ThermoFisher SCIENTIFIC

Exploring the surface in depth with XPS analysis

Depth profiling of surfaces and interfaces with the Hypulse Surface Analysis System

thermo scientific

The need for surface and interface analysis

In today's rapidly evolving technological landscape, precise material analysis is crucial for the development and optimization of advanced materials and devices. X-ray photoelectron spectroscopy (XPS) is an established technique for the characterization of material surface chemistry, capable of revealing compositional information several nanometers into a sample. Depth profiling is a method that extends the analysis range of XPS; by alternating material removal and XPS analysis, it can reveal how composition changes from the surface to the bulk, or across interfaces between different compounds in a sample. This information can be just as critical as how a material's surface interacts with its environment, and can provide a more complete picture of the material's behavior and properties.

The Thermo Scientific™ Hypulse™ Surface Analysis System is a fully featured XPS instrument with a range of additional analytical capabilities, including reflected electron energy loss spectroscopy (REELS) and low-energy ion scattering spectroscopy (ISS). The system is equipped with a Thermo Scientific MAGCIS Dual-Mode Ion Source and a novel femtosecond laser-ablation system (fs-LA) for XPS depth profiling.

This eBook explores XPS depth profiling in detail and shows how the Hypulse System is ideally suited for this technique, helping you uncover critical surface and sub-surface information.

Understanding XPS depth profiling

The basics of XPS depth profiling

Depth profiling analyzes the composition and properties of a material from the surface down to the interior of a sample, detecting interfaces or changes in the bulk. This analysis is essential for understanding how materials behave under different conditions and for optimizing their performance in various applications.

Experimentally, XPS depth profiling is fairly straightforward: a surface is first analyzed and then the material is removed.

The newly exposed area is then also analyzed, and the process is repeated. The data collected at each level is processed and combined into a compositional plot that shows how the sample changes with increasing depth (Figure 1).

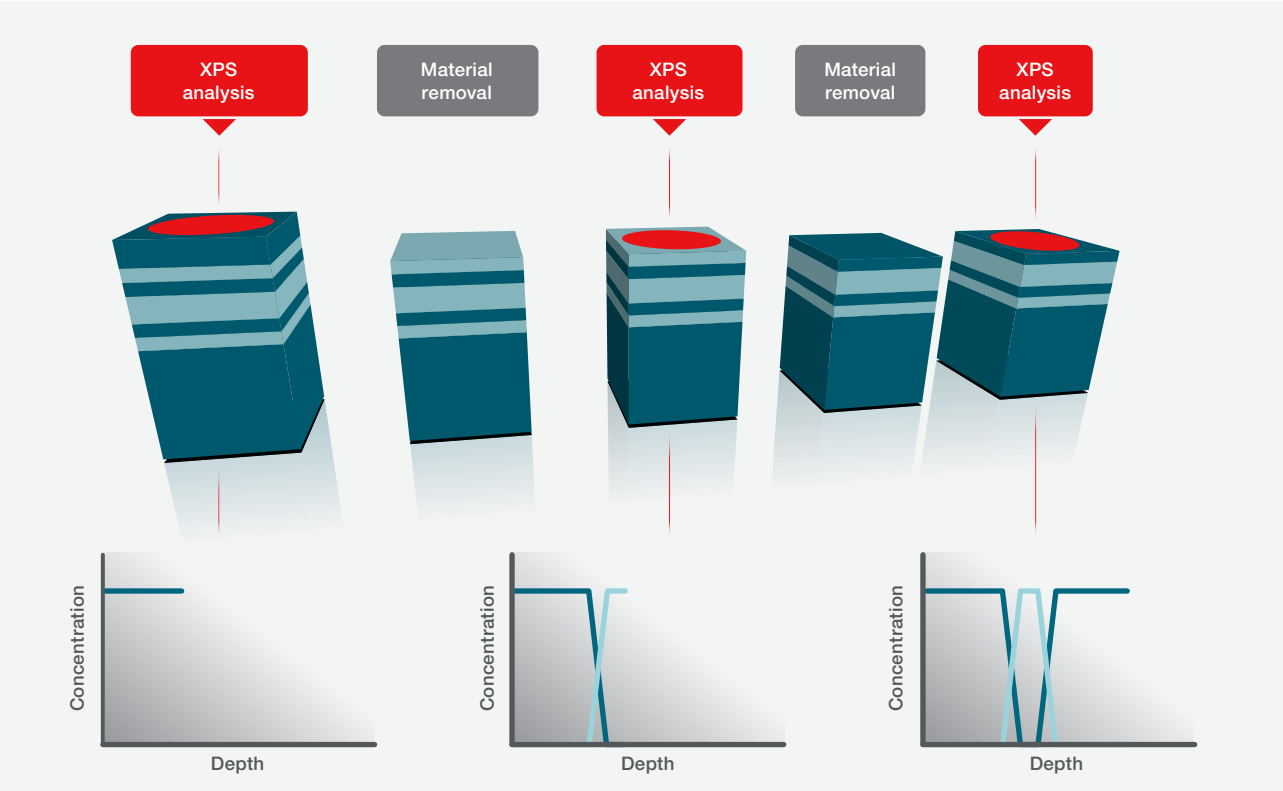


Figure 1. Schematic of the depth profiling process, along with a simplified representation of a resulting depth profile.

Depth profiling is used in numerous industries as part of research and development, as well as in diagnostic processes to examine material quality and failure. It enables researchers and engineers to:

- **Optimize material properties:** Understanding a material's composition and structure beyond the surface allows it to be tailored to meet specific requirements, leading to improved performance and longevity.
- **Enhance product quality:** Depth profiling can be used to identify sub-surface defects and impurities, helping to ensure higher product quality and reliability.
- **Innovate on new materials:** Depth profiling supports the development of novel, layered materials with unique properties.
- **Meet regulatory compliance:** Accurate analysis of materials helps products meet industry standards and regulatory requirements.

Ion beam depth profiling methods

XPS analysis is performed by irradiating a material with X-rays and measuring the amount and the kinetic energy of the electrons that then escape from the top layers of the material. This data can be used to determine the elemental composition, chemical state, and electronic state of the material's surface.

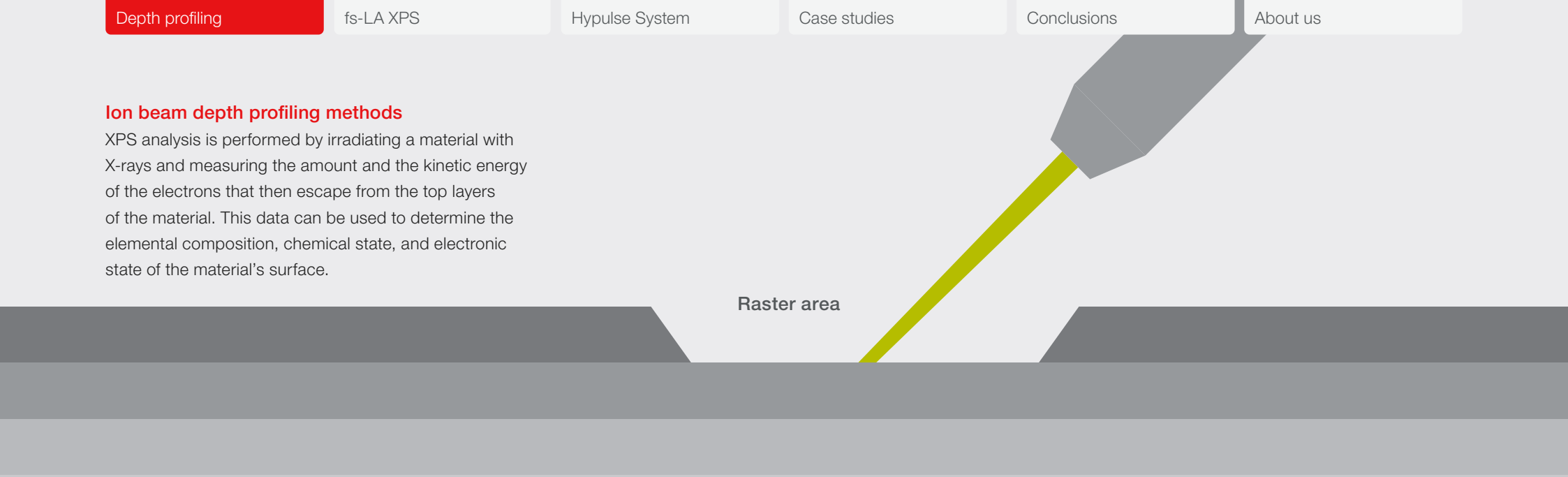


Figure 2. Schematic representation of material removal with an ion beam.

A. Monatomic ion beam depth profiling

Material removal in an XPS instrument was originally carried out with a focused beam of ionized argon, referred to as an ion source or ion gun. In these sources, gas is introduced at a low pressure and is then ionized by electron bombardment from a hot filament. The resulting ionized atoms are focused into a beam and raster-scanned across a sample surface; the ions collide with enough energy to remove surface material. The etched area is typically ~5x the size of the analysis area so that measurements are made from the flat area at the center of the ablated region, which prevents edge effects (Figure 2).

The ion beam energies commonly used in XPS systems range from 100-200 eV up to 4-5 keV, offering a variety of material removal rates, from very slow for the analysis of thin films and layers, to fast ablation for the measurement of multiple thick layers. Low-energy beams can also be used to clean samples, removing only the surface contamination.

B. Cluster ion beam depth profiling

Certain classes of material cannot be etched successfully with monoatomic beams, including, notably, polymers, as their chemical structure is often damaged by the beam. The resulting depth profiles tend to under-represent the functional groups of the polymer as they are preferentially removed from the sample surface, instead leaving an excess of C-C bonding.

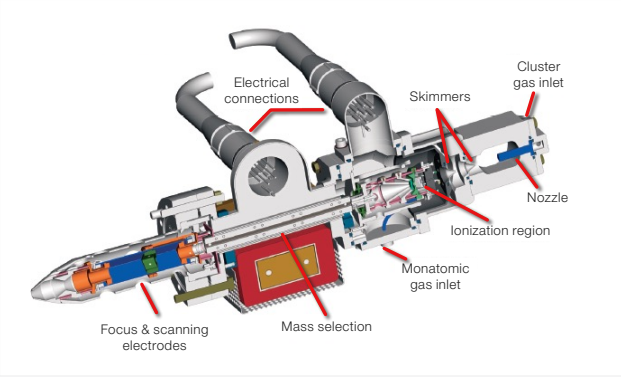


Figure 3. Schematic of the Thermo Scientific MAGCIS Dual Mode Ion Source, a combination monoatomic and gas-cluster ion-beam source.

Gas-cluster ion beams were developed as an alternative to monoatomic ion beams to reduce sample damage during depth profiling. As the name suggests, these ions are composed of loosely bound gas atoms in clusters of 10s – 1,000s. They are formed by expanding a gas from a high pressure into a low-pressure region through a specially shaped nozzle; this cools the gas and allows the clusters to form. A single atom on the cluster is then ionized in the same way as in a monatomic source. The charged clusters can then be size-selected so that only clusters of a desired size are focused and scanned across the surface.

The mass of the cluster causes material removal, but also prevents it from penetrating significantly into the surface. (I.e., one of the mechanisms by which monatomic ion beams can damage samples.) Cluster size and acceleration energy, which translate to the beam's energy per atom, determine the source's ablation rate.

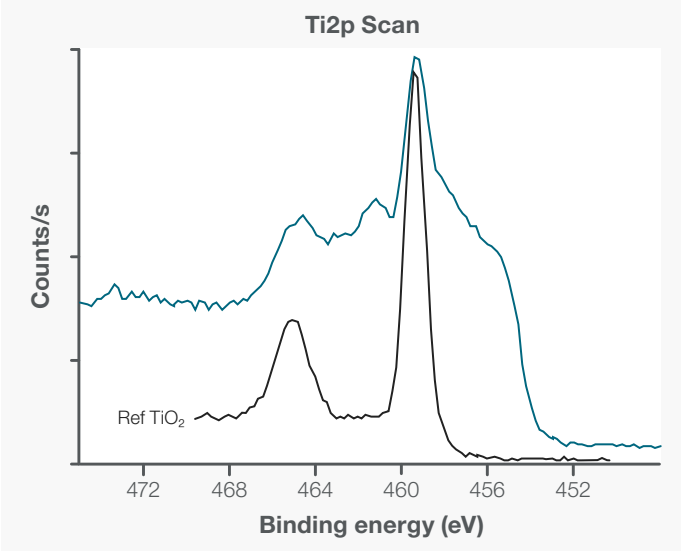


Figure 4. Example of preferential sputtering of a TiO_2 sample. Ion beam exposure (blue spectrum) caused oxygen to be removed at a greater rate than titanium, leading to reduced titanium oxide species being observed in the XPS data compared to a reference TiO_2 sample.

Challenges of ion beam depth profiling

Both monatomic and gas-cluster ion beams can cause preferential sputtering of samples, particularly metal oxides. This is because ion beam etching is primarily a ballistic process, and mass differences between surface atoms can result in an increased removal rate of lighter element. Sample heating induced by ion impact can also cause preferential removal of sample components that have low sublimation points in vacuum compared to the rest of the surface.

The following section shows how femtosecond laser ablation can address these challenges, facilitating XPS characterization of a wide variety of samples with the Hypulse System.

Introduction to femtosecond laser ablation XPS

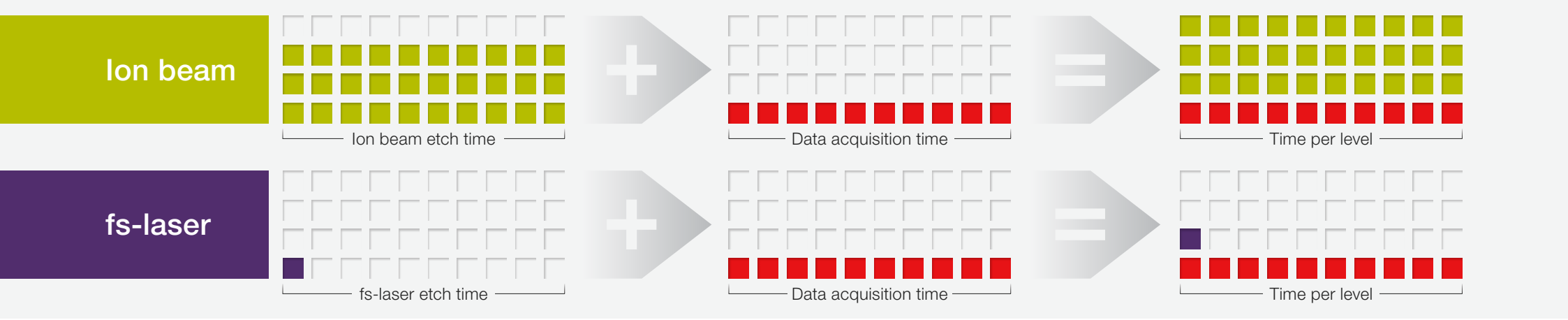


Figure 5. Illustration showing the time difference between fs-LA and typical ion beam depth profiling. Each box represents one second. The data acquisition time (red) is the same for both methods. The fs-LA substantially reduced the time required for the ablation step.

How is depth profiling different with fs-LA?

Femtosecond laser ablation (fs-LA) utilizes ultrafast laser pulses to remove material from a sample surface. This enables precise and controlled removal of material layers without chemical damage to the remaining sample, helping to ensures that data collection is representative of the material's composition. fs-LA XPS provides highly accurate and detailed analysis for a wide range of materials, making it a powerful tool for surface analysis.

Material ablation with femtosecond laser pulses

The mechanism by which a laser ablates material is highly dependent on the length of the laser pulse. At longer pulse lengths (picoseconds or longer), thermal processes dominate as the electrons excited by the laser pulse relax and dissipate energy. The resulting heat can vaporize or expand the sample while also potentially changing the composition of the remaining material in the surface. Shorter pulse lengths (i.e., femtoseconds) do not provide enough time for these heating processes to propagate, preventing chemical changes from occurring within the sample. Instead, material removal is caused by either a rapid solid/vapor transition (for metals) or electrostatic processes such as Coulombic explosion (for dielectrics and polymers).

Additionally, as this method of bond breaking is electrostatic rather than ballistic (as seen in ion sputtering), there is no momentum transfer between the beam and the sample, and mass differences between sample components do not lead to preferential sputtering.

The other benefit of fs-LA is that material removal steps are dramatically shorter compared to ion beam etching (Figure 5). As a profile is made up of dozens if not hundreds of ablation steps, this can substantially reduce the total experiment time, making it practical to analyze deeper into the sample, or to repeat experiments for increased accuracy.

Advanced features of the Hypulse Surface Analysis System

System configuration

The Hypulse System is based on the established Thermo Scientific™ Nexsa™ G2 Surface Analysis System, and features multiple analytical techniques in addition to XPS; reflected electron energy loss spectroscopy (REELS) and ion scattering spectroscopy (ISS) are included as standard, UV photoelectron spectroscopy (UPS) is available as an option. This multi-technique capability provides comprehensive insights into the surface chemistry and structure of materials.

The Hypulse Surface Analysis System is controlled by Thermo Scientific Avantage Software, which provides full system control and data processing, both on the instrument and offline. A large sample holder and automated sample handling enable high-throughput analysis.

Optional accessories include an inert gas transfer system to move samples between the Hypulse System and a glove box, a sample heating accessory, and the capability to perform angle-resolved XPS (ARXPS).

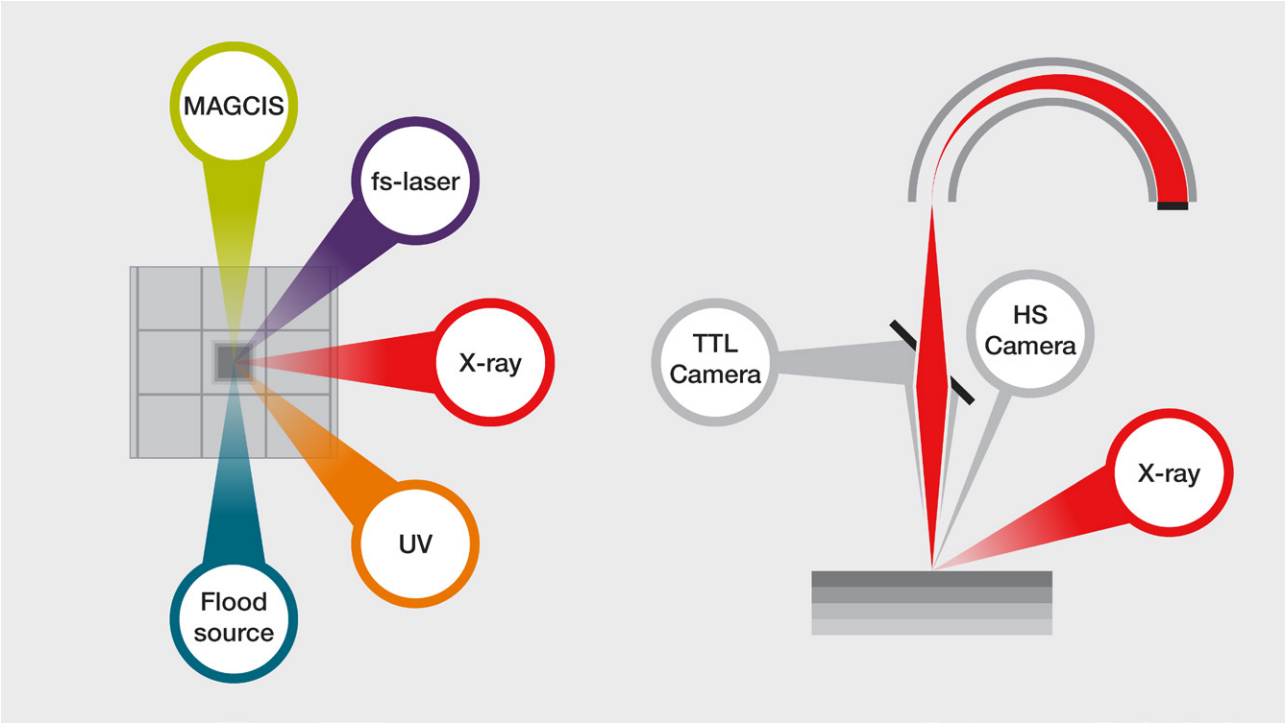
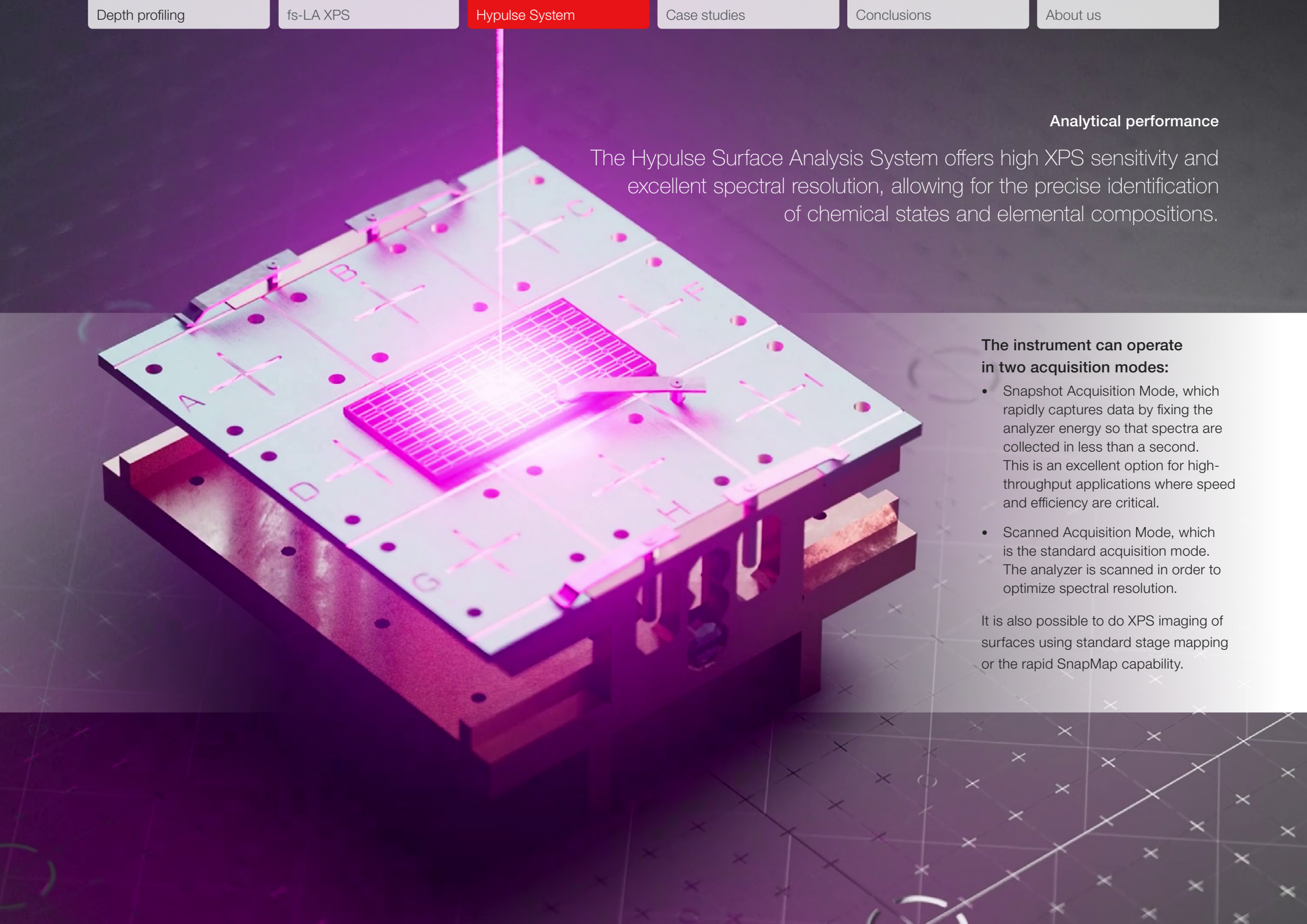


Figure 6. Layout of the Hypulse Surface Analysis System, showing the source arrangement and sample viewing system.



Analytical performance

The Hypulse Surface Analysis System offers high XPS sensitivity and excellent spectral resolution, allowing for the precise identification of chemical states and elemental compositions.

The instrument can operate in two acquisition modes:

- Snapshot Acquisition Mode, which rapidly captures data by fixing the analyzer energy so that spectra are collected in less than a second. This is an excellent option for high-throughput applications where speed and efficiency are critical.
- Scanned Acquisition Mode, which is the standard acquisition mode. The analyzer is scanned in order to optimize spectral resolution.

It is also possible to do XPS imaging of surfaces using standard stage mapping or the rapid SnapMap capability.

Depth profiling capabilities

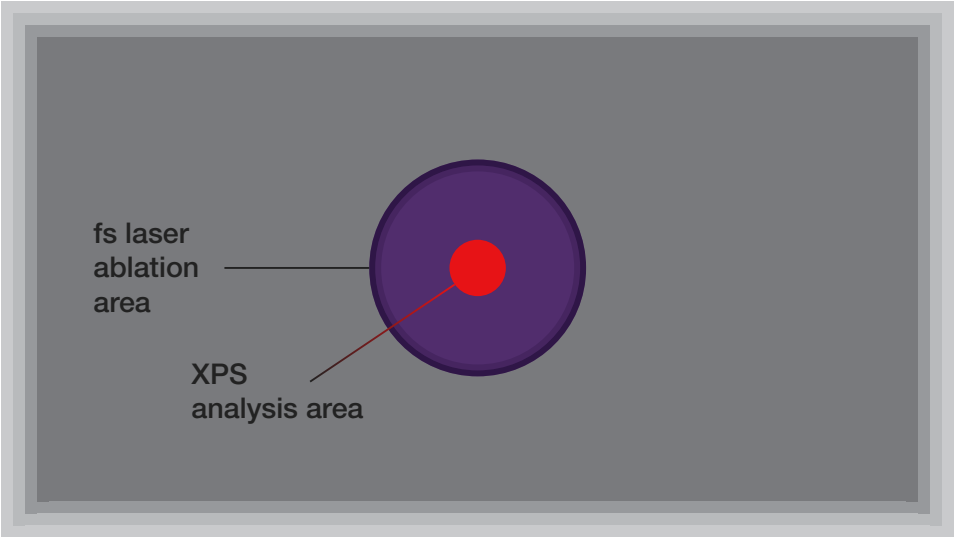
The Hypulse System has two modes for depth profile acquisition.

Femtosecond laser ablation

Unique to the Hypulse System (compared to the rest of the Thermo Scientific XPS portfolio) is the 1,030-nm fs-laser ablation system. The laser source is fully integrated into the platform to ensure Class 1 laser safety, which allows the system to be installed in a standard laboratory rather than a dedicated laser room. fs-LA depth profiles are controlled through Avantage Software, facilitating the management of laser parameters and data acquisitions.

Monatomic and gas-cluster ion sputtering with the MAGCIS Ion Source

The MAGCIS Dual Mode Ion Source can produce both monatomic and gas-cluster ions, allowing it to depth profile a range of materials, from metals and oxides to polymers and composites. The source is also able to use helium for ISS.



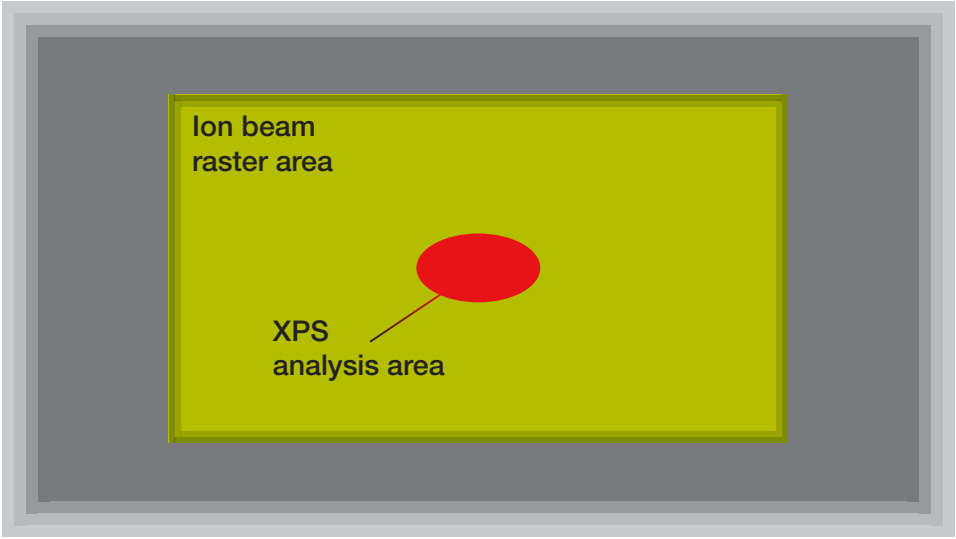
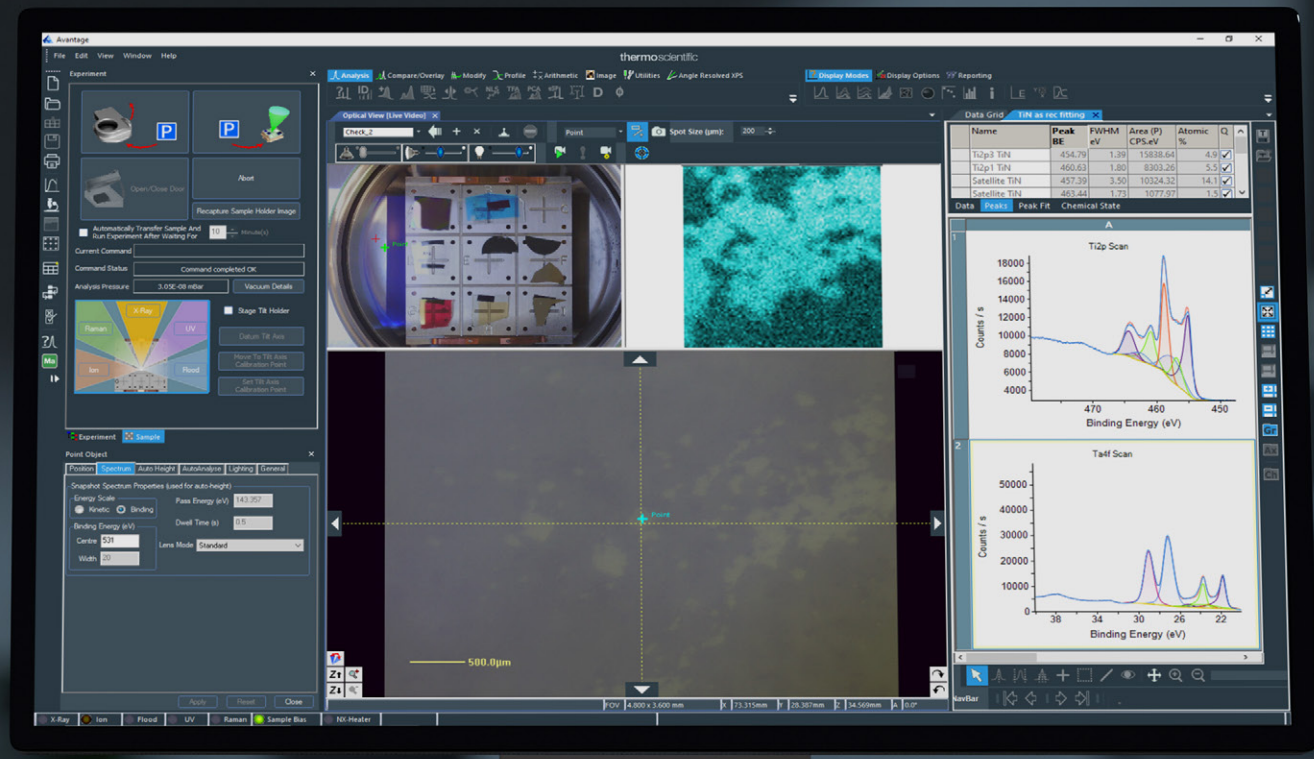


Figure 7. Illustration of a typical ion-beam raster area, laser-ablation area, and an XPS-analysis area tuned for a fs-LA experiment.

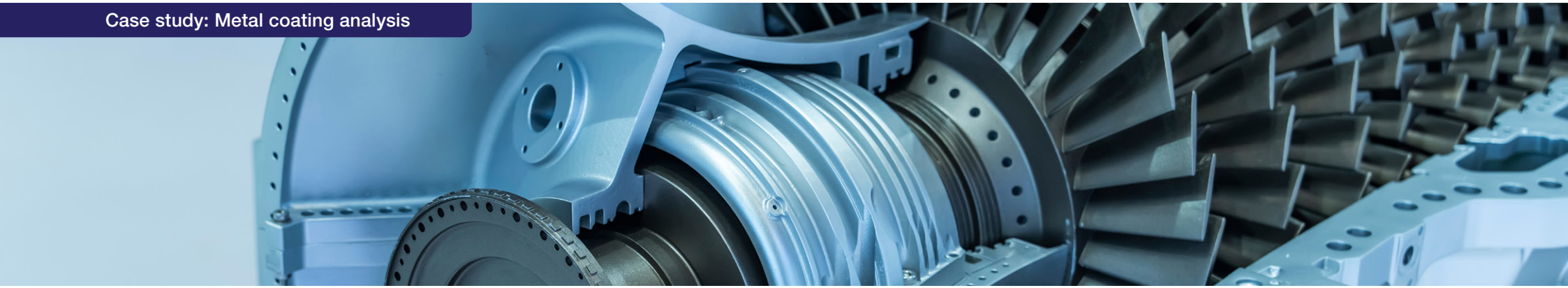
Advanced data analysis software

The Hypulse XPS System is equipped with Avantage Software, which simplifies the interpretation of complex datasets. It offers spectrum identification, peak fitting, and guidance through the Knowledge View feature, enabling you to obtain comprehensive and accurate results with minimal effort.



Case studies and real-world applications

Case study: Metal coating analysis



Necessity for improved materials analysis

In the field of metallurgy, the composition and structure of metal coatings and substrates play a critical role in the properties of the final material. Characterization of these layers with traditional ion sputtering can lead to preferential material removal and chemical damage, affecting the accuracy of the analysis. This is particularly problematic for complex, multi-layered structures and coatings.

Depth profiling with fs-LA XPS

Femtosecond laser ablation with the Hypulse Surface Analysis System addresses these challenges, significantly improving the accuracy and reliability of metallurgical analysis.

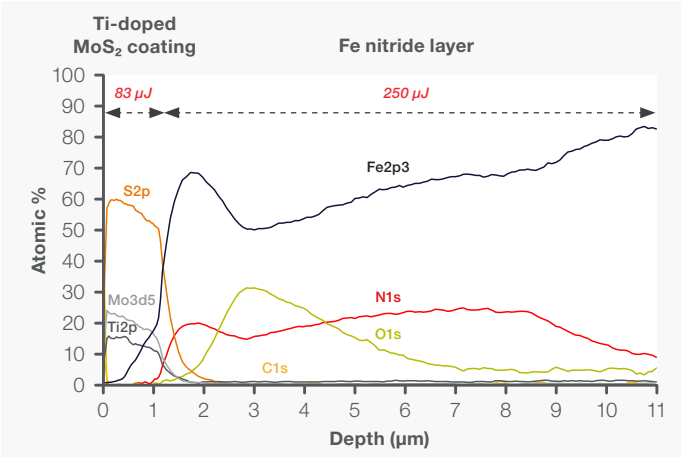


Figure 8. fs-LA depth profile of a nitride steel sample, showing relative atomic percentages to an approximate depth of 11 µm. ***Reproduced from Baker et al. under*** CC BY 4.0.[1]

For instance, in the depth profiling of a nitrided steel with a PVD Ti-doped MoS_2 coating, fs-LA XPS provided detailed insights into the elemental composition and chemical states across different layers (Figure 8).[1]

The damage-free ablation process preserved the stoichiometry and chemical integrity of the material, leading to more accurate and reliable results. This enhanced understanding of material properties can facilitate the development of more durable and efficient coatings, improving the overall performance of metallurgical products.

Learn more

Reference

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.** *Applied Surface Science* 654 (2024). doi: 10.1016/j.apsusc.2024.159405

Case study: Photovoltaic analysis

Enhanced understanding of photovoltaic materials

Solar cells, particularly those based on emerging materials like perovskites, require precise depth profiling to optimize their efficiency and stability. Traditional XPS methods often fall short in analyzing the complex, multi-layered structures of these cells due to ion-beam-induced damage and limited depth profiling capabilities.

Depth profiling helps optimize solar cell efficiency

When used to depth profile a perovskite solar cell, the Hypulse System allowed the elemental and chemical composition of each layer to be examined in detail, without unwanted damage.[2]

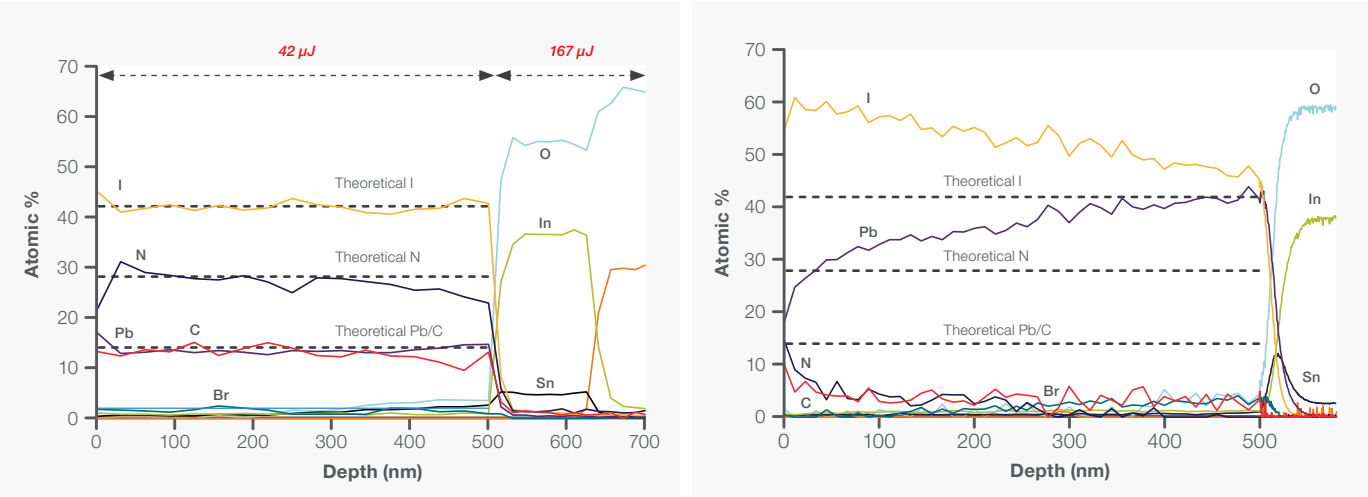


Figure 9. fs-LA depth profiles of a solar cell sample, showing the relative atomic percentages down to the ITO layer.
***Reproduced from Chandler et al. under CC BY 4.0.*[2]**

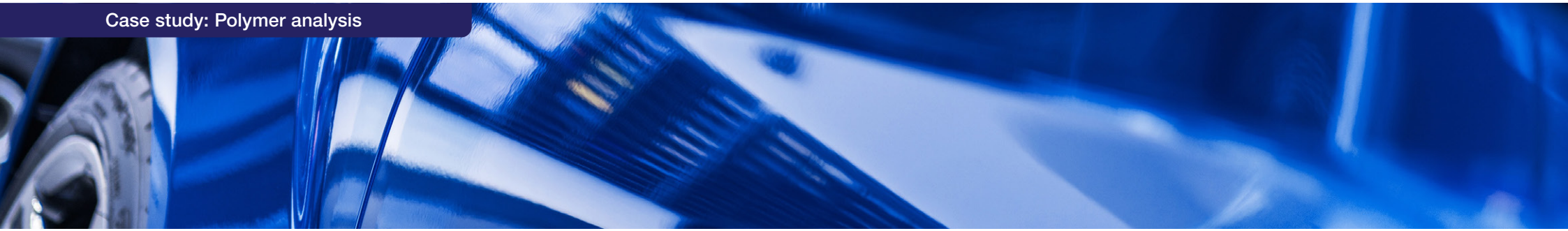
This precise analysis provided critical insights into the material's properties, allowing researchers to optimize fabrication processes and improve the efficiency of solar cells. The ability to achieve accurate depth profiles up to tens of micrometers deep was instrumental in understanding and enhancing the performance of these advanced photovoltaic materials.

Learn more

Reference

2. Chandler, CW, *et al.* **Femtosecond Laser Ablation (fs-LA) XPS Depth Profiling of Lead Halide Perovskite Thin Film Solar Cells.** *Surface and Interface Analysis* 57:3 (2025). doi: 10.1002/sia.7374

Case study: Polymer analysis



Measuring changes in polymer chemistry with depth

XPS is an established method for polymer characterization due to its ability to determine both elemental composition and chemical states, allowing for the identification of polymer surfaces and interfaces with minimal sample preparation. Monatomic and gas-cluster ion beam methods have traditionally been used for polymer depth profiling, but they are time-consuming and, in the case of monatomic ion beams, can cause chemical damage to organic materials, limiting their effectiveness. The introduction of fs-LA XPS has greatly enhanced polymer characterization due to its ability to provide rapid, chemical-damage-free depth profiling, significantly reducing analysis time (i.e., from hours to minutes).

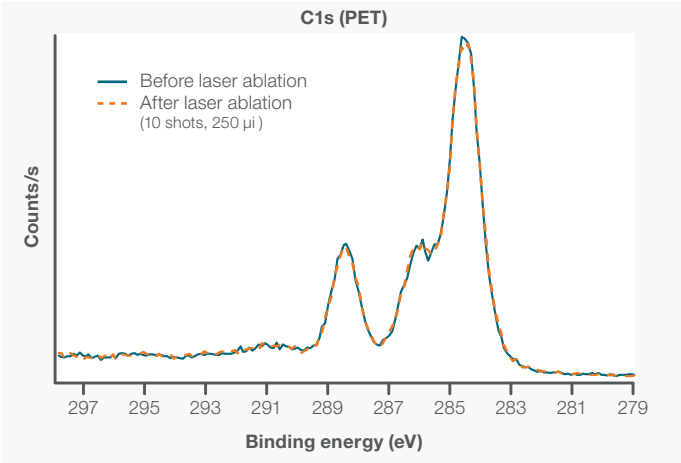


Figure 10. XPS spectra of the C1s region of PET before and after femtosecond laser ablation.

fs-LA XPS accurately captures polymer composition

The Hypulse Surface Analysis System was used to profile several polymer standards and complex samples, such as a multi-layer paint sample provided by collaborators at the University of Surrey, UK.[3] Figure 11 shows an example depth profile of a paint sample that consists of an aluminum substrate coated in a 5 µm polyurethane primer layer and a 25 µm PMMA/PVdF topcoat.

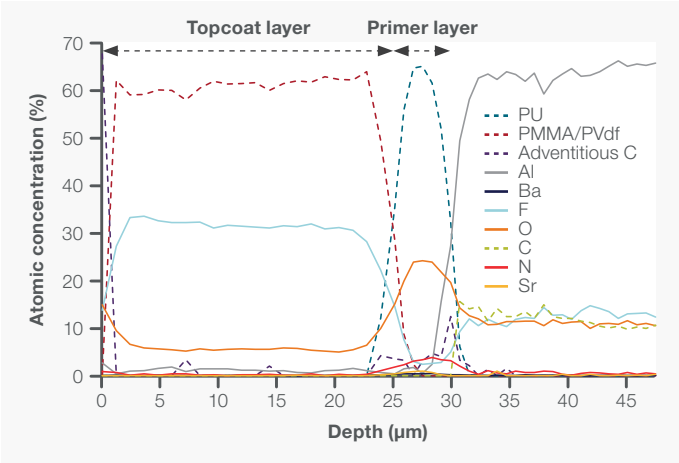


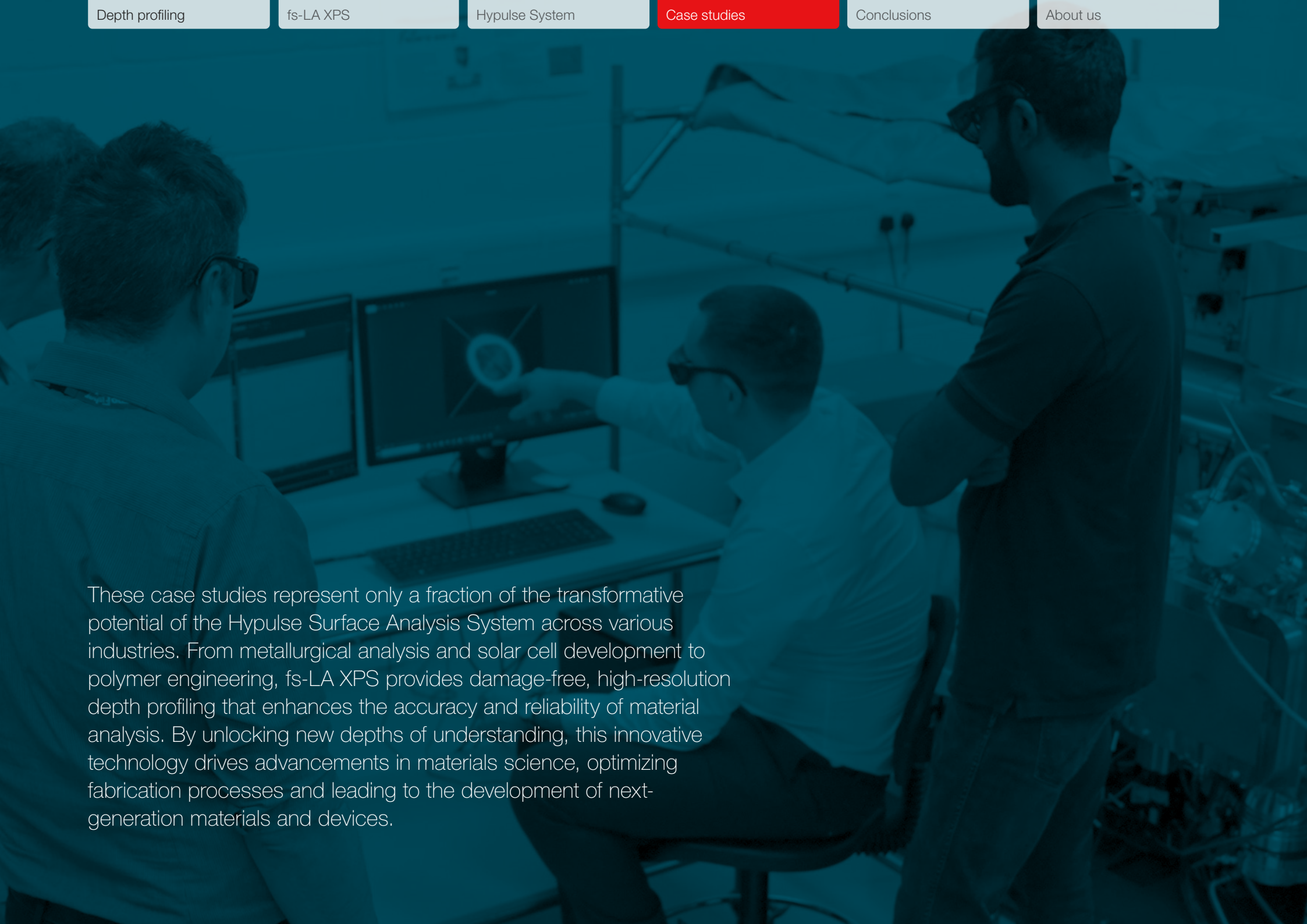
Figure 11. fs-LA XPS depth profile of a paint sample composed of an aluminum substrate coated in a 5 µm PU primer layer and a 25 µm PVdF/PMMA topcoat.[3]

The system used a 30 µm X-ray spot and a 1,030-nm laser to perform the fs-LA XPS depth profiling, revealing distinct layers and even minor contamination within the sample. This demonstrates the detailed depth profiles that can be obtained with the Hypulse System without compromising the chemical integrity of the analyzed material.

Learn more

Reference

3. Hinder SJ, *et al.* **Surface and interface analysis of complex polymeric paint formulations.** *Surf Interface Anal* 38:4 (2006). doi: 10.1002/sia.2325



These case studies represent only a fraction of the transformative potential of the Hypulse Surface Analysis System across various industries. From metallurgical analysis and solar cell development to polymer engineering, fs-LA XPS provides damage-free, high-resolution depth profiling that enhances the accuracy and reliability of material analysis. By unlocking new depths of understanding, this innovative technology drives advancements in materials science, optimizing fabrication processes and leading to the development of next-generation materials and devices.

Conclusions

The Hypulse Surface Analysis System, with its integrated femtosecond laser ablation technology, provides versatile, damage-free analysis and depth profiling across a wide range of materials.

By overcoming the limitations of traditional XPS methods, it offers researchers and industry professionals a powerful tool for detailed and accurate chemical analysis, at the surface and beyond.

Real-world applications and case studies highlight how this technology is already revolutionizing materials analysis across various industries, from semiconductor manufacturing to metallurgy and solar cell development. As we continue to push the boundaries of material science, the Hypulse System is poised to play a crucial role in future innovations, helping researchers enhance the properties of advanced materials, optimize renewable energy technologies, and more.

How can we help?

NanoPorts

The teams at our four NanoPorts around the world provide tailored solutions for your applications and on-site or remote demonstrations, plus they act as research collaboration centers. The NanoPorts also help R&D, factory, and field service teams provide optimized outcomes and improved solutions.

Global service logistics and field service assistance

We maintain an extensive network of central warehouses, regional hubs, and local stock locations to fulfill your needs more quickly. From installation services to on-site and remote maintenance agreements, our team of experts is here to support you at every step.

Application support

After your system is installed, our team of applications experts can help you quickly get up to speed. From training and documentation to troubleshooting and more, we're with you every step of the way to help your research succeed.

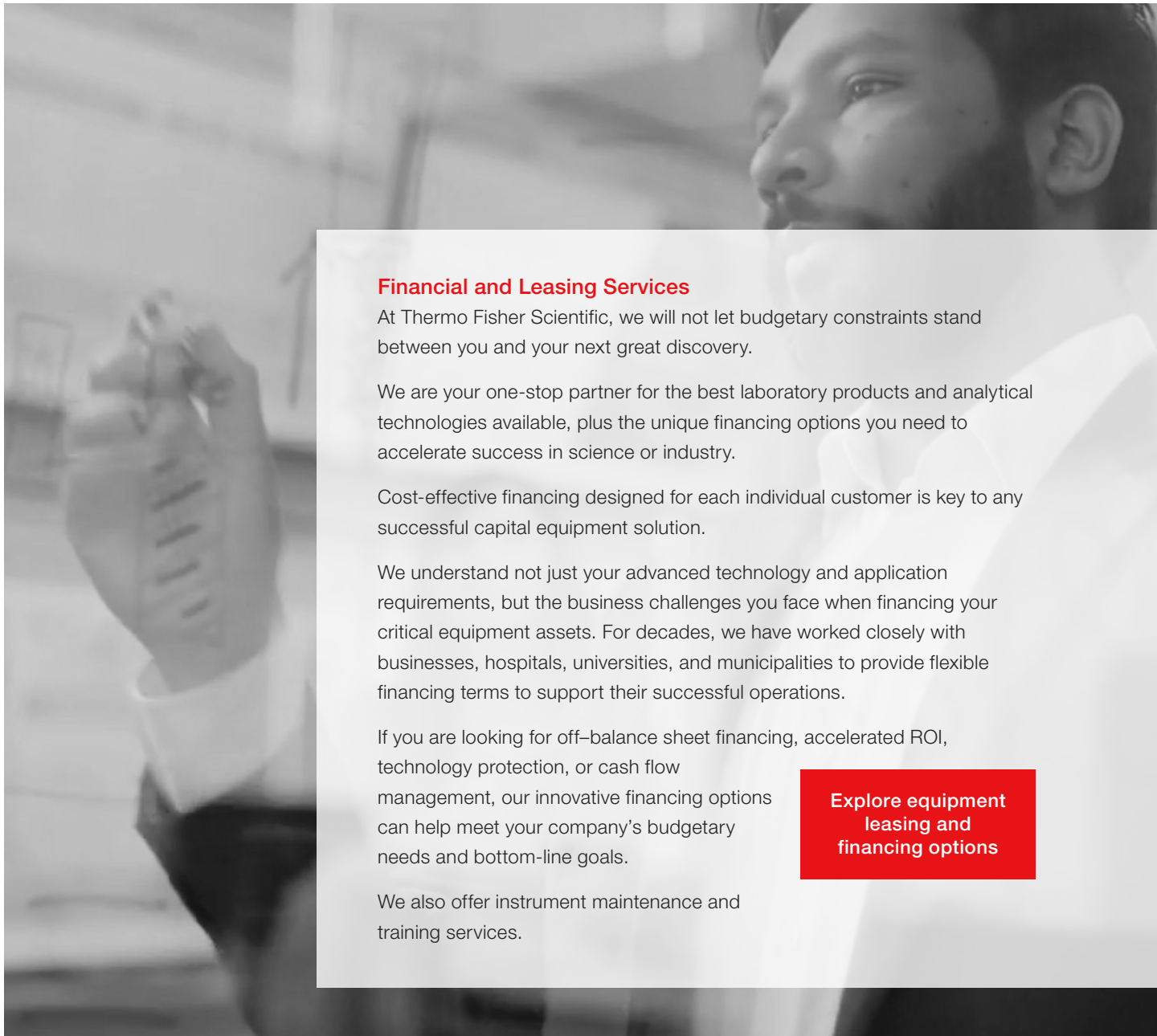
Need more information? Our representatives are here to help. **Contact us**

About Thermo Fisher Scientific

We are the world leader in serving science. Our Mission is to enable our customers to make the world healthier, cleaner and safer.

Learn about the mission of Thermo Fisher Scientific. Duration 1:23.

Our innovative solutions for electron microscopy, surface analysis, and microanalysis help materials science researchers advance their sample characterization to gain deeper insight into the physical and chemical properties of materials from the macroscale to the nanoscale. Our multiscale, multimodal solutions cover a broad range of applications across dozens of industries and research fields, serving customers in academia, government, and industry. Our TEMs, DualBeam™ FIB-SEMs, comprehensive portfolio of SEMs, XPS, and microanalysis solutions, combined with software suites, take customers from questions to usable data by combining high-resolution imaging with physical, chemical, elemental, mechanical, and electrical analysis across scales and modes.



Financial and Leasing Services

At Thermo Fisher Scientific, we will not let budgetary constraints stand between you and your next great discovery.

We are your one-stop partner for the best laboratory products and analytical technologies available, plus the unique financing options you need to accelerate success in science or industry.

Cost-effective financing designed for each individual customer is key to any successful capital equipment solution.

We understand not just your advanced technology and application requirements, but the business challenges you face when financing your critical equipment assets. For decades, we have worked closely with businesses, hospitals, universities, and municipalities to provide flexible financing terms to support their successful operations.

If you are looking for off–balance sheet financing, accelerated ROI, technology protection, or cash flow management, our innovative financing options can help meet your company's budgetary needs and bottom-line goals.

Explore equipment leasing and financing options

We also offer instrument maintenance and training services.

ThermoFisher SCIENTIFIC

Learn more about fs-LA XPS depth profiling at **thermofisher.com/hypulse**

thermo scientific

For research use only. Not for use in diagnostic procedures. For current certifications, visit thermofisher.com/certifications