Characterizing Materials for Energy Generation Using X-ray Photoelectron Spectroscopy (XPS)

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Introduction

In order to meet the challenges of more economical and environmentally benign energy production, a new generation of complex materials and devices are being developed, including thin film solar cells, fuel cells, and batteries. In all stages of development there is a requirement for materials characterization and analysis, from the initial development stages through to testing of the finished product. Most materials need to be analyzed for compositional homogeneity across surfaces and also for confirmation of film thickness and layer chemistry.

Recent developments in spectrometer hardware and software design have made the unique capabilities of X-ray photoelectron spectroscopy (XPS) more accessible to scientists and engineers working on thin film devices. Thin film solar cell and fuel cell design and fabrication rely on materials engineering at the nm scale; thus, it is important that techniques able to achieve chemical characterization on the same scale are available. In this article, we address the characterization requirements for two important thin film devices: the copper indium gallium (di)selenide (CIGS) solar-cell and the proton exchange membrane fuel cell (PEMFC). These devices represent the latest in thin film fabrication technology in their respective fields.

Precise control of surface, thin film, and interface composition is essential to product viability and efficiency. Most modern devices such as solar cells are reliant on the use of a combination of conductive, semi-conductive, and insulating layers, where the composition of specific layers is engineered to deliver particular physical, chemical, and electrical properties. Deviations from desired chemistry can often occur during the fabrication process; this is especially true at the crucial interfacial regions where precise materials engineering meets its greatest challenges. Few analytical techniques have the ability to analyze completely all these materials in a single analysis session, however, owing to its surface sensitivity, XPS can provide characterization on the nm scale for ultra-thin films and interfaces. Accuracy within these limits is not without its difficulties; however, improvements in instrumentation and analytical capabilities have allowed XPS to become an essential component of the engineer's toolkit.

Introducing XPS

Historical perspective. XPS data has been widely published for more than 50 years with the technique gaining increasing commercial momentum over the past 40 years. P.D. Innes is credited with recording the first XPS spectrum in 1907, but the real "father of XPS" as an analytical technique is considered to be Kai Siegbahn (1918–2007) who produced the first high-resolution spectrum of sodium chloride in 1954. By the late sixties he had performed many wide-ranging studies that proved the value of the technique. In 1969 he cooperated with Hewlett-Packard in the USA to produce the first commercial XPS instrument. In recognition of his work in the field of surface analysis, Siegbahn received the Nobel Prize for Physics in 1981. To emphasize the fact that XPS provides a method for the chemical characterization of a surface, Siegbahn referred to the technique as ESCA (electron spectroscopy for chemical analysis), a term that continues to be used alongside the term XPS [1].

The basics. As the name implies, XPS relies on the photoelectric effect, in which an X-ray photon removes an electron from an atom located in the surface region of the sample to be analyzed. A particular electron will only be emitted provided that the photon has energy in excess of the electron's binding energy to the target atom nucleus. The remaining energy imparted by the photon manifests itself as the kinetic energy of the emergent photoelectrons. In an XPS spectrometer, it is the kinetic energy of the photoelectron that is measured as it leaves the surface. This process is described simply by the following equation:

$$\text{Kinetic energy (KE)} = \text{Photon energy } (h\nu) - \text{Binding energy (BE)}$$

Typically an X-ray source of a known energy (for example, Al $K\alpha$ radiation $h\nu = 1486.6$ eV) is used in the equation (Figure 1B). This allows the BE of the emergent electron to be easily calculated by rearranging the above equation. Principally, the binding energy of the photoelectron is dependent on the identity of the parent atom and the electron orbital from which it came. Basic interpretation of wide scan survey data, collected by scanning the analyzer through the full range of accessible kinetic energies (the accessible range being dependent on the photon energy), can lead to quantitative determination of the surface elemental composition (of all elements heavier than He). To a first approximation, quantification of the data is achieved by the application of elemental and transition-dependent matrix factors during data processing, which removes the need for the use of external calibration standards. Refinements to these factors that take into account the attenuation length of the photoelectron and its kinetic energy lead to improvements in quantification accuracy. These factors are generally supplied by the instrument data system and lead to a detection limit for the technique of about 0.1 atomic%. This elemental information is useful; however, the real strength of XPS lies in the fact that the chemical environment of the emitting atom induces subtle changes in binding energy of the photoelectron. As a consequence, detailed high-resolution XPS spectra also contain valuable chemical state information.

The basic components of an XPS spectrometer include an X-ray source, electron energy analyzer, and detection system

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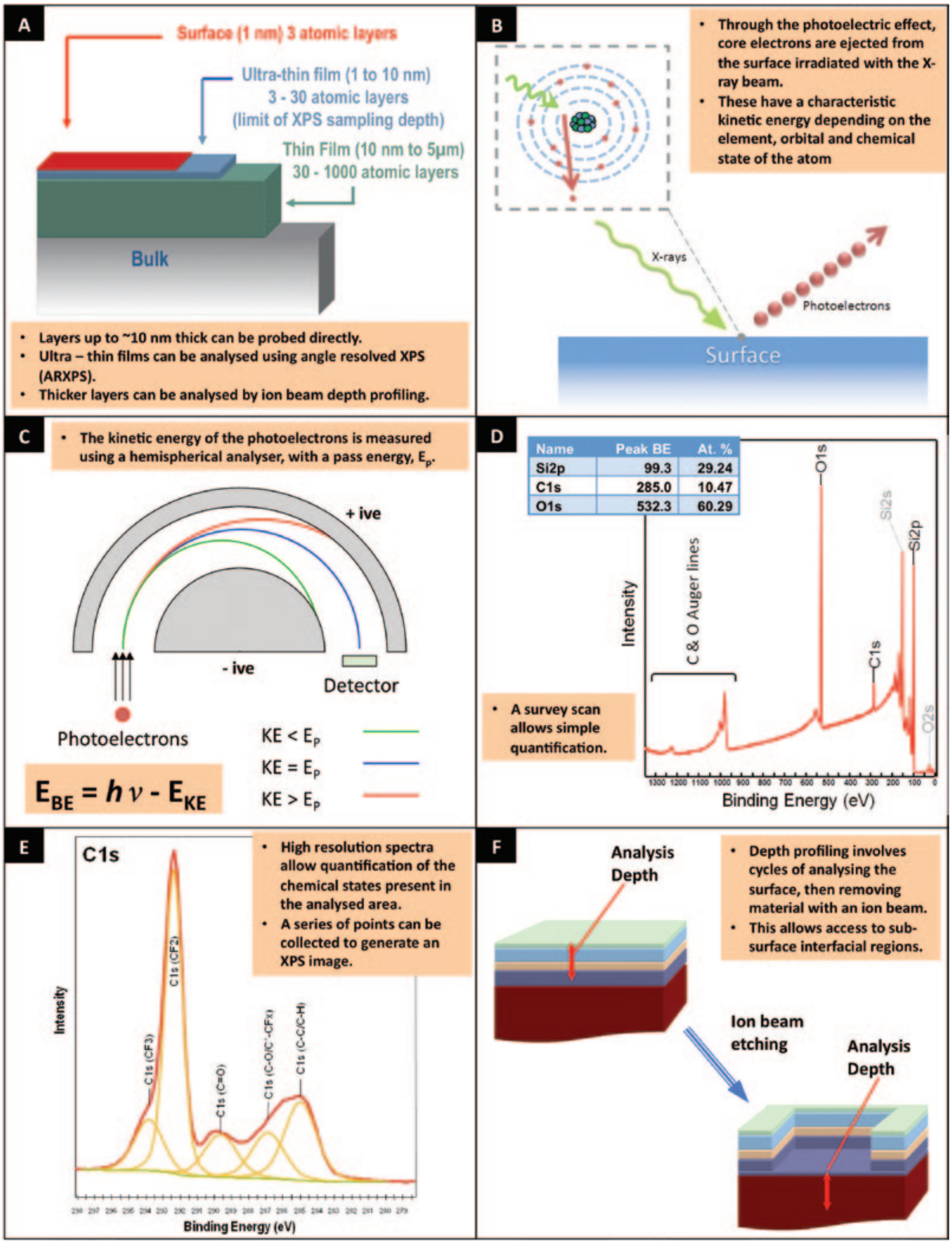
(Figure 1C). Within the XPS spectrometer, the emitted photo-electrons need to travel a considerable distance before they reach the detector. To ensure that energy losses due to collisions with gas molecules are kept to a minimum, XPS spectrometers need to be operated under ultra-high vacuum conditions, typically 1 × 10^{-7} mbar (7.5 × 10^{-8} torr) or better. Any solid sample that is compatible with these conditions can be analyzed and requires little or no prior sample preparation.

XPS spectrometers are available in a number of forms, from highly configurable, multi-technique platforms to dedicated, fully automated spectrometers. Figure 2 shows a schematic illustrating a typical XPS system, including additional components such as a low-energy electron flood source for insulator analysis, an argon ion source for depth profiling applications, and a camera system for aligning the sample with the analysis position.



- Layers up to ~10 nm thick can be probed directly.
- Ultra – thin films can be analysed using angle resolved XPS (ARXPS).
- Thicker layers can be analysed by ion beam depth profiling.

- Through the photoelectric effect, core electrons are ejected from the surface irradiated with the X-ray beam.
- These have a characteristic kinetic energy depending on the element, orbital and chemical state of the atom

- The kinetic energy of the photoelectrons is measured using a hemispherical analyser, with a pass energy, E_P.

Name	Peak BE	At. %
Si2p	99.3	29.24
C1s	285.0	10.47
O1s	532.3	60.29

- A survey scan allows simple quantification.

- High resolution spectra allow quantification of the chemical states present in the analysed area.
- A series of points can be collected to generate an XPS image.

- Depth profiling involves cycles of analysing the surface, then removing material with an ion beam.
- This allows access to sub-surface interfacial regions.

Figure 1: The XPS process. (A) The information depth of XPS, ~10 nm, which can be extended by depth profiling to a few microns. (B) The generation of photoelectrons. (C) Kinetic energy selection of photoelectrons using an electrostatic hemispherical analyzer. (D) A survey spectrum, used for elemental quantification. (E) A high-resolution region spectrum used for quantifying chemical states. (F) Depth profiling through a layered sample.

Why is XPS so surface-sensitive? When considered relative to other electron microscopy techniques, XPS has comparatively poor lateral spatial resolution; however, this is mitigated by its extreme surface sensitivity, which results in a vertical depth resolution on the nm scale (typically less than 10 nm). The surface sensitivity of XPS is often mistakenly attributed to X-ray penetration depth or the analysis geometry. In reality the surface specificity of XPS is a consequence of the strong interaction of photoelectrons with condensed matter. When X rays strike a solid, they penetrate the material to a great depth causing photoemission along the whole of their path of travel. However, as the emitted photoelectrons travel through the material, they undergo inelastic collisions with other atoms in the solid. Only photoelectrons originating at or close to the surface (within the top 5 to 10 nm, depending on the material) have a reasonable probability of escaping without energy loss. The XPS spectrum consists of sharp peaks on a broad background. See Figure 1(D,E). Electrons generated close enough to the surface to escape without energy loss contribute to the peaks, whereas those that escape having lost some energy through the aforementioned inelastic collisions contribute to the spectrum background.

Modes of operation. The simplest form of XPS analysis is a single-point analysis, as shown in Figure 3A, where such measurements can be obtained from areas down to about 10 μm in diameter. Imaging XPS is possible by using either parallel detection systems or stage mapping (Figure 3B). Current state of the art capabilities result in elemental or chemical state

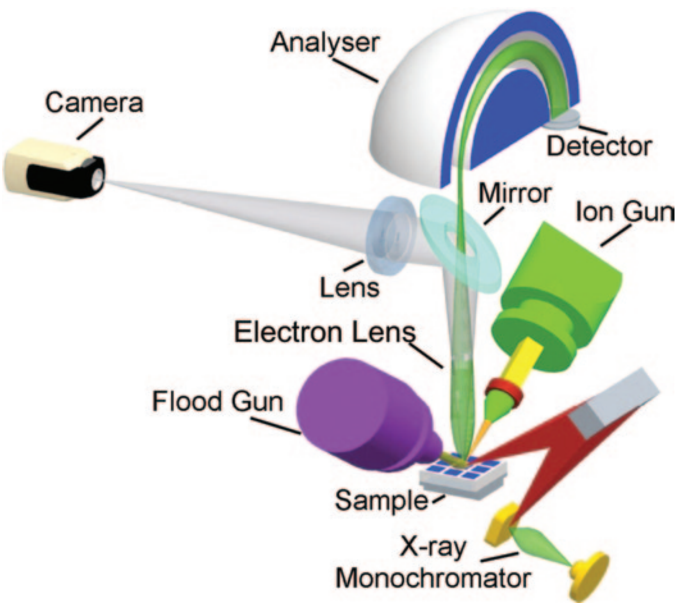


Figure 2: A schematic of the internal configuration of the Thermo Scientific K-Alpha showing the principal components of a modern XPS spectrometer. The sample is irradiated with monochromatic X rays, and the resultant photoelectrons are collected by a transfer lens. The photoelectrons are selected based on their kinetic energy by the hemispherical analyzer and collected at the detector. The low-energy electron flood gun facilitates the analysis of insulating materials, and the ion gun permits sample cleaning and composition depth profiling.

images with a spatial resolution on the order of 3 µm. If XPS measurements are interleaved with Ar-ion-beam etch cycles, then it is possible to produce a chemical composition depth profile (Figure 3C). This makes it possible to determine the composition of films that are much thicker than the escape depth of the electrons.

Common applications. The range of application areas that XPS addresses is extensive, encompassing both academic and industrial R&D [2–6]. With the recent explosion of manufacturing processes that use thin film fabrication methods, XPS has now been adopted for quality assurance and control purposes. Common uses for XPS are:

- Measuring surface contaminants
- Ultra-thin film and oxide thickness measurements
- Characterization of surface defects, stains, and discolorations
- Measuring effectiveness of surface-preparation treatments
- Surface composition of powders and fibers
- Chemical characterization of plasma-modified polymer materials
- Measurement of coating thickness and conformity
- Composition-depth profiling for multilayer and interface analysis

Case study 1: Characterization of Fuel Cell Components

Proton exchange membrane fuel cells (PEMFC) are currently being developed for both stationary and transport applications, such as remote telecommunications base stations and motor vehicles. PEM fuel cells have several advantages over current solid oxide fuel cells (SOFC), including higher conversion efficiencies and considerably lower operating temperatures (typically <100°C), which leads to improved start-up performance.

At the heart of the fuel cell is a membrane electrode assembly (MEA) containing the central layers shown in Figure 4. The MEA contains layers of Pt in carbon black, which catalyzes the reaction of hydrogen and oxygen. A polymer electrolyte (typically Nafion®) is used to separate the anode and cathode electrodes. In MEA manufacture or development, the aim is to maximize the surface area of Pt that is electrically connected to the conducting support; loss of surface area decreases the efficiency of the device. Platinum loss can occur when high currents corrode the carbon-black support, liberating the active metal and allowing it to migrate to the adjacent polymer

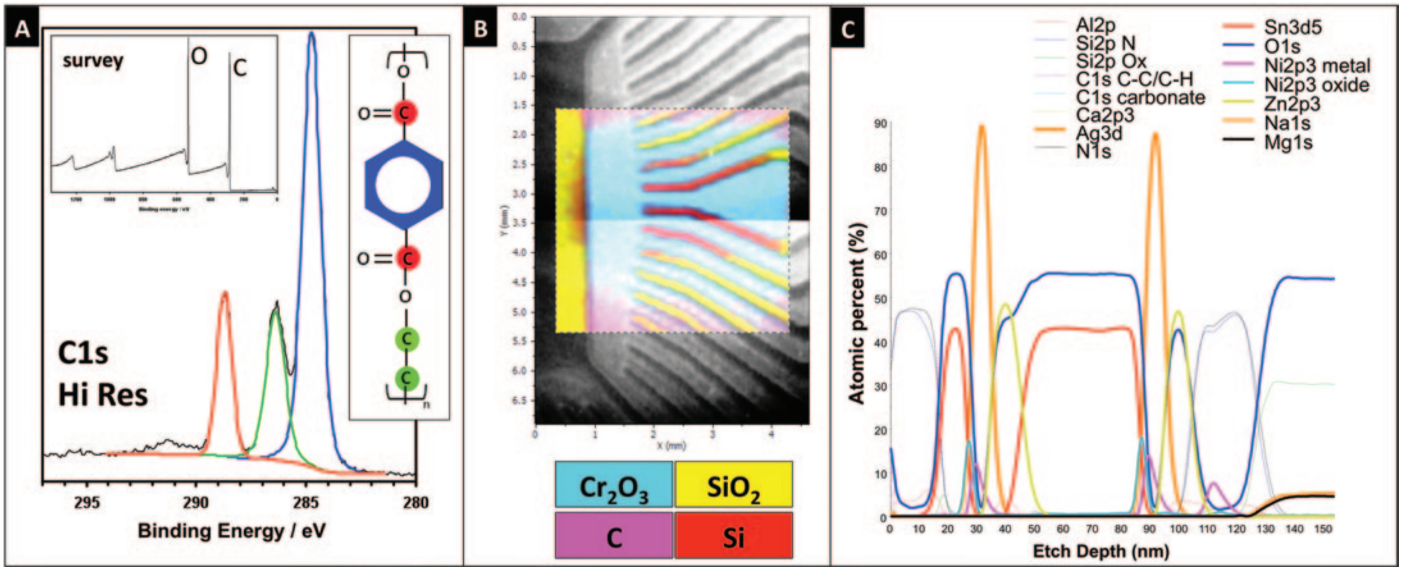


Figure 3: Examples of XPS data. (A) A C1s high-resolution spectrum of PET. The color-coding of the peaks relates to the highlighted chemistry in the molecule. The inset is a survey spectrum from the same sample. (B) An XPS image, showing a concentration map overlaid on an image of the analysis area, showing an etched area of a patterned wafer. (C) A depth profile through a multilayer sample.

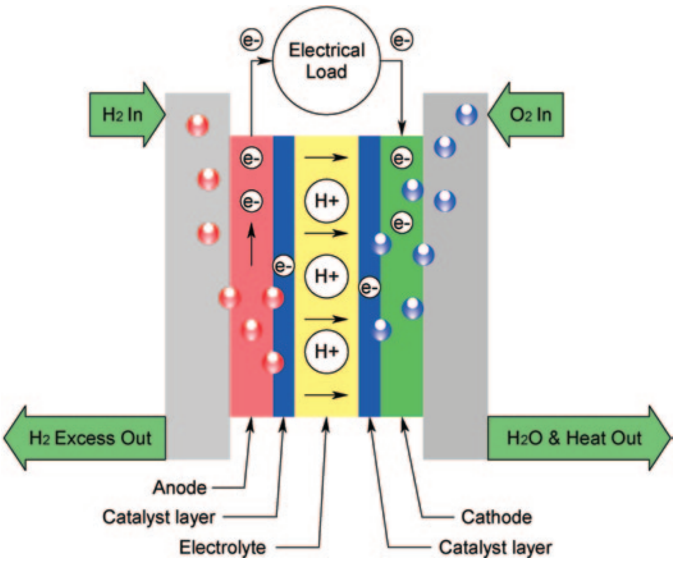


Figure 4: Schematic of a PEMFC. Platinum catalyst layers sandwich the polymer solid electrolyte. A high-surface area of Pt is required, which can lead to migration of catalyst into the membrane.

electrolyte. Additionally, the presence of Pt in the Nafion hinders hydrogen ion mobility in the electrolyte. The purpose of the analysis here is to determine if the Pt has migrated from the catalytically active layers into the adjacent Nafion electrolyte.

The MEA layers are typically too thick for conventional XPS depth profiling, so sectioning was required before the XPS analysis could commence. A simple 90° cross section would reveal layers that would be too narrow for XPS analysis, making it impossible to detect the subtle diffusion of Pt from one layer to another. The solution to this was to mount the sample in epoxy and to use ultra-low angle microtomy (ULAM) to cross-section the MEA at an angle of 1° or 2°. ULAM sectioning effectively stretches the available analysis area, making the exposed internal layer dimensions several times larger than the X-ray probe size, which allows the analyst to obtain in-depth information across the internal layer. Sections for this analysis were prepared by Oak Ridge National Laboratory, Tennessee, USA.

Figure 5 shows the C1s region of the XPS spectrum of the Nafion and epoxy areas of the sample. The Nafion spectrum has a strong peak associated with CF_2 groups in the polymer. It also has a peak at lower binding energy associated with adventitious carbon contamination. The epoxy spectrum has components associated with aromatic, aliphatic, and carboxyl type carbon bonding. From the mapping data in Figure 5, it was possible to determine the elemental surface composition of the MEA-ULAM sample at the three different areas, as shown in Figure 6. Fluorine and sulfur were observed in the catalyst layer; these are expected because a small amount of Nafion containing sulfur was mixed into the platinum-carbon layer during manufacture. Although sulfur is not a contaminant in the platinum layer, these results demonstrate the capability of the XPS tool to detect potential contaminants at low concentration.

Despite the concentration of catalytically active Pt being less than 0.5 at%, a high signal-to-noise spectrum was acquired from the catalyst layer. As shown in Figure 6, no Pt was detected in middle of the Nafion layer suggesting minimal Pt migration.

Case study 2: Compositional analysis of a CIGS solar cell

Solar cells based on $Cu(In,Ga)Se_2$ (CIGS) thin films have demonstrated high efficiencies and offer the potential of a low-cost alternative to bulk, silicon-based, solar cells. They consist of a thin-film stack on a substrate (typically glass), as shown in Figure 7. The Mo and the ZnO layers form the electrical contacts, the p-type CIGS film acts as the sunlight absorber layer, and a thin n-type CdS layer forms a p-n junction. The most common manufacturing methods involve evaporation and/or sputter deposition of the components onto a substrate. For the CIGS layer, the Cd, In, and Ga are deposited first before the film is exposed to Se vapor that reacts with the metals in order to establish the final film composition.

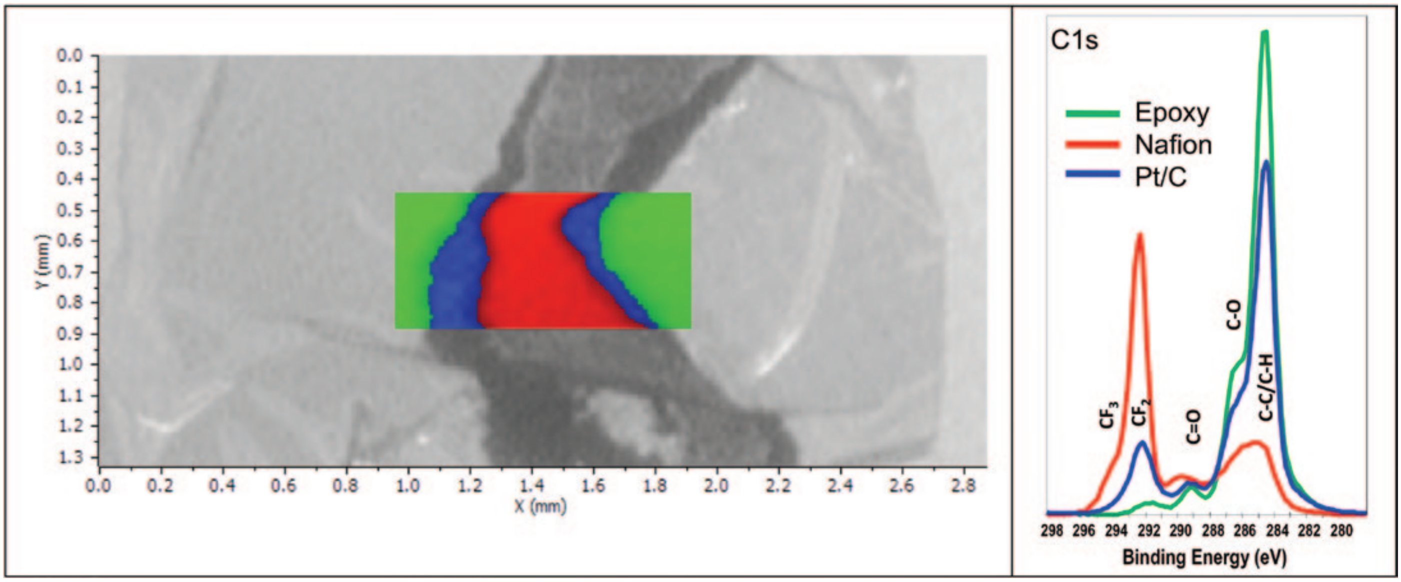


Figure 5: Light optical image of the prepared MEA sample with an overlay of the XPS map data (left). Average C1s spectra (right) from the three identified phases (green = epoxy, blue = Pt on carbon black, red = polymer electrolyte). Some fluorine contamination from the membrane is visible in the Pt/C section.

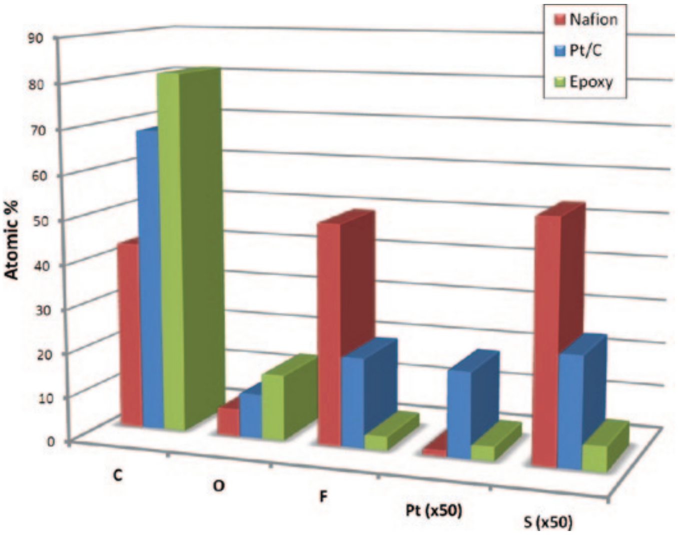


Figure 6: Quantitative analysis results from the three regions of the MEA sample.

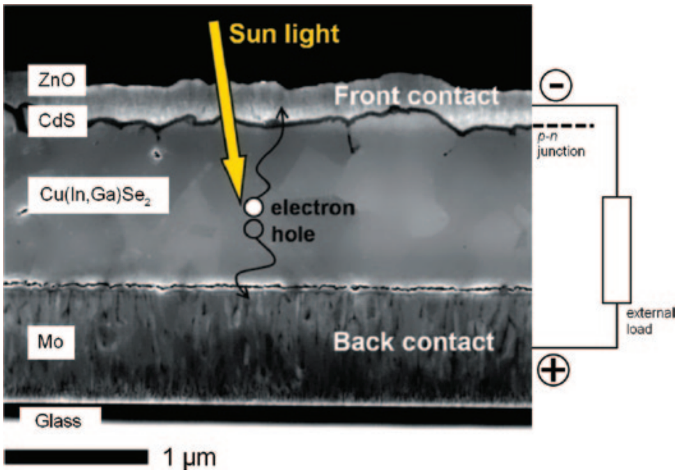


Figure 7: Scanning electron micrograph of a Cu(In,Ga)Se_2 solar cell (cross section) and its mode of operation.

One of the major challenges in producing these devices is the control film composition; hence, reproducibility of layers in commercial volumes has been problematic. This is critical to performance, as the electrical properties of the cell are dependent on the exact composition of the various layers. Depth profiling with XPS can determine both the composition through the structure and the nature of the chemistries formed at the interfaces. This is essential for understanding how to control the band gap to provide efficient operation of the light-adsorbing layer.

The analysis in this example takes the form of an XPS depth profile acquisition. As with most depth profiles, Argon ions were used to generate the sputter crater. Depth-concentration profile results can be seen in Figure 8. The depth calibration scale was confirmed using the SEM cross-section image as a reference.

The depth profile clearly follows the expected structure of the solar cell: the transparent ZnO front contact layer, the thin n-type CdS layer, the light-adsorbing p-type CIGS layer, and finally the Mo back contact. The profile highlights the composition gradient of gallium and indium within the CIGS layer. Controlling the composition of this gradient is critical because it is known to influence the band gap of the material and therefore the overall efficiency of the device. The quality of this profile demonstrates the capability of modern day XPS spectrometers to produce composition profiles from complex multi-component films while maintaining good depth resolution throughout.

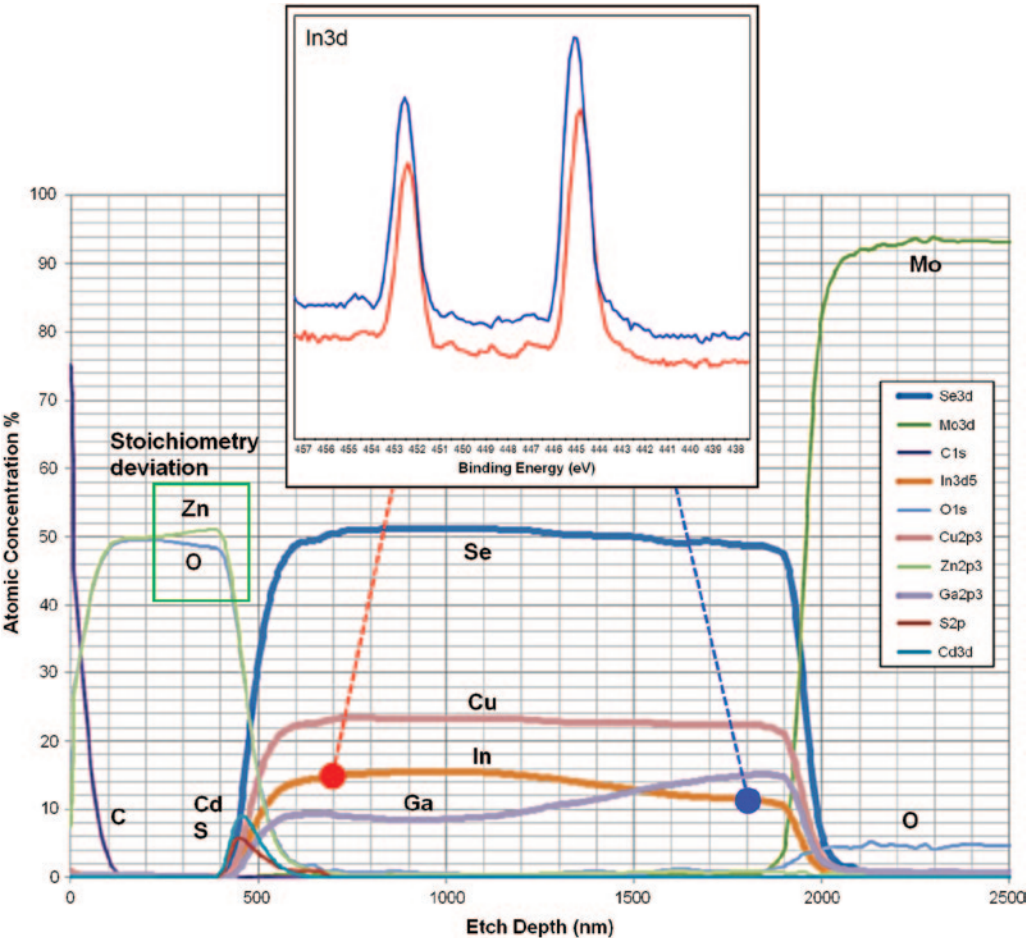


Figure 8: Depth profile of the CIGS solar cell. Variation in the In3d peak position is indicative of the changing chemical environment through the CIGS layer. The thin CdS layer is apparent at the ZnO-CIGS interface.

The profile also highlights a change in stoichiometry within the ZnO layer as the n-type CdS layer is approached. This is likely to be caused by reduction of the ZnO layer as it interacts with the CdS layer. This interfacial effect is likely to have some significance to overall device performance. Further inspection of the data set reveals subtle chemical differences within the absorber layer. The inset showing the In3d XPS transition confirms that the indium oxidation state changes with increasing Ga concentration. This will have a direct influence on the electronic structure and therefore the band gap of the device. The analysis could be extended to look for dopants, such as sodium, in the layers, which can further enhance (or be detrimental) to the performance of the device.

Conclusion

As demand for new thin film devices for cleaner power sources increases so will the need for tools that can elucidate the chemical properties of ultra-thin films and interfaces. It is rare that a single technique can meet all the analysis requirements, and therefore a complementary approach involving several techniques is often demanded. Both energy dispersive spectroscopy (EDS) and Raman spectroscopy are clear candidates to be included within this experimental portfolio, adding rapid composition mapping and molecular contrast. The case studies included in this article demonstrate the important role that XPS analysis can play as a cornerstone of such multi-technique investigations.

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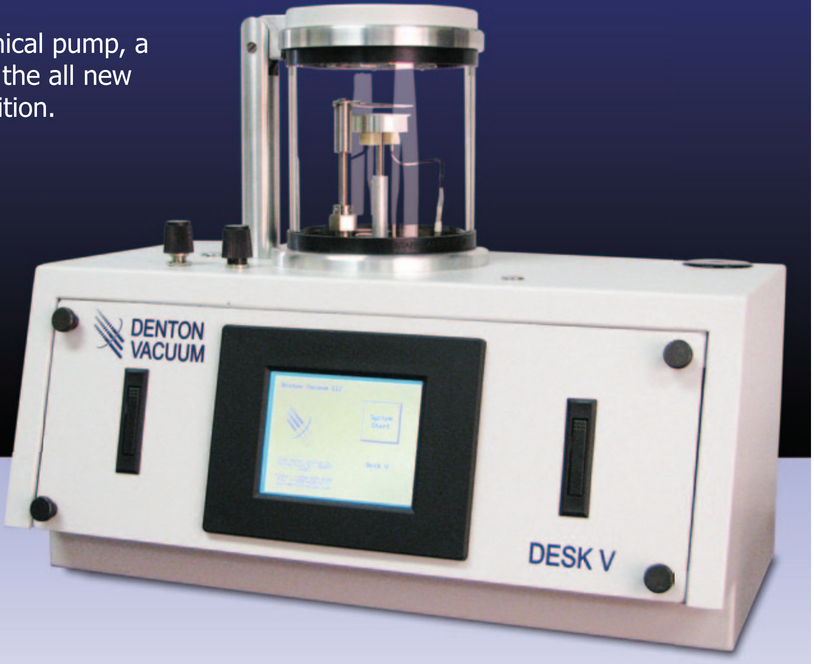

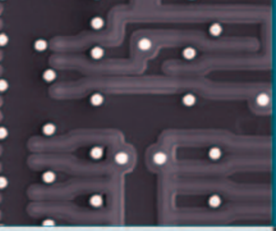

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