Application Note #220801

KeyWords
XPS, Gas Cluster Ion Beam, Iodine
Sputter Depth Profiling, Organic Films

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Sputter Depth Profiling of Iodine in Organic Thin Films

This application note presents how the optional GCIB source of the EnviroESCA can be used for sputter depth profiling of iodine-containing (bio)organic thin film samples using Argon cluster Ar_n^+ (n= 500-5000).

Motivation

XPS is a powerful surface analysis technique providing elemental and chemical information from the first 3-10 nm of a surface. However, many modern technological devices show multi-layered structures, and a complete analysis of such devices needs a stepwise removal of the individual layers.

Gas cluster ion beams (GCIB) enable depth profiling analysis of biological or organic films, e.g., polymers with minimal loss of chemical information due to ion beam damage. This is crucial in analysis of modern multi-layer structures, such as OLEDs, but also shows a marked improvement in analysis of well-established materials.

Combining XPS with GCIB has extended the range of materials that can be analyzed in-depth with XPS. Now sputter etching and depth profiling up to several dozens of nanometers and even microns can be realized for samples, e.g., organic, and biological ones, which are otherwise sensitive to ion beam damage.

The whole process can be compared with sandblasting a surface but using snowballs instead of sand grains. Thereby the damage to the sample is minimized, the abrasion is smooth, and the depth of removed material is significantly reduced which is a great improvement compared to monoatomic sputter etching.

Fig. 1 Sample of an organic thin film coated on silicon used for sputter depth profiling with argon gas clusters

Methods

EnviroESCA utilizes X-ray Photoelectron Spectroscopy (XPS) as analytical technique, see Fig. 1. Here an electron beam is generated inside the X-ray source and focused on an aluminum anode. The deceleration of the electrons on the anode generates X-rays. This X-ray beam is monochromated and focused on the sample.

X-ray photons impinging the sample excite electrons in the material which are subsequently emitted with a specific kinetic energy determined by their binding energy and the photon energy of the incoming X-rays. In case of solid samples only electrons from atoms down to a depth of about 10 nm can leave the surface.

These electrons propagate through the lens system of the electron analyzer into the hemisphere which acts as a spherical capacitor forcing the electrons onto circular paths with radii depending on their kinetic energy. The path of photoelectrons ends at an electron sensitive

detector where the electrons are amplified and measured as intensity in counts per second.

A photoelectron spectrum is recorded by sweeping the voltage of the spherical capacitor while measuring the number of electrons per second on the detector. From these spectra a quantitative analysis of the atomic composition of the sample surface can be done.

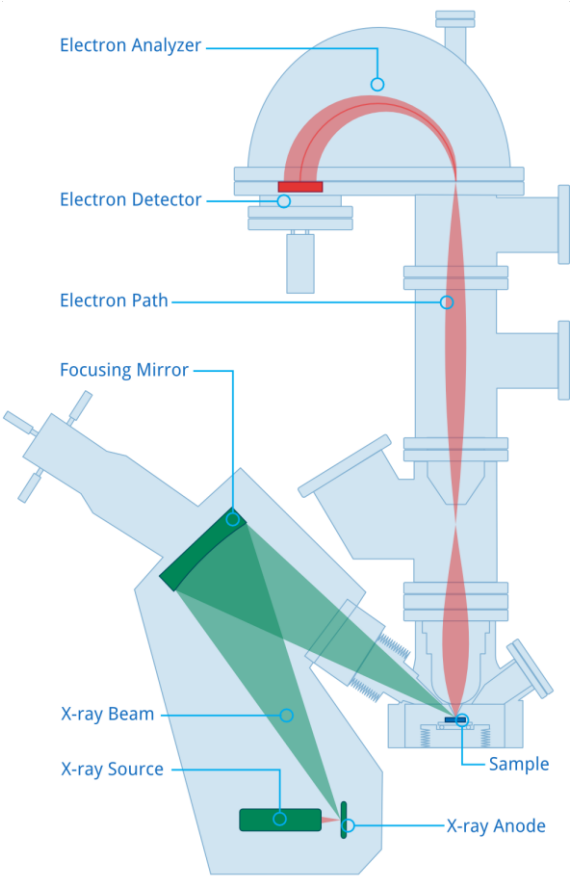

Fig. 2 XPS with EnviroESCA

Gas cluster ion beams (GCIB) are high energy beams of ionized clusters, ideal for the sputtering and analysis of organic matter. They are incredibly versatile ion sources, as both the beam-type and the properties of the beam can be varied as needed. This allows the users to tune the beam to the needs of their experiment.

Sputter beams have three characteristic features: high current, large spot size, and wide field of view. They are designed to deliver a large dose of ions over a wide area as quickly as possible to optimize etch rates. GCIBs are the ideal choice for sputtering organic matter. Etch rates of organic materials are several orders of magnitude higher than for metallic or semiconductor materials. This makes cluster beams such as the IONOPTIKA GCIB 10S an excellent tool for cleaning surfaces prior to analysis. The large cluster species also produce little fragmentation or sub-surface damage, thus their performance on those aspects is even better than with C_{60}.

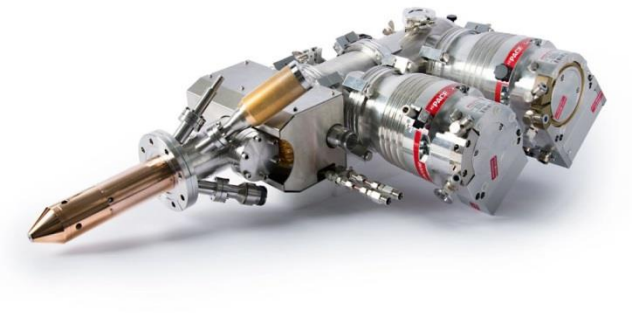

Fig. 3 IONOPTIKA 10 keV Gas Cluster Ion Beam System GCIB 10S

Ions are generated in the ion source by a 2-stage process. Firstly, argon clusters are formed by the adiabatic expansion of argon gas through a nozzle, starting at high pressure and passing into a region which is pumped to low vacuum. Then, passing through skimmer apertures into the next vacuum stage, the clusters enter an ionization chamber, and are ionized by electron bombardment.

The cluster ions are accelerated into an ion column which contains a Wien filter, a gate valve (for isolating the source from an instrument during maintenance), a bend to remove neutrals, scan plates and a final focusing lens. The Wien filter can select single cluster sizes for the small clusters; for the larger clusters, the beam consists of a mass distribution around the nominal cluster size. The size of cluster is a vital parameter and may be tuned over a wide range by adjusting the source conditions.

Experimental Section

EnviroESCA can work under vacuum and near ambient pressure (NAP) conditions up to several dozens of mbar. Thus, it is very well suited to investigate a multitude of organic and biologic samples at elevated pressures.

As used in this study, the EnviroESCA can optionally be equipped with an IONOPTIKA GCIB 10S to enable cluster beam sputtering for sample cleaning and depth profiling.

The basic principle of GCIB sputtering is shown in Fig. 4 for an organic film sample on a solid support, here silicon. The sample is bombarded with a beam of Ar_n^+ clusters consisting of *n* Argon atoms with energies of several keV. Upon impact of Ar_n^+ clusters on the surface a shallow crater is formed, thus some of the (organic) material from the uppermost surface layer is removed and the cluster itself is destroyed. Depending on the beam energy the amount of removed material per time, the sputter rate, can be controlled.

Sequential removal of individual layers from the sample surface by Ar_n^+ cluster sputtering and XPS analysis yields a compositional profile in terms of atomic concentration of all elements (except H) over sputter time (or depth if the sputter yield is known).

A simplified cartoon-like version of the used thin film samples is shown in Fig. 4. The samples are made of a very thin organic film of Povidone-iodide (PVP-I) or a mixture of agarose and PVP-I on a silicon wafer. The organic film is formed by spin coating of aqueous solutions of the respective organic compound on the silicon substrate [1].

The agarose thin film samples are selected as a model system for the exopolysaccharide matrix of biofilms. And PVP-I is used as an antibacterial agent with iodine as a specific marker element for XPS detection.

A full description of the sample preparation and experimental details as well as a detailed discussion of the results are given in reference [1].

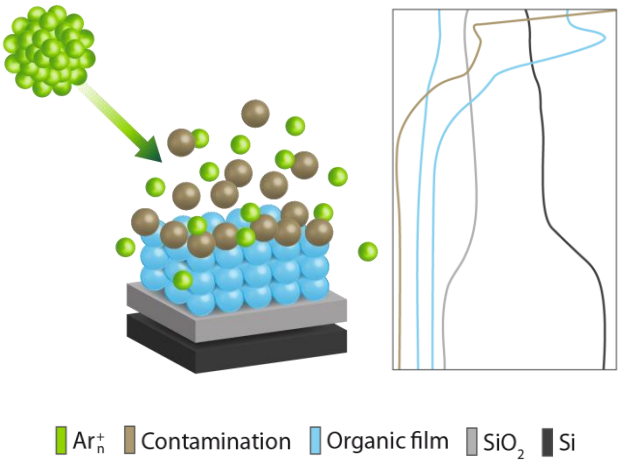

Fig. 4 Gas cluster ion beam (GCIB) sputtering of organic thin films

Results

Cluster ion beams enable depth profiling analysis of polymers with minimal loss of chemical information due to ion beam damage. This is crucial in analyses of organic and biological structures.

Here, sequential argon gas cluster sputtering combined with XPS analysis was used to quantify the in-depth distribution of iodine (cf. Fig. 5) in the mixed agarose/PVP-I films.

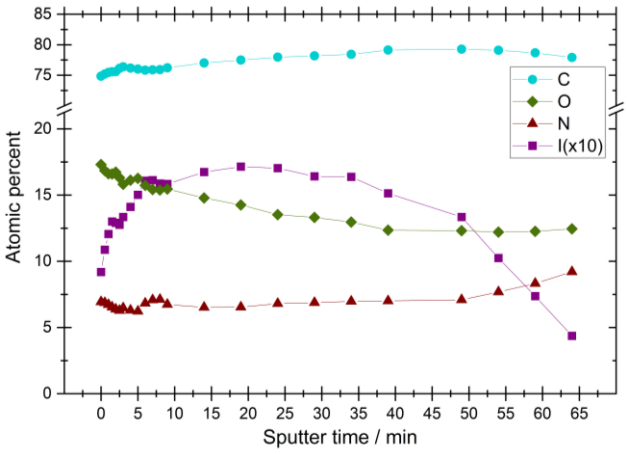

Fig. 5. XPS sputter depth-profile of a mixed PVP-I/agarose thin film (thickness 114 ± 8 nm, average sputtering rate 1.9 nm/min) using Ar^+_{2000} gas clusters (5 keV).

From the sputter depth profile shown in Fig. 5 it becomes obvious that iodine is depleted in the uppermost surface layers of the mixed agarose/PVP-I film.

Further sputtering into the film reveals a wide plateau of constant iodine concentration and when approaching the thin film substrate (Si wafer) interface a decrease of the iodine intensity.

A potential segregation effect in the mixed film was investigated in detail on a pure PVP-I thin film and the corresponding depth profile is shown in Fig. 6. Again, a depletion of iodine is observed in the topmost surface layers of the film corresponding to the upper 10 nm of the pure PVP-I sample (film thickness 33 ± 4 nm, average sputter rate 1.1 nm/min).

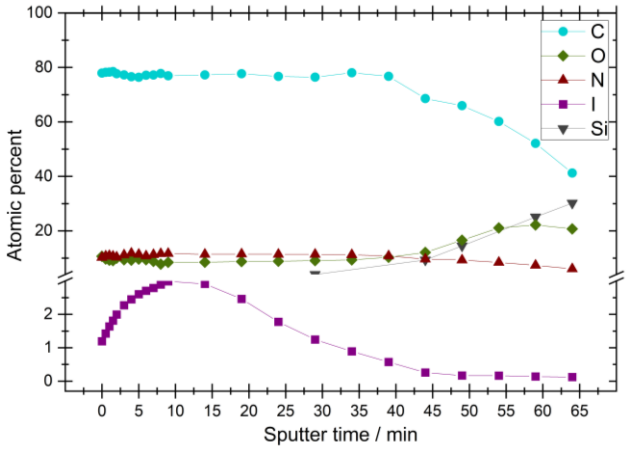

Fig. 6. XPS sputter depth-profile of a pure PVP-I thin film (thickness 33 ± 4 nm, average sputtering rate 1.1 nm/min) using Ar^+_{2000} gas clusters (5 keV).

Also, in the pure PVP-I film a plateau of about 5–10 nm and a decay of the iodine concentration at the interface between thin film and silicon substrate is present. From that finding it can be assumed that a PVP-I-related effect alone is inducing the observed iodine depletion in the pure PVP-I and the mixed agarose/PVP-I film.

The detailed peak fitting analysis of the I 3d core-level spectra indicates that the iodine depletion in the topmost surface layers of these thin films correlates with a loss of molecular iodine [1]. A significant loss of I_2 occurs when storing the PVP-I samples in (ultrahigh) vacuum (UHV). There are also losses of molecular iodine during the argon cluster sputter process, but these are minor effects compared to an extended UHV exposure.

Conclusion

EnviroESCA with its ability to work in vacuum and near-ambient pressure conditions using different gas atmospheres allows *in situ* and *operando* surface characterizations of a variety of samples and devices.

Gas cluster ion beams (GCIB) enable depth profiling analysis of organics with minimal loss of chemical information due to ion beam damage. This is crucial especially when analyzing biological and organic samples or modern multi-layer structures.

Here we presented sputter depth profiling of (bio)organic thin films as a typical application of a gas cluster ion beam (GCIB) source that can be added as an option to the EnviroESCA. Ar^+_n gas cluster ion sputter depth profiling was used to measure the in-depth distribution of iodine in artificial biofilm model layers. Consecutive cycles of surface layer removal by sputtering and XPS analysis yield compositional depth profiles of each sample in terms of atomic concentration over sputter time as shown in Fig. 5–6.

Both films the mixed agarose/PVP-I and the pure PVP-I thin film showed an iodine depletion in the outermost surface layer and a homogeneous distribution of iodine in the depth region between that surface layer and the region in the film near to the interface to the silicon substrate. Since the samples are inevitably exposed to (ultrahigh) vacuum conditions during the sputter process a surface depletion of iodine will occur due to the loss of excess molecular iodine [1].

This example shows the unique capabilities of the EnviroESCA combined with the GCIB 10S gas cluster ion source from IONOPTIKA.

[1] Paul M. Dietrich, Marit Kjærvik, Elizabeth A. Willneff, Wolfgang E. S. Unger *Biointerphases* **2022**, *17*, 031002

We gratefully acknowledge Marit Kjærvik and Wolfgang E. S. Unger from BAM, Prof. Sven L. M. Schroeder and Dr. Elizabeth Willneff from Leeds University as well as Ionoptika Ltd. for a very inspiring cooperation and fruitful discussions.