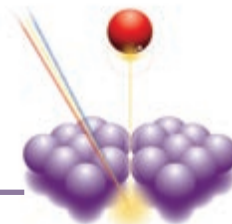


Measurements & Characterization • National Center for Photovoltaics

SURFACE ANALYSIS



Surface analytical techniques help to determine the chemical, elemental, and molecular composition, and electronic structure of material surfaces and interfaces. The properties of the surface and outer few micrometers of a material often control the electrical, chemical, or mechanical properties of that material—hence, this region is of extreme importance.

Our techniques use ions, electrons, and X-ray or ultraviolet photons in high vacuum to probe surfaces and interfaces of a material. We map the elemental and chemical composition of specimens, study impurities and grain boundaries, gather bonding and chemical-state information, measure surface electronic properties, and perform depth profiles to determine doping and elemental distributions. We have analyzed a wide range of materials, including photovoltaics, microelectronics, polymers, and biological specimens.

We work collaboratively with you to solve materials- and device-related R&D problems. This sheet describes our major technique capabilities.

FIELD EMISSION AUGER ELECTRON SPECTROSCOPY (FE-AES) WITH SCANNING AUGER MICROSCOPY (SAM)

In Auger electron spectroscopy (AES), a sample surface is bombarded with a focused beam of high-energy (2- to 10-kV) electrons. The incident electrons lose energy to the sample atoms, generating Auger electrons that have discrete kinetic energies characteristic of the emitting atoms.

This technique is particularly useful for determining the elemental composition of the surface because Auger electrons have a limited escape depth. A key capability of the FE-AES is its ability to focus the electron beam to a small spot, with resolutions similar to an electron microscope. By scanning the electron beam across the surface, we can generate both element-specific Auger maps and secondary-electron microscope (SEM) images from the same region of the sample.

Applications

- **Elemental surface analysis.** Identifies and quantifies elemental compositions of solid surfaces, with a sensitivity to 0.5 at.% for elements from lithium to uranium.
- **Depth profiling.** Argon ions are used to remove successive layers, thus allowing elemental analysis as a function of depth. Especially useful for quantitative bulk and volumetric analysis of thin-film materials, and for exploring impurities and diffusion present at junctions and grain boundaries.
- **Small-feature analysis.** The field-emission electron source produces a small spot size (> ~25 nm) that can be used to explore the composition and structure of small particles or intricate features, such as those found in microelectronics or polycrystalline thin-films.
- **Imaging.** By using raster scanning with a highly focused electron beam ≥ 25 nm in diameter, SEM micrographs can be obtained with up to 20,000x magnification. Using the same raster scan, SAM can produce elemental composition maps of a surface.

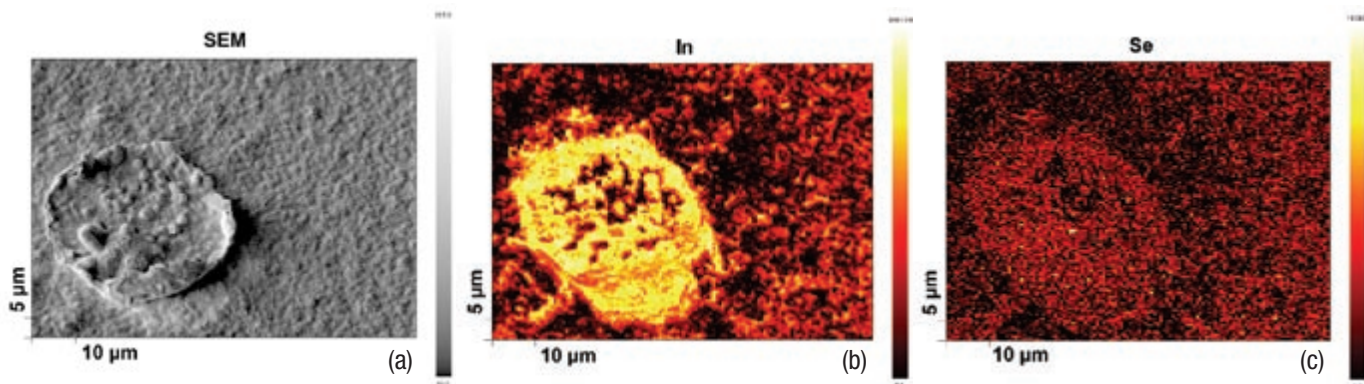
X-RAY AND ULTRAVIOLET PHOTOELECTRON SPECTROSCOPY (XPS/UPS)

Photoemission techniques use either X-rays or ultraviolet photons to bombard the surface of a sample. The incident photons cause the emission of electrons (photoelectrons) from atoms in the near-surface region (about the top 4 nm) of the sample.

In XPS, the photoelectrons have energies characteristic of the atom they came from, thus allowing elemental and chemical determinations to be made. Ultraviolet photons used for UPS have lower energies and probe the electrons in the outermost valence levels of the surface atoms, yielding surface electronic structure information such as work function and valence band-edge.

MAJOR INSTRUMENTATION FOR SURFACE ANALYSIS

Analytical Technique	Instrumentation	Typical Applications	Probing species	Spot Size	Signal Detected	Elements Detected	Detection limit	Lateral Resolution	Depth Profiling/Resolution	Mapping?	Organic Info.?
Auger electron spectroscopy	Physical Electronics PHI 670	Elemental surface analysis, small-feature analysis	Electrons	25 nm	Auger electrons	Li to U	0.5–1 at.%	25 nm	Yes, 10 nm	Yes	—
X-ray and ultraviolet photoelectron spectroscopy	Physical Electronics PHI 5600	Elemental and chemical surface analysis, surface electronic properties	X-ray or ultraviolet photons	50 μ m (XPS), 1 mm (UPS)	Photoemitted electrons	Li to U	0.5–1 at.% (XPS)	50 μ m (XPS)	Yes, limited, 100 nm both	Limited	Yes
Dynamic SIMS	Cameca IMS-5F & IMS-3F	Trace-element contaminant and dopant analysis	Ions (Cs, O, Ar)	1 to 200 μ m	Ions (+/-)	H to U and all isotopes	ppm–ppb (cm^{-1})	1 μ m	Yes, <10 nm	Yes	—
Static TOF SIMS	IONTOF TOF SIMS IV	Surface elemental and molecular information	Ions (Ga, Ar, O)	To 0.3 μ m	Ions (+/-)	H to U, all isotopes, mass range >1000 amu	ppm–ppb (cm^{-2})	0.5 μ m	Yes, <5 nm	Yes	Yes



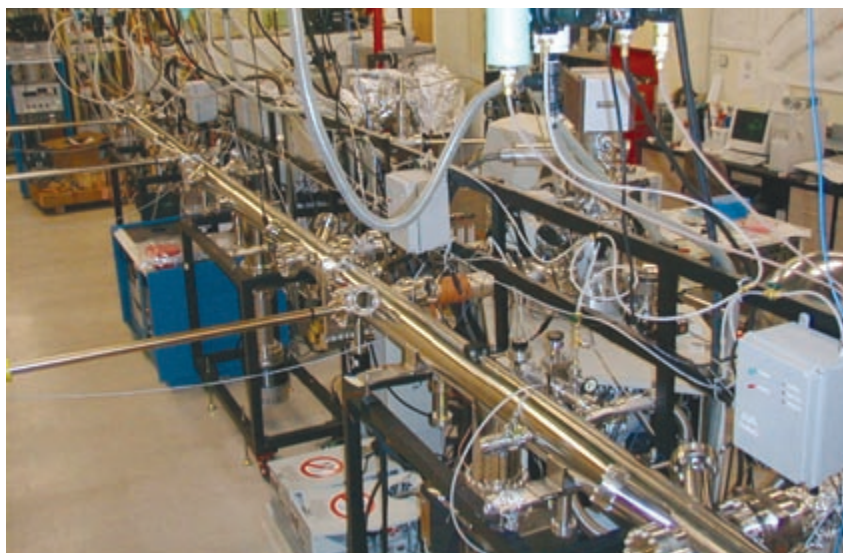
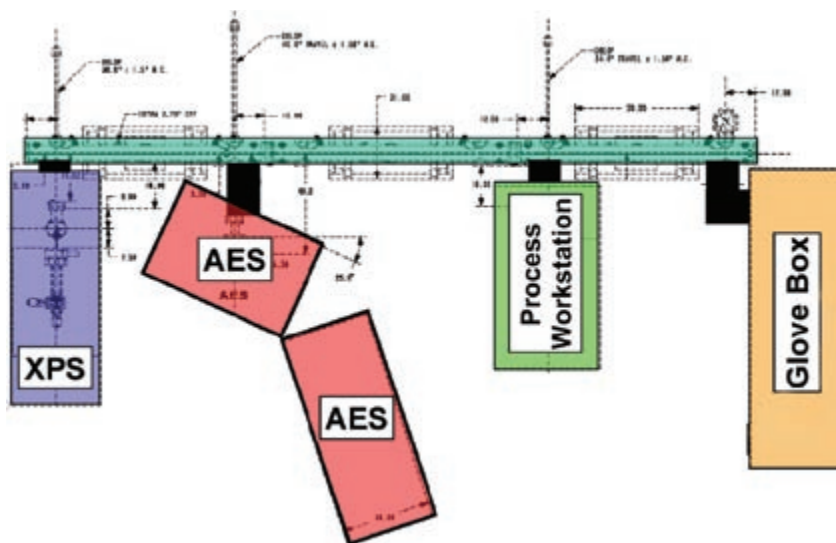
(a) SEM and (b) SAM images of a surface defect in Cu(In,Ga)Se₂. SAM analysis shows the defect to be an In-rich region (b), indicating that the likely origin was an “In-spit” during precursor deposition that was subsequently selenized during downstream processing (b,c).

Applications

- Chemical state.** Evaluate bonding environments of surface layers via XPS, and valence states via UPS. Ultrahigh vacuum facilitates sample cleanliness. Aluminum, magnesium, and monochromated Al K α radiation allow a variety of analytical conditions. A high-resolution electron energy analyzer minimizes the spread of photoelectrons, allowing accurate determination of energies and enhanced peak separation for accurate chemical identifications.
- Elemental analysis.** Quantitative identification of elements from lithium to uranium by XPS, with detection levels down to 0.5 at.%.
- Depth profiling.** Argon ion gun equipped for sputter cleaning of the surface and for limited compositional depth profiles of layers <1 μm thick.
- Polymers.** Especially valuable for analyzing functional groups in polymers and other organic materials. Particularly useful in this regard when used as a complementary tool with static SIMS analysis.
- Versatile sample capabilities.** Accommodates standard semiconductor materials, but also, insulators, powders, irregular geometries, polymers, catalyst particles, and biological and cell materials.
- Non-destructive depth profiling.** Using angle-resolved photoelectron spectroscopy (ARPES), photoelectron spectroscopy is performed from a variety of angles—from normal to the surface to nearly parallel to it—changing the sampling depth for photoelectrons. This yields a non-destructive method for producing depth profiles of near-surface regions.
- Variable-temperature manipulator.** Allows the acquisition of XPS and UPS data at variable temperatures (-50° to +800°C). Useful for in-situ cleaning of sample surfaces and temperature-programmed XPS/UPS studies.

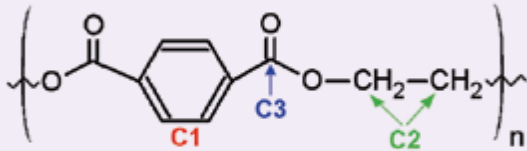
SURFACE ANALYSIS CLUSTER TOOL (INCLUDES AES, XPS/UPS, UHV DEPOSITION SYSTEM, TDMS, INERT-ATMOSPHERE GLOVEBOX)

This cluster system is a newly developed tool stemming from the need for integrated analysis, growth, and processing capabilities, such as will be available in NREL's new Science and Technology



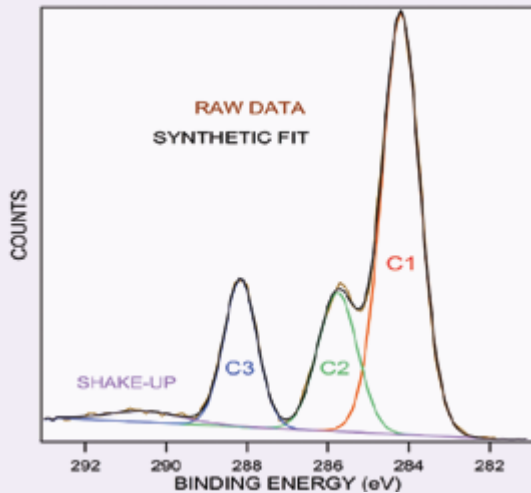
Schematic diagram and photograph of the surface analysis cluster tool.

Polyethylene Terephthalate



Ratio of Different Carbon Atoms
C1:C2:C3 = 3:1:1

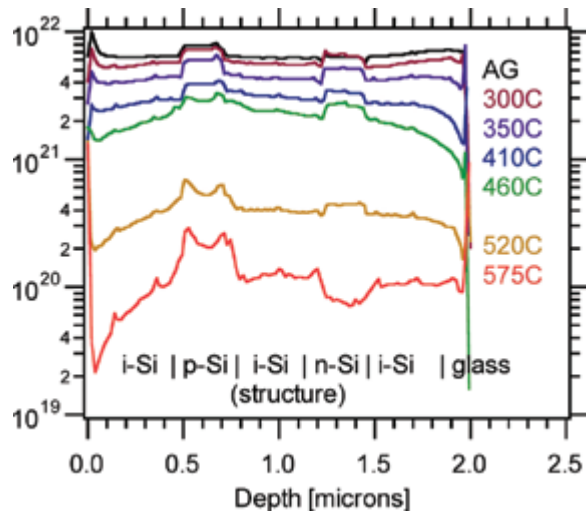
PET CARBON 1S



High-resolution XPS spectra of carbon 1s from polyethylene terephthalate backsheet material, showing excellent quantitative agreement between measured and predicted peak area ratios. Subtle differences in polymer functionality are assessed by deviations from stoichiometry.

DYNAMIC SECONDARY-ION MASS SPECTROMETRY (SIMS)

Dynamic SIMS uses a continuous, focused beam of primary ions to remove material from the surface of a sample by sputtering. The fraction of sputtered material that is ionized is extracted into a double-focusing mass spectrometer, which uses electrostatic and magnetic fields to separate the ions according to their mass-to-charge ratio. Ions of different mass-to-charge ratios are selected by adjusting the strength of the magnetic field. Dynamic SIMS is extremely sensitive—able to detect fractions in the range of parts per million to parts per billion—and is used to determine the elemental composition and levels of trace impurities and dopants in solid materials.



SIMS depth profiles of hydrogen for a series of a-Si films undergoing solid-phase recrystallization at different temperatures. Hydrogen loss is greater for higher temperatures. However, the rate of loss for a given temperature is also affected by the type of dopant and proximity to the surface.

Applications

- **Elemental analysis.** Identifies all elements or isotopes present in a material, from hydrogen to uranium. Different primary-ion sources (cesium and oxygen) allow the choice of conditions for the best analytical sensitivity across the Periodic Table, down to parts per billion for many elements. High mass resolution ($M/\Delta M$ of up to 6000) allows the separation of nominally identical masses (e.g., ^{31}P from ^{30}SiH). This is the only surface analysis technique for directly detecting hydrogen and deuterium in materials.
- **Depth profiling.** Sputtering into a material generates a profile of the concentration of impurities or dopants as a function of depth. Depth resolution of better than 10 nm is possible, and the technique can be quantitative with standards.
- **Interface analysis.** By sputter-removing material from the sample, dynamic SIMS determines the changes in composition or the diffusion of impurities from layer to layer. Variable primary-ion conditions allow depth resolutions of <10 nm.
- **Image analysis.** Raster scanning or the unique direct-imaging capability of the instruments can produce secondary-ion images for detecting the lateral distribution of trace impurities. Image analysis, combined with depth profiling, produces three-dimensional maps of elemental distributions.

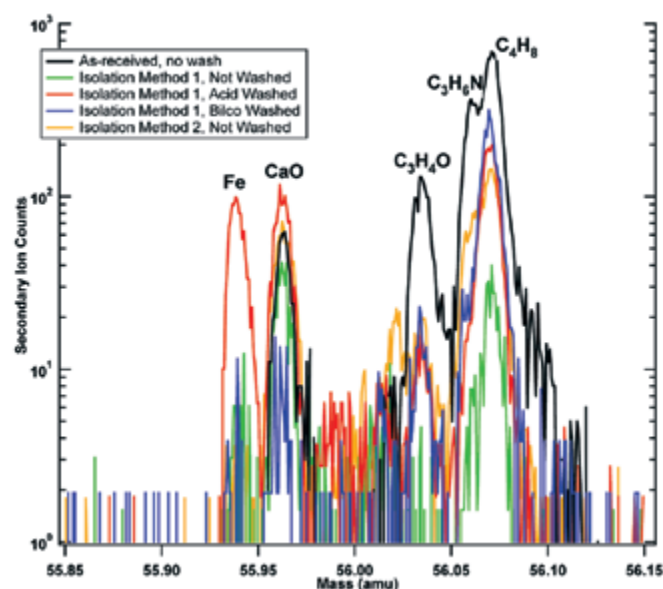
Facility. We developed and built a unique tool for the in-situ study of surface chemical changes that occur during growth and processing of materials under various conditions. In addition, using this tool, we developed capabilities to study reactions and kinetic processes at surfaces. We joined our previously stand-alone XPS/UPS and AES instruments to a custom ultrahigh-vacuum thin-film deposition system and a nitrogen-ambient glovebox, via a UHV trolley system, to form an ultrahigh-vacuum cluster tool.

The cluster tool greatly enhances the capabilities of our stand-alone tools by allowing controlled surface modification and processing, as well as adding the new analysis tools of thermal desorption mass spectrometry (TDMS), reflection high-energy electron diffraction (RHEED), and low-energy electron diffraction (LEED), and the capability for in-situ spectroscopic ellipsometry during film deposition. In addition, our variable-temperature manipulator for the photoemission system allows us to monitor chemical and electronic properties during temperature-programmed experiments.

Our expert staff is available to discuss how this tool and our experience in surface science experimental design can aid you in understanding issues related to surfaces and interfaces of your materials.

STATIC TIME-OF-FLIGHT SECONDARY-ION MASS SPECTROMETRY (TOF SIMS)

Static SIMS uses a pulsed primary-ion beam to sputter-remove material from the top monolayer of a sample. Secondary ions are collected and focused into a reflectron time-of-flight (TOF) mass spectrometer. The combination of low primary-ion density (low surface damage) and high transmission of the TOF analyzer (high sensitivity) makes the technique extremely useful for studying the top monolayer of a surface. The large mass range of the TOF analyzer makes the instrument well suited for detecting trace levels of organic contaminants on surfaces. Depth profiling is also possible in combination with high-current, low-energy cesium and argon sputter sources. Information on chemical structure is especially useful when combined with XPS analysis.



We used the high mass resolution and mass accuracy of TOF SIMS to study surface cleanliness of tin-oxide-coated glass after different types of isolation scribes and cleaning processes. Not all processes were equal. As-received tin oxide was heavily contaminated with silicone oils (not shown). An acidic wash resulted in contamination by Fe and other metals. Without high mass accuracy, the CaO signal might be mistaken for Si_2 , or Fe mistaken for CaO.

Applications

- **Surface sensitive.** Low doses of primary ions ensure that below the static limit, every secondary ion comes from an undisturbed region of the surface. High vacuum promotes a clean specimen surface. Multiple ion sources (liquid-metal gallium and argon) promote analytical flexibility.
- **Elemental and molecular analysis.** Performs mass analysis to determine the elemental and/or molecular composition of the top monolayer of a material's surface. Can distinguish elements and molecules whose masses range from 1 to >10,000 amu. High mass resolution ($M/\Delta M > 7000$) allows precise differentiation of secondary-ion species.
- **Wide range of materials.** Can be used for a wide range of organic and inorganic materials, including thin films, solid-state materials, ceramics, polymers, biological samples, and catalyst particles.
- **Imaging.** Using a rastered probe, we can generate images to determine the lateral distribution of surface elemental and molecular species, with spot sizes down to 0.5 μm for the gallium liquid-metal ion source. Collecting a complete spectrum at every pixel allows for retrospective analysis of the image data.
- **Depth profiling.** Low-energy cesium, and argon or oxygen sputter guns for depth profiling provide high-resolution depth-profiling capabilities. Collecting an entire spectrum for each point allows for retrospective analysis of depth-profile data.



National Renewable Energy Laboratory
1617 Cole Blvd., Golden, CO 80401

NREL is a national laboratory of the U.S. Department of Energy, Energy Efficiency and Renewable Energy, operated by Midwest Research Institute • Battelle

Measurements and Characterization is within the National Center for Photovoltaics at NREL
Web site: www.nrel.gov/pv/measurements
Phone: (303) 384-6675 • Fax: (303) 384-6604
Contract No. DE-AC36-99-GO10337
NREL/BR-520-40122 • June 2006

NOTICE—This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste