White paper

The evolution of XPS depth profiling

Introduction

X-ray photoelectron spectroscopy (XPS) is a surface-sensitive technique that quantifies the elemental composition and empirical formula of a material, as well as the corresponding chemical and electronic states of its elements. XPS is used across a wide range of applications including corrosion studies, polymer engineering, as well as semiconductor and clean energy research. XPS uses X-rays to irradiate a sample, causing photoelectrons to be emitted from its surface (i.e., the photoelectric effect). By measuring the kinetic energy of these electrons, the binding energy of the elements and their chemical states can be determined using $E_B = hv – E_K – \Phi$, where E_B is the binding energy, hv is the X-ray photon energy, E_K is the kinetic energy of the emitted electrons, and Φ is the spectrometer's work function.

XPS is widely utilized in materials science, chemistry, and physics for surface composition analysis, chemical state identification, and thin film investigation. It offers non-destructive, high-surface-sensitivity analysis, typically within a 0–10 nm depth range. This technique requires ultra-high vacuum conditions and, due to its extreme surface selectivity, careful sample handling, preparation, and investigation in order to avoid the effects of contamination. Additionally, important information is sometimes located below the surface of the sample, and may not be immediately accessible with XPS.

To compensate for these issues, it is common to include a method to gently clean the sample surface within the XPS instrument. This can also be used to remove material more extensively, enabling changes in composition to be measured with increasing depth, a process referred to as "depth profiling." This white paper will describe how sample removal technology has evolved, allowing XPS to meet the changing demands posed by the novel materials being investigated with this technique.

Monatomic ion beams

Originally, sample cleaning and depth analysis in an XPS instrument relied on a focused ion beam of argon for material removal. The hardware, typically referred to as an ion source or ion gun, ionizes low-pressure gas by electron bombardment from a hot filament. The ionized gas can then be accelerated and focused by electrostatic lenses towards the specimen. The beam is generally raster scanned across the sample surface to create an etched area that is typically five-times the size of the analysis area. This ensures that measurements are made from the flat area at the center of the ablated region, preventing edge effects.

Ion beams in XPS systems commonly have energies from around 100–200 eV up to 4–5 keV, and are chosen to ensure a range of material removal rates, from very slow for ultra-thin film analysis, to faster ablation for the measurement of thicker layers. Low energy beams can also be used to clean samples, removing only the surface contamination, or to create composition profiles for thin layers.

Initially, monatomic ion beams were the only way of creating depth profiles, and they were used to investigate a wide range of application areas. For instance, Figure 1 shows a depth profile from a sample of low-emissivity glass, which is composed of a series of metal oxide and metal layers deposited onto a glass surface. The silver metal layers are the key components of the stack, creating the infrared reflection that the coating is designed to achieve. The other layers are there to protect the silver, offering either chemical or scratch protection to ensure that the coating is effective. Checking the composition of the material is an important step in the development of the coating, and XPS depth profiling offers the necessary chemical quantification and depth resolution. The monatomic ion beam profile easily reveals a variety of information for the stack, despite the fact that it is only 120 nm thick.

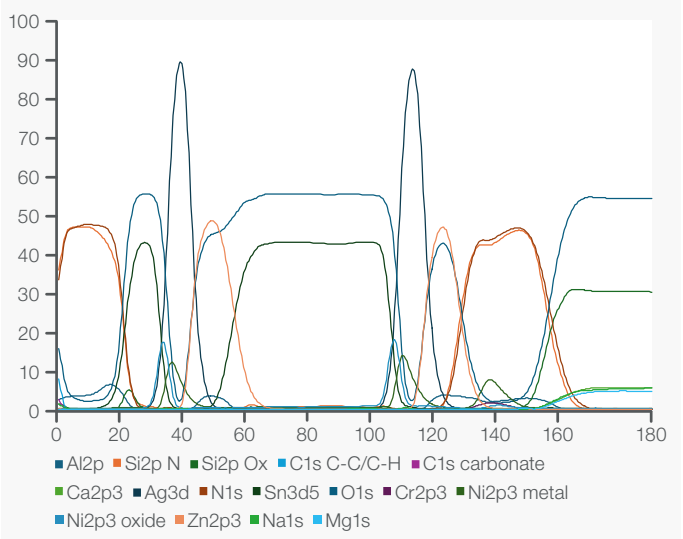

Figure 1. Depth profile of a low-emissivity glass, obtained with monoatomic ion beam profiling.

Gas cluster ion beams

While monatomic ion beams are highly useful, it is not possible to measure certain classes of materials with this technology. One such group is polymers; in a majority of cases their chemical structure is damaged when exposed to a monatomic ion beam. The depth profiles generated from such polymer samples tend to under-represent functional groups at the surface, as they are preferentially removed, leaving an excess of C-C bonding. An example of such changes occurring to a polyimide sample is shown in Figure 2B.

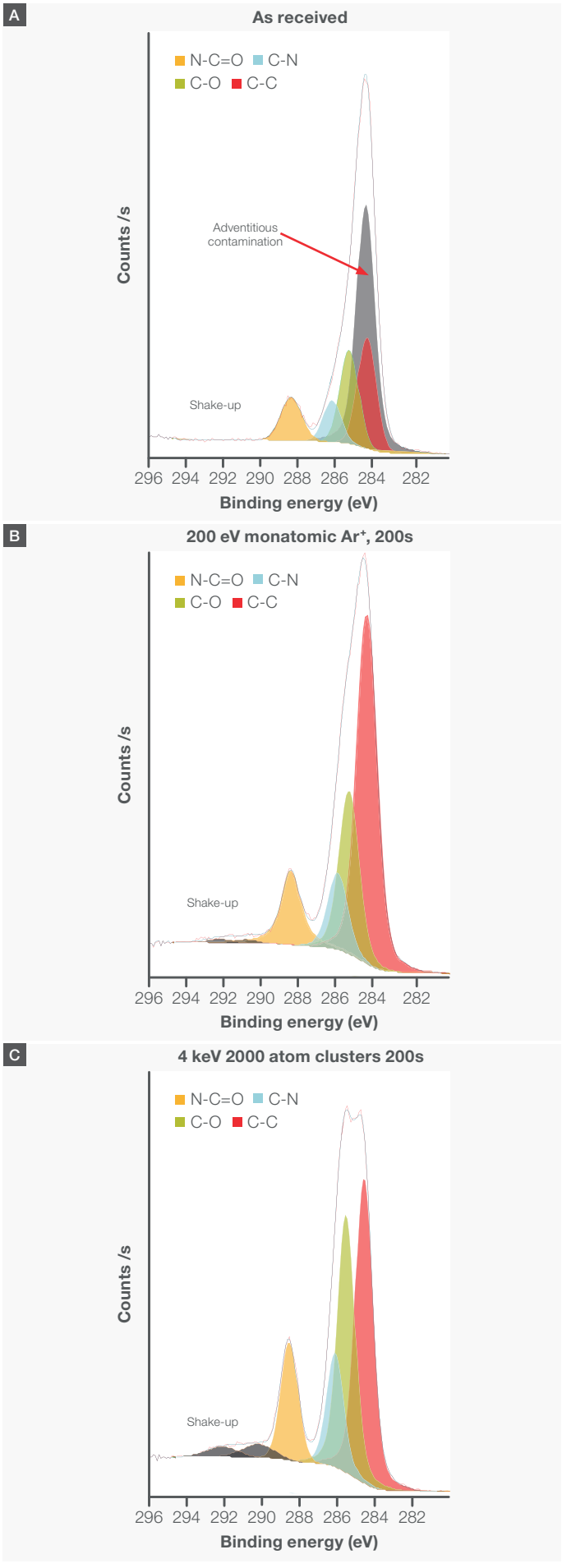

Figure 2. A polyimide sample cleaned using B) 200 eV monatomic ions and C) 4 keV 2000 atom cluster ions.

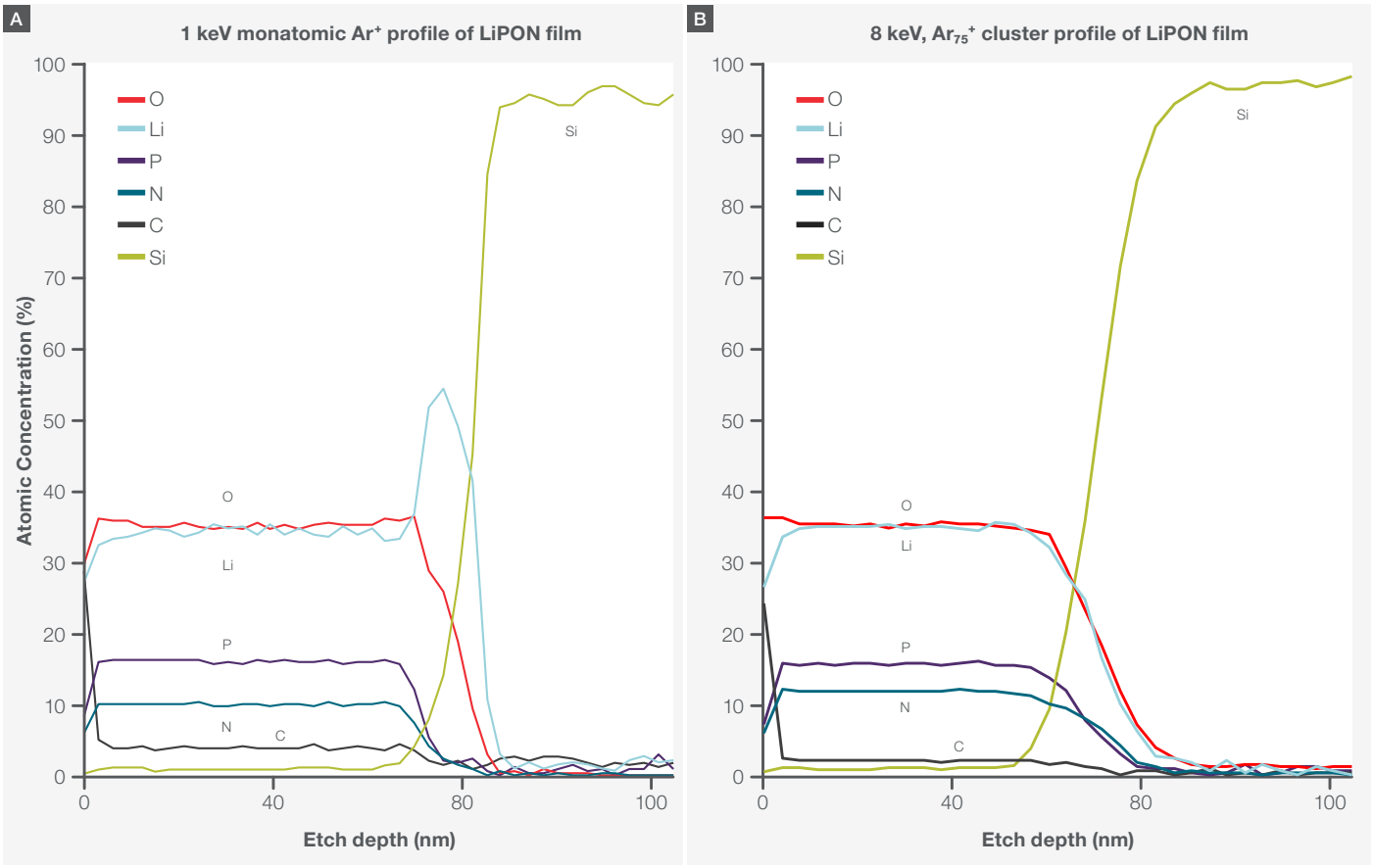

Figure 3. Monoatomic (A) and cluster (B) ion profiles of a solid electrolyte film. The monoatomic profile incorrectly identifies an accumulation of lithium at the interface of the film with the silicon wafer.

To reduce the damage to the sample during depth profiling, new ion sources were developed, such as the Thermo Scientific MAGCIS Dual-Mode Ion Source, which can generate a gas-cluster ion beam that is composed of loosely bound gas atoms in clusters of tens to thousands. These are formed by expanding gas from a high- to low-pressure region through a specially shaped nozzle. This cools the gas, allowing clusters in a range of sizes to form. A single atom in each cluster is ionized in the same way as in a monatomic source, forming charged clusters. These can then be size selected so that only clusters of the desired size are focused and scanned across the sample surface. The mass of the cluster causes material removal, but also prevents significant penetration into the surface (which is one of the ways damage is caused by monatomic ion beams). The energy per atom of the cluster beam (impacted by cluster size and acceleration energy) is what determines the ablation rate.

An example, comparing monoatomic and gas cluster ion profiles for a solid electrolyte LiPON film, is shown in Figure 3. The film was deposited onto a silicon wafer; depth profiling was used to understand if the film was uniform. Analysis with a monoatomic ion beam showed an excess of Li at the interface with the wafer. The cluster profile, meanwhile, showed the correct stoichiometry throughout the LiPON layer, with no increase in Li at the interface. It can be concluded that the accumulation of Li in the monatomic profile is due to the ability of the monoatomic ion beam to induce “drift” in alkali metal ions, which then move until they hit a barrier, such as the silicon substrate.

It is worth noting that the MAGCIS Ion Source is able to generate both monatomic and gas cluster ion beams, thereby facilitating experiments on a wide range of samples.

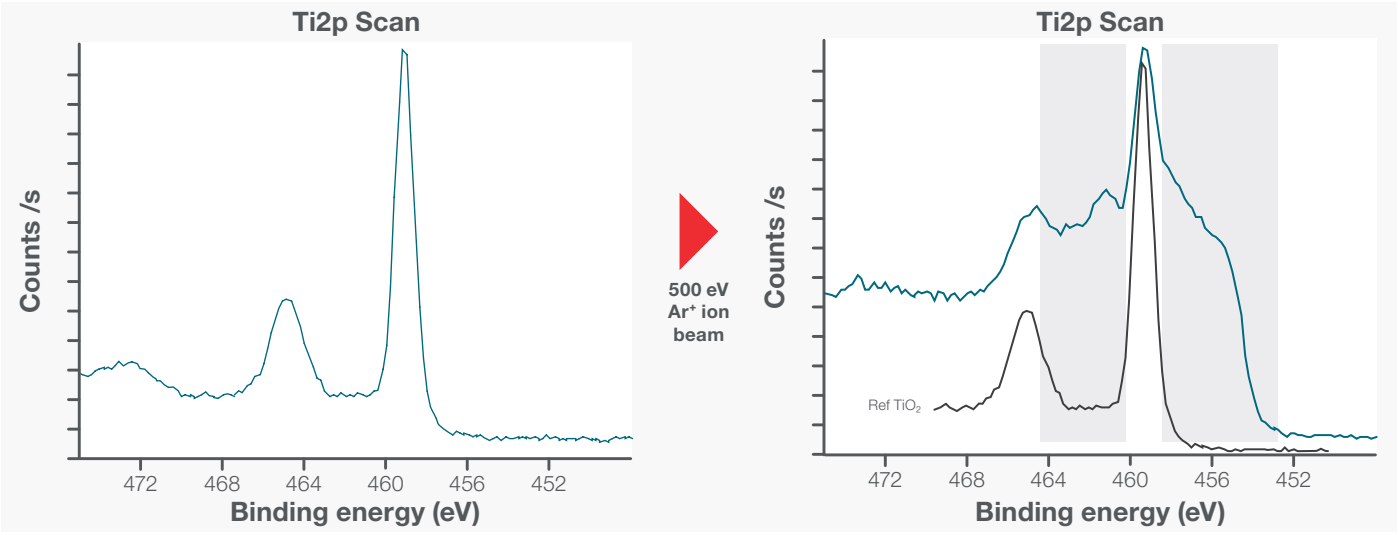

Figure 4. TiO_2 exposed to a low-energy monatomic ion beam.

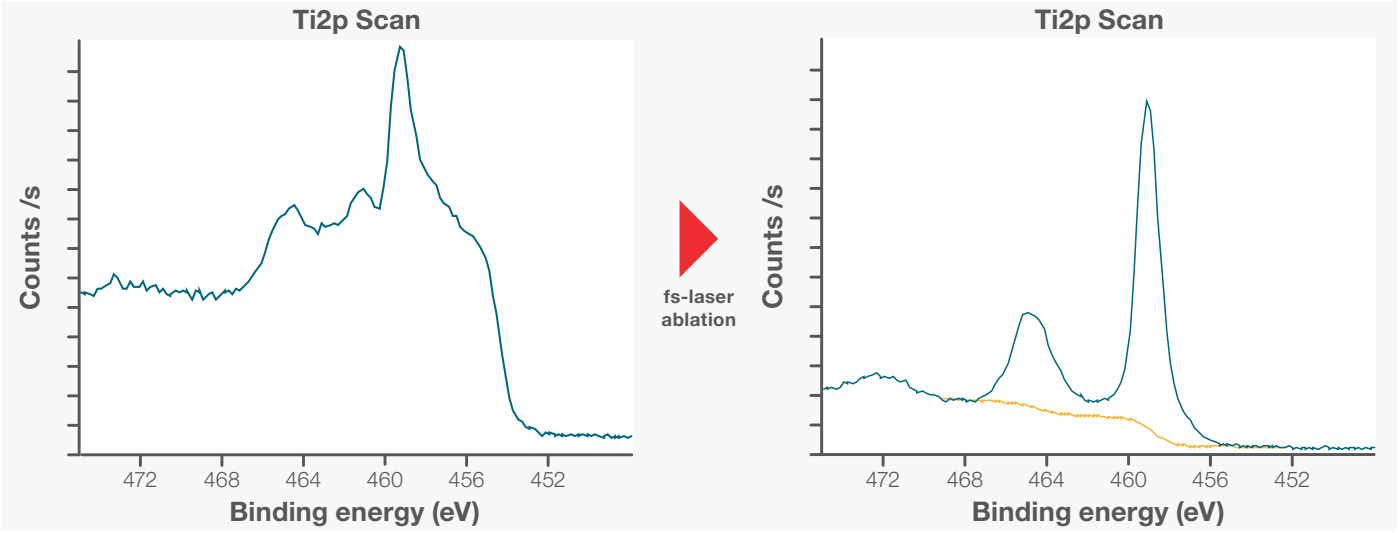

Figure 5. Femtosecond laser ablation used to remove ion-beam-damaged TiO_2.

Femtosecond laser ablation

There are materials where even cluster ion beams are not able to provide accurate profiles. For instance, both monatomic and gas cluster ion beams can cause preferential sample sputtering, particularly for metal oxides. As ion beam etching is primarily a ballistic process, the mass difference between atoms in the surface can cause an increased removal rate for the lighter element. Sample heating induced by the ion impacts can also cause preferential removal of a component if it has a low sublimation point in vacuum compared to the other components in the sample.

As a result, alternate techniques are being investigated, such as material removal using a femtosecond (fs) laser. This approach uses ultra-short laser pulses and is known for its high precision and the minimal thermal damage it causes to the material around the impact site.

When the laser pulse interacts with a material, its energy is absorbed almost instantaneously, rapidly exciting the material's electrons. The high peak intensity of the pulse induces nonlinear ionization effects, such as multi-photon and avalanche ionization, generating a high density of free electrons. These quickly transfer their energy to the material's lattice through electron-phonon interactions, causing a rapid increase in lattice temperature on a picosecond timescale. This localized heating leads to a phase transition, resulting in material ablation through melting, vaporization, or Coulombic explosion. The ultra-short pulse duration minimizes heat diffusion, ensuring that the surrounding material remains largely unaffected, allowing for high-precision material removal with minimal damage to the remaining surface.

Laser ablation enables depth profiling of materials that cannot be accurately measured using ion beam methods. A classic example of this is titanium dioxide, which reduces under both monatomic and cluster ion beams due to the preferential removal of oxygen. Figure 4 shows the changes that occur to a pristine TiO_2 surface when it is exposure to a low energy monatomic ion beam; Figure 5 shows how this damage can be reversed with fs-laser ablation. This illustrates how the laser can be used to remove material from sensitive samples without inducing chemical damage to the remaining specimen. The speed of laser ablation also makes it easier to measure interfaces deep within a sample, as compared to slower ion beam experiments.

Summary

XPS depth profiling is an important experimental method which allows researchers to understand changes in chemical composition at increasing depth within their samples. All the methods described in this white paper have their distinct advantages, and are all available as part of the Thermo Scientific™ Hypulse™ Surface Analysis System, ensuring that an exhaustive range of materials can be investigated. The integration of femtosecond laser ablation in particular expands the variety of experimental options available, ensuring that the instrument can address challenging materials now, and in the future.

Reference

1. 1. Baker, MA, et al. **Femtosecond laser ablation (fs-LA) XPS – A novel XPS depth profiling technique for thin films, coatings and multi-layered structures.** Appl Surf Sci 654 (2024). doi: 10.1016/j.apsusc.2024.159405

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