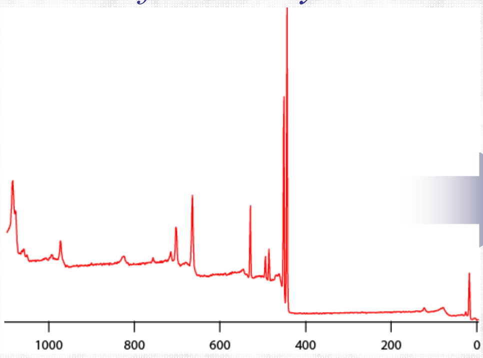
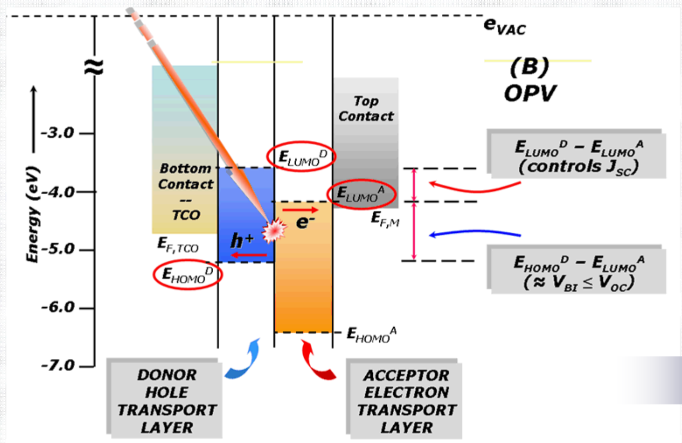
Using Surface Science to Probe Critical Interfaces in Organic and Hybrid Systems

SAND2010-1772P

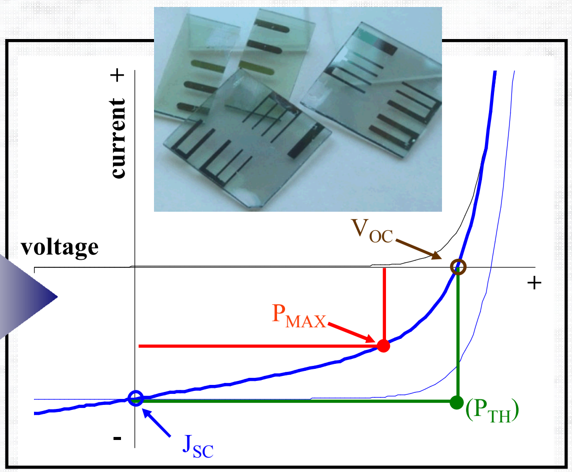
Surface analysis



Band structure



Real devices



Post-Doctoral and Recent Staff Seminar Series

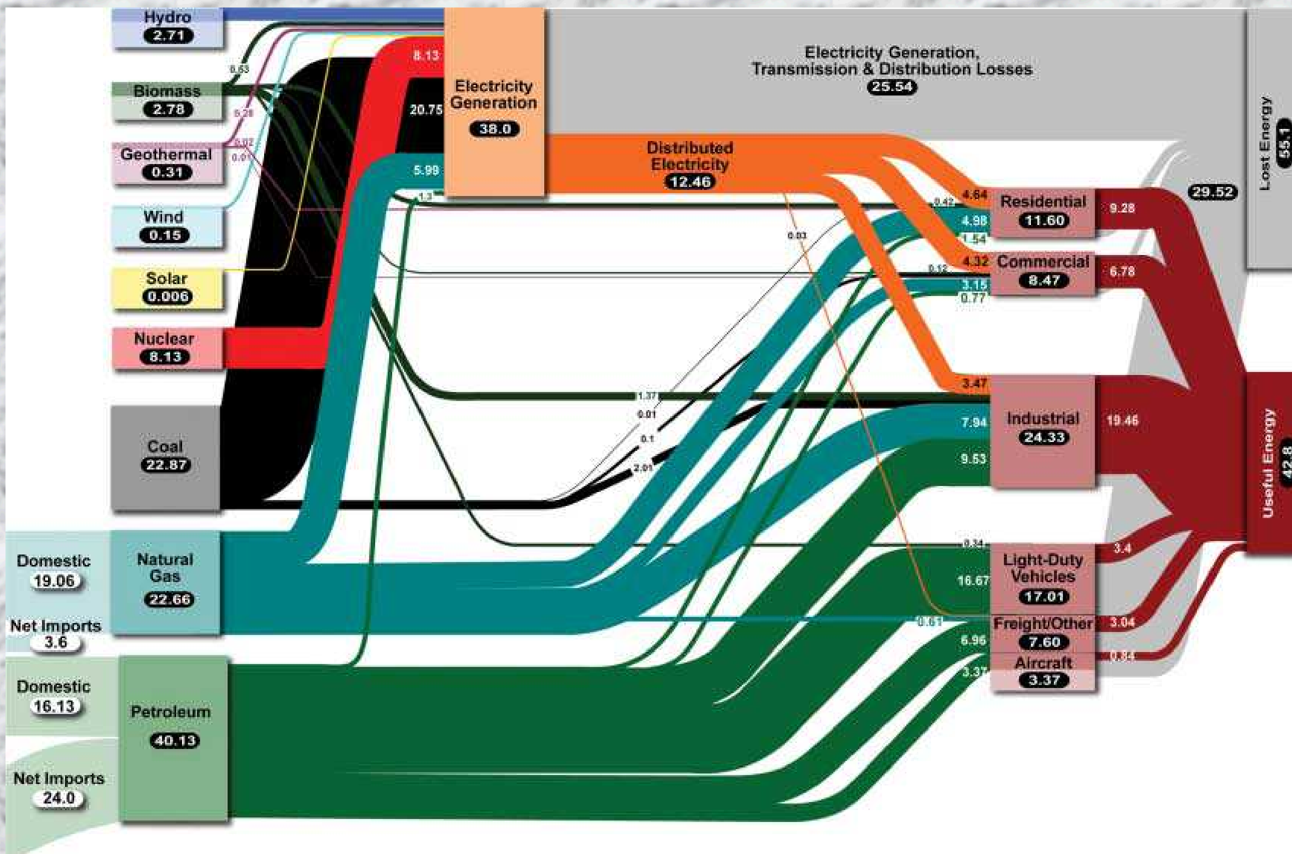
March 25, 2010

Michael T. Brumbach
1822 Materials Characterization (Surface Science Laboratory)

Sandia National Laboratories Laboratory Directed Research and Development Program
Sandia National Laboratories is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94Al8500.

Pursuit of Sustainable Energy Technologies

The Energy Story: U.S.A. $_{2005}$



Photovoltaic technology has tremendous potential: The supply of energy from the Sun to the Earth = 3 x 10^{24} J/year = 10,000 times the global energy usage

PV efficiency must increase (OPVs must reach 10-12%) *Cost* must decrease (DOE goal: $0.33/W)

Energy storage required to make PVs viable.

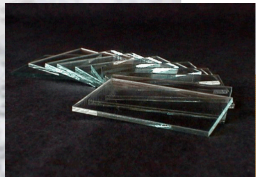
Sustainable energy devices require significant improvements for widespread utilization. Surface science is critical for understanding their operation and for leading rational design and optimization of these devices.

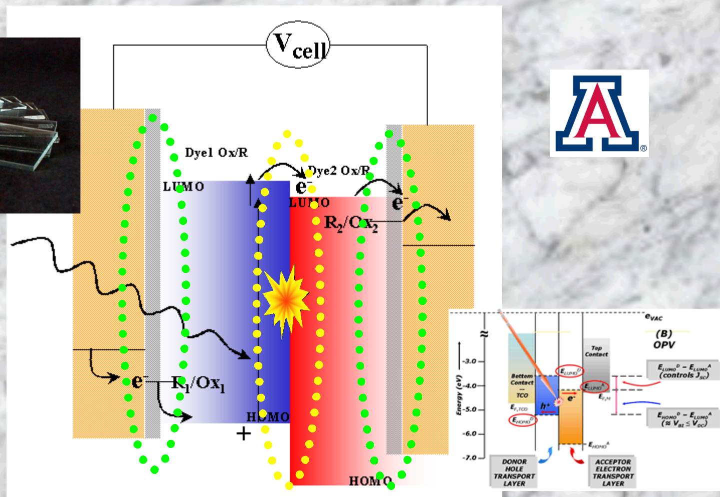
Units in Quads → 1 Quad = 10^{15} BTU

G. Whitesides. *Science*, (2007) **315**, 796.

Outline

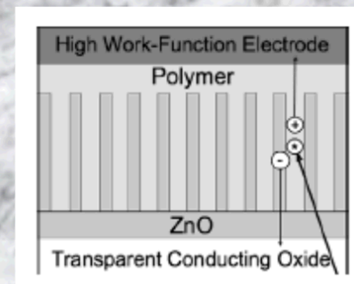
XPS/UPS and Organic Photovoltaics

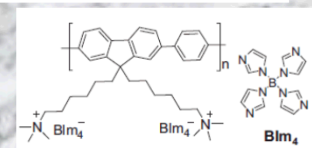


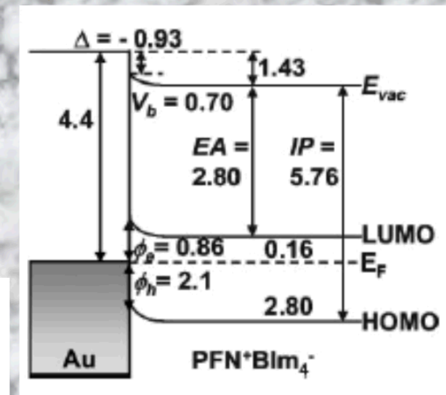


Proposed Work on Hybrid Interfaces

- Early Career LDRD – Inorganic/Polymer interfacial characterization

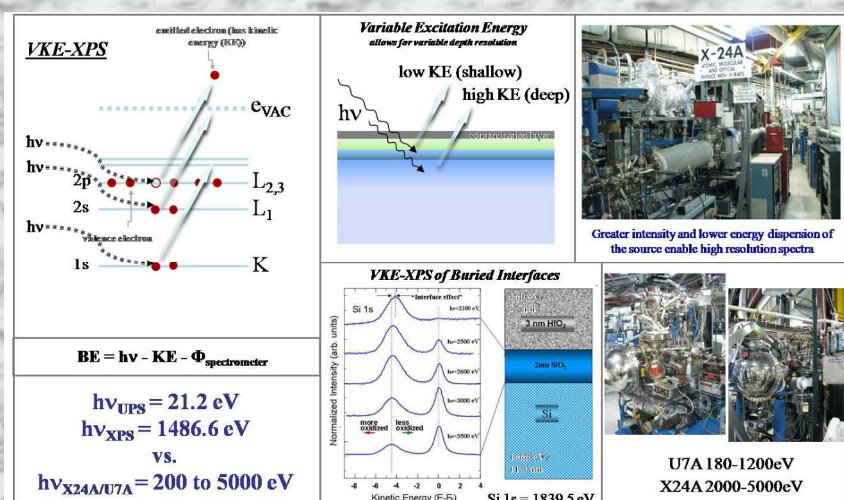






Variable Energy XPS

- National Synchrotron Light Source – RTBF - Erbium



Surfaces Science Lab

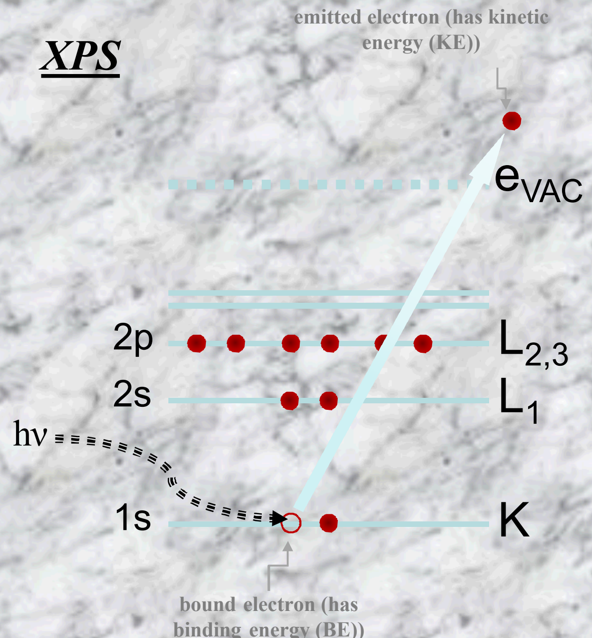
- VKE-XPS – NEXAFS – ToF-SIMS – AES – AFM -

Introduction to X-ray Photoelectron Spectroscopy

XPS characterizes core level electrons

- Chemical Analysis – Chemical Environment – Oxidation State – Electronic Environment -

XPS

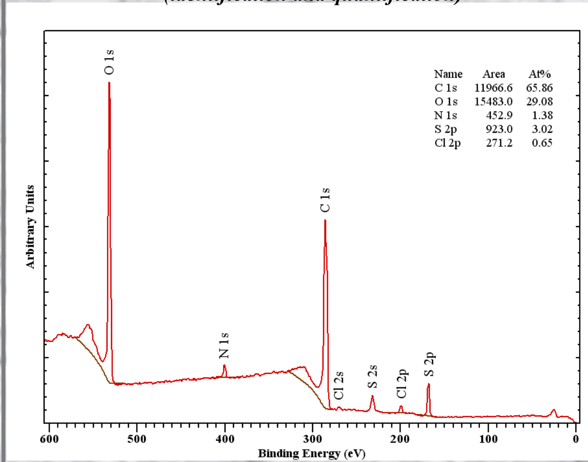


$$BE = h\nu - KE - \Phi_{spectrometer}$$

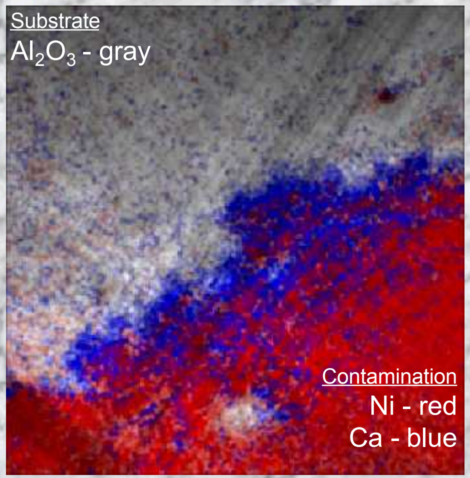
The inelastic mean free path (IMFP or λ) of an emitted electron makes XPS a very surface sensitive technique.

Compositional Analysis

(identification and quantification)

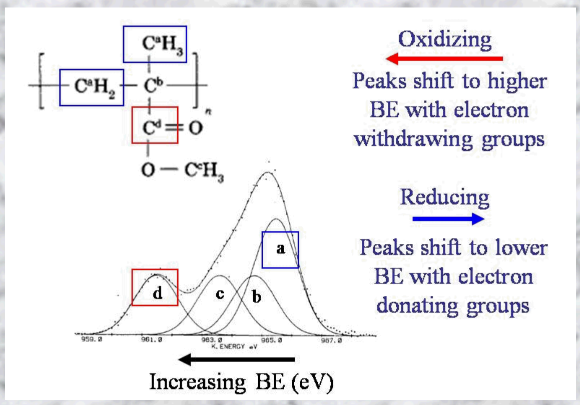


Chemical Imaging



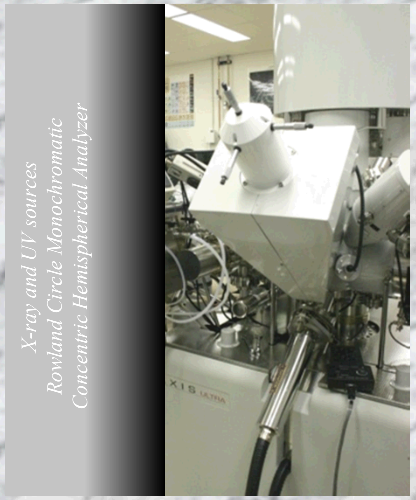
Peak Fitting for Chemistry

(valence and chemical environment)



Pijpers, Donners, *J. Polym. Sci. Chem. Ed.* (1985) **23**, 453.

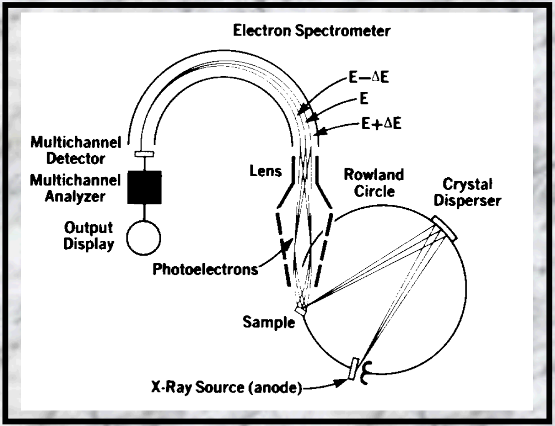
Kratos Axis Ultra DLD



Introduction to X-ray Photoelectron Spectroscopy

XPS characterizes core level electrons

- Chemical Analysis – Chemical Environment – Oxidation State – Electronic Environment -



XPS Instrumentation

-- X-ray (Al Kα @ 1486.6 eV, Mg),
-- UV (Omicron, He I @ 21.2 eV, He II)
-- Rowland Circle monochromator
-- Concentric Hemispherical Analyzer, DLD detector
-- 0.3 to 0.4 eV resolution

$$\mathbf{BE = h\nu - KE - \Phi_{spectrometer}}$$

Inelastic mean free path (IMFP or λ): the average escape depth for electrons in a particular material

-Initial e^- energy

-Nature of the medium

Compositional Analysis

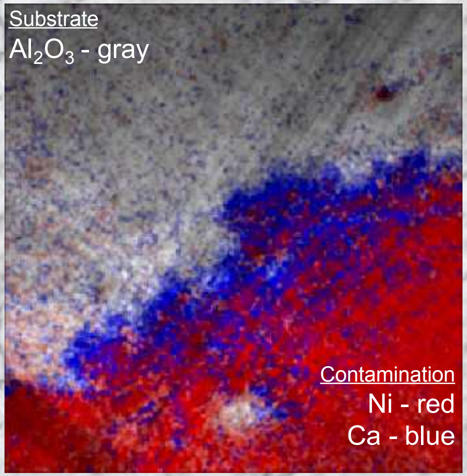
(identification and quantification)

• Surface Sensitive!

•What is the chemical nature of my material?

•Identification/quantification of composition *(~1% LOD) - Peak areas proportional to concentration – depth profiling (surface vs. bulk), segregation?*

Chemical Imaging



Peak Fitting for Chemistry

(valence and chemical environment)

• Surface Sensitive!

•How are adsorbants interacting with the surface? – ***surface bonding***

•What is the ***oxidation state*** *of species within my material? At the surface vs. bulk?*

•How is charge flowing from one material to another at an interfacial contact?

Kratos Axis Ultra DLD

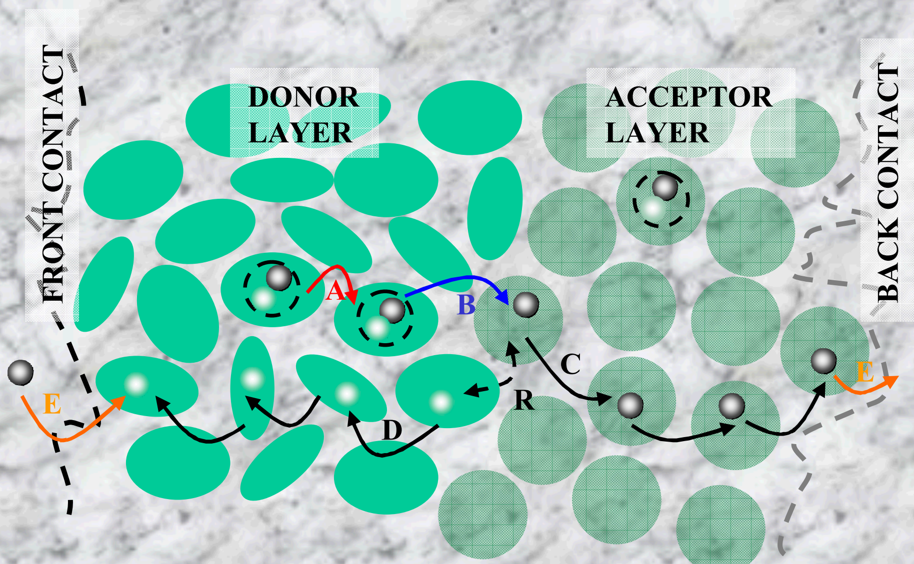
--

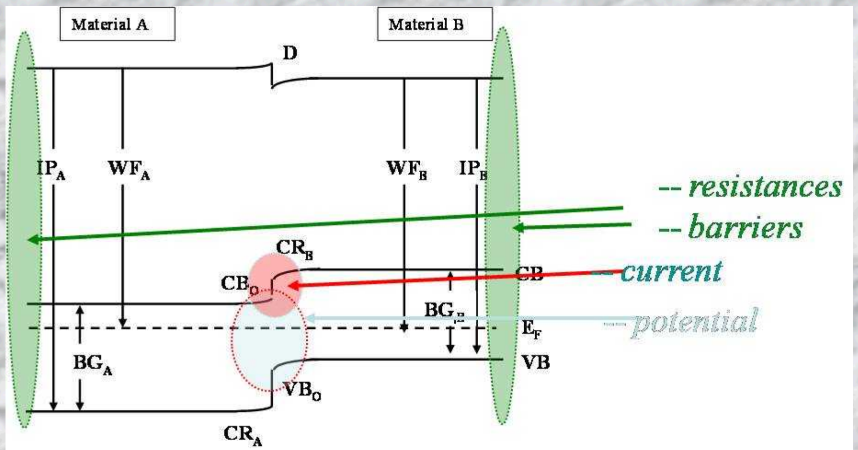
-- imaging (spatial resolutions as low as 10 microns)
-- depth profiling
-- valence band analysis
-- integrated Ar glove box for inert sample transfer
-- all elements (except H and He)

Photovoltaic Devices and Interfaces

Charge generation, separation, and collection occur at interfaces.

Bilayer Organic Photovoltaicc





The efficiency of a solar cell is a combination of the efficiencies of multiple individual processes, all of which can be evaluated by understanding an energy level diagram.

Light absorption (solar spectrum)

Exciton dissocation (recombination)

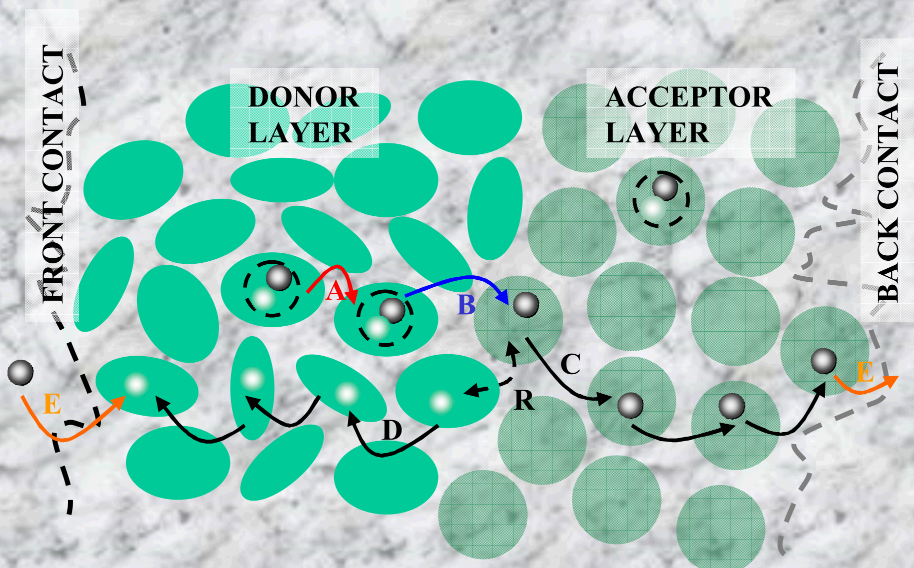
Charge transport (resistance)

Charge collection (barriers)

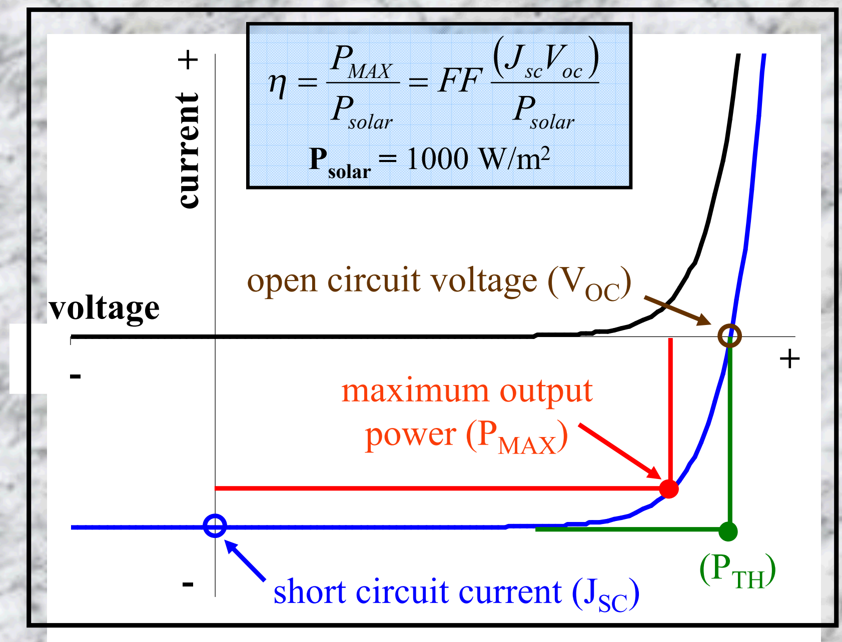
Photovoltaic Devices and Interfaces

Charge generation, separation, and collection occur at interfaces.

Bilayer Organic Photovoltaicc



Photovoltaic Performance
Current as a function of Voltage

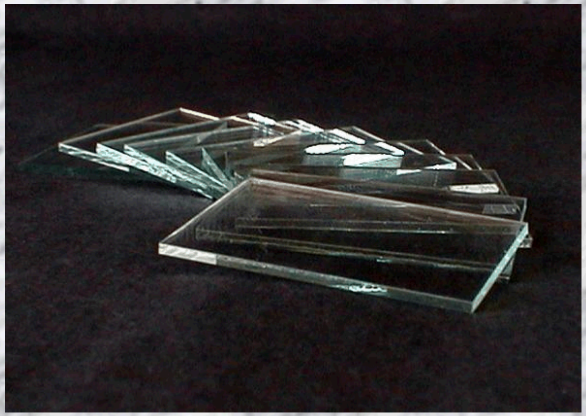


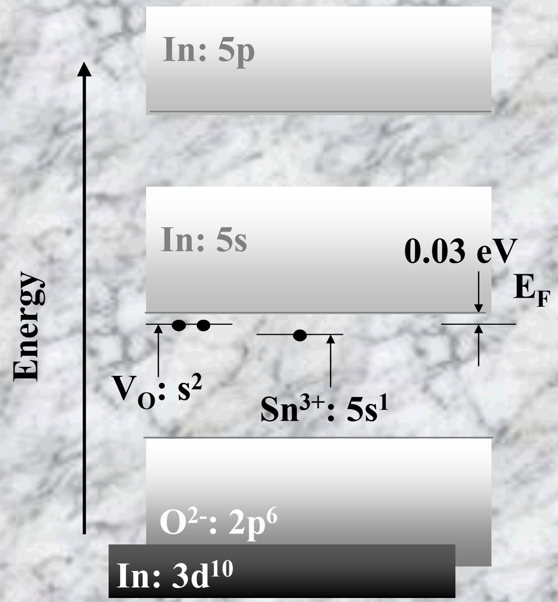
Interface properties must be understood and controlled to optimize the performance of the organic photovoltaic.

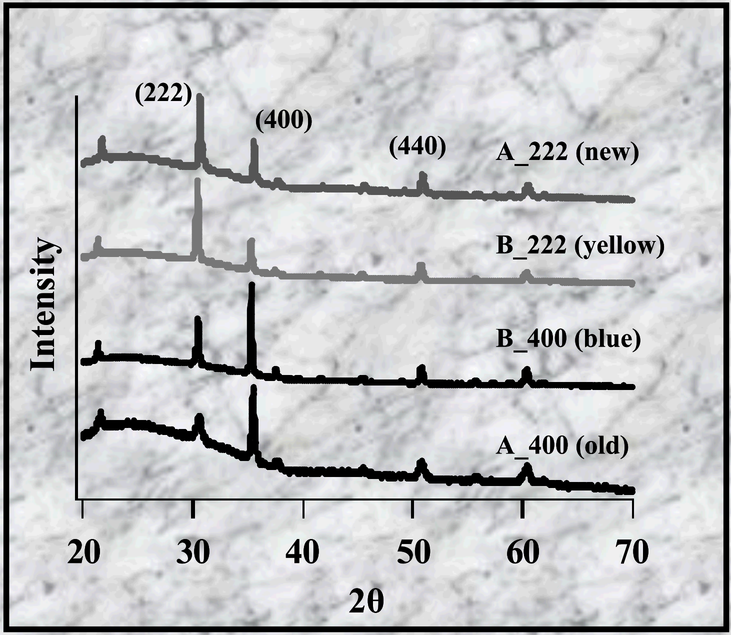
Focus on understanding the physical and electronic structure of these interfaces.

Indium Oxide (ITO) is a Critical TCO

- ITO acts as the substrate for the entire OPV structure → can influence device fabrication
- ITO is used as a key electrode for multiple technologies (LED, PV, electrochromics)
- Surface properties of ITO can dictate charge transfer properties







Commercial ITO is poorly characterized and controlled.

Batch-to-batch variations

-Doping – Crystallinity – Thickness – Conductivity – Transparency – Roughness –

Thin film deposition (sputter deposition) parameters must be stringently controlled.

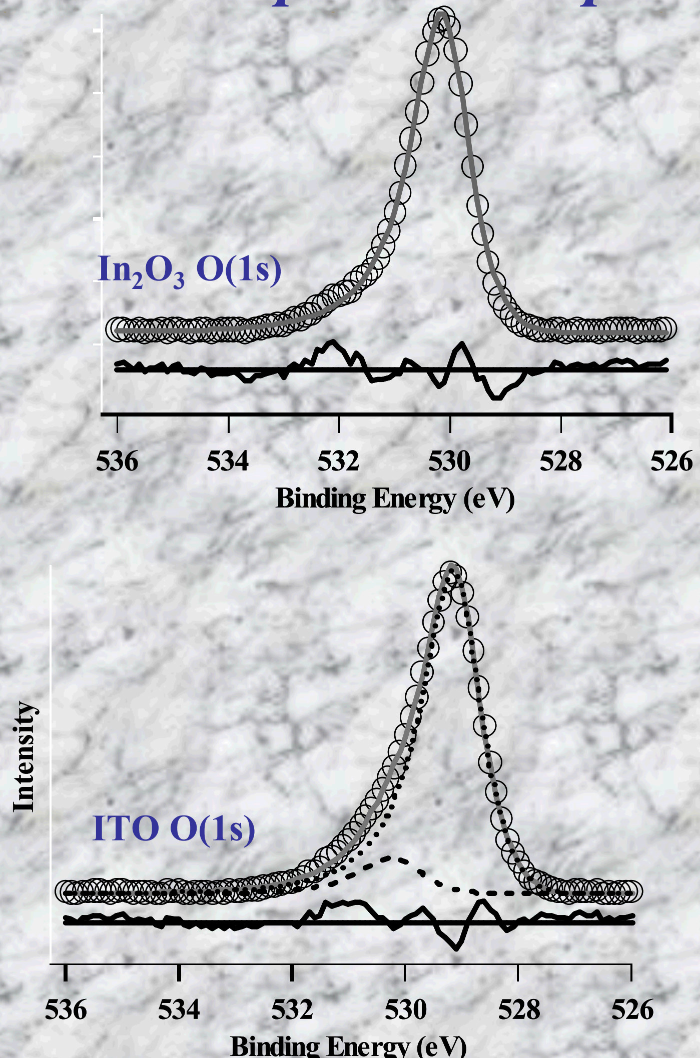
Doping levels: tin and oxygen vacancy concentration

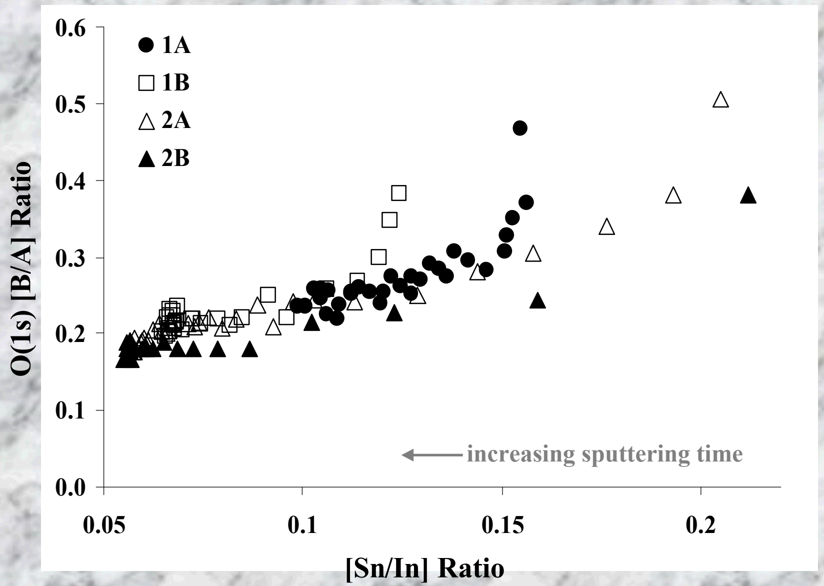
Annealing conditions

Fan and Goodenough, *J. Appl. Phys.* (1977) **48** 3524.

Identification of O(1s) Component Related to Tin

Comparison of native In_2O_3 surface with native ITO reveals a spectral component of the O(1s) related to tin.





- Baseline spectral components for ITO O(1s) established.

- Identification of O(1s) component related to tin doping.

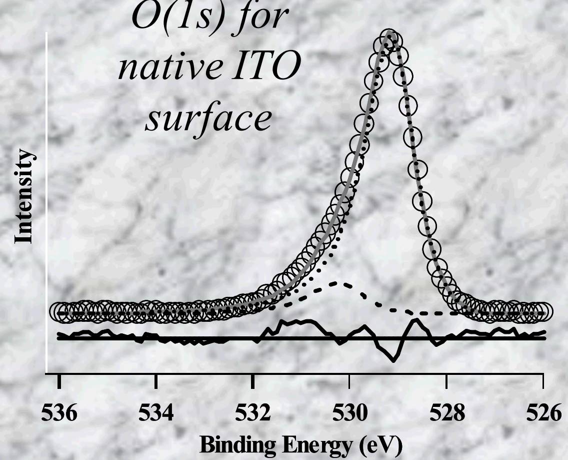
w/ Thomas Schulmeyer

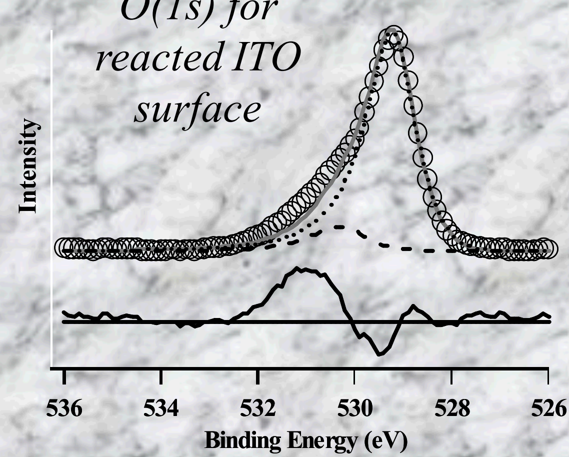
Brumbach, *et. al., Langmuir.* (2007) **23**, 11089-99.

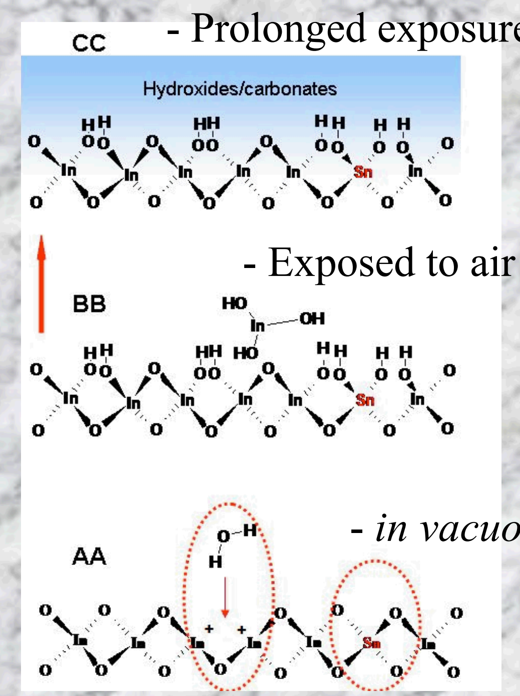
Indium Tin Oxide (ITO) – Baseline O(1s) Spectra

Hydroxylation of ITO occurs rapidly

Passive layer formation between electrode and active organics!







Exposure to atmosphere leads to extensive hydroxylation, ill-defined contamination

- Difficult to adequately remove contamination and control ITO surface

- Presence of passive/insulating layer leads to contact resistance in a device!

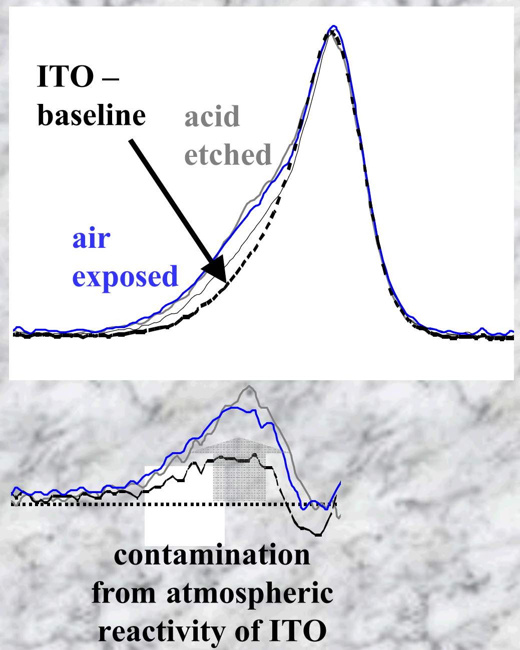
w/ Thomas Schulmeyer

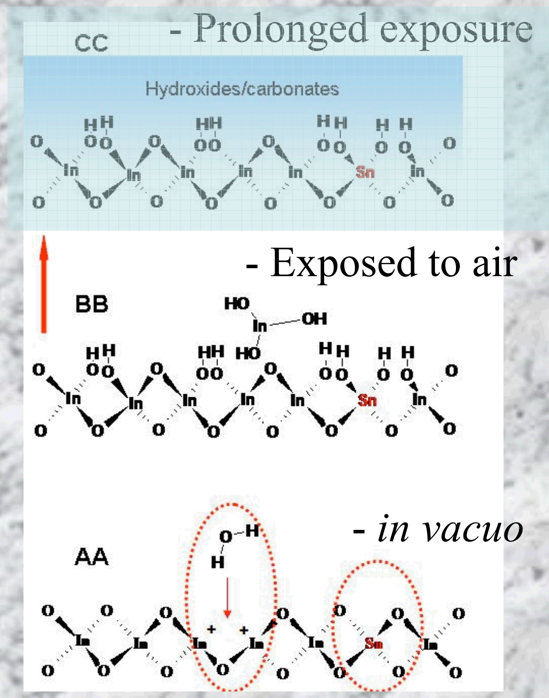
Brumbach, *et. al., Langmuir.* (2007) **23**, 11089-99.

Acid Etching for Surface Preparation

Controlled acid etching removes contamination and produces clean, native surface

Passive layer formation occurs spontaneously, but can be controlled and reproduced.





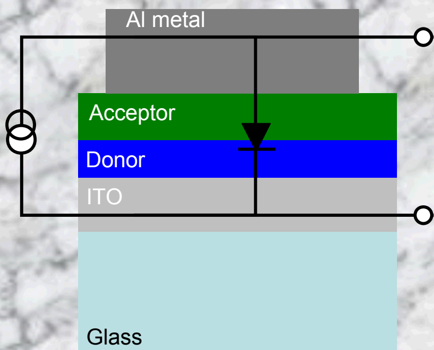
Strong halo-acids etch ITO (HI, HCl/HNO_3, $HCl/FeCl_3$) - brief exposure to remove surface layer.
Creates clean, reproducible surface.
Other "cleaning" procedures merely modify the contamination layer – previous XPS studies.
Changing contamination layer has led to "erroneous" device data.

Brumbach, *et. al.*, *Langmuir.* (2007) **23**, 11089-99.

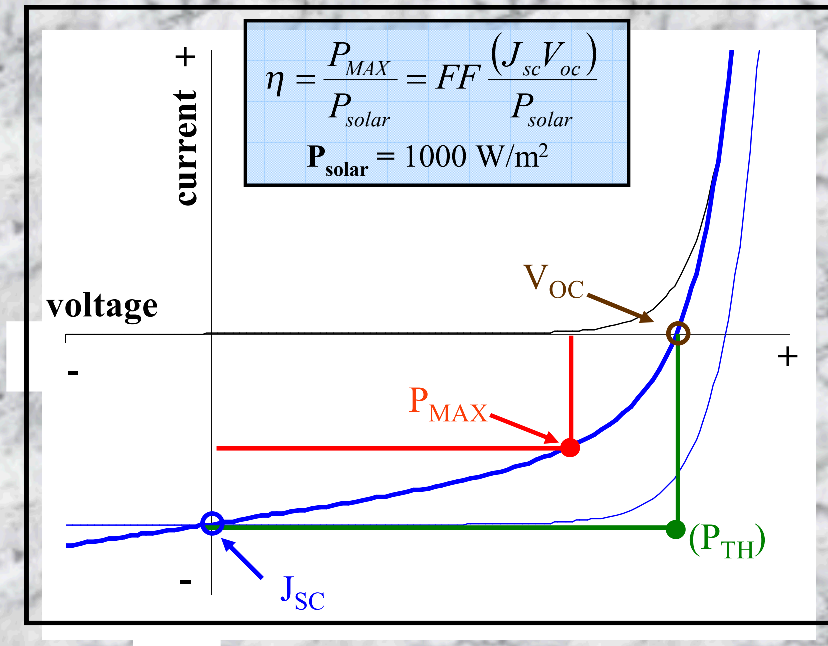
Real OPV Performance

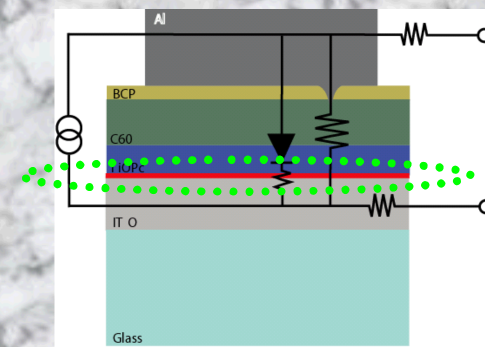
Real device performance deteriorates from ideal behavior

- Parasitic resistances - Contact resistance – Leakage pathways -



$$J = J_o\left(\exp\left(\frac{V}{n_o k_B T/e}\right)-1\right)$$



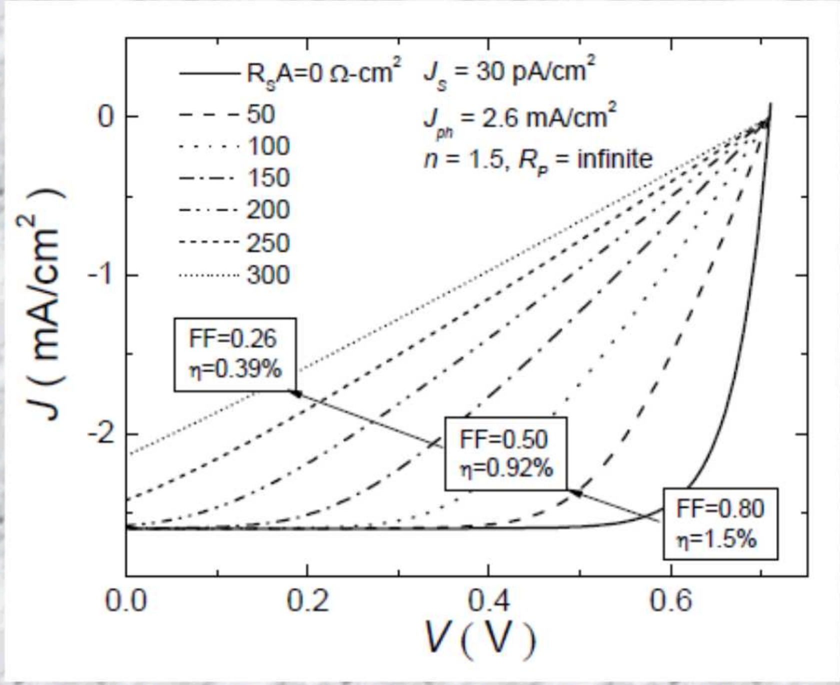


$$J = J_o\left(\exp\left(\frac{V - JR_s A}{n_o k_B T/e}\right)-1\right) + \frac{V - JR_s A}{R_p A}$$

The contact at the ITO interface can be influenced by contamination leading to a contact resistance in the device.

Influence of Series Resistance

Seunghyup Yoo, *PhD Dissertation, University of Arizona.* (2005).



Increasing series resistance degrades FF and J_{SC}.

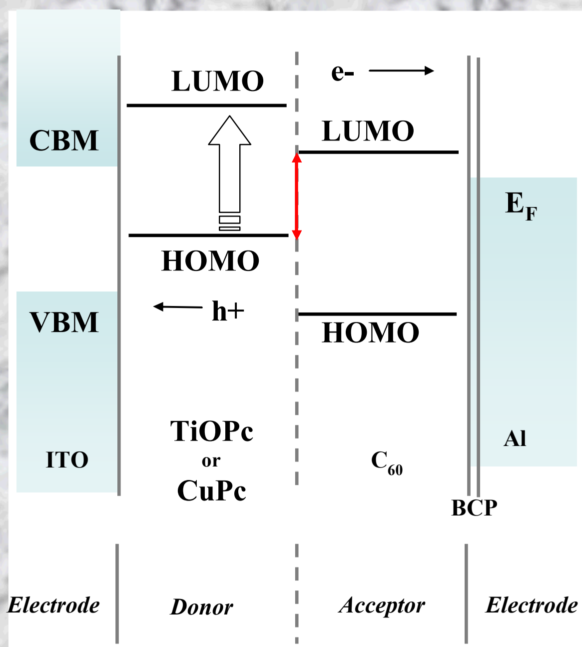
Strategies for reducing surface contamination are required to reduce contact resistance and overall series resistance…

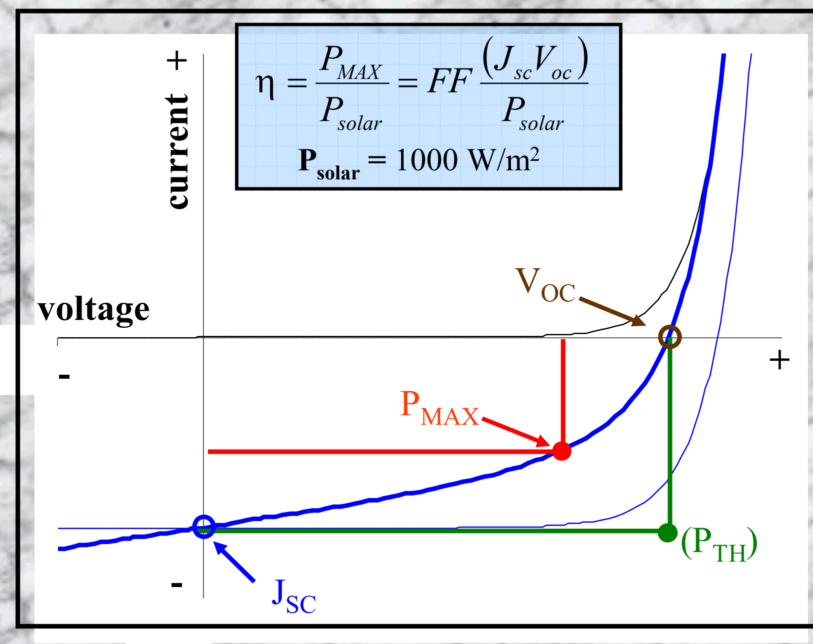
Acid etching of surface

Surface modification

TiOPc for Planar Heterojunction OPVs

Utilizing UPS to understand the role of organic/organic' heterojunctions in bilayer OPVs.





Donors

Copper Phthalocyanine (CuPc)

Titanyl Phthalocyanine (TiOPc)

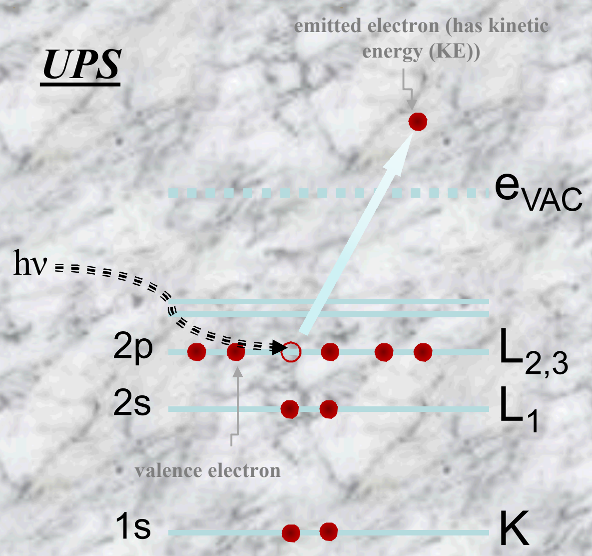
Acceptor

C_{60}

Introduction to UV Photoelectron Spectroscopy

UPS characterizes valence band electrons

- Material work function – Ionization potential – Highest occupied molecular orbital (HOMO) -



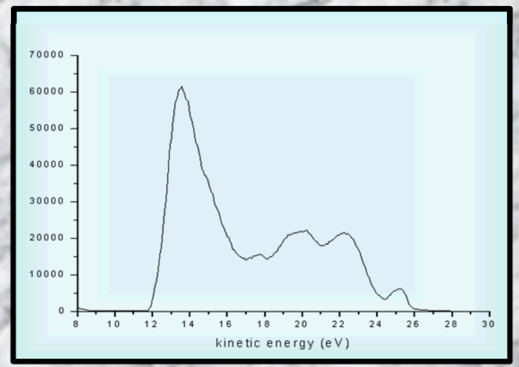
BE = hν - KE - $\Phi_{spectrometer}$

$h\nu_{UPS}$ = 21.2 eV

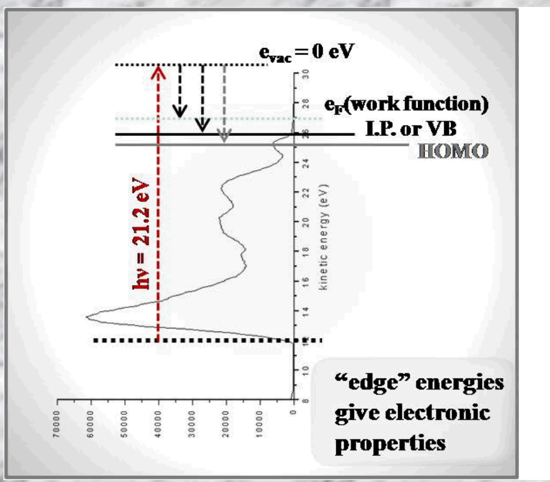
vs.

$h\nu_{XPS}$ = 1486.6 eV

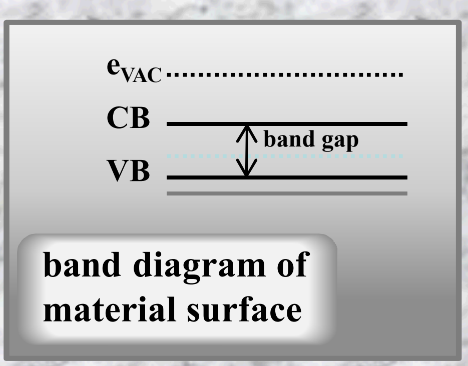
UPS spectrum of an organic thin film



Spectral Interpretation



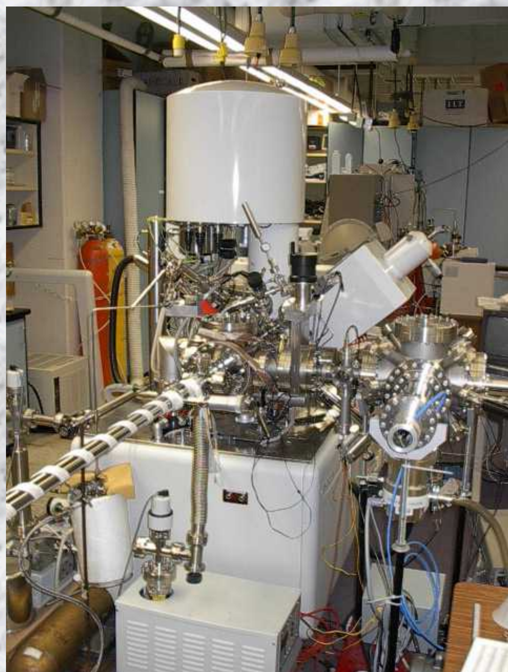
Band Diagram

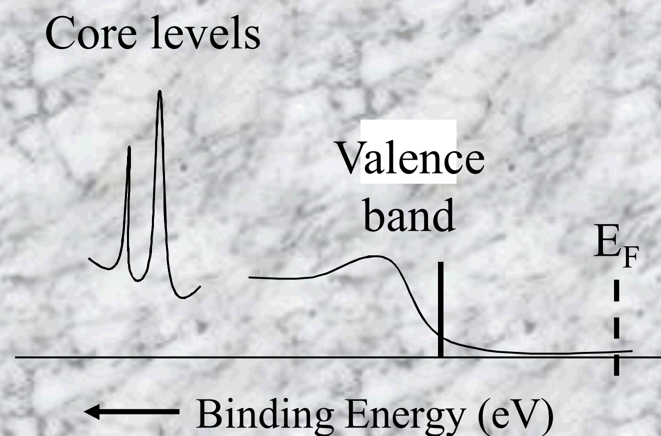


- *What is the **work function**? – electrode selection*
- *How does the work function change with adsorbants? – **charge injection barriers, surface dipoles***
- *What is the material **ionization potential**?*

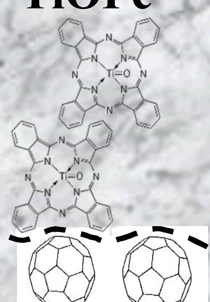
Energy Level Alignments - Methodology

In situ interface preparation - sequential growth of film on substrate – track shifts.





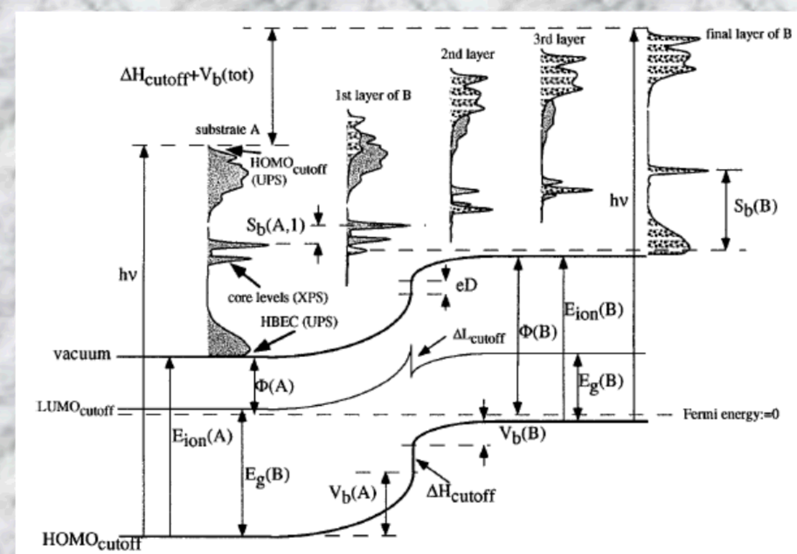
TiOPc



C_{60}

C(1s)
Ti(2p) or Cu(2p)
O(1s)
N(1s)
VBM

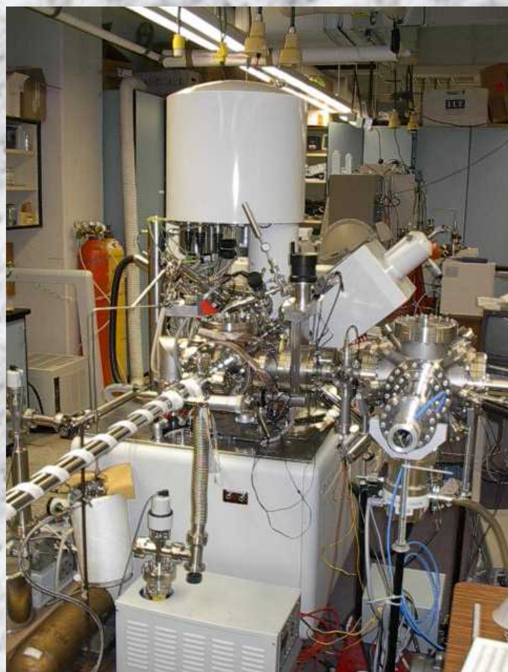
(issues for organics: resolution, interferences, lack of VBM)



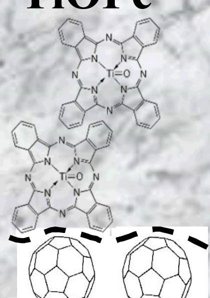
Schlaf, *et. al., J. Phys. Chem. B.* (1999) **103**, 2984-92.

Energy Level Alignments - Methodology

In situ interface preparation - sequential growth of film on substrate – track shifts.



TiOPc



C_{60}

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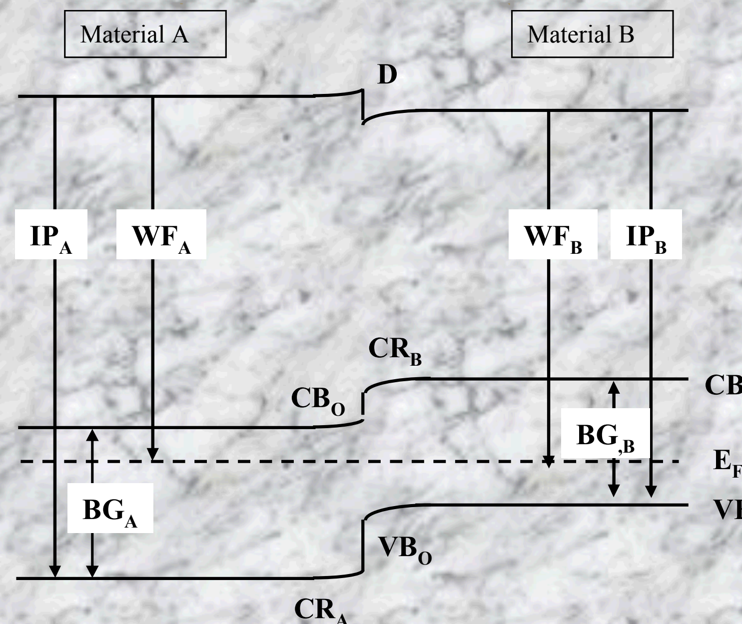


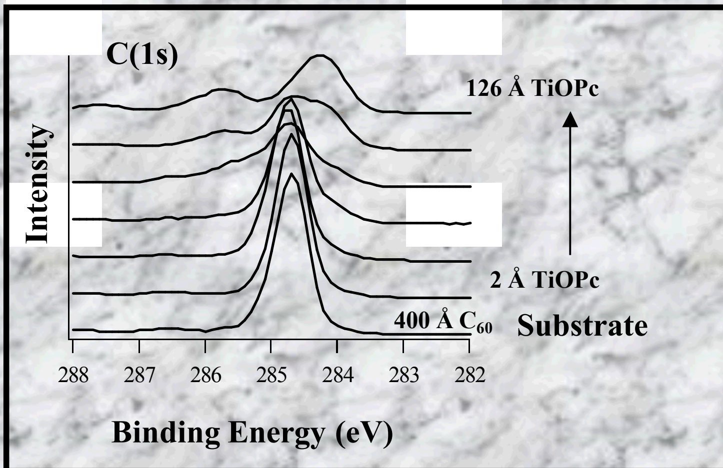
IP = ionization potential
WF = work function
BG = band gap
CR = charge redistribution
CB_O = conduction band offset
VB_O = valence band offset
D = dipole

Band Alignment at p/n junction

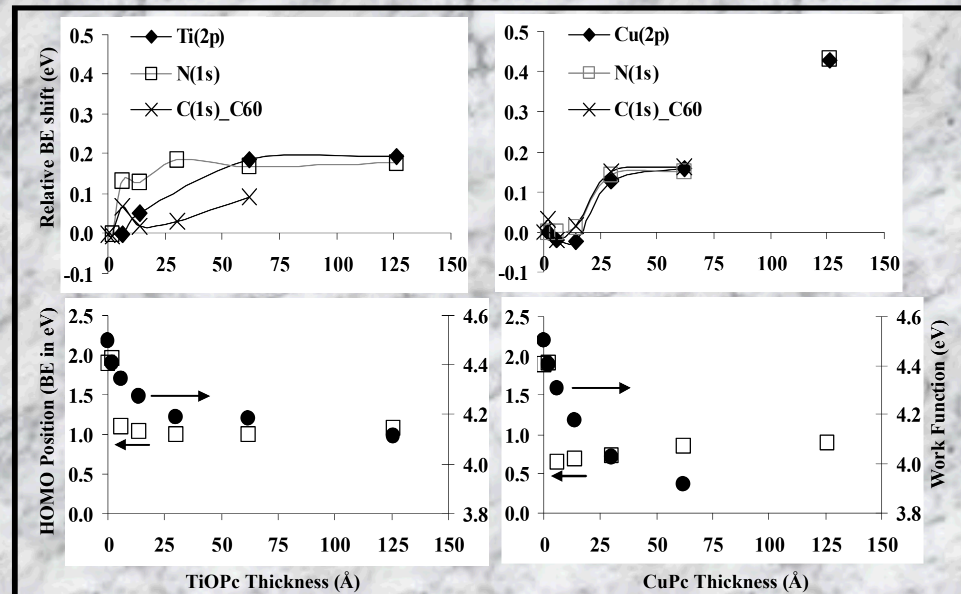
dipole, band bending/charge redistribution, work function, ionization potential, ...

Energy Level Alignments – Energy Level Shifts

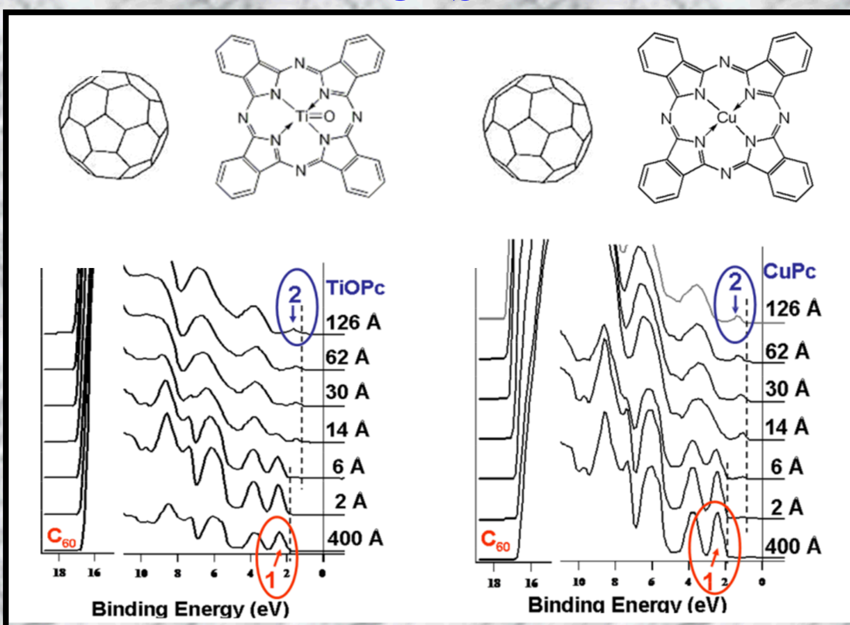
XPS



XPS: shifts in the core levels → charge redistribution
UPS: work function, ionization potential, HOMO position



UPS



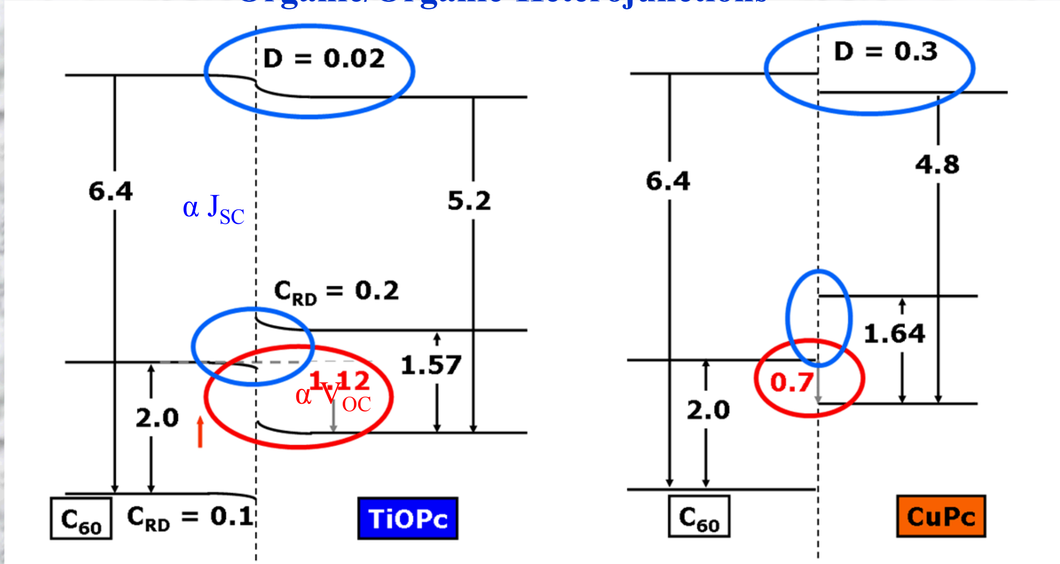
Core level shifts of Ti(2p) and N(1s) indicate charge redistribution (CR) in TiOPc.
Core level shift of C(1s) indicates CR in C_{60}.
Large step in HOMO position suggests dipole.
Charging apears to dominate shifts in CuPc spectra.

Brumbach, *et. al., J. Phys. Chem. C.* (2008) **112**, 3142-51.

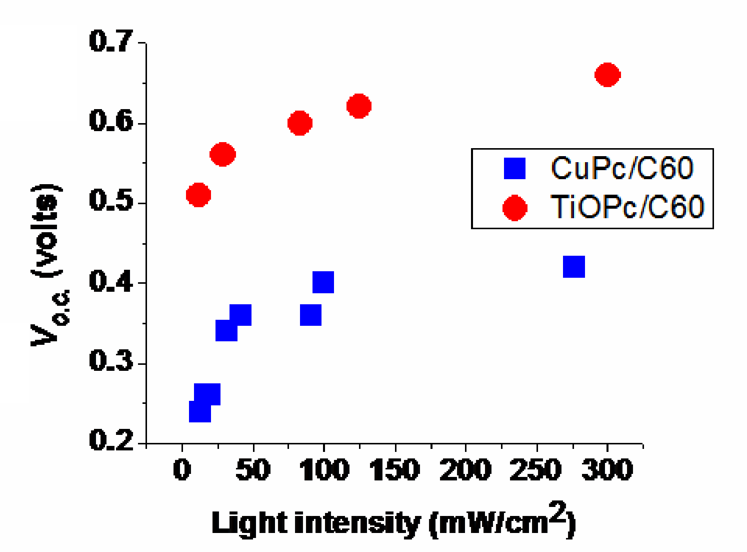
Energy Level Alignment and V_{OC}

Energy level alignments explain multiple device performance characteristics. (J_{SC}, V_{OC}, diode properties) Some parameters of the energy level alignment (offset magnitudes, charge redistribution, dipoles, etc.) still require further investigation.

Energy Level Alignments for Bilayer Organic/Organic Heterojunctions



Open Circuit Potential Correlates to HOMO/LUMO Offset of Bilayer



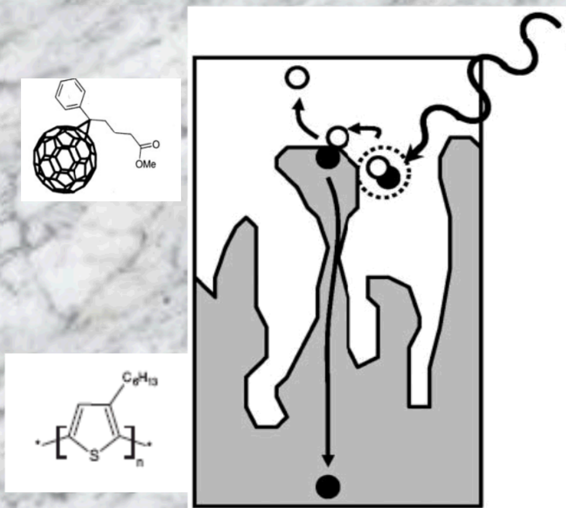
	Electrochemical Potential	Ionization potential	Offset Potential	V_{OC} (mV)
TiOPc	1.39 V	5.2 eV	1.12 eV	600 ± 20
CuPc	1.19 V	4.8 eV	0.7 eV	350 ± 10

Brumbach, *et. al., J. Phys. Chem. C.* (2008) 112, 3142-51.
Armstrong, Brumbach, *et. al. Macromolecular Rapid Communications (2009) 30, 717-31.*
Armstrong, Brumbach, *et. al. Accounts of Chemical Research (2009) 42, 1748-57.*

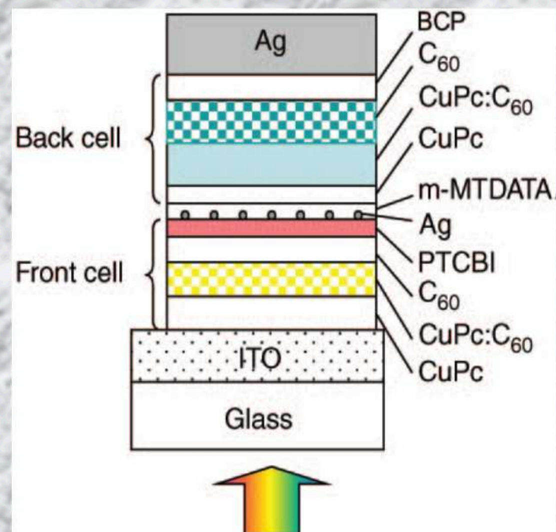
OPV Nanosystems

Strategies for improving efficiency → 3D (nano)architectures
→ create a device which is mostly interface

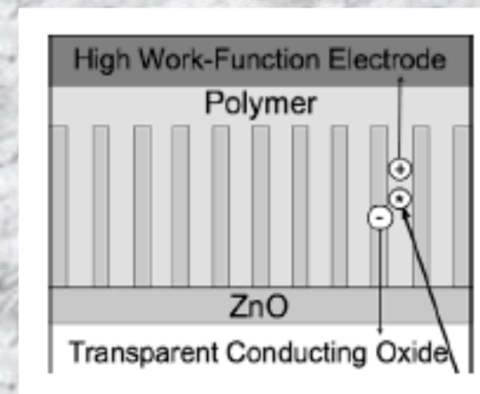
Bulk Heterojunction



Tandem Devices



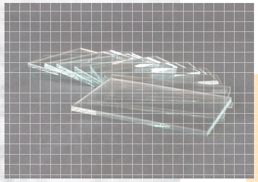
Hybrid Devices

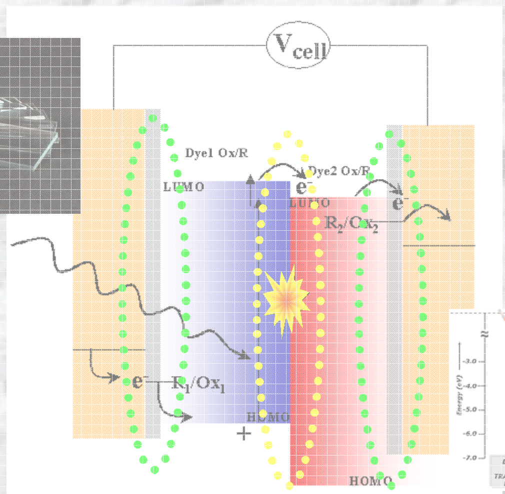


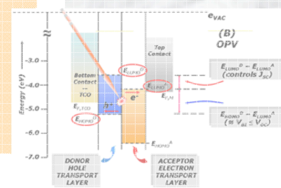
Optimization of interface energetics becomes increasingly more critical as interfacial contact areas begin to comprise the structure of a device

Outline

XPS/UPS and Organic Photovoltaics

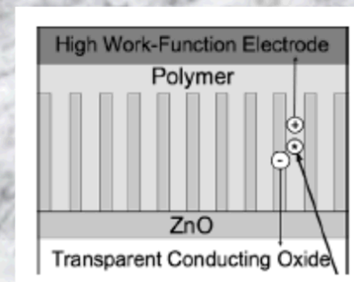


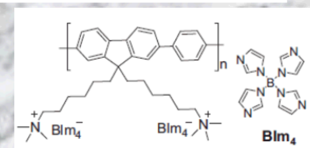


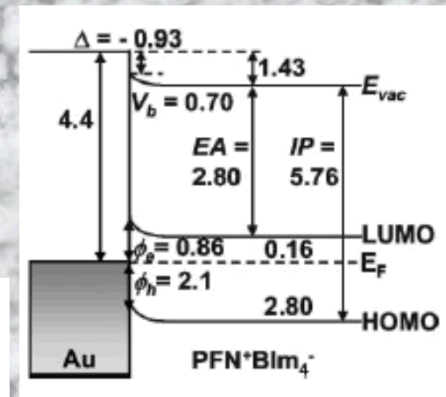


Proposed Work on Hybrid Interfaces

- Early Career LDRD – Inorganic/Polymer interfacial characterization

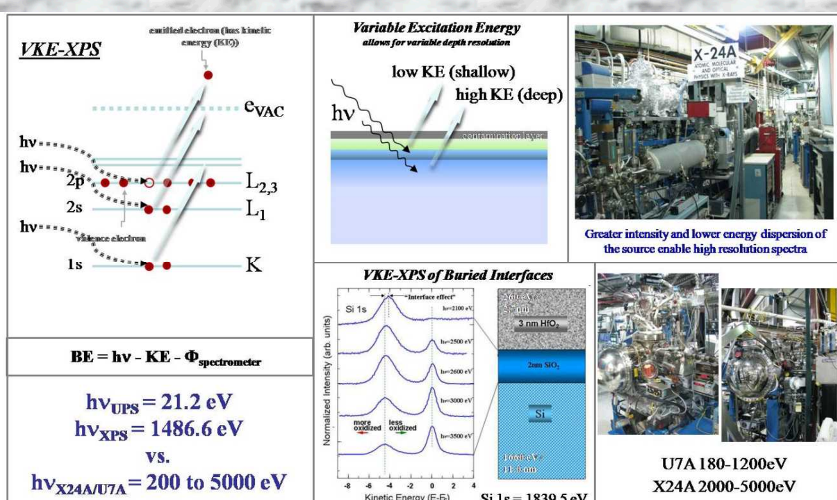






Variable Energy XPS

- National Synchrotron Light Source – RTBF - Erbium

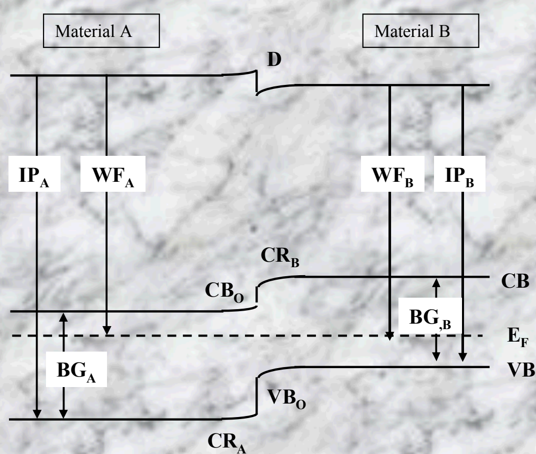


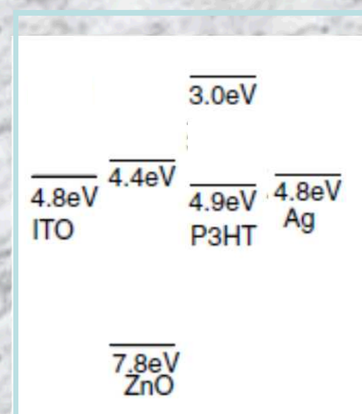
Surfaces Science Lab

- VKE-XPS – NEXAFS – ToF-SIMS – AES – AFM -

Polymer Interfaces are Not Well Characterized

Energy level alignments for many organic/organic and organic/inorganic systems are not known.
→ Reported values are inconsistent!
→ correct values? or just wrong? -Different measurements
→ different results - Interfacial chemistry and effect of structure have not been examined.
Offsets are unknown. Band bending not evaluated. (polymer morphology) (doping/dedoping)
→effect of band bending is unknown





Most work has assumed bulk properties remain unchanged at the interface.

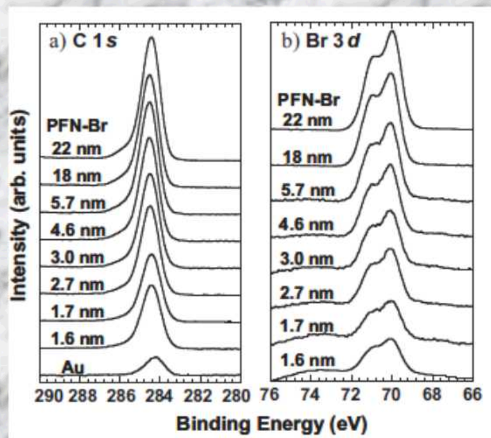
Complications for hybrid (inorganic/polymer) interfaces:
Polymers must be deposited ex situ.
- characterization experiments are more difficult to perform
- "contamination" is always present in experiments performed ex situ
Surface contamination is present in real devices, but has generally been excluded in characterization experiments. *(the impact/effect of contamination is essentially unknown!)*

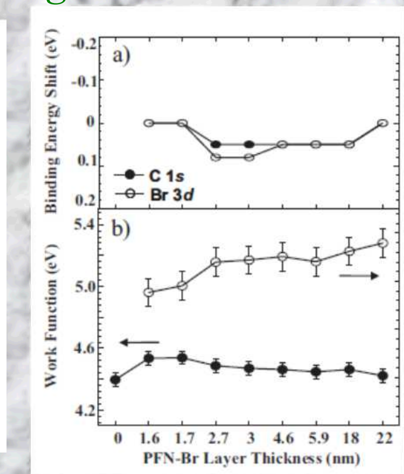
Previous Polymer Characterizations

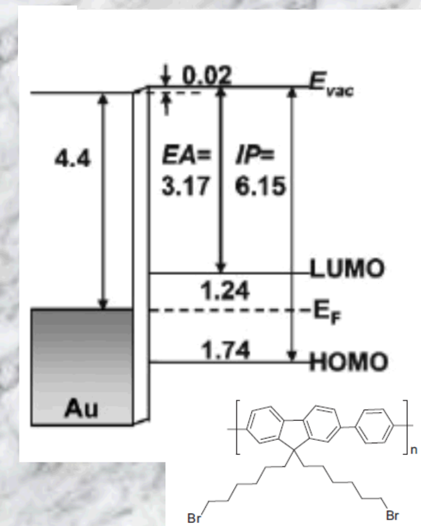
Nguyen, *et. al. Adv. Mater.* (2009) **21**, 1006-11.

Some examples of electronic characterization of hybrid interfaces are emerging in the literature. Characterizations typically follow established protocols for inorganic systems.

XPS for characterizing charge redistribution



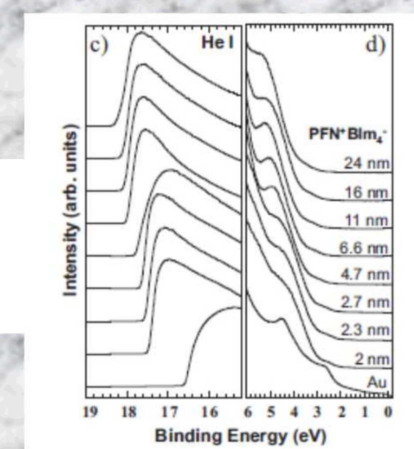


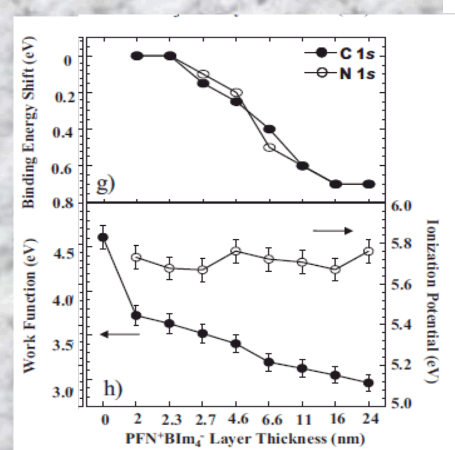


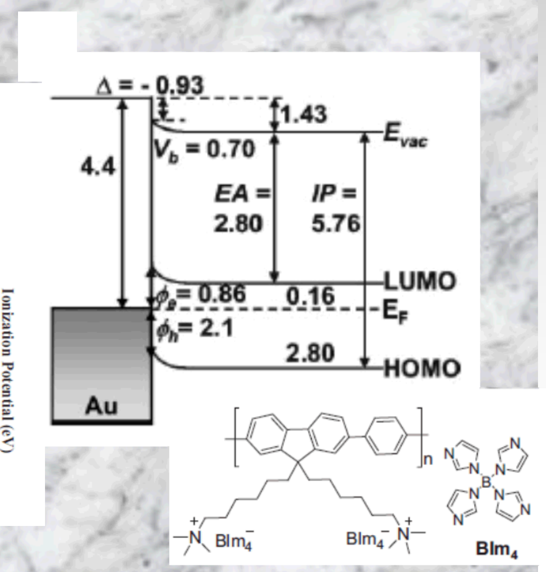
Schlaf
- in situ electrospray
  - MEH-PPV/ITO
  - MEH-PPV/Ag
  - P3HT/HOPG
  - P3HT/ITO

Ramsey
Koch
Kahn
- vacuum deposition of small molecules, IPES
  - organic/metal

UPS for characterizing W.F., I.P.







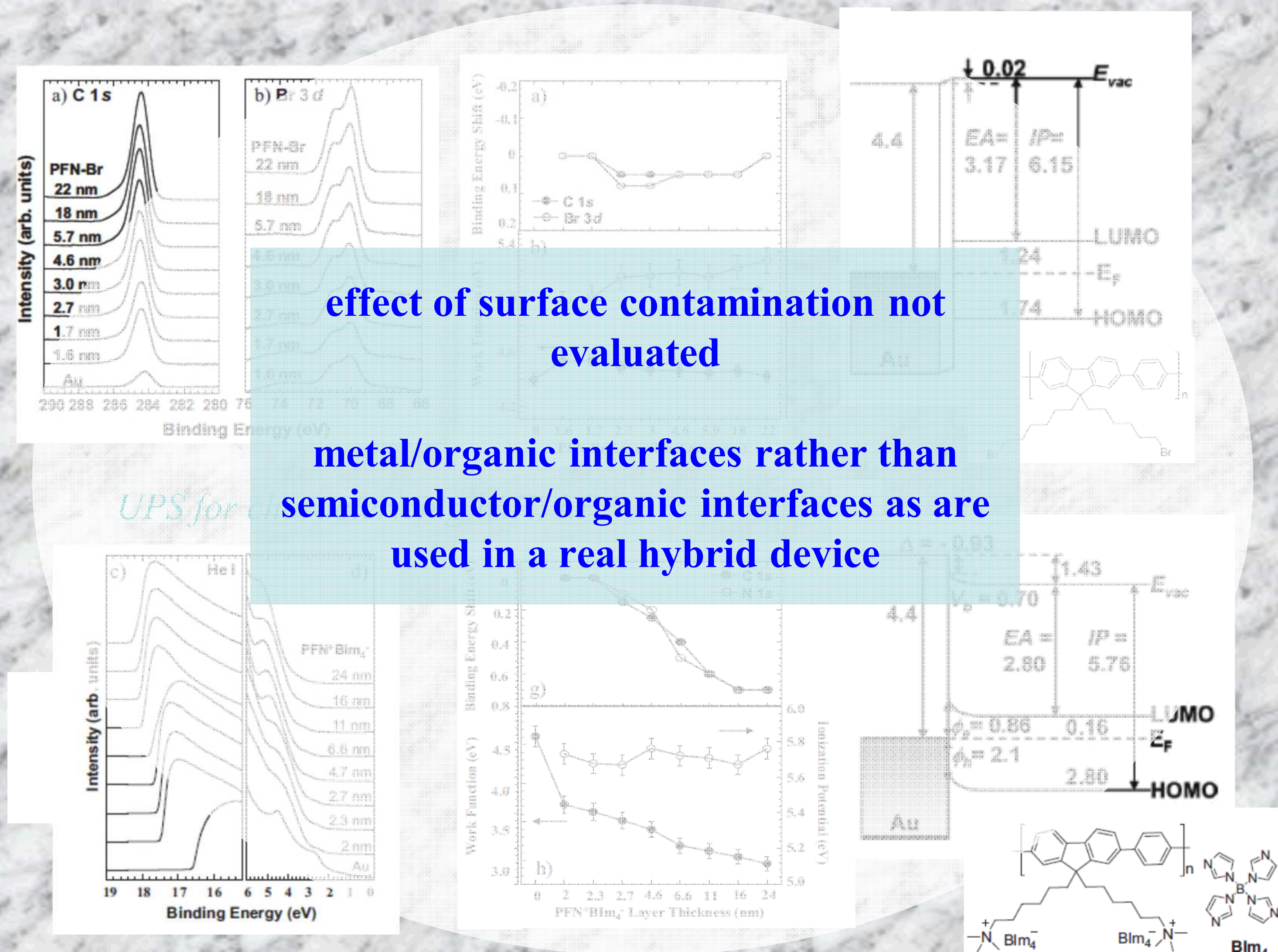
Previous Polymer Characterizations

Previous measurements follow typical procedures precluding a correlation to real interfaces.

Schlaf
- in situ electrospray
  - MEH-PPV/ITO
  - MEH-PPV/Ag
  - P3HT/HOPG

Ramsey
Koch
Kahn
- vacuum deposition of small molecules, IPES
  - organic/metal

poor/unknown correlation to real interfaces



UPS for el...

effect of surface contamination not evaluated

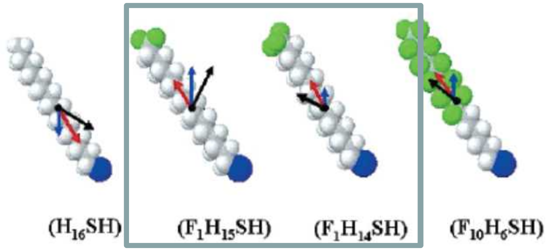
metal/organic interfaces rather than semiconductor/organic interfaces as are used in a real hybrid device

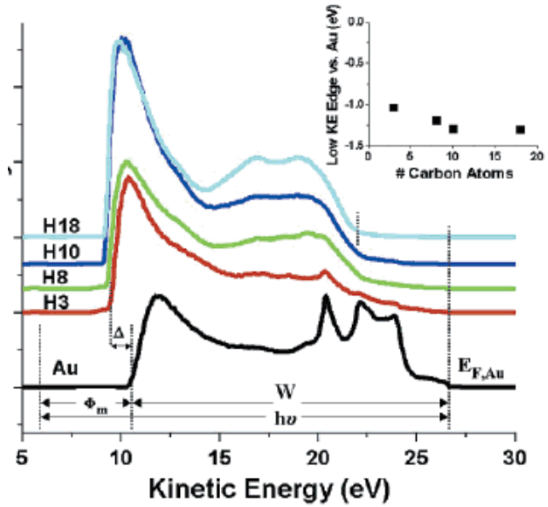
UV Photoelectron Spectroscopy – Surface Dipoles

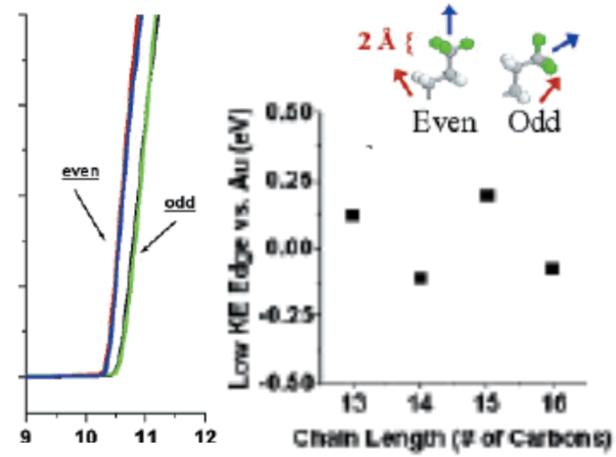
Alloway, Armstrong, *et. al. J. Phys. Chem. B.* (2003) **107**.

UPS is an extremely sensitive technique for evaluating surface electronic properties

Dipole effects from molecular orientation can be detected by UPS







Work function can be "tuned" at a material surface through modification

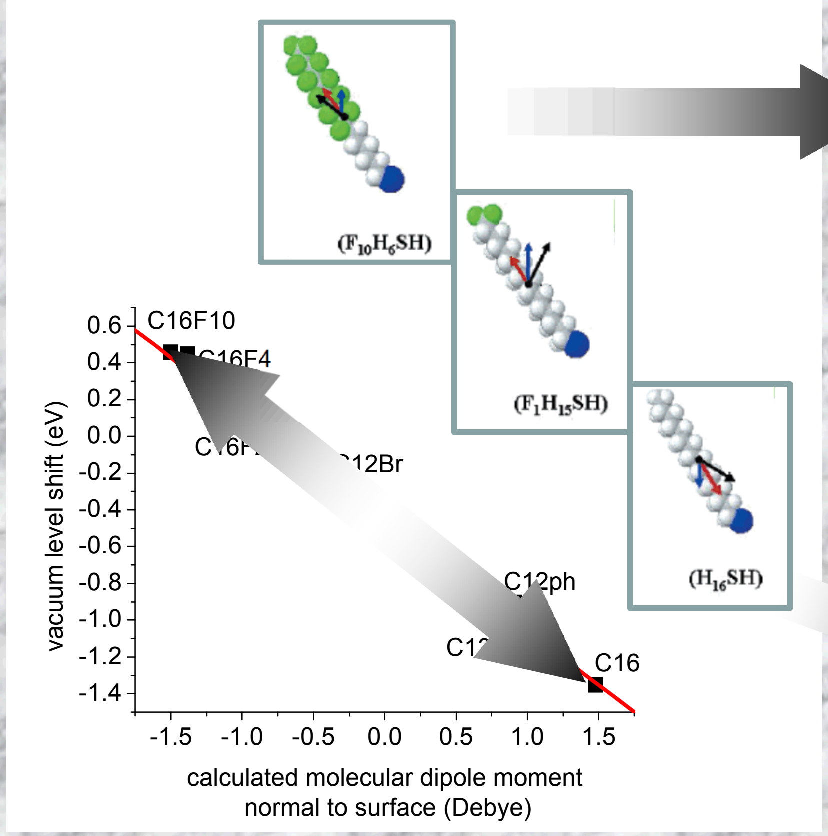
Injection barriers

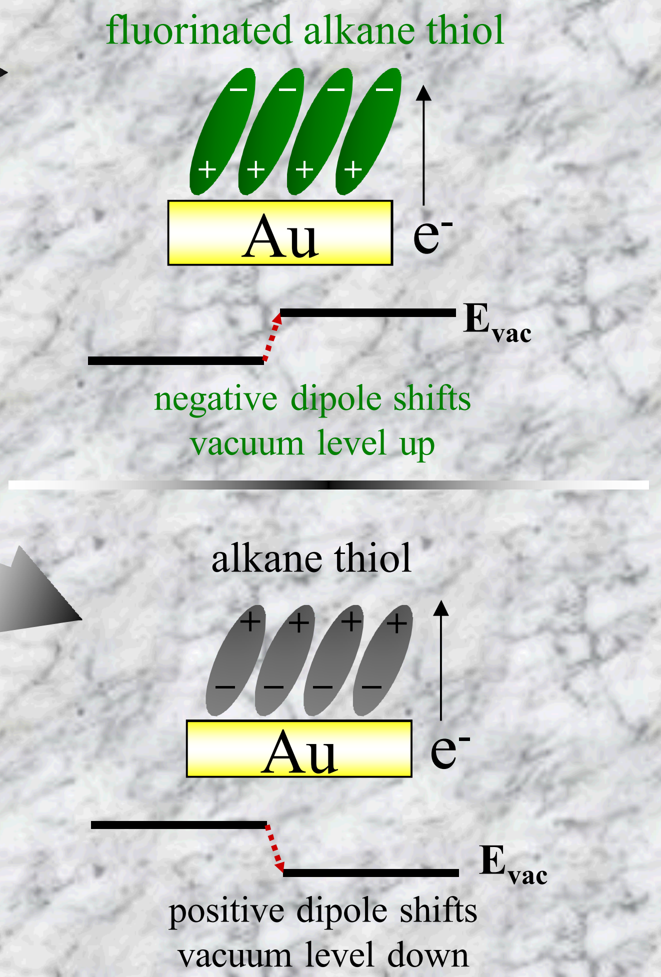
UV Photoelectron Spectroscopy – Surface Dipoles

Alloway, Armstrong, *et. al. J. Phys. Chem. B.* (2003) **107**.

"Tuning" of work function of gold surface through surface modification

Work function variation over ~ 2 eV range (~40% of WF of clean Au)





Work Function "tuning" by variations in concentration

Salzmann, *et. al. JACS.* (2008) **130**.

Ionization energy can be continuously tuned by concentration of variously dipolar species.

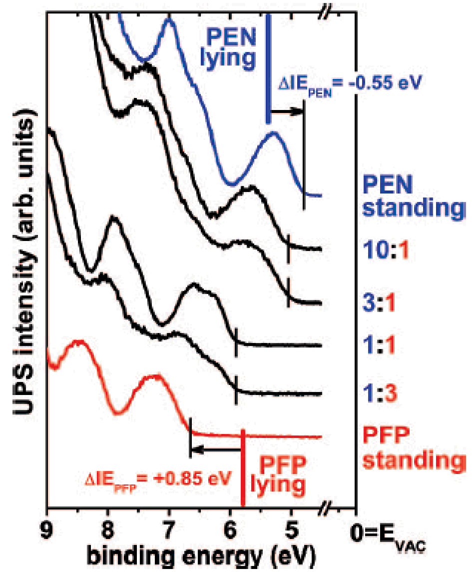


Figure 1. UPS spectra of pure and mixed films of standing PEN and PFP on SiO_x. The vertical lines indicate the photoemission onsets, i.e., the IE (values of lying PEN and PFP on Au(111)[13] are given for comparison).

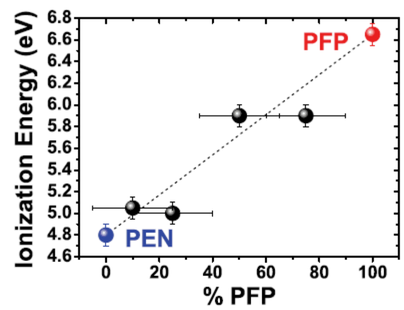
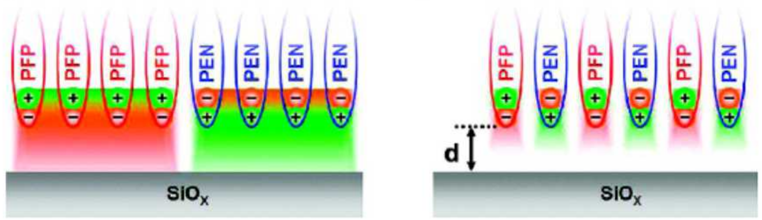


Figure S3: Ionization energies deduced from the UPS spectra of Fig. 1 in dependence of the PFP ratio.

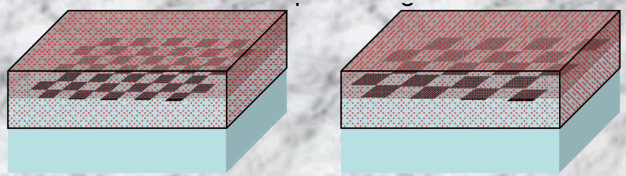


Not spatially organized.

Tunable Surface by Spatial Organization

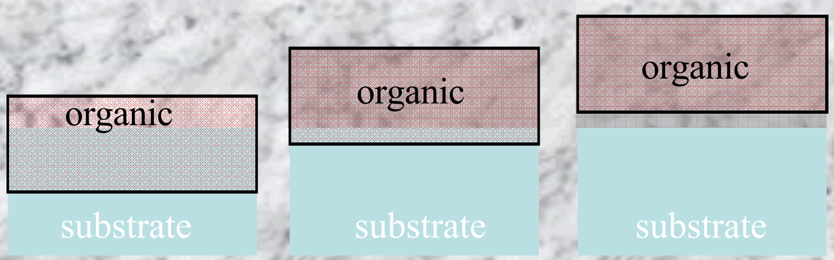
Assemblies of surface modifiers with controllable functionalities and dimensions.

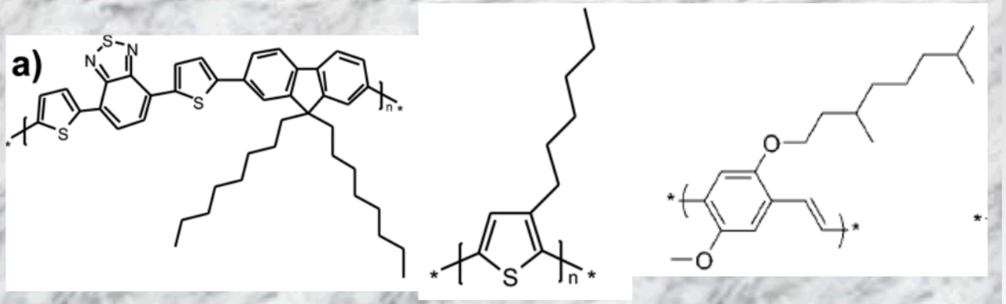
Vary lateral (2D) dimensions with only two dipolar surface modifiers… Control surface work function in a spatially controlled system.



Effect of spatial distribution of molecular components in a mixed assembly on spectra
-- continuous vs. superposition?

Spatially organized SAMs for work function tuning has not been evaluated.
Effects are unknown.





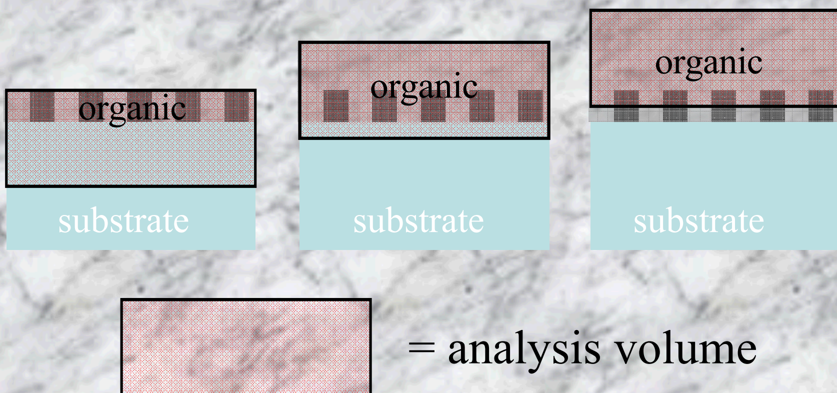
Real surfaces are likely to be a heterogeneous, dispersed array of contaminants.

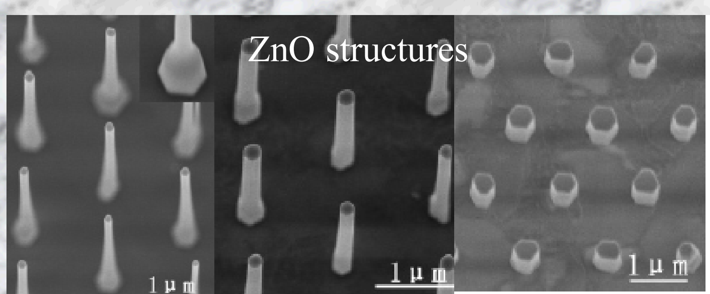
Observations from known arrays of specified dimensions could be used to infer constraints on the effects of otherwise unknown surface contaminants on real surfaces.

Electronic Characterization of Hybrid Interfaces

Vertical (3D) Dimensions - *evaluate unknown effect of surface structure*

Strategically design interfacial structure and chemistry to tailor sample for the analysis capabilities of photoelectron spectroscopy!

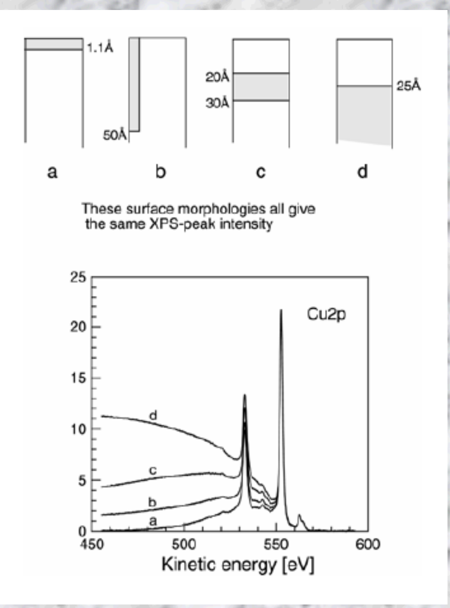




Liu, *et. al.*, *Nano. Let.* (2006) **6**, 2375-8.

Interfacial areas and distribution from interface can be designed to optimize analyses volumes.

There is some precedence for evaluating nanostructure via photoelectron spectroscopy.
-- Cu/CuO stripe reconstruction
-- Tougaard

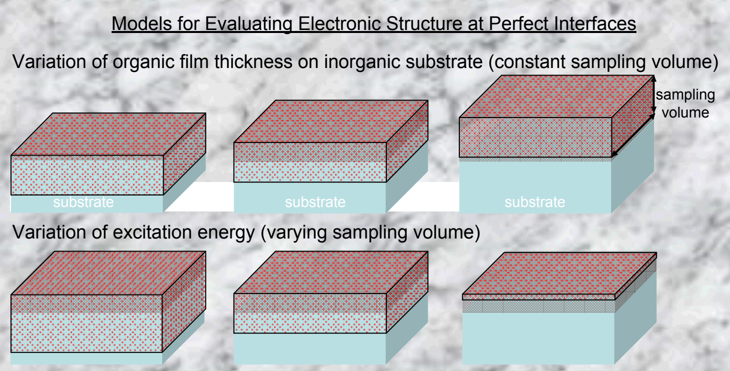


Koller, G.; Netzer, F. P.; Ramsey, M. G. *Appl Phys Lett* **2003,** *83*, 563.
Tougaard, S. *Appl Surf Sci* **1996,** *100*, 1.

Corroborating Depth Profiling with VKE-XPS

Unique Capability:* *Sandia beamline at Brookhaven!
-- variable excitation energies – tune sampling depth!!
electronic characterization
non-destructive depth profiling

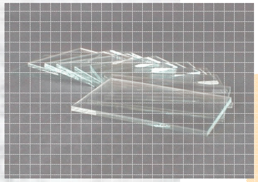
Confirm and support experiments with variable excitation PES!

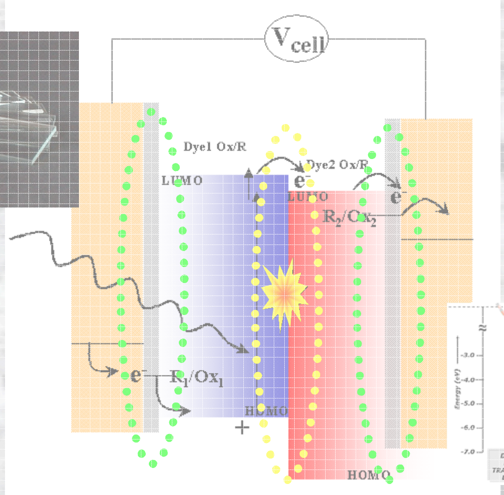


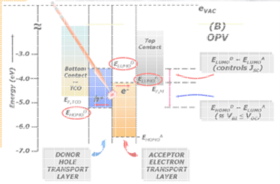
Systematically step through the interfacial regime at high resolution.
-- Vary the polymer thicknesses to be above and below the XPS/UPS sampling depth.
Spin coating, electrodeposition, and/or electrospray deposition will be used for thin film deposition.
-- Adjust the sampling depth using variable excitation energies (1 to 10 nm, synchrotron source).

Outline

XPS/UPS and Organic Photovoltaics

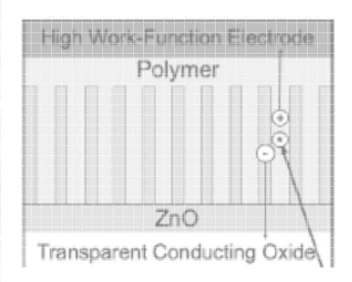


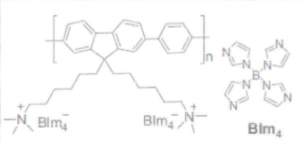


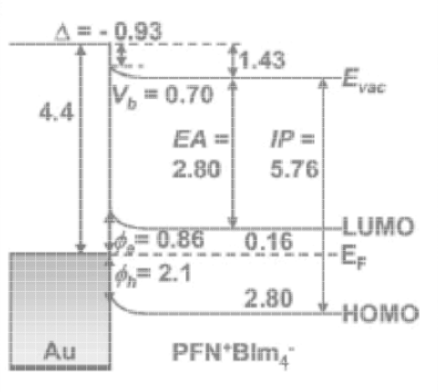


Proposed Work on Hybrid Interfaces

- Early Career LDRD – Inorganic/Polymer interfacial characterization

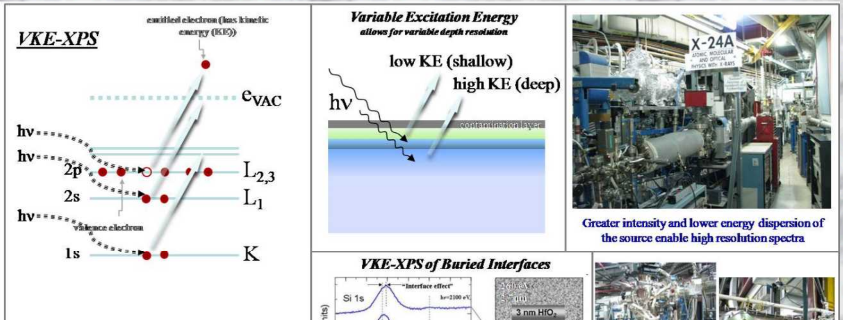






Variable Energy XPS

- National Synchrotron Light Source – RTBF - Erbium



$BE = h\nu - KE - \Phi_{spectrometer}$

$h\nu_{UPS} = 21.2$ eV
$h\nu_{XPS} = 1486.6$ eV
vs.
$h\nu_{X24A/U7A} = 200$ to 5000 eV

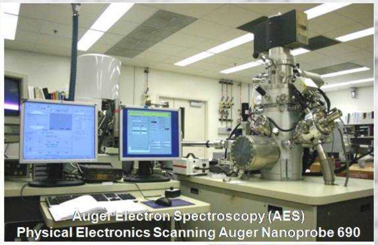
Si 1s = 1839.5 eV

U7A 180-1200eV
X24A 2000-5000eV

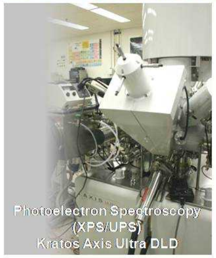
Surfaces Science Lab

- VKE-XPS – NEXAFS – ToF-SIMS – AES – AFM -

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) Ion-ToF SIMS 5

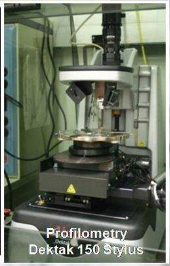


Auger Electron Spectroscopy (AES) Physical Electronics Scanning Auger Nanoprobe 690



Photoelectron Spectroscopy (XPS/UPS) Kratos Axis Ultra DLD

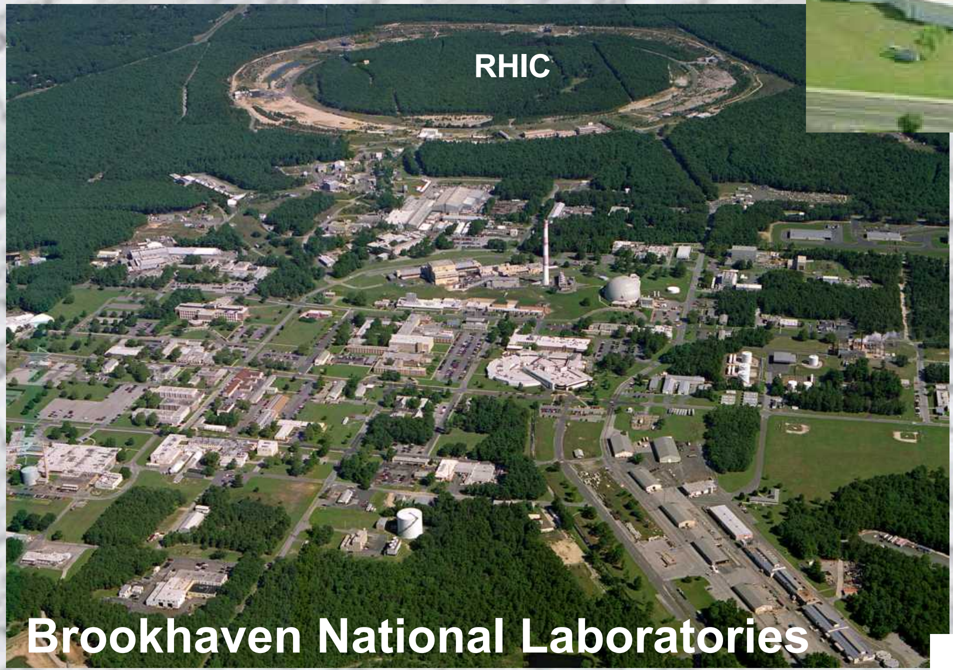
Atomic Force Microscopy (AFM, STM, SPM) Veeco Dimension Icon

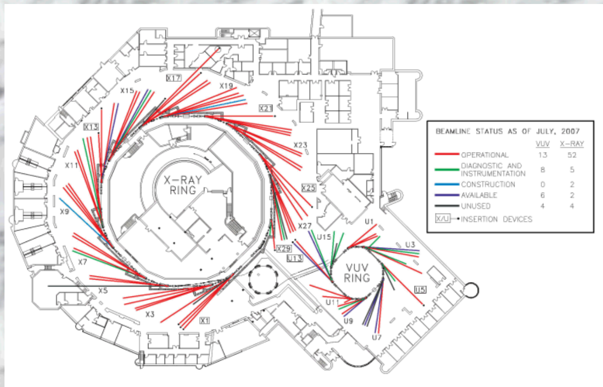


Profilometry Dektak 150 Stylus

NSLS (National Synchrotron Light Source) @ BNL

- Over 2000 users from around the world with 800-1000 publications per year.
- Provides high-brightness radiation from far-infrared to 100keV x-rays
- 49 beamlines on the x-ray ring and 16 beamlines on the VUV-IR ring.
- Operational since 1982
- DOE User Facility





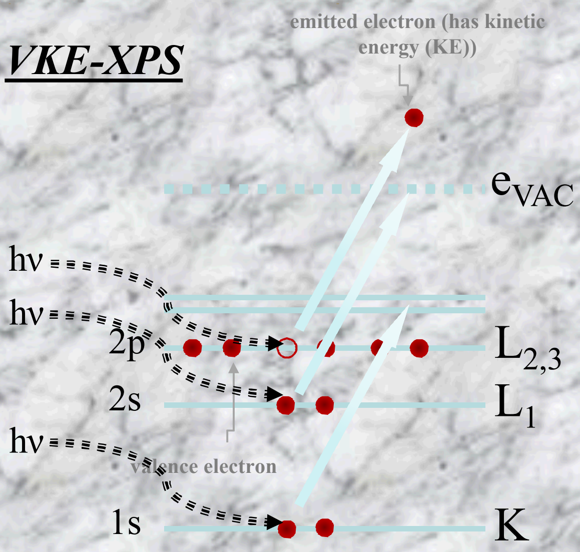
U7A 180-1200eV
X24A 2000-5000eV

Introduction to VKE-XPS

VKE-XPS characterizes

- Non-destructive depth profiling – buried interfaces – subtract out contamination layer – optimize cross section -

VKE-XPS



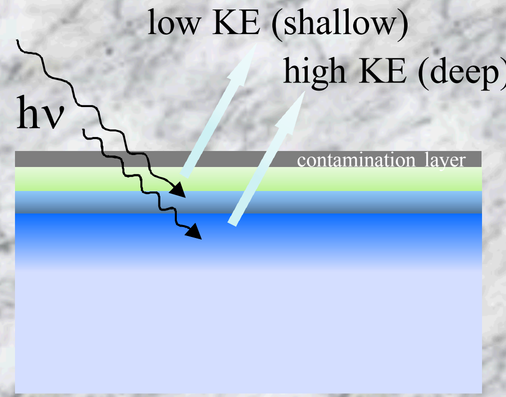
Higher energy source probes deeper core levels.

$$BE = h\nu - KE - \Phi_{spectrometer}$$

$$h\nu_{UPS} = 21.2\ eV$$
$$h\nu_{XPS} = 1486.6\ eV$$
vs.
$$h\nu_{X24A/U7A} = 200\ to\ 5000\ eV$$

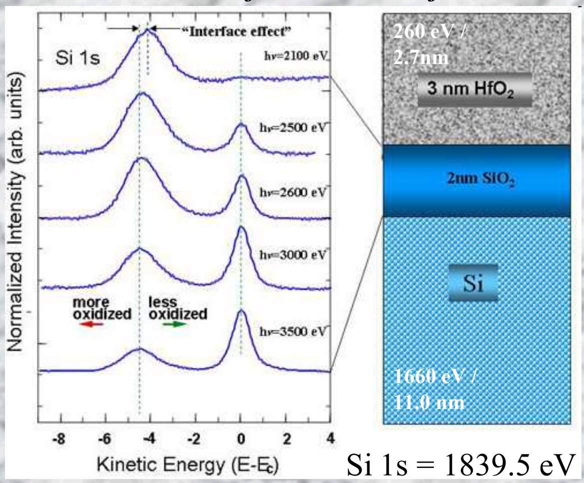
Variable Excitation Energy

allows for variable depth resolution

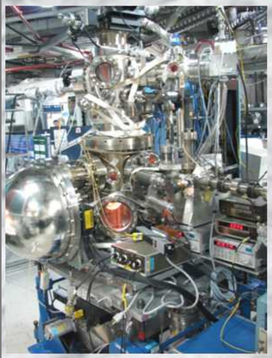


Greater intensity and lower energy dispersion of the source enable high resolution and good S/N.

VKE-XPS of Buried Interfaces



Si 1s = 1839.5 eV



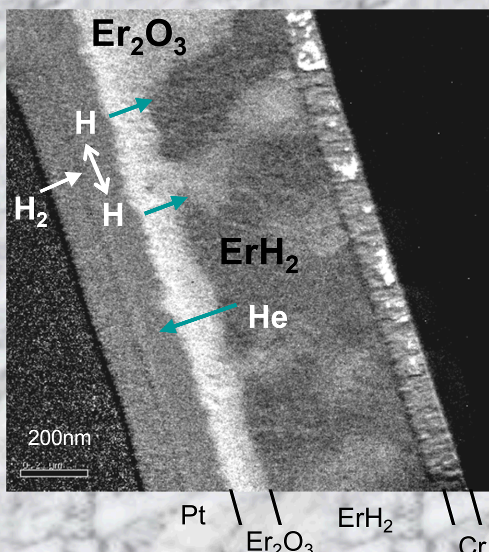
U7A 180-1200eV
X24A 2000-5000eV

Lysaght, *et al*. *J. Appl. Phys.* **101**, 024105 (2007).

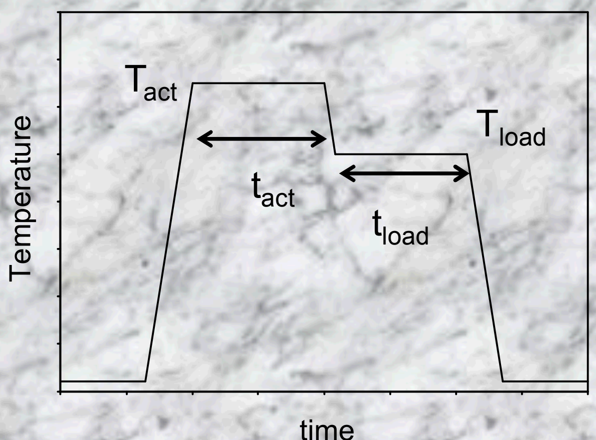
thermal activation of the oxide surface on the metal

Erbium is a critical material for hydrogen storage.
Hydrogen loading requires an "activation" process.

Synchrotron-based photoelectron spectroscopy (variable energy XPS) can be used to provide nondestructive depth profiling to determine the fate of the initial surface O during the activation process.



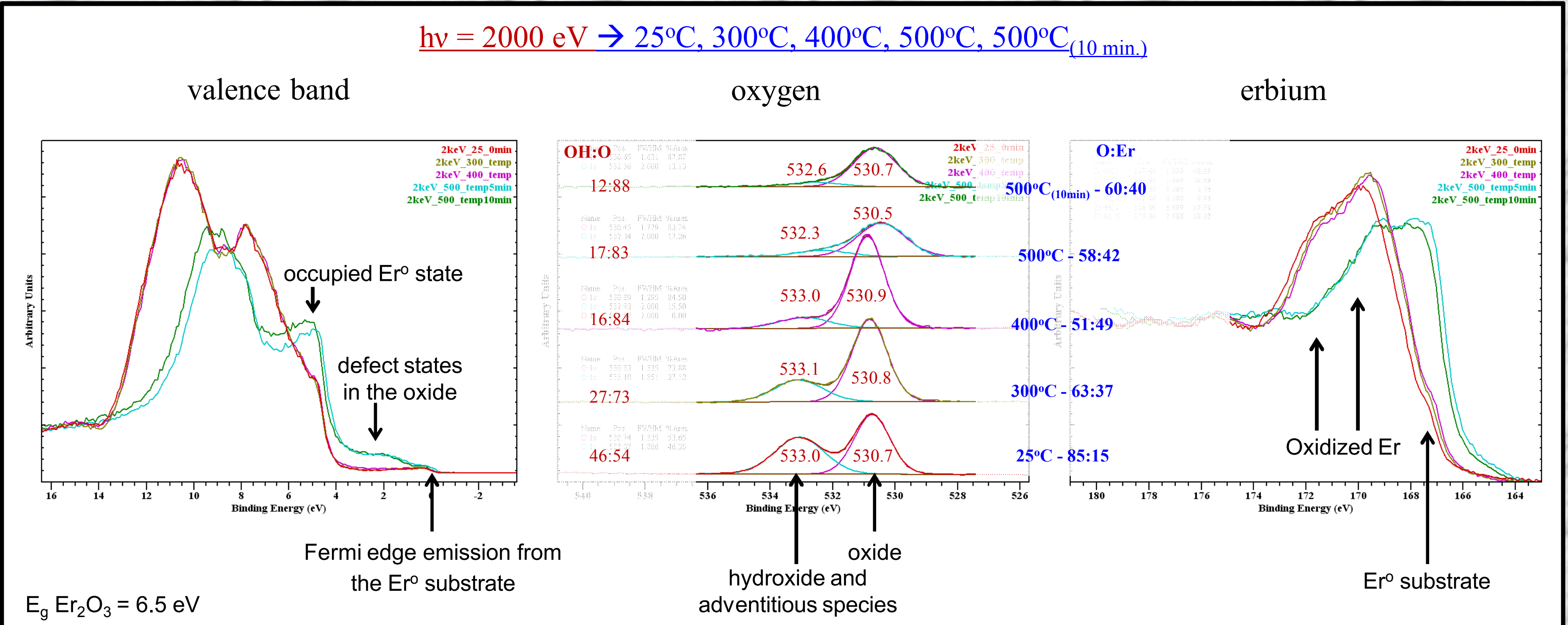
C. Parish, C. Snow, L. Brewer



Erbium hydriding: a passive surface oxide is thermally activated to yield a H_2 accommodating surface

- Define O distribution at the activation and load states of the Er film
  - Explore the kinetics of the redistribution of O within the Er film
  - Provide chemical input for performance models of target films

XPS (hν = 2000eV) – thermal activation



Heat treatment requires a temperature above 400°C for thermal activation.

Activation includes: *1. Removal of hydroxyls and adventitious species from the surface*

2. Depletion of oxygen in near surface region

3. Defect state formation in the oxide

(continued heating leads to a redistribution of oxygen to the surface – oxide reformation (single component O 1s))

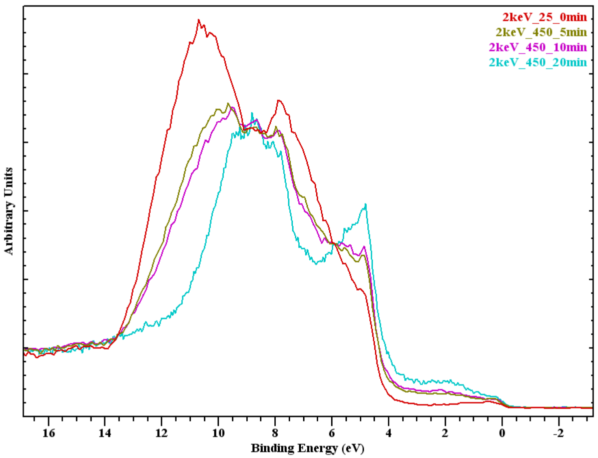
(emergence of Er^0 peaks in Er 4d show that oxide has thinned)

K. Zavadil

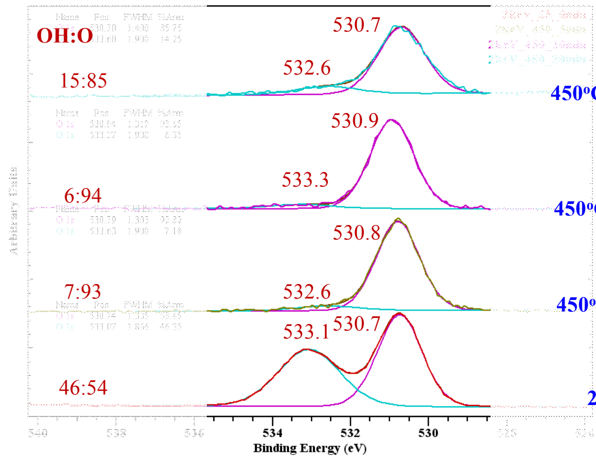
XPS (hν = 2000eV vs. 3000eV) – heat duration

hν = 2000 eV → 450°C for 0, 5, 10, 20 minutes

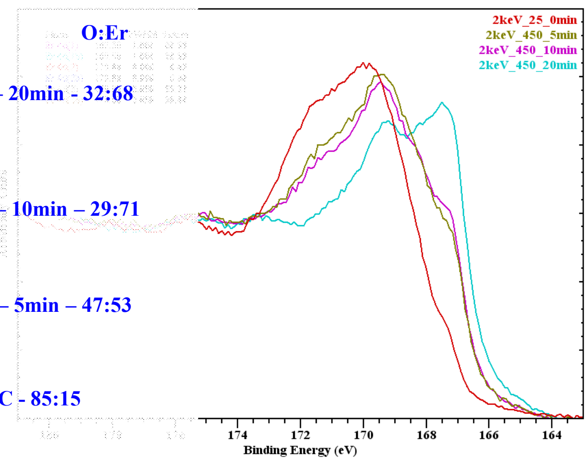
valence band



oxygen

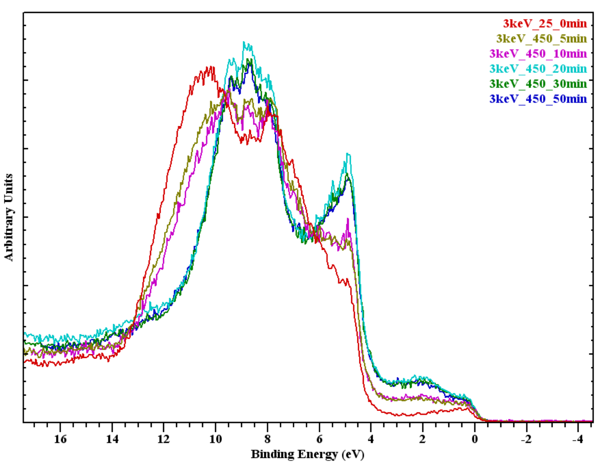


erbium

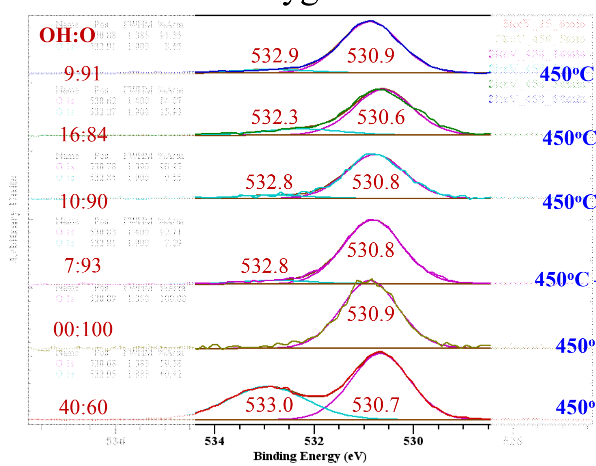


hν = 3000 eV → 450°C for 0, 5, 10, 20, 30, 50 minutes

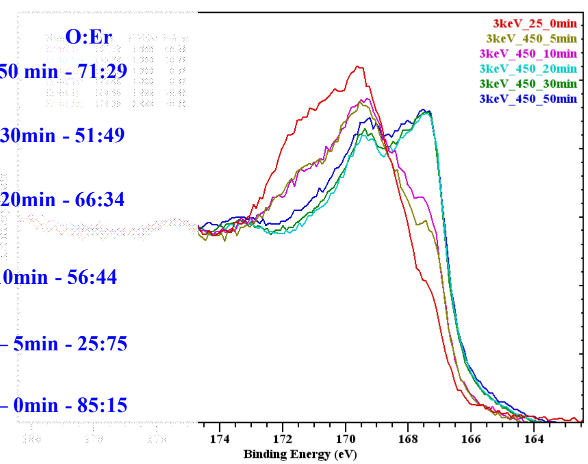
valence band



oxygen



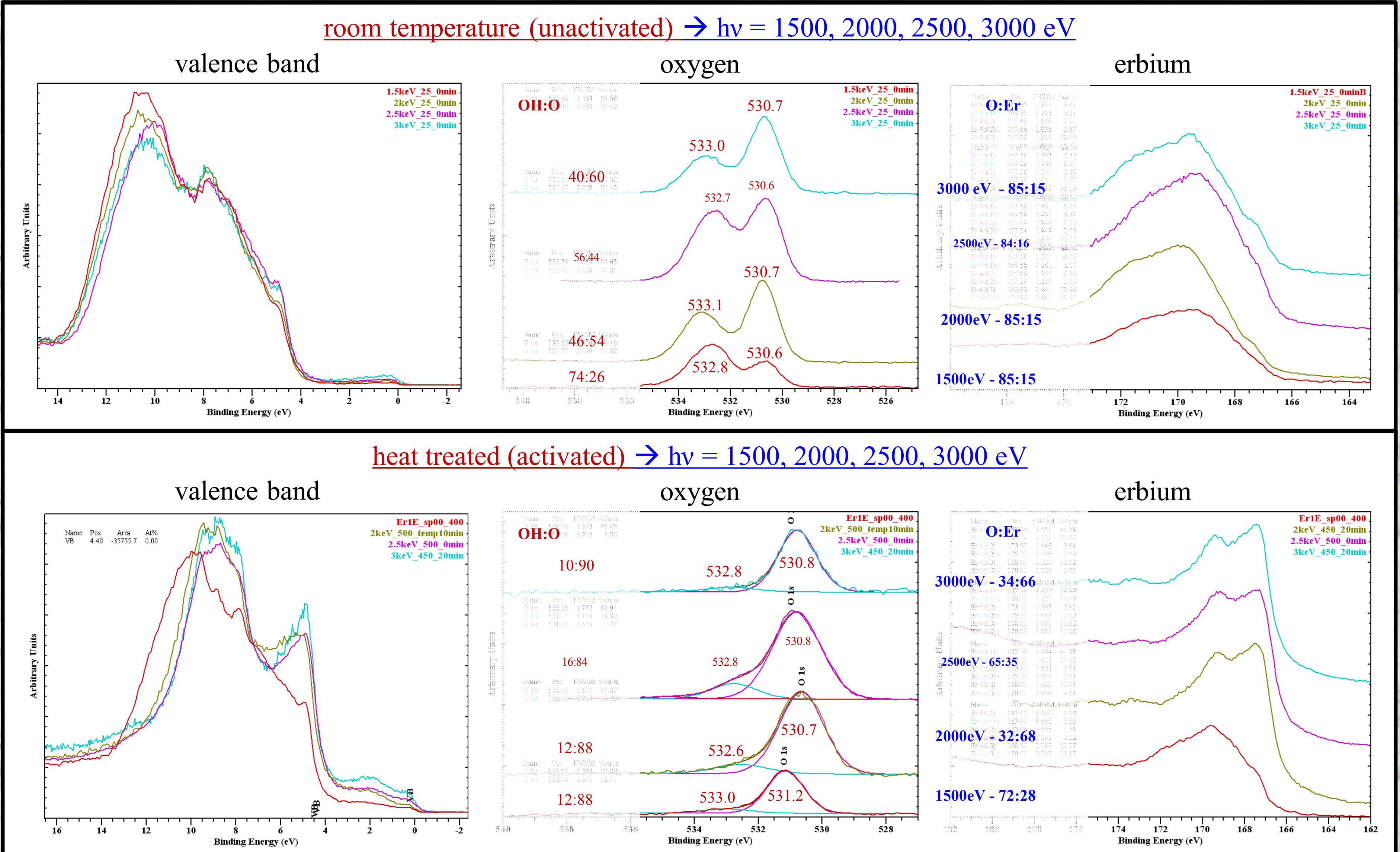
erbium



Higher energy XPS allows for the full depth of the surface oxide to be analyzed.
Two stage thermal activation: *Stage 1. Thinning of the oxide*
Stage 2. Defect formation and reconfiguration of the oxide

K. Zavadil

Variable Depth Analysis – VKE-XPS (hν = 1.5, 2, 2.5, 3 keV)

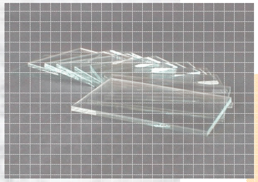


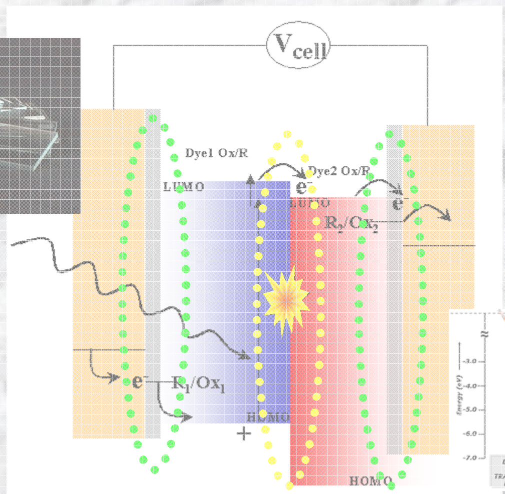
Unactivated surface has a thick, ill-defined hydroxide/oxide/Er^0 surface.
Activated surface has a thin reconfigured oxide with high density of defects.

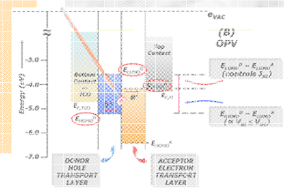
K. Zavadil

Outline

XPS/UPS and Organic Photovoltaics

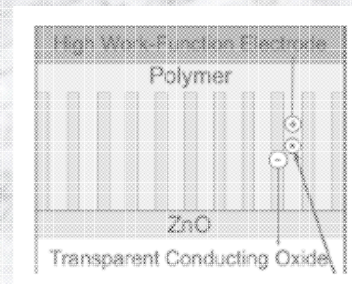


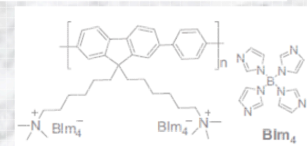


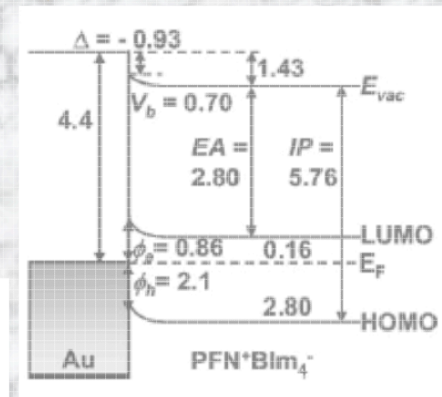


Proposed Work on Hybrid Interfaces

- Early Career LDRD – Inorganic/Polymer interfacial characterization

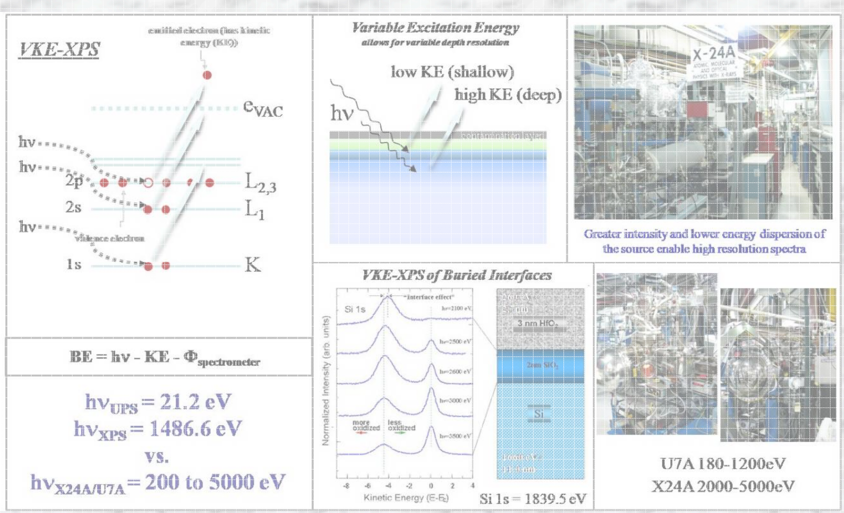






Variable Energy XPS

- National Synchrotron Light Source – RTBF - Erbium



Surfaces Science Lab

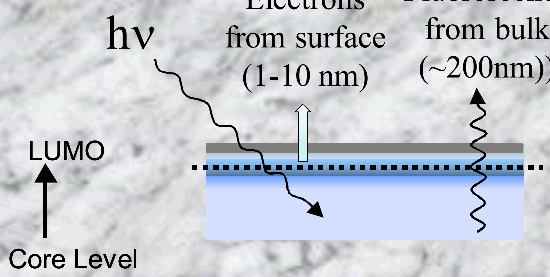
- VKE-XPS – NEXAFS – ToF-SIMS – AES – AFM -

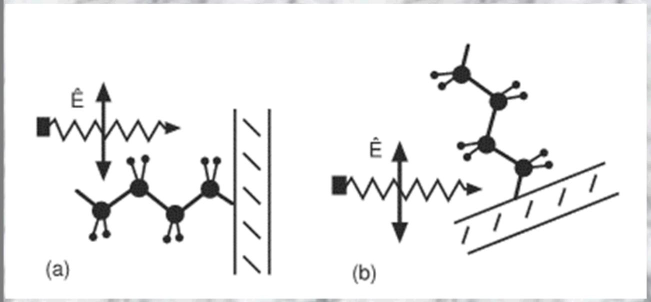
Introduction to NEXAFS

Near Edge X-ray Absorption Fine Structure

- C, N, O, F – chemical state identification – molecular orientation – monolayers – segregation -

NEXAFS



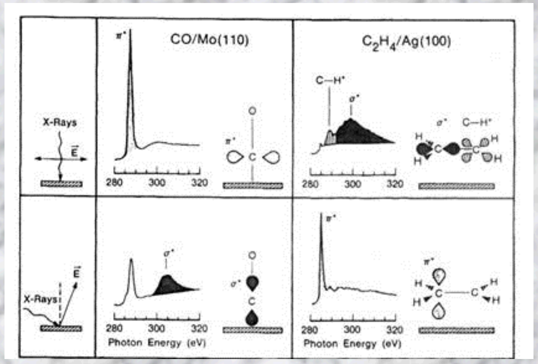


The maximum intensity of transition is achieved when the electric field vector is parallel to the respective bonding orbital; thus, when the beam is normal (a) the dominant transition will be the C-H* and at glancing angle geometry (b) the major transition will be the C-Cσ.

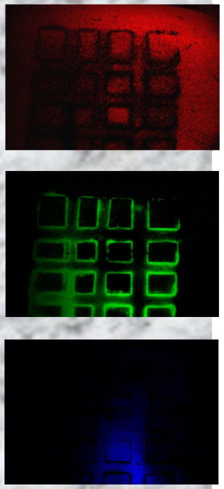
(*J. Mat. Sci. Let.*, **17** (1998) 1223-1225.)

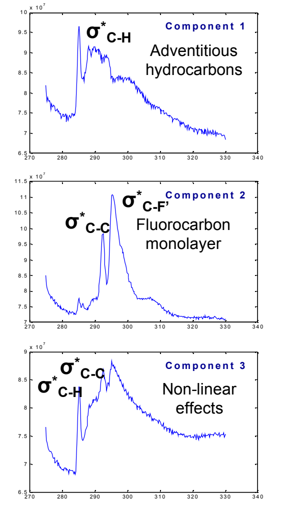
Molecular Orbital Orientation

Resonance with incoming X-ray



NEXAFS Spectroscopy, Joachim Stöhr, Springer, 2003





NEXAFS

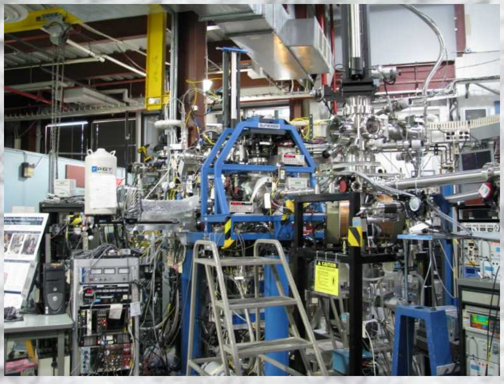
A synchrotron-generated variable energy X-ray beam (180-1200eV) irradiates the sample surface.

A monochromator selects energy and directs the beam to the sample.

The x-rays at a given energy are absorbed when they match electron energies (resonance).

Intensity of ejected electrons (or photons) are plotted versus x-ray energy.

Polarized light from the synchrotron allow probing of molecular orientation.

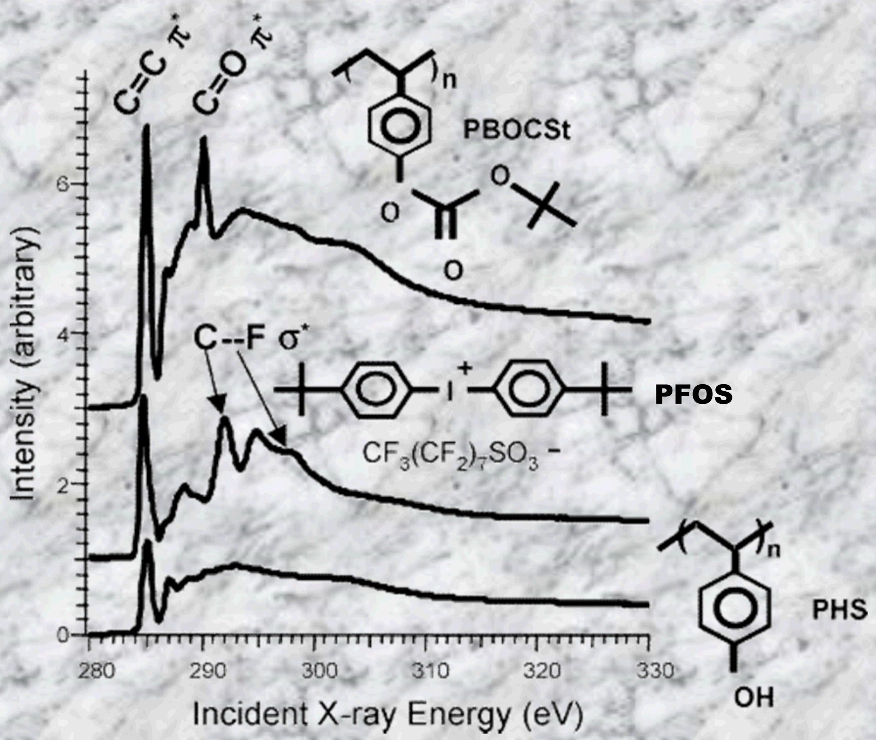


U7A
180-1200eV

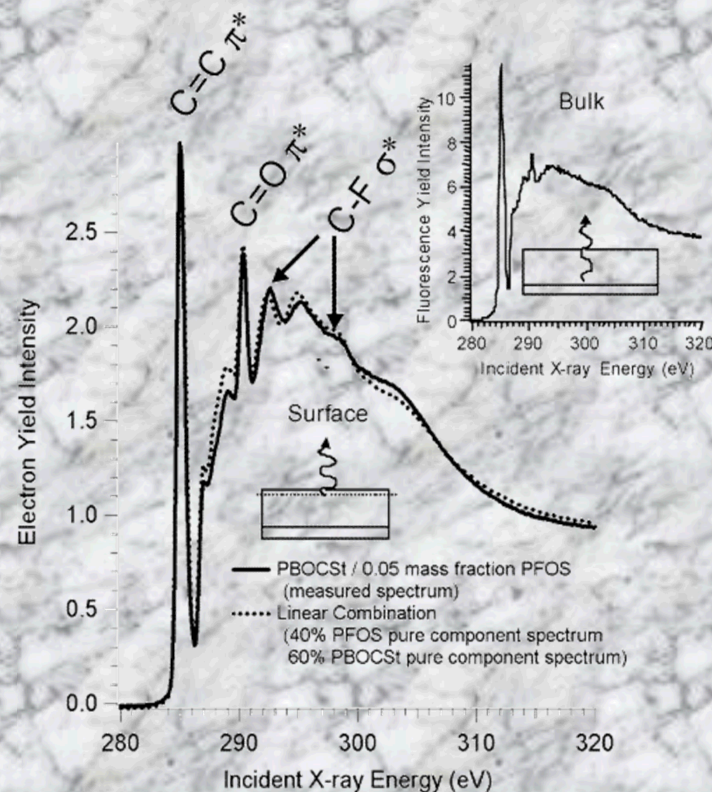
NEXAFS to Probe Surface Composition in Photoresist Films

Lenhart, et. al., *Langmuir* **2005**, *21*, 4007-4015.

Measure the surface segregation of film components in photoresist.



NEXAFS spectra of pure resist components.



- Fit of surface spectrum reveals an enhancement of PFOS on the surface.
- Bulk spectrum shows little PFOS.

NEXAFS to Probe Surface Composition in BHJ-SC

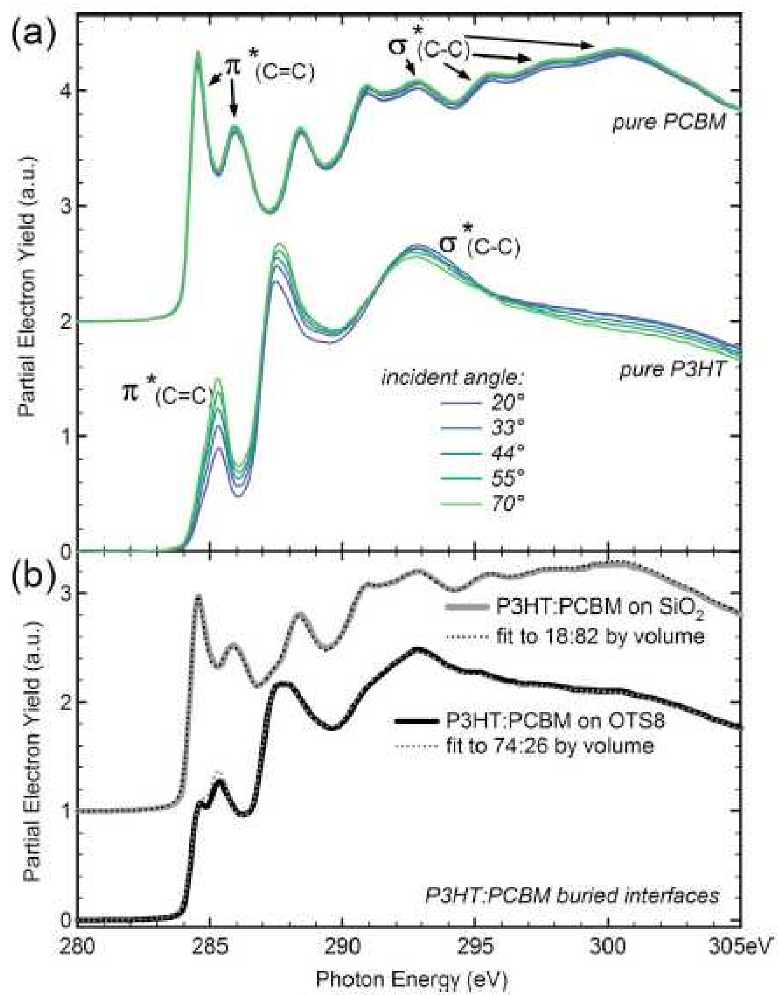
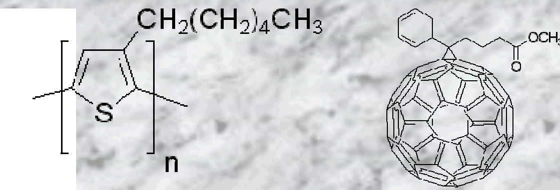


FIG. 1. (Color online) (a) Neat P3HT and PCBM NEXAFS spectra. (b) Spectra of the P3HT:PCBM buried interface on OTS8 and SiO_2 with composition fits. Spectra offset for clarity. Standard uncertainty in PEY is ± 2%; photon energy ± 0.2 eV.



P3HT and PCBM segregation is dependent on the surface energy of the substrate

APPLIED PHYSICS LETTERS 94, 233303 (2009)

Substrate-dependent interface composition and charge transport in films for organic photovoltaics

David S. Germack,[1] Calvin K. Chan,[2] Behrang H. Hamadani,[2] Lee J. Richter,[3] Daniel A. Fischer,[1] David J. Gundlach,[2] and Dean M. DeLongchamp[1,a)]

[1]*Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8541, USA*

[2]*Electronics and Electrical Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8541, USA*

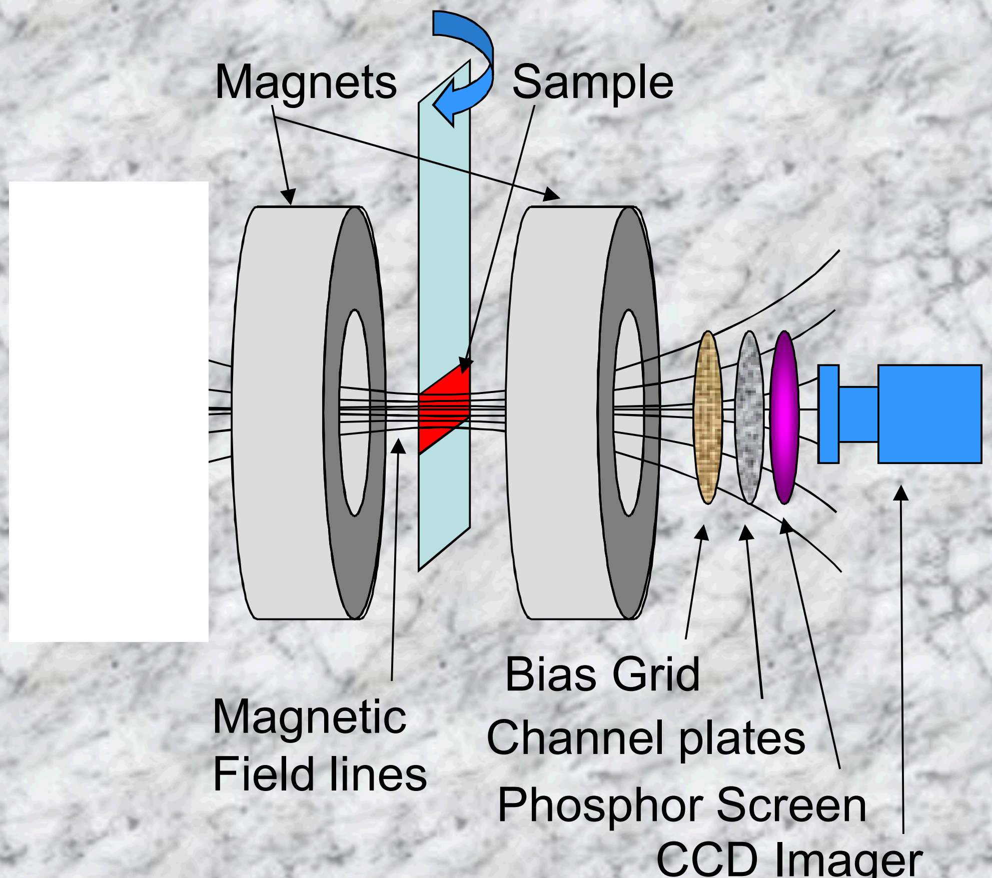
[3]*Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899-8541, USA*

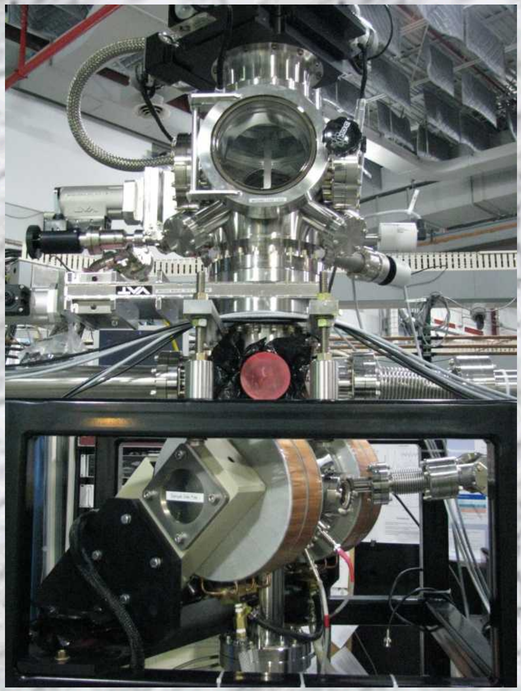
Linear combination of PCBM spectrum and P3HT spectrum gives contribution of each to the measured spectrum.

Buried interface – delaminated and examined.

Imaging NEXAFS

- A synchrotron-generated variable energy x-ray beam (180-1200eV) irradiates the sample surface.
- A monochromator selects energy and directs the beam to the sample.
- The x-rays at a given energy are absorbed when they match electron energies (resonance).
- Secondary electrons travel along magnetic field lines to a channel plate amplifier then phosphor screen.
- A CCD directly images the phosphor, recording the spatially resolved intensity of ejected electrons.

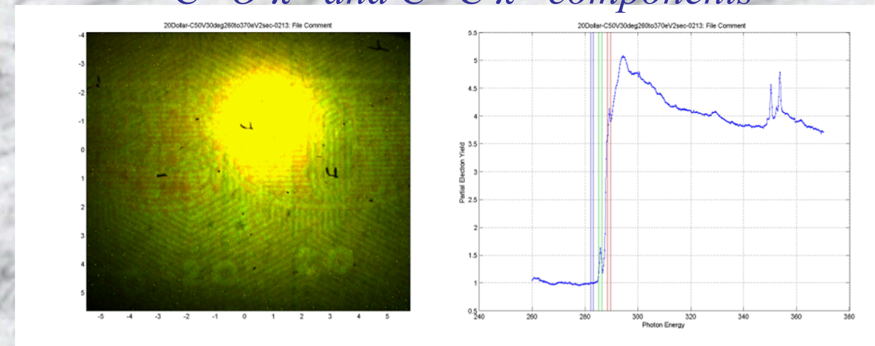




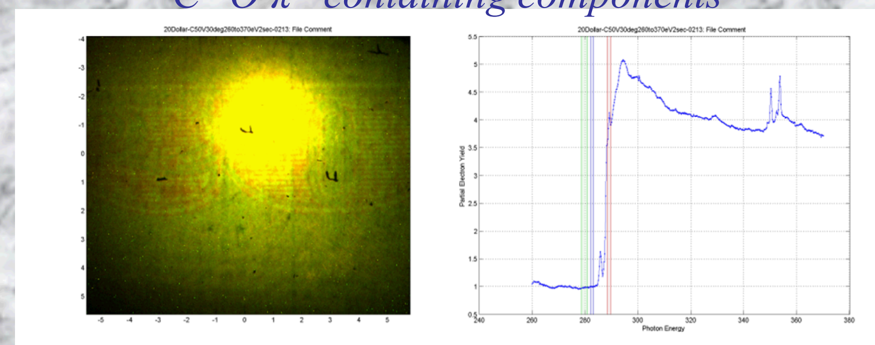
James (Tony) Ohlhausen (1822)
Mark Van Benthem (1822)
Dan Fischer (NIST)
Cherno Jaye

Imaging NEXAFS – Dyes in a Twenty Dollar Bill

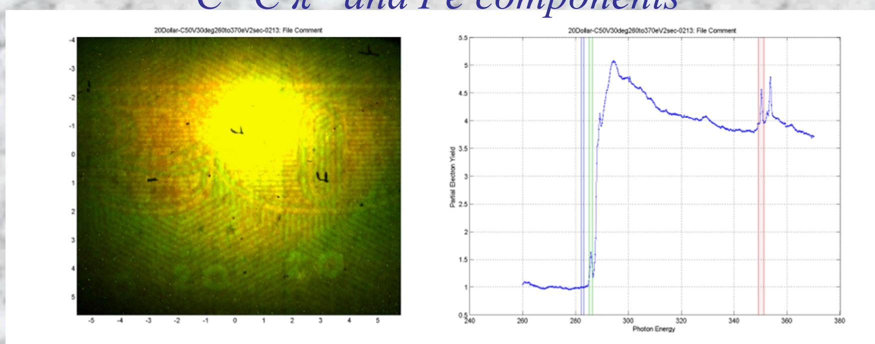
C=O π and C=C π* components*



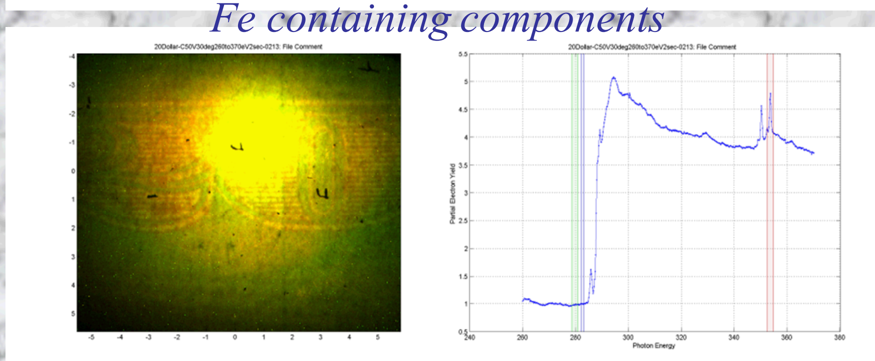
C=O π containing components*



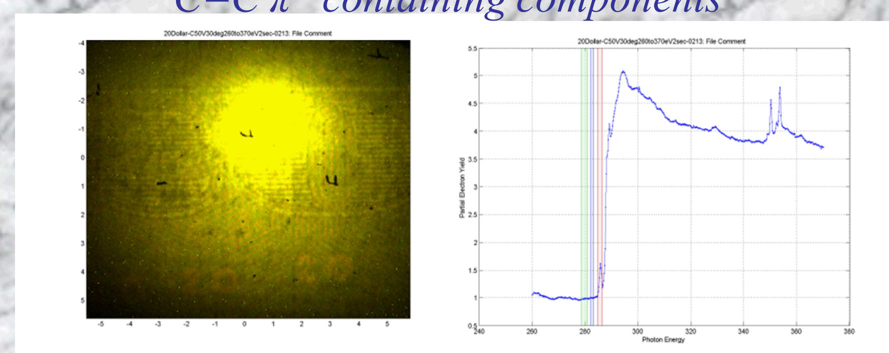
C=C π and Fe components*



Fe containing components



C=C π containing components*



NSLS II

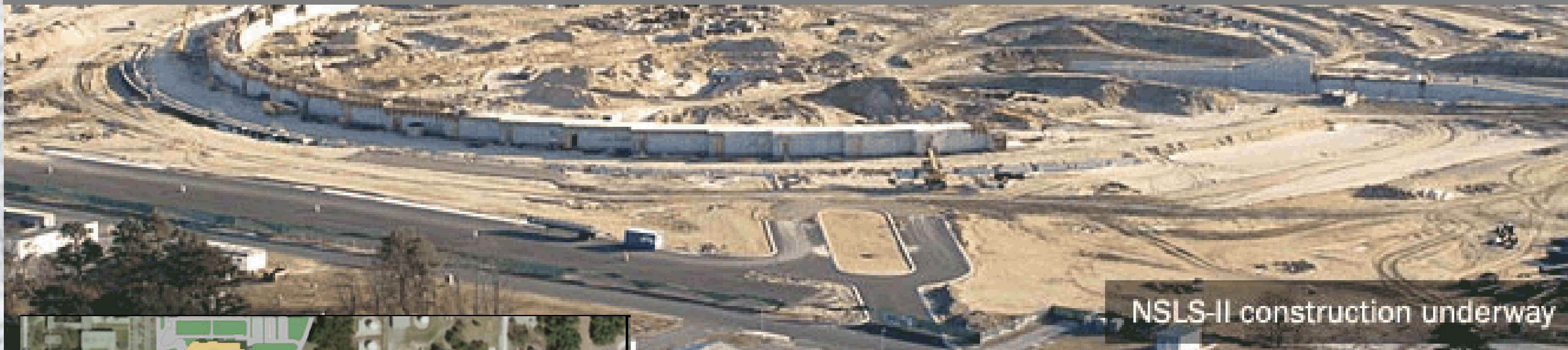
Next generation synchrotron light facility (2015)

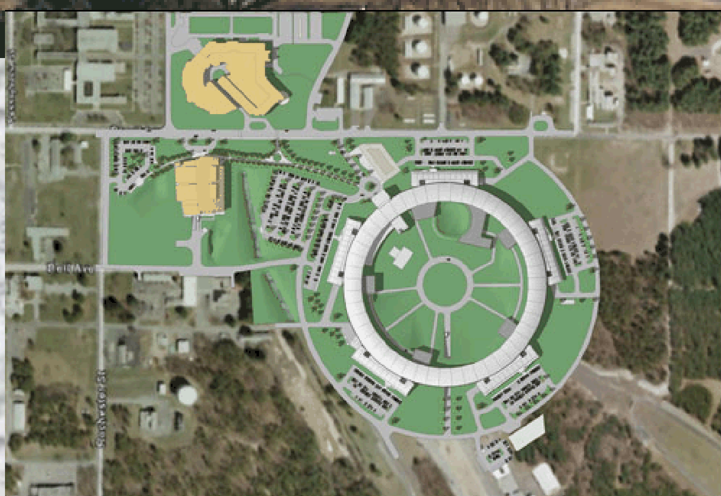
10,000 times brighter than NSLS

High-current electron beam, sub-nm-rad horizontal emittance (0.5 nm-rad) and diffraction-limited vertical emittance (8 pm-rad)

Stable beam position, angle, dimension, intensity

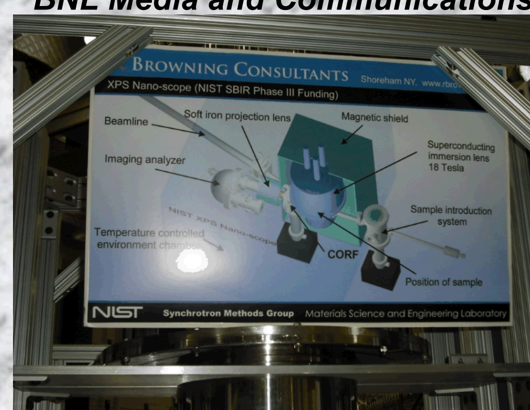
Wide spectral range (0.1 meV (1cm^{-1}, far IR) to 300 keV (hard X-ray))

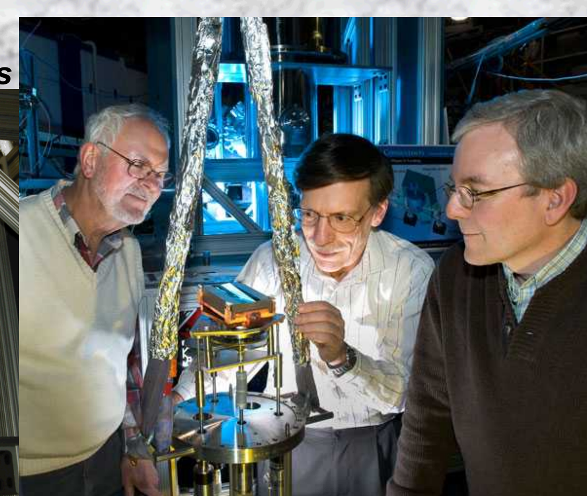




New Microscope Construction Builds New York State Business Opportunities

BNL Media and Communications

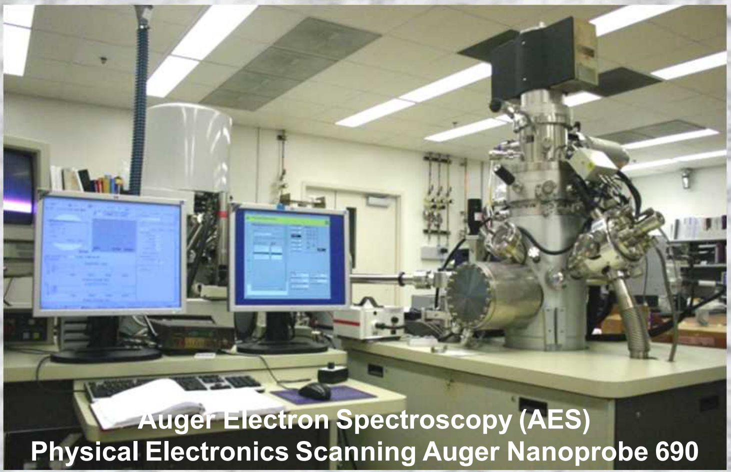




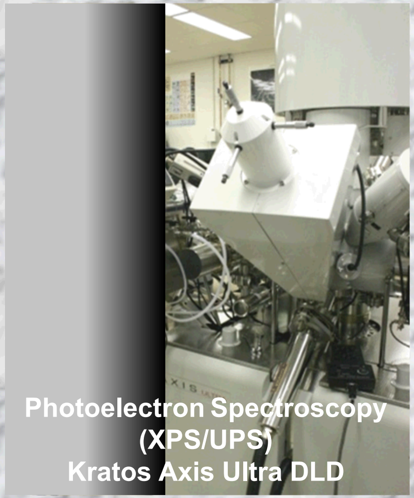
Surface Analysis Laboratory (701/1226b) – Dept. 1822

James (Tony) Ohlhausen, William (Bill) Wallace, Michael (Mike) Brumbach, James (Jim) Aubert

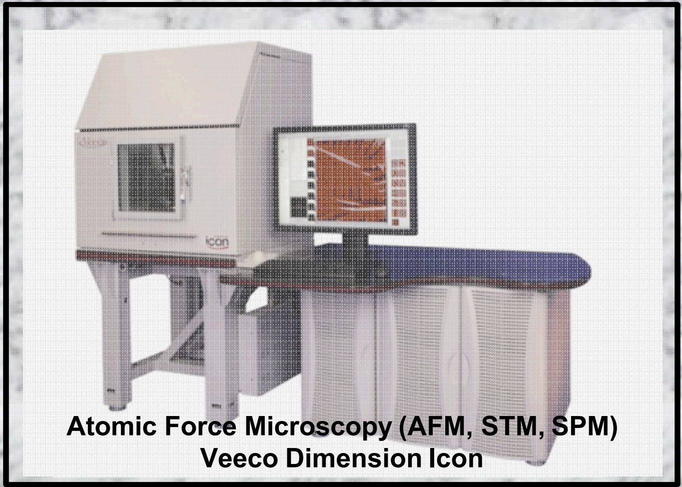
Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) Ion-TOF.SIMS 5



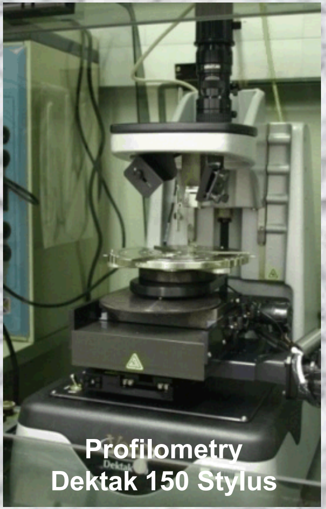
Auger Electron Spectroscopy (AES)
Physical Electronics Scanning Auger Nanoprobe 690



Photoelectron Spectroscopy (XPS/UPS)
Kratos Axis Ultra DLD



Atomic Force Microscopy (AFM, STM, SPM)
Veeco Dimension Icon



Profilometry
Dektak 150 Stylus

High mass resolution and accuracy
High sensitivity
Can analyze whole periodic table
Ion imaging (200nm resolution)
Depth profiling
Isotopic ratios
Molecular detection

Detection limits < 1 at%
High spatial resolution (15 nm)
Quantification by standards
Elemental mapping
Elemental depth profiles

Morphology
Electrical properties

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Chet Carter
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Chemistry and Electrical Engineering
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Bernard Kippelen
Simon Jones
Seth Marder

-- NSF (Chemistry, STC-MDITR)
-- ONR

Linfield College
Alfred University
Whiteware Research Center

Post-Doctoral work on Nano-composites for Ultracapacitors
Bruce Bunker
Jim Voigt
Dave Wheeler
Mark Roberts
Erik Spoerke
Chris Orendorff
Geoff Brennecka
Todd Alam
Bob Nilson
Graham Yelton
Sarah McIntyre
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Ralph Tissot
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Terry Garino

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Tony Ohlhausen
Bill Wallace
Kevin Zavadil

NIST – Dan Fischer

-- SNL Laboratory Directed Research and Development Program
-- RTBF
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