

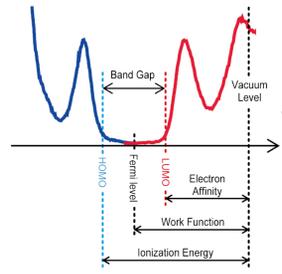
Characterization of Electronic Materials Using the PHI VersaProbe 4 Multi-Technique Scanning XPS Microprobe



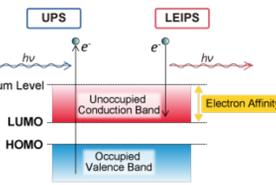
PHYSICAL ELECTRONICS
A DIVISION OF ULVAC-PHI

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- Organic and organic/inorganic hybrid materials are of interest for optoelectronic applications such as light-emitting diodes (OLED) and photovoltaics (OPV)
- Characterization of the electronic band structure is vital to designing efficient charge transport systems
- Parameters of interest include work function, ionization potential, band gap, and electron affinity
- Ultraviolet photoelectron spectroscopy (UPS) is typically reported in the literature, but only provides half of the story of the band structure
- New and upgraded techniques are now available on PHI VersaProbe multi-technique XPS systems to fully characterize the entire band structure of organic electronic materials**



UPS provides valence band information only. With additional techniques, more information can be gained.



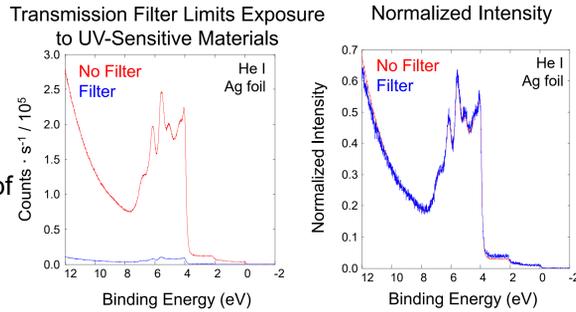
LEIPS is the inverse process of UPS and provides information on conduction band states.

Technique	Information Gained	Advantage of VersaProbe 4
UPS	Work Function Ionization Potential Valence Band Spectrum Highest Occupied Molecular Orbital (HOMO)	Optional source filter to reduce UV exposure of sensitive materials
LEIPS	Electron Affinity Conduction Band Spectrum Lowest Unoccupied Molecular Orbital (LUMO)	Low-energy incident electrons to minimize damage to organic materials

UPS (Ultraviolet Photoelectron Spectroscopy)

NEW Features:

- UV source operation fully integrated into SmartSoft acquisition software
- Optional filter attachment for reducing photon flux for analysis of UV-sensitive samples
- Decreased beam size: ~1.5 mm diameter



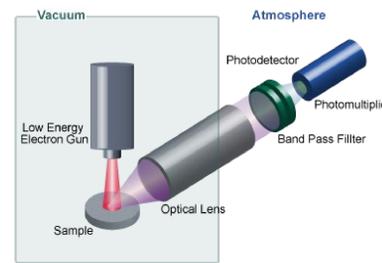
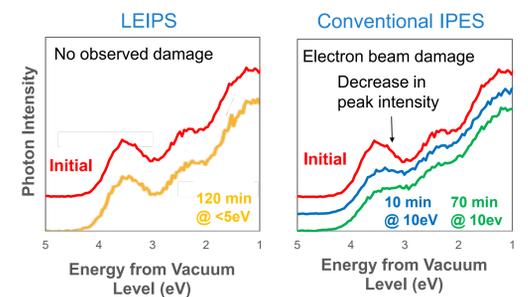
LEIPS (Low Energy Inverse Photoemission Spectroscopy)

How it Works (Isochromat mode):

- Electrons are emitted from BaO electron neutralizer source
- Sample stage is biased to achieve net electron incident energy < 5 eV
- As electrons fill unoccupied conduction band states, photons are emitted and detected using fixed wavelength detector
- Total electron current to sample is also measured for calibration of energy scale to calculate sample electron affinity

Key Features:

- Minimal damage to organic materials due to low energy of incident electrons
- Ability to measure electron affinities up to 6.42 eV with selectable band pass filters

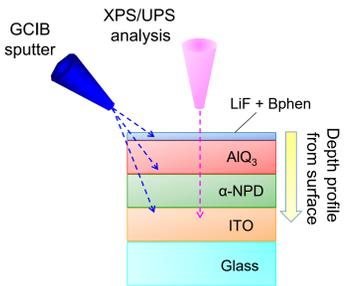


Schematic of LEIPS

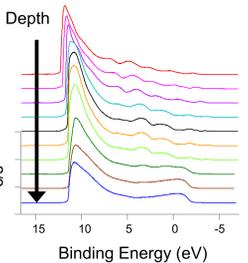
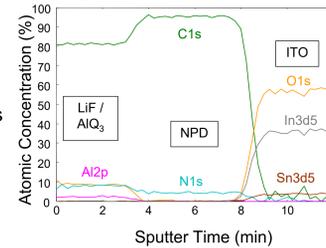
Conduction band spectra of C₆₀ film:

- (Left) LEIPS spectra uses < 5 eV electrons and shows minimal change to the peak shape and intensity even at long analysis times
- (Right) Using 10 eV electrons, similar to a conventional inverse photoemission spectroscopy (IPES) experiment, peak intensity and features show changes, suggesting chemical damage to the sample and lower confidence when determining electron affinity values.

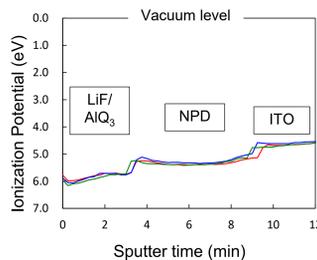
Application: XPS / UPS Depth Profile of Ionization Potential in Multilayer Film



XPS depth profile of a multilayer film stack using 5 keV Ar₂₅₀₀⁺ gas cluster ion beam (GCIB). In combination with UPS, it is possible to probe the individual layers and interfaces for chemical and electrical properties.

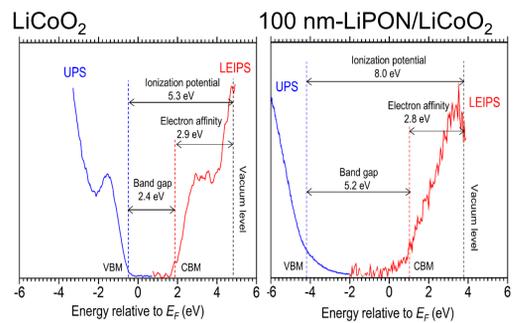
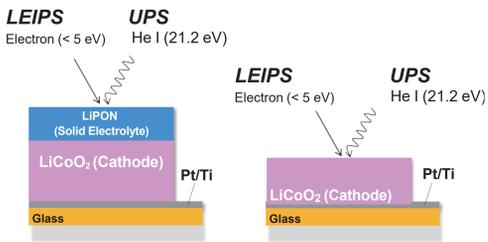


UPS spectra collected at each sputter cycle. -5V bias was applied to the stage during acquisition in order to measure both HOMO and secondary electron cutoff energy.

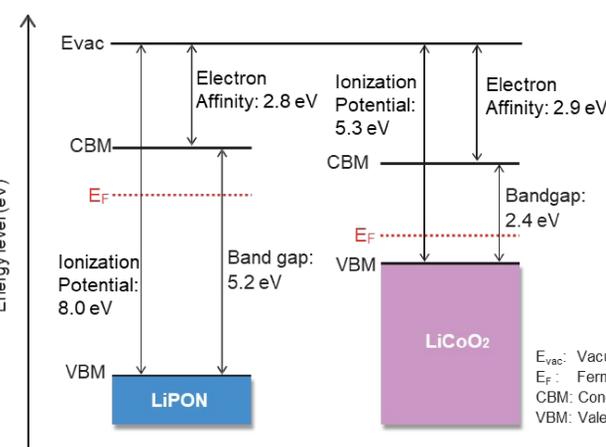


Depth profile of ionization potential as calculated from UPS spectra. Data from 3 similar samples shown for comparison.

Application: Energy Diagram of All Solid-State Battery



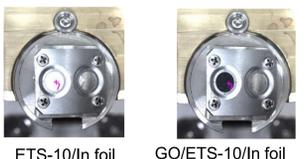
- Heating during the manufacturing process stimulates electron excitation in LIPON
- Electrons diffuse from LiPON to LiCoO₂ and facilitate Co reduction



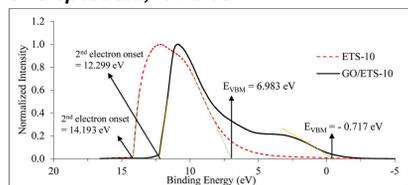
Oxidation/reduction of solid-state battery electrodes is greatly affected by its electrical characteristics. The energy diagram obtained by UPS/LEIPS enables predicting the chemical state and chemical reaction at the electrolyte/electrode interface! Solid electrolytes are often sensitive to electron beam irradiation and higher energy conventional IPES can cause significant damage to such samples. LEIPS, using a low-energy electron beam, is essential for proper energy diagram evaluation!

Evac: Vacuum levels
EF: Fermi energy
CBM: Conduction Band Minimum
VBM: Valence Band Maximum

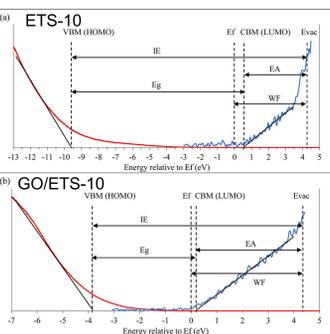
Application: Photocatalytic performance of Engelhard Titanosilicate-10



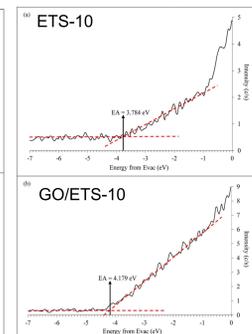
UPS spectrum, -5V bias



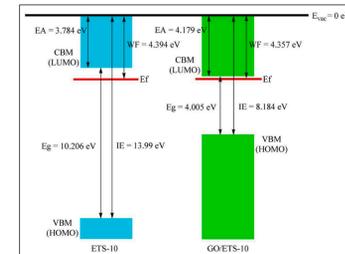
Combined UPS and LEIPS spectra



LEIPS spectrum



HOMO-LUMO energy level alignment diagram



GO/ETS-10 has lower Eg (4.0 eV) with HOMO and LUMO bands that were located closer to the Fermi level (EF), and a smaller work function (WF) indicating GO/ETS-10 requires lower thermodynamic energy to release an electron from a solid to a point in the vacuum immediately outside the solid surface

Acknowledgement

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References

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