Application Note #000401

KeyWords
XPS, Gas Cluster Ion Beam, Sputtering, Depth Profiling, XPS, Surface Analysis

Gas Cluster Ion Beam (GCIB) sputtering with EnviroESCA

This application note presents how the optional GCIB source at the EnviroESCA can be used to clean samples prior to XPS analysis to get reproducible analytical data and reliable quantification results. Moreover, Argon cluster Ar_n^+ (n= 500-5000) sputtering and depth profiling of (bio)organic samples is possible which cannot be done when using monoatomic Ar_n^+ sputtering.

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 different layers.

Gas cluster ion beams (GCIB) enable depth profiling analysis of ultra-thin 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 greatly extended the range of materials that can be analyzed in-depth with XPS. Now sputter etching and depth profiling up to several dozen 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 very smooth, and the depth of removed material is significantly reduced which is a great improvement compared to monoatomic sputter etching.

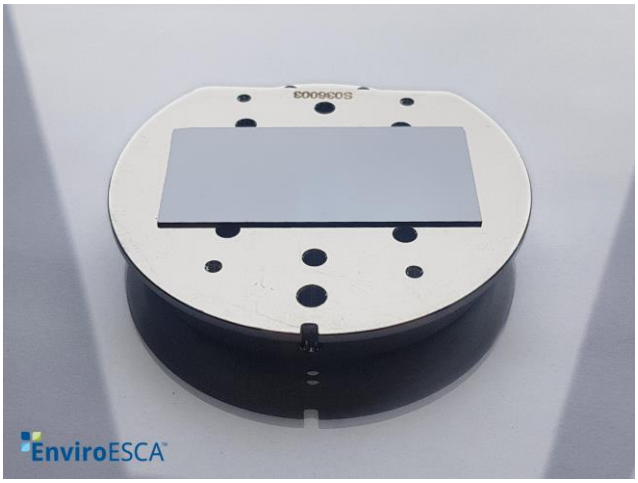

Fig. 1 Sample of an ultra-thin organic film on silicon used for sputter depth profiling with argon gas clusters

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 X-ray 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 X-rays. In case of solid samples only electrons from atoms down to a depth of about 10 nm are able to 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.

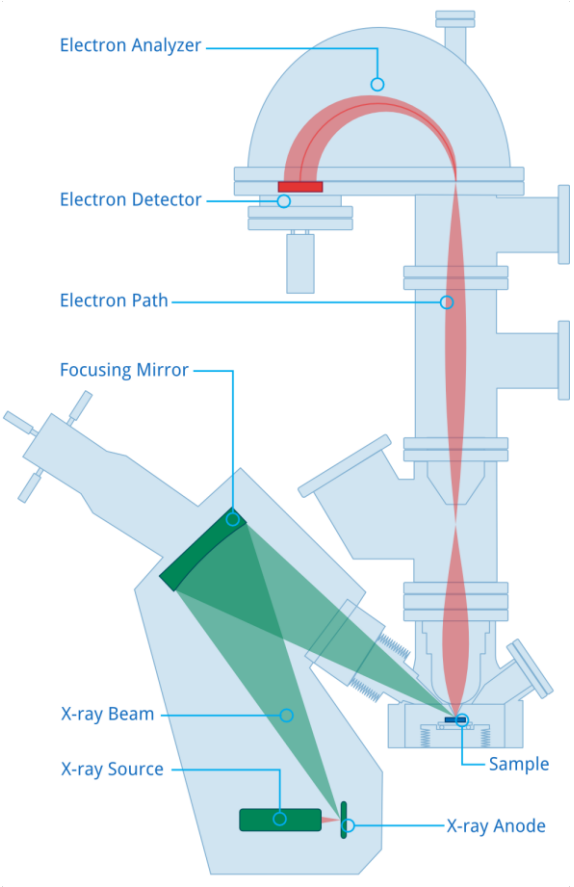

Fig. 2 XPS with EnviroESCA

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 user 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, in order 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 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 very little fragmentation or sub-surface damage, thus their performance on those aspects is even better than with C_{60}.

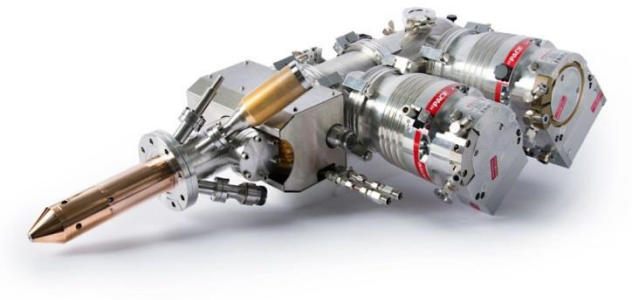

Fig. 3 IONOPTIKA 10 keV Gas Cluster Ion Beam System GCIB 10S

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 they 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 as well as near ambient pressure (NAP) conditions up to several dozens of mbar. Thus, it is very well suited to investigate all kind 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).

The sample used for sputter depth profiling is shown in a simplified cartoon-like version in Fig. 4. The sample is made of a very thin organic film on a silicon (100) wafer. The organic film is formed by a reaction between an organic precursor molecule a so-called silane (dimethylsilylpropylbenzylamide, DMSPBA) and the native oxide layer on the Si(100) substrate.[1,2]

The nominal thicknesses of the DMSPBA and native oxide layer were determined to be 1.4±0.5 nm and 1.7±0.5 nm, respectively. [1,2] As indicated in Fig. 4 a shallow contamination layer on top of the sample is also present. Its origin is not known but prolonged storage and handling in laboratory atmosphere could be possible reasons.

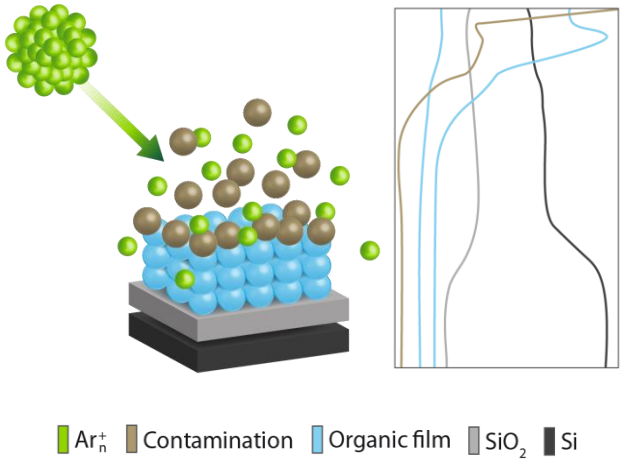

Fig. 4 Gas cluster ion beam (GCIB) sputtering of organic thin films

Results

Sample cleaning

First the GCIB was used to clean an "old" gold foil which was stored in open laboratory atmosphere for several months. Gentle sputtering conditions using Ar_{3000}^+ at 10 keV (3.3 eV per Ar atom) were used to remove the organic contamination layer. The C 1s core-level spectra shown in Fig. 5 demonstrate the effective removal of almost all adventitious carbonaceous material after 10 min of sputtering.

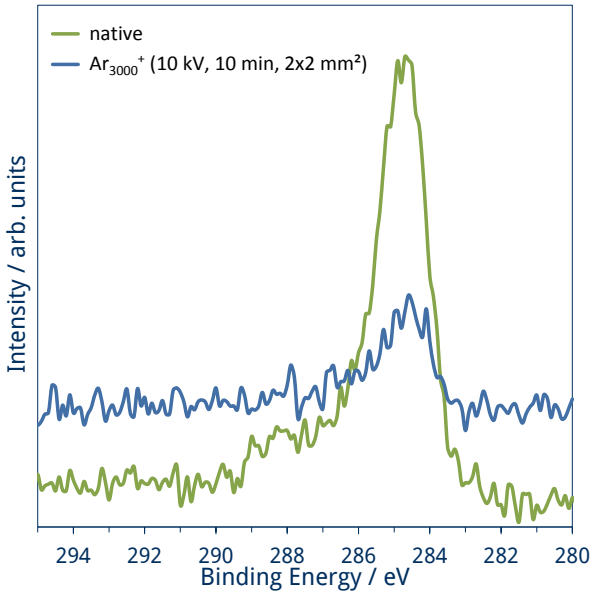

Fig. 5. C 1s core-level spectra of a gold sample before (green) and after (blue) GCIB sputtering (2x2 mm² area, Ar_{3000}^+ 10 kV, 10 min)

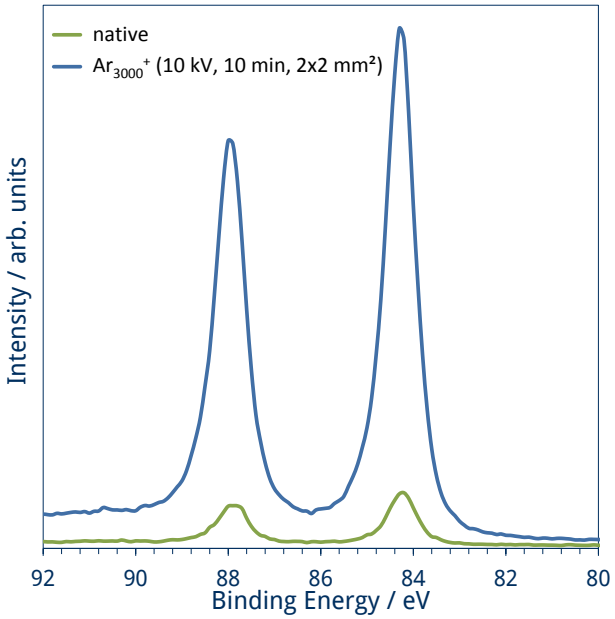

Fig. 6. Au 4f core-level spectra of a gold sample before (green) and after (blue) GCIB sputtering (2x2 mm² area, Ar^+_{3000} 10 kV, 10 min)

At the same time the Au 4f core-level spectra shown in Fig. 6 exhibit a tenfold increase of the Au $4f_{7/2}$ peak intensity after cleaning. Surface composition (Au/C in atom-%) of the gold foil sample changes from 10/90 before cleaning to 90/10 after 10 min sputter cleaning with Ar^+_{3000} at 10 keV as calculated from Au 4f and C1s core-level data.

Depth Profiling of Organic Monolayers

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.

A thin film of DMSPBA on Si(100) with a nominal thickness of 1.4±0.5 nm was used to demonstrate the capabilities of the GCIB option.[1,2] First, sample cleaning was done by a very gentle GCIB sputtering with Ar^+_{3000} at 5 keV accounting for 1.7 eV per Ar atom.

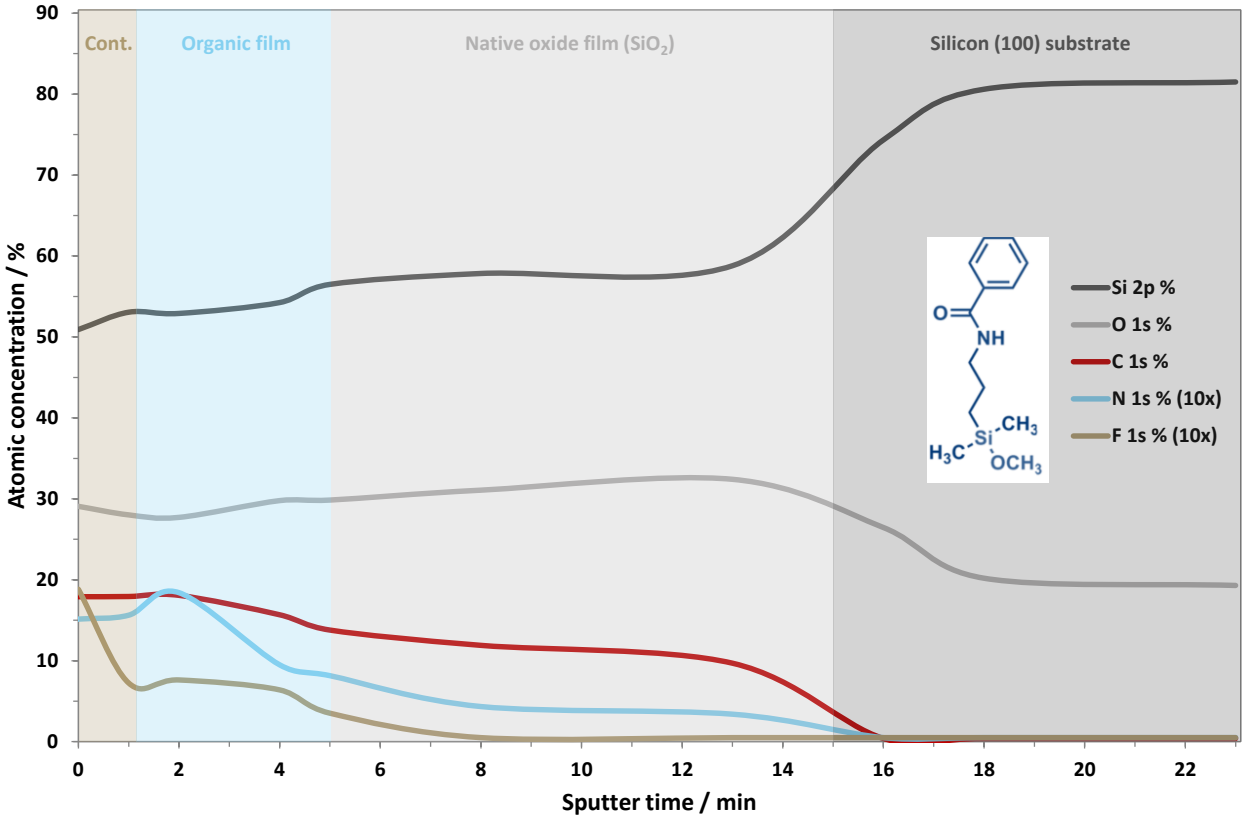

Fig. 7. XPS sputter depth profile of an ultra-thin DMSPBA film (1.4±0.5 nm) on a SiO_x/Si(100) surface. The chemical structure of DMSPBA is given as inset. The sample was sputtered using an argon GCIB with Ar_n^+ clusters first at 5 kV (4 min Ar^+_{3000}, 9 min Ar^+_{2000}, 1 min Ar^+_{1000}) then at 10 kV (Ar^+_{2000}). A raster size of 5×5 mm² was used. Elemental compositions are given in atomic percent.

Cleaning was monitored using the contamination-related fluorine F 1s peak. The fluorine content was reduced from about 2.0 at.-% to less than 0.5 at.-% within 2 min of Ar^+_{3000} sputtering without any detectable damage to the organic layer as controlled by C 1s and N 1s core-level spectra. The depth profile in Fig. 7 reveals that the chemistry remains mainly unchanged except for slightly increased carbon and nitrogen contents at sputter times around 2-3 min due to a decreased peak attenuation by the contamination.

Further sputtering with Ar^+_{2000} at 5 kV, corresponding to 2.5 eV per Ar atom, affects the organic film. Then the silane film is abrasively removed as indicated by decreasing C 1s and N 1s intensities.
Continuation of sputtering then removes the substrate-related native silicon oxide layer yielding spectra with pronounced characteristics of elemental silicon after approximately 15 min.

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 in analysis of modern multi-layer structures, such as OLEDs.

Here we presented two typical applications, sample cleaning and sputter depth profiling, of a gas cluster ion beam (GCIB) source that can be combined optionally with the EnviroESCA.

Effective surface cleaning prior to analysis was demonstrated on a typical sample an “old” gold foil. A gentle argon gas cluster sputtering with Ar^+_{3000} at 10 keV (3.3 eV per Ar atom) was used to remove the presumably organic contamination layer from the gold.

Depth profiling XPS was demonstrated using a nanometer thin organic film on a silicon wafer. Consecutive cycles of surface layer removal by Ar^+_n cluster sputtering and XPS analysis gives a compositional depth profile of the sample in terms of atomic concentration over sputter time as shown in Fig. 7.

First, surface cleaning was done to remove a fluorine-related contamination, which is realized without damaging the underlying organic layer. Proceeded sputtering with Ar^+_{2000} at 5 kV (2.5 eV per Ar atom) then removes the organic film. Continuation of sputtering for 15 min or more results in removal of the native silicon oxide layer giving Si 2p core-level spectra with pronounced characteristics of elemental silicon.

These two examples demonstrate the unique capabilities of the EnviroESCA combined with the GCIB 10S gas cluster ion source from IONOPTIKA.

[1] P. M. Dietrich, C. Streeck, S. Glamsch, C. Ehlert, A. Lippitz, A. Nutsch, N. Kulak, B. Beckhoff, and W. E. S. Unger *Quantification of Silane Molecules on Oxidized Silicon: Are there Options for a Traceable and Absolute Determination?* Analytical Chemistry **2015**, 87 (19), 10117-10124.

10.1021/acs.analchem.5b02846

[2] P. M. Dietrich, S. Glamsch, C. Ehlert, A. Lippitz, N. Kulak, W. E. S. Unger *Synchrotron-radiation XPS analysis of ultra-thin silane films: Specifying the organic silicon* Applied Surface Science **2016**, 363, 406-411. 10.1016/j.apsusc.2015.12.052.

We gratefully acknowledge Prof. Sven L. M. Schroeder and Dr. Elizabeth Willneff from Leeds University and Ionoptika Ltd. for a very inspiring cooperation and fruitful discussions.