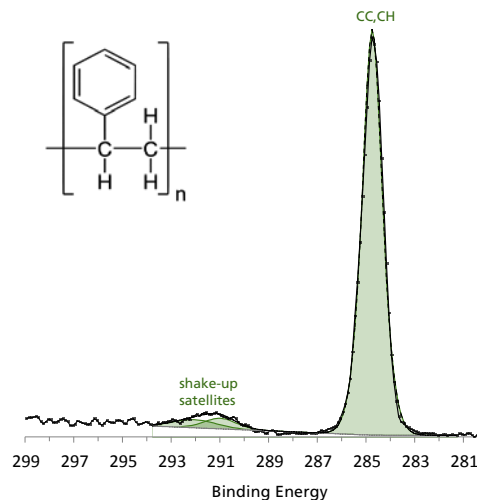


Figure 3(b) C 1s spectrum from layer 35 (PS) demonstrating retention of chemistry through the depth profile.

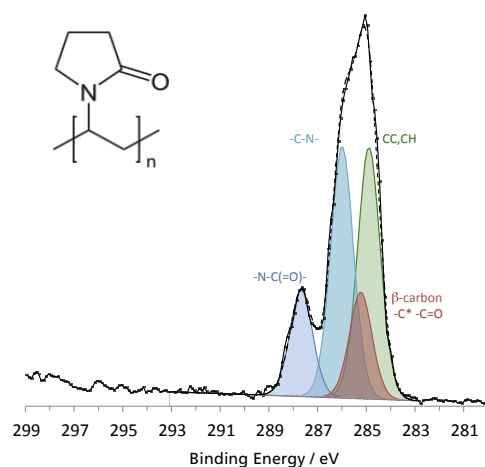


Figure 3(c) C 1s spectrum from layer 36 (PVP) demonstrating retention of chemistry throughout the depth profile.

KRATOS
ANALYTICAL
A SHIMADZU GROUP COMPANY

Kratos Analytical Ltd, UK

Wharfside, Trafford Wharf Road,
Manchester, M17 1GP, U.K.

Telephone: +44 (0)161 888 4400

Fax: +44 (0)161 888 4402

www.kratos.com

© Copyright August 2017