Emerging Areas in Photoelectron Spectroscopy (you can teach an old spectrometer new tricks)

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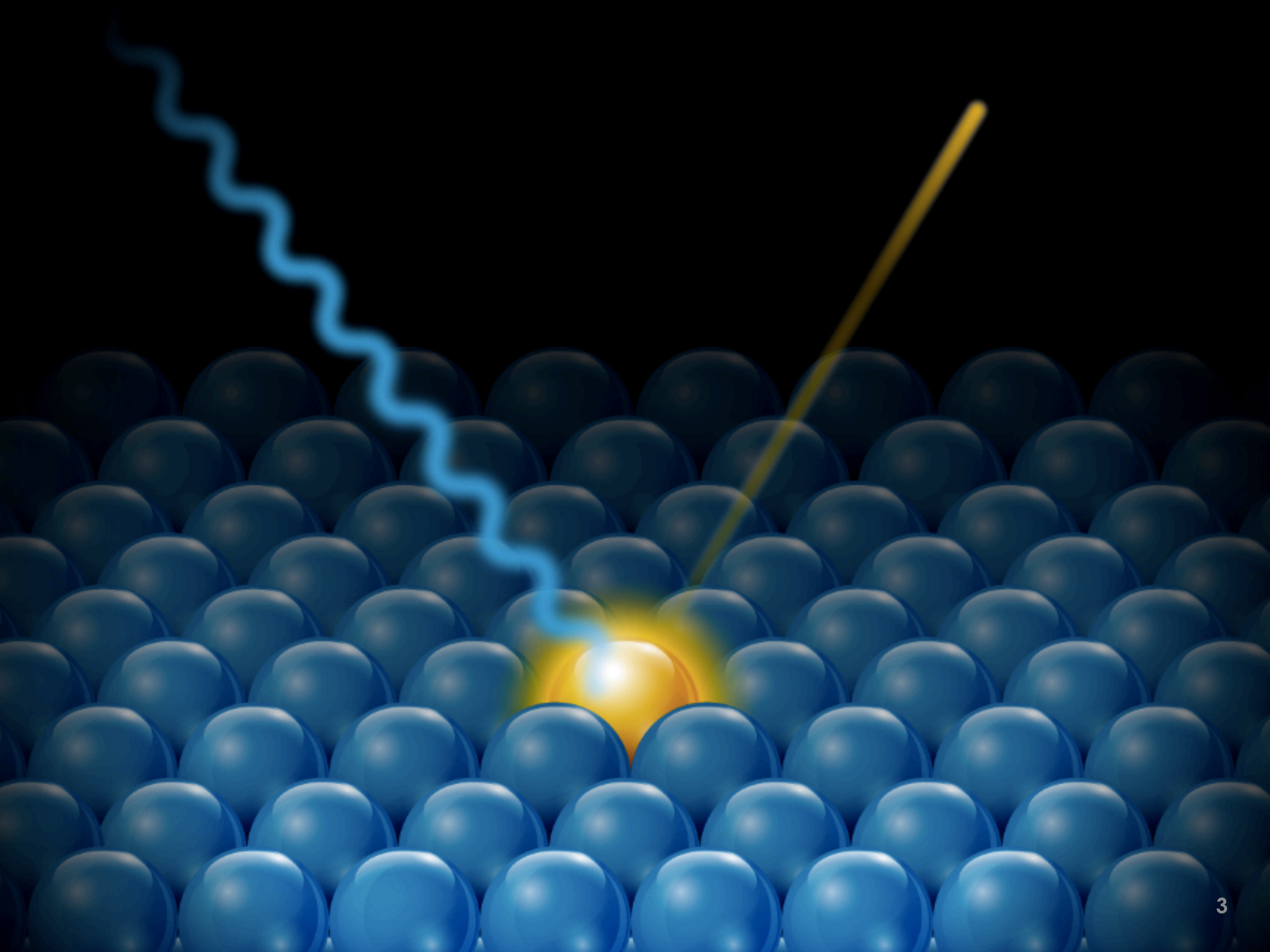
What I Won't Talk About

- Standing Wave PES
- HAXPES – Hard X-rays
- Res-PES
- 2-PPE
- Spin resolved PES
- NEXAFS, XANES, variable energy PES or other beamline techniques
- The election

What I Will Talk About

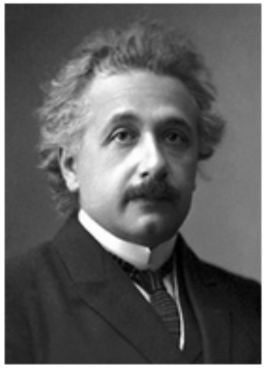
- Photoelectric Effect
- XPS & UPS
- Apparatus
- Full spectral analysis
- Example Studies
  - Dipoles
  - NP interfaces
  - X-ray induced degradation
- New Areas in PES



Early Photoelectric Discovery

- 1887 – Hertz
- Hallwachs – showed UV increases positive charge to metal
- 1899 – Lenard demonstrated that the increasing charge is emission of electrons and that their velocity is independent of light intensity, depending rather on energy – disagreed with prevailing concepts
- Photoelectric effect – 1905
- Verified by Millikan and students
- "Einstein's Law has become the basis of quantitative photo-chemistry in the same way as Faraday's Law is the basis of electro-chemistry."

The Nobel Prize in Physics 1921

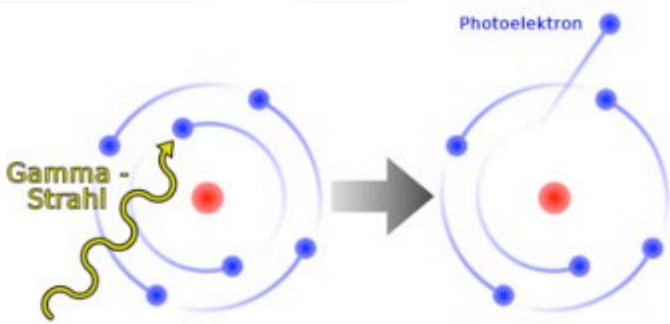


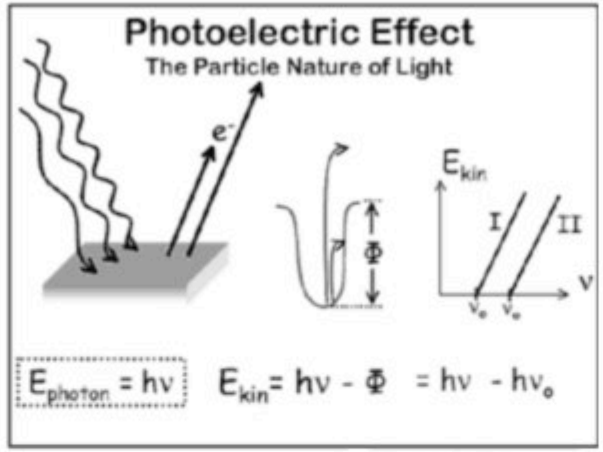
Albert Einstein
Prize share: 1/1

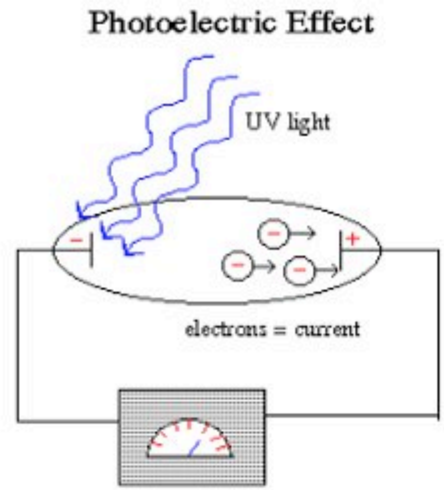
The Nobel Prize in Physics 1921 was awarded to Albert Einstein *"for his services to Theoretical Physics, and especially for his discovery of the law of the photoelectric effect"*.

- From Nobel Lectures, Physics 1901-1921, Elsevier Publishing Company, Amsterdam, 1967
- https://en.wikipedia.org/wiki/Photoelectric_effect
- http://einsteinpapers.press.princeton.edu/vol2-trans/100?ajax

E10 Photoelectric Effect

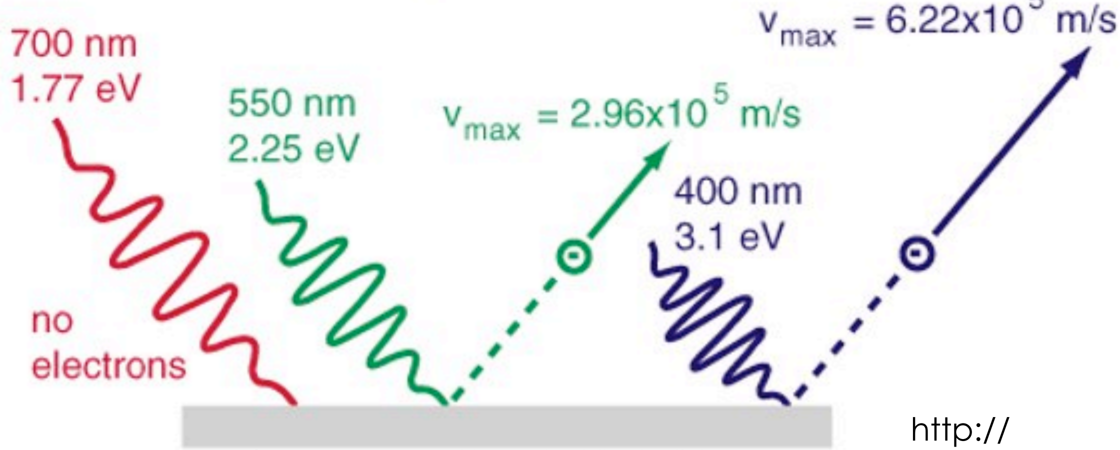






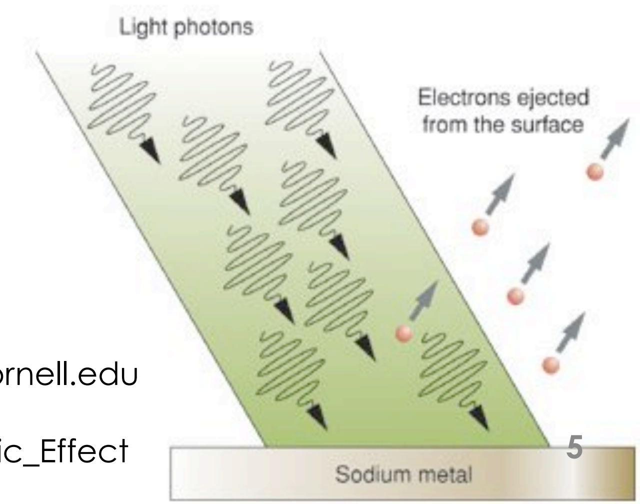
$$E_{photon} = h\nu$$

photon = wave particle of light



Potassium - 2.0 eV needed to eject electron

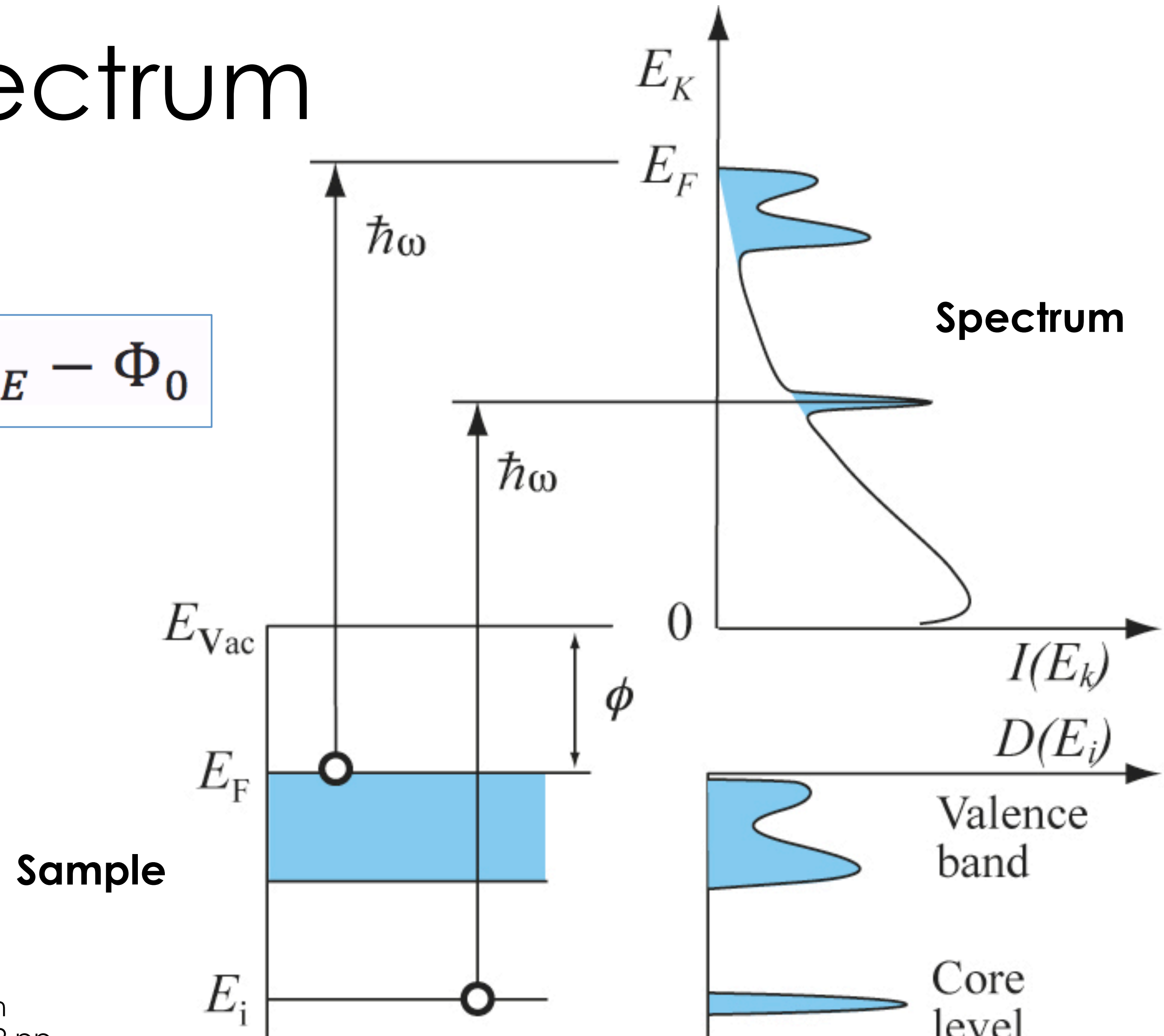
Photoelectric effect



http://pages.physics.cornell.edu/p510/E-10_Photoelectric_Effect

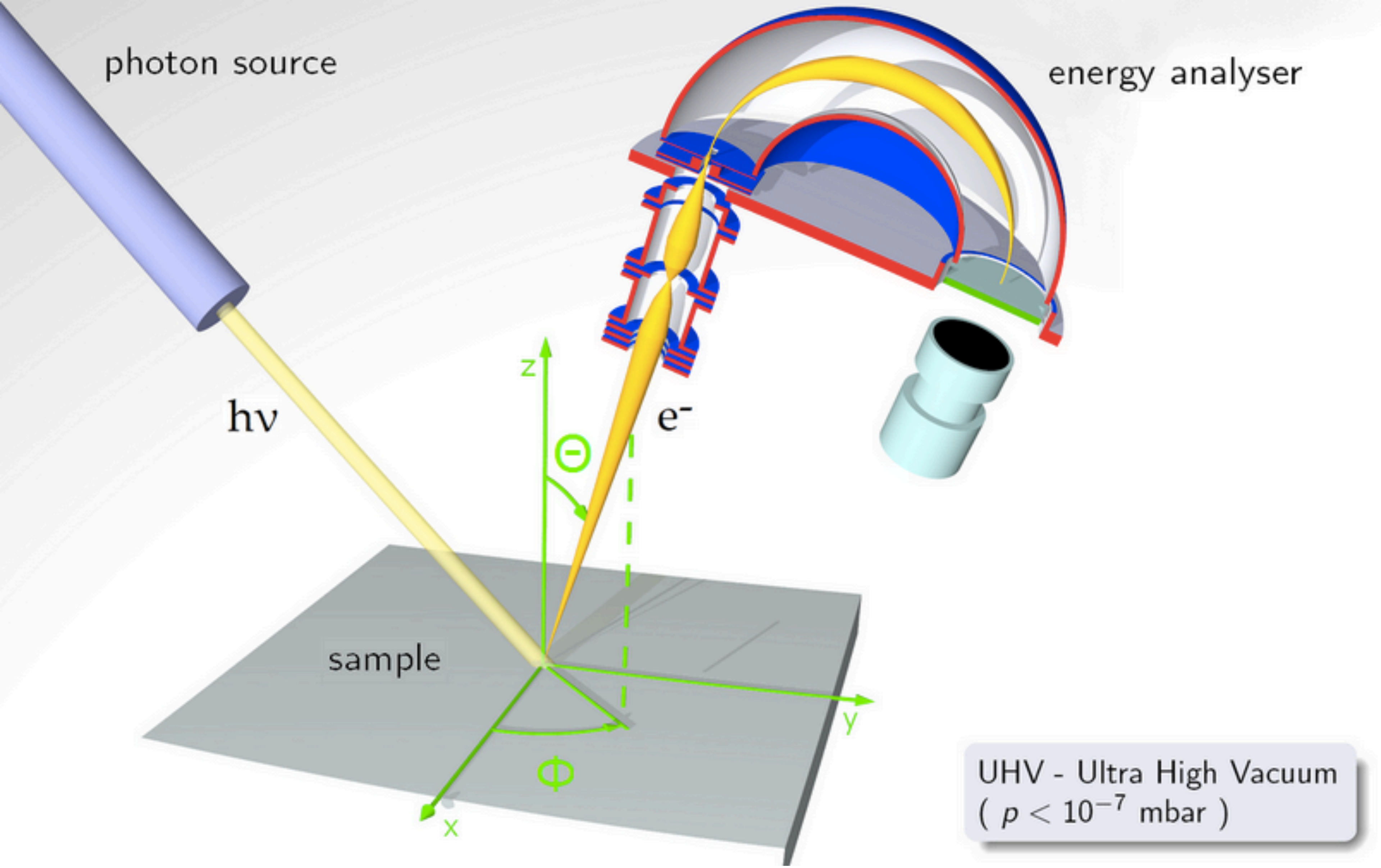
PES Spectrum

$$E_{KE} = hv - E_{BE} - \Phi_0$$



Oura K. et al. Surface Science: An Introduction // Springer, 2010 - 452 pp.

http://eng.thesaurus.rusnano.com/wiki/article1915

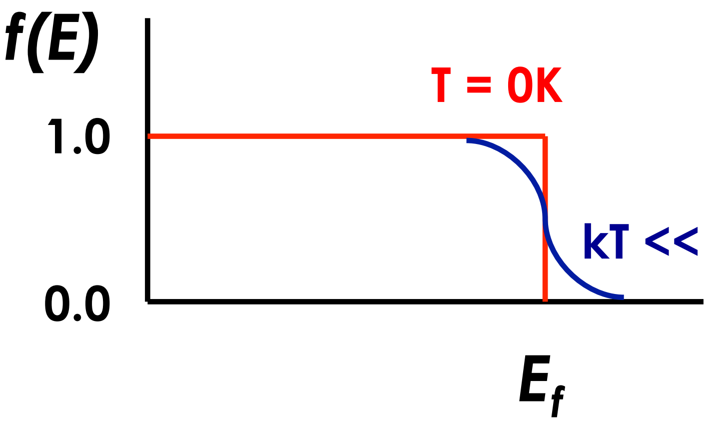


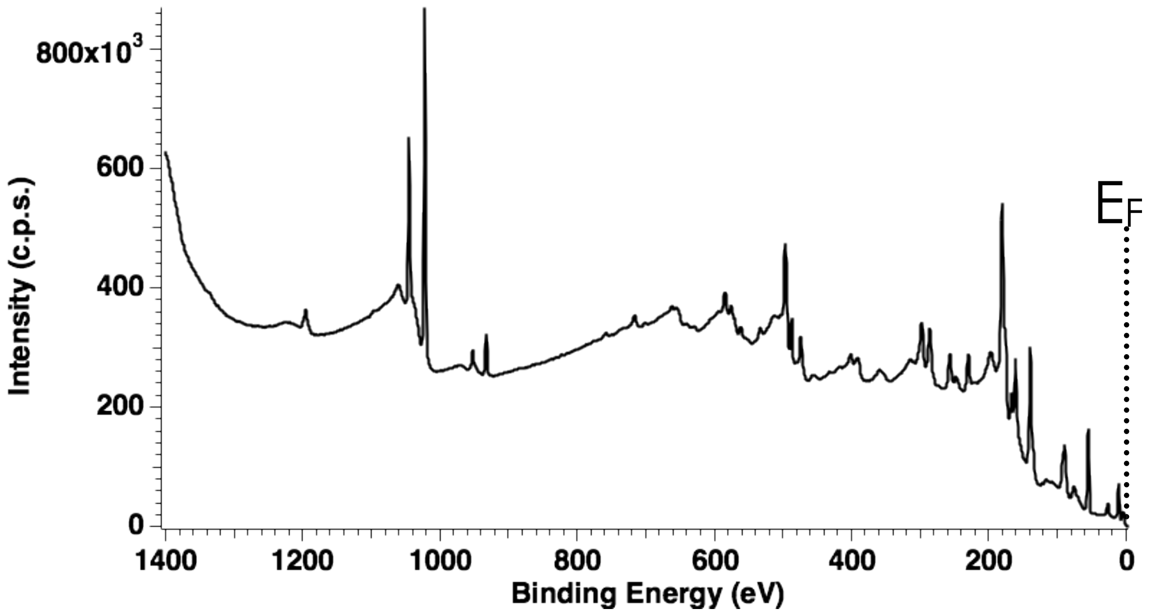
1 mbar = 0.75 torr

https://www.khanacademy.org/science/chemistry/electronic-structure-of-atoms/electron-configurations-jay-sal/a/photoelectron-spectroscopy

Fermi Level Reference

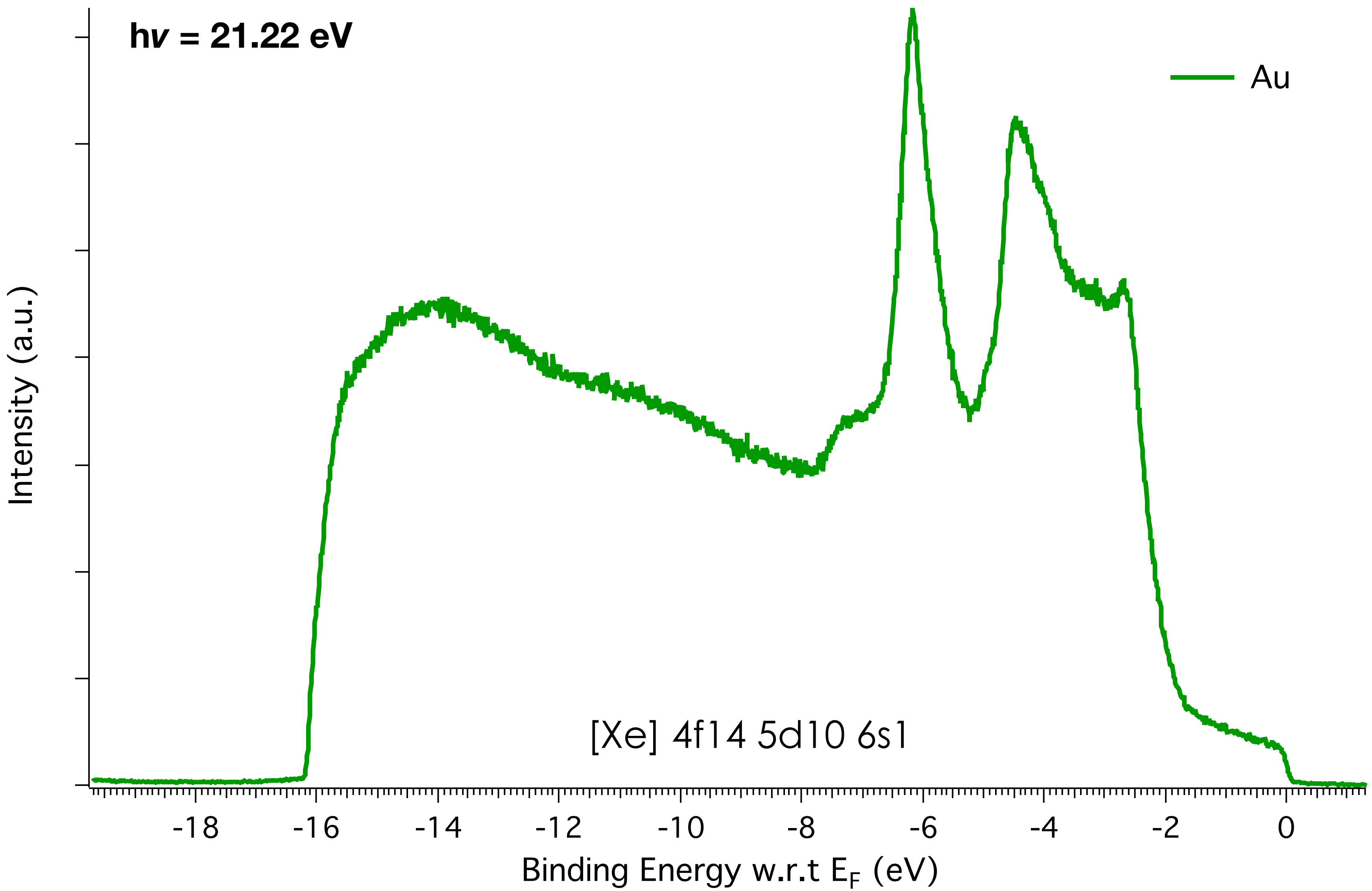
$$f(E) = \frac{1}{\exp\left[\frac{E - E_f}{kT}\right] + 1}$$





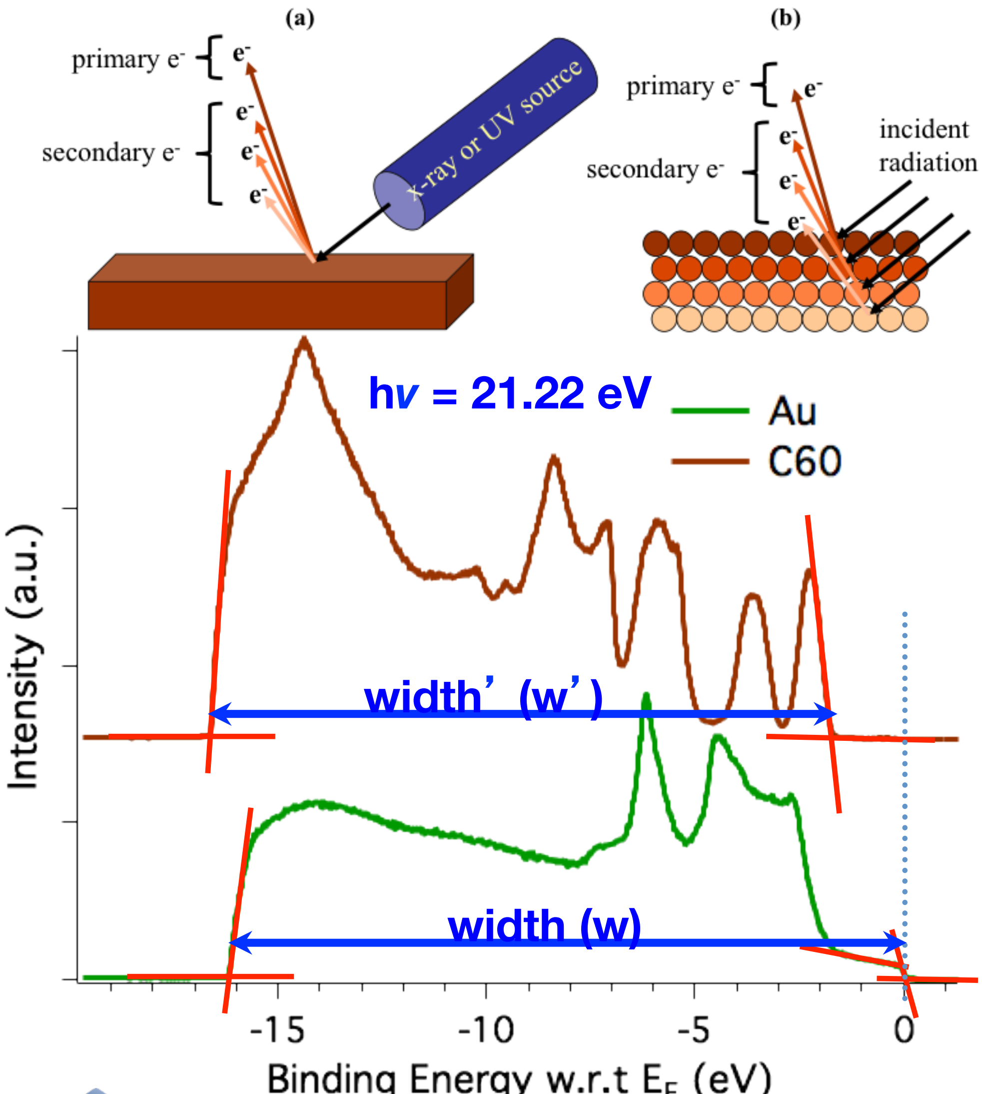
T = 0K — $f(E)=1$ for $E < E_f$; $f(E)=0$ for $E > E_f$

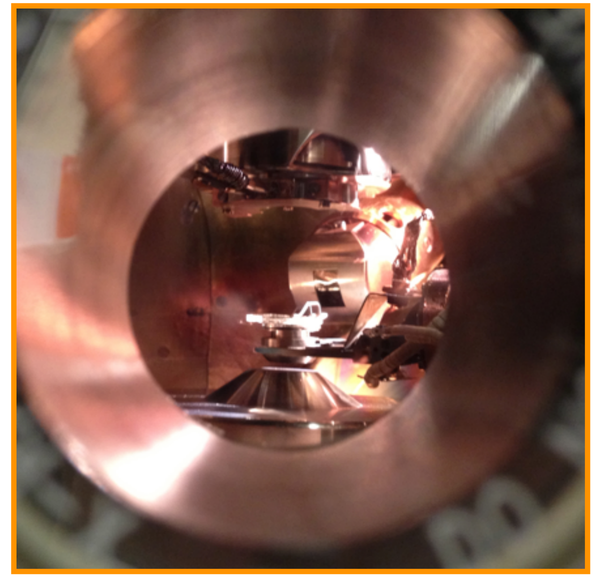
$kT << E_f$ — $f(E)=0.5$ for $E = E_f$



hv = 21.22 eV
Au
Intensity (a.u.)
[Xe] 4f14 5d10 6s1
-18
-16
-14
-12
-10
-8
-6
-4
-2
0
Binding Energy w.r.t E_F (eV)

Ultraviolet photoelectron spectroscopy





$$\phi = h\nu - (E_{\text{Fermi}} - KE_{\text{low}})$$

$$\text{IP} = h\nu - (KE_{\text{high}} - KE_{\text{low}})$$

Spectral Analysis

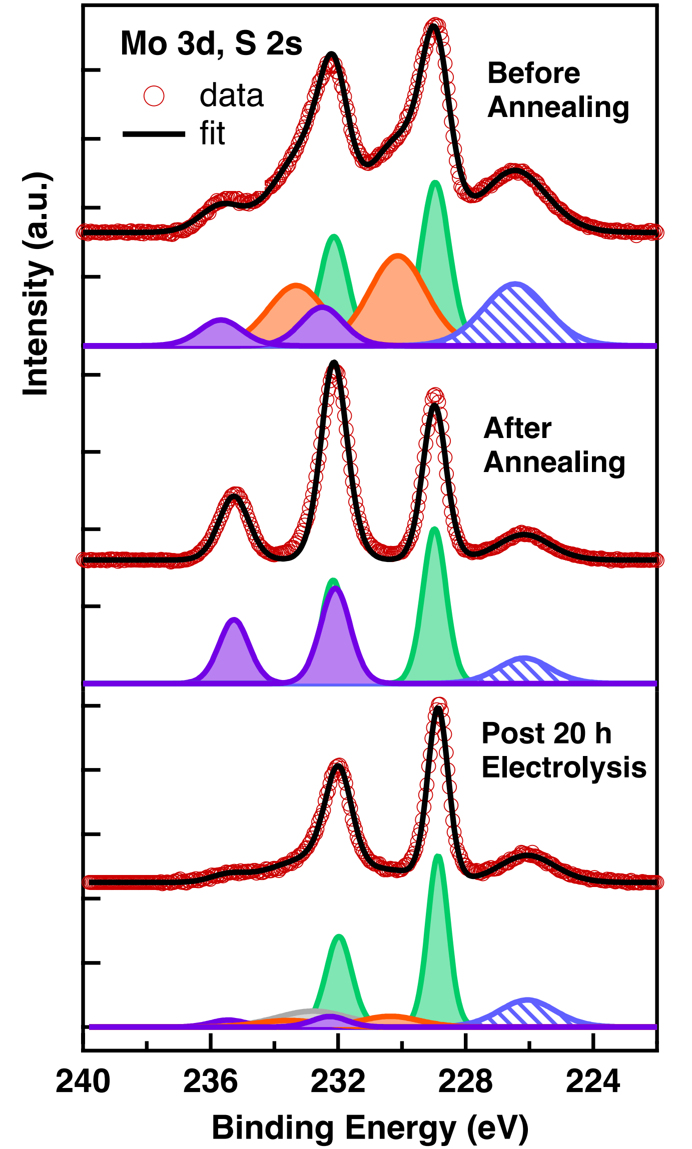
- Sample charging
- Auger transitions
- Plasmon loss
- X-ray satelites
- X-ray “ghosts”
- Overlapping peaks
- Spectral ID
- Chemical shifts

$\ell =$ 0…s
1…p
2…d
3…f

n → $\mathbf{3d_{5/2}}$

$j = \ell - s$

$j = \ell + s$

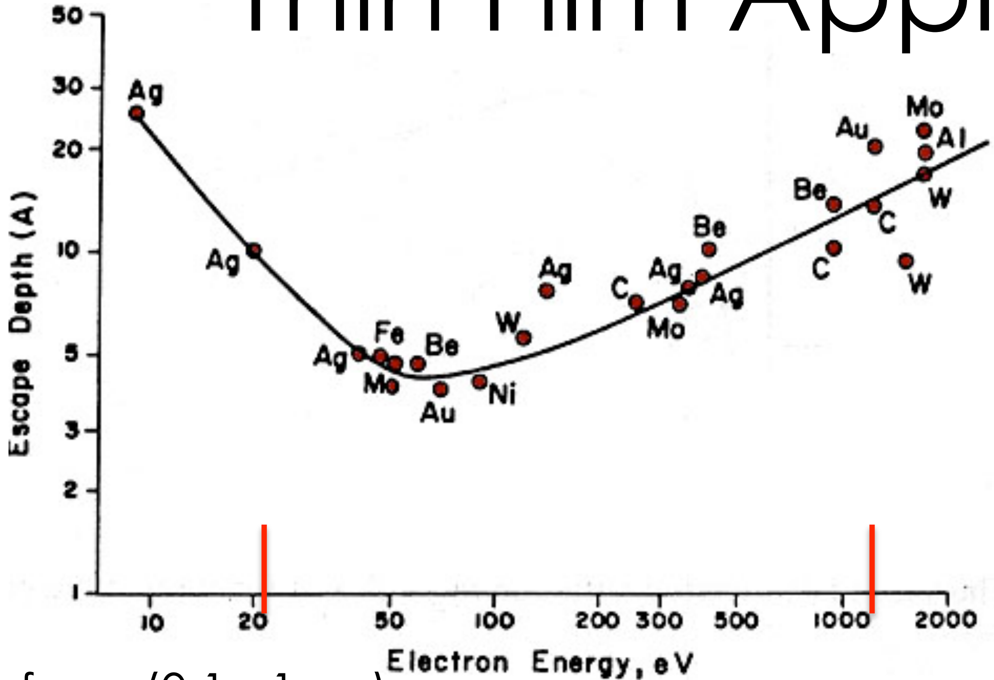


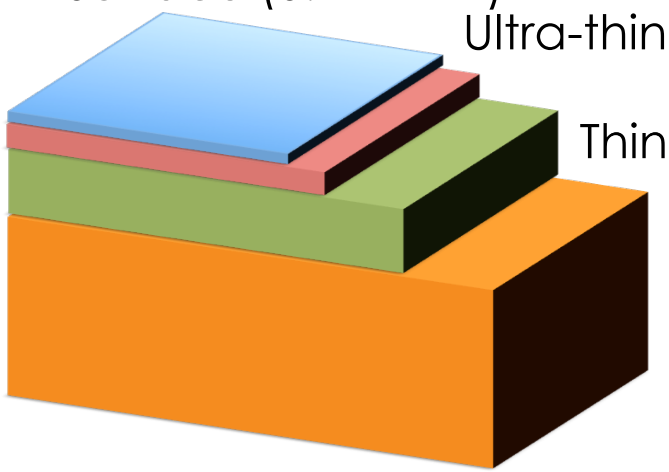
Gu, Aguiar, Ferrere, Steirer , Yan, Xiao, Young, Al-Jassim, Neale, Turner, *Nature Energy*, 2016 accepted

PES as a Research Tool

- Limitations
  - Requires high vacuum $$
  - Slow data acquisition/ processing
  - Large Area Required
  - H and He not Measureable
    - Only Li and up
- Advantages
  - Non-destructive
  - Surface Sensitive ~few nm
  - Quantitative Composition
  - Identifies Chemical States
  - Measures Electronic Structures of Surfaces and Interfaces

Thin Film Applications



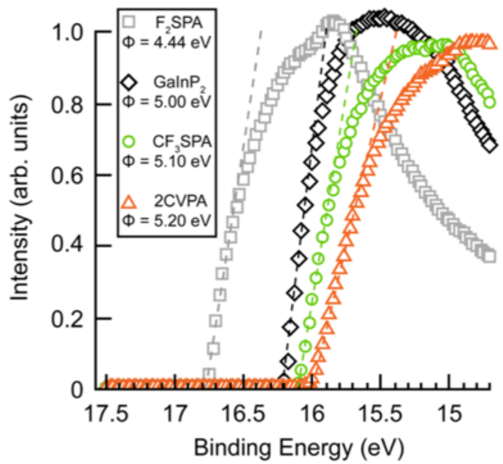


- Surfaces:
  - Wetting
  - Soldering
  - Catalysts
  - Work Function
  - Optics
  - Diffusion
- Ultra-Thin Films
  - Contacts
  - Oxidation
  - Passivation
  - Tribology
  - Gate Dielectrics
  - Optics
  - Diffusion

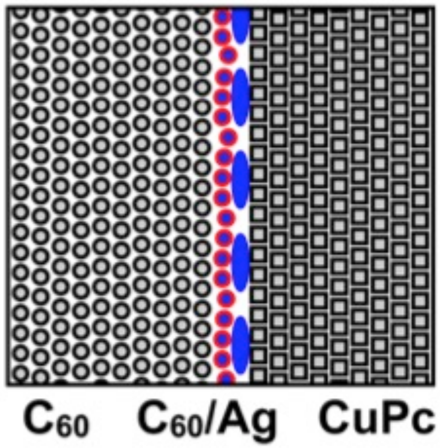
- http://xpssimplified.com/whatisxps.php
- http://www.virginia.edu/ep/SurfaceScience/electron_interactions.htm

PES Research Topics

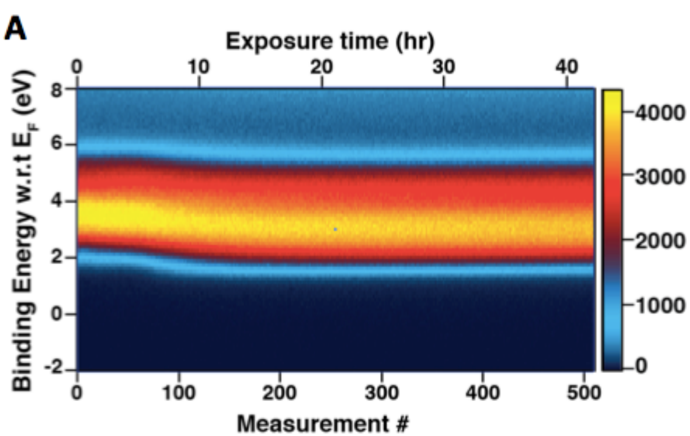
Dipole Studies



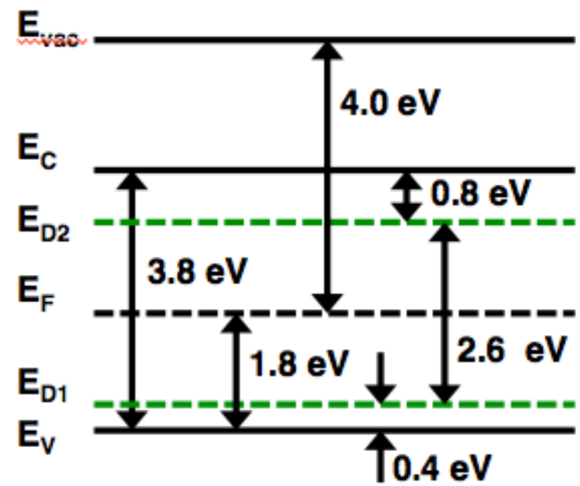
Nanostructured Interfaces



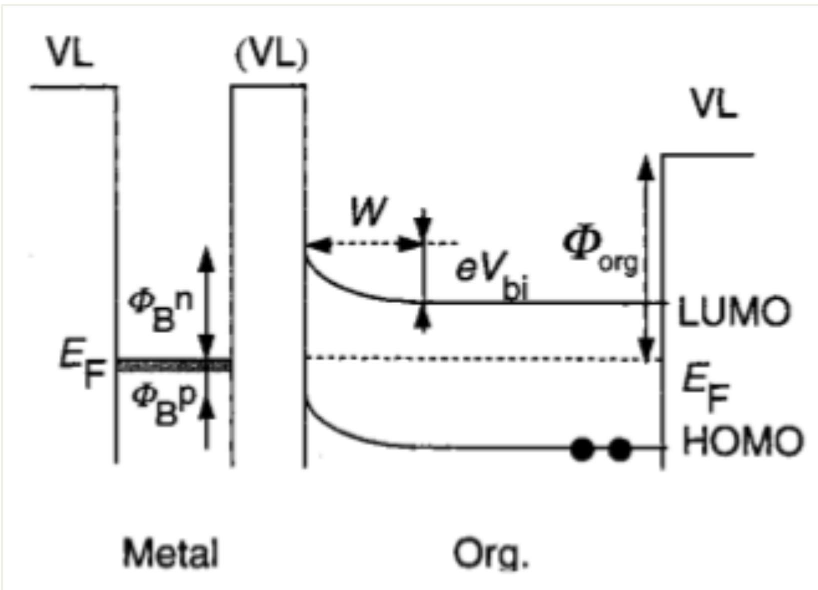
Phase Transformations

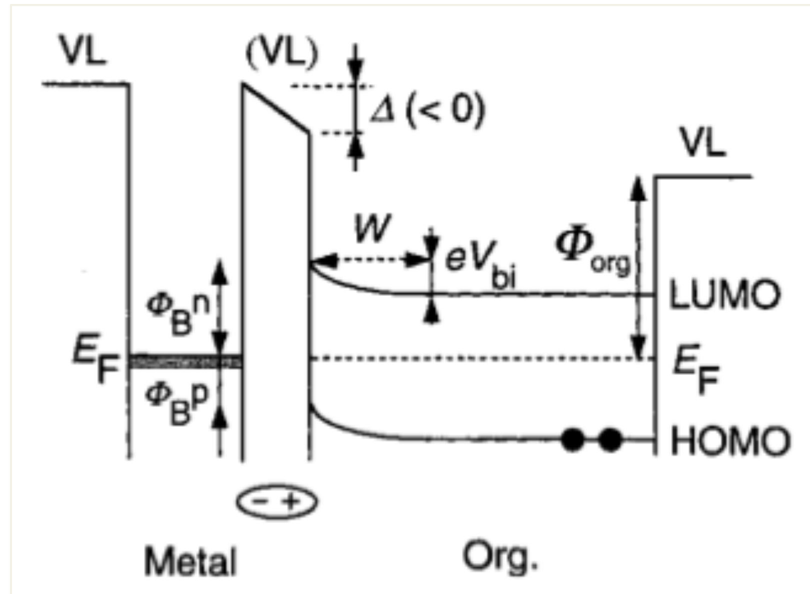


Defect Assessments



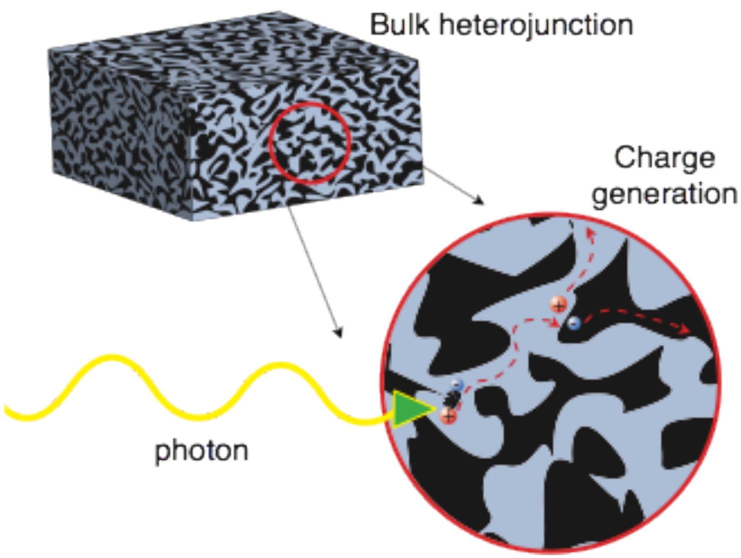
Interface dipole effects



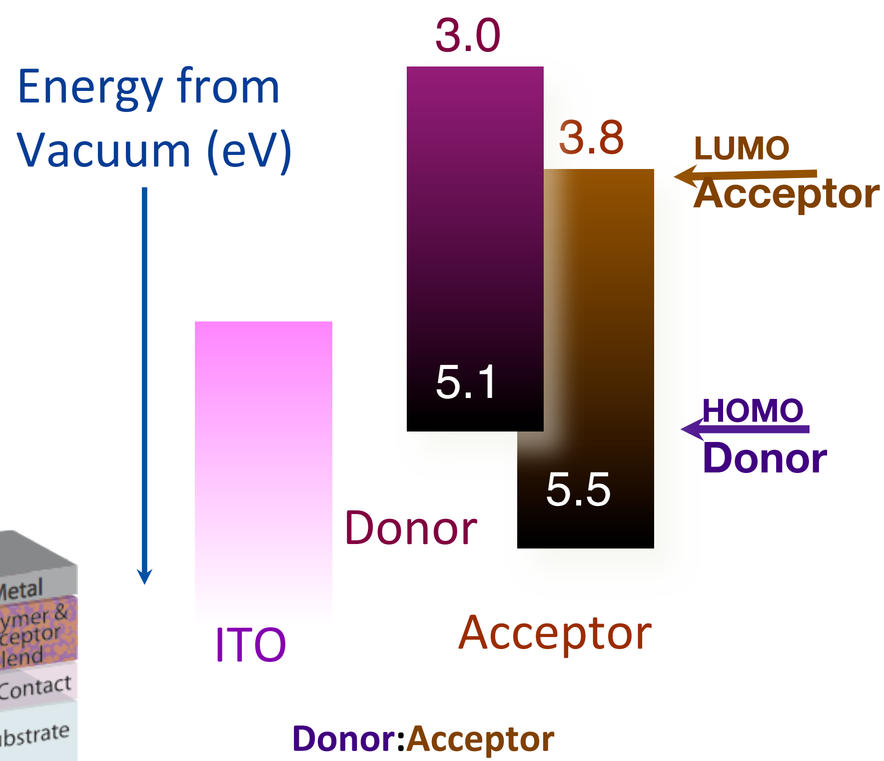


Ishii, H., Sugiyama, K., Ito, E. & Seki, K. *Adv. Mater.* **11,** 605–625 (1999).

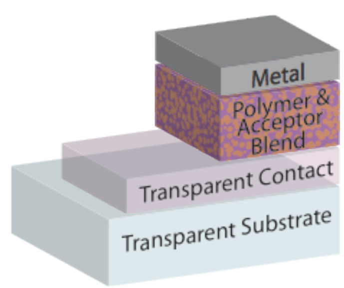
Bulk Heterojunction PV



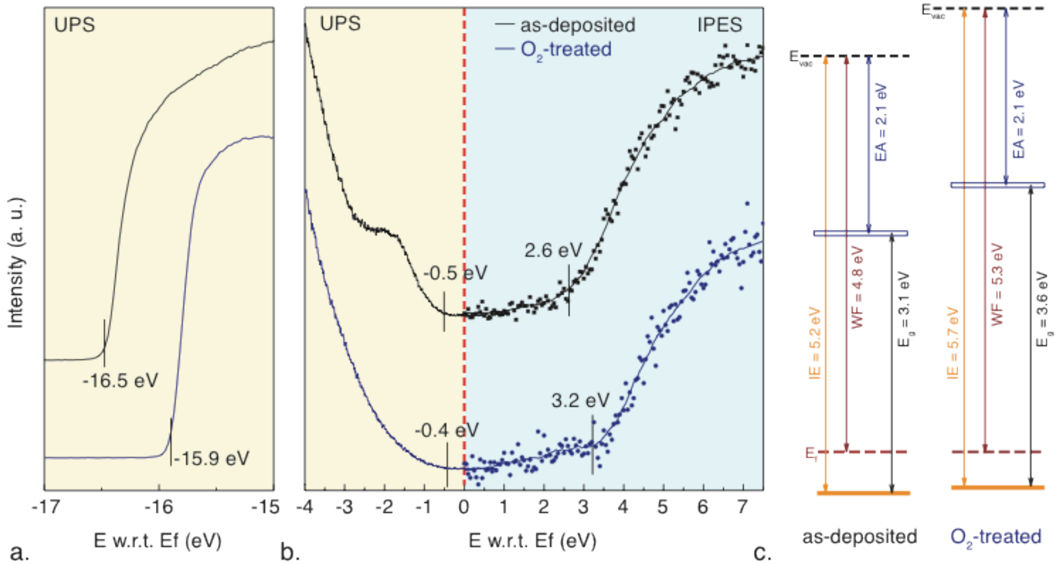
$$V_{OC} \leq \frac{1}{q}|\mathrm{LUMO_A} - \mathrm{HOMO_D}| - 0.3V$$



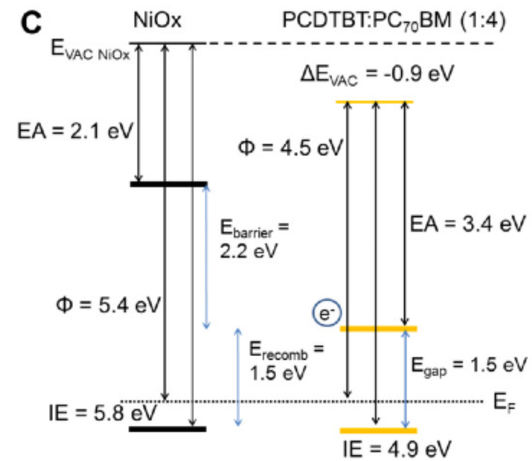
- Hole contact affects:
  - Photovoltage
  - Photocurrent
  - Diode behavior



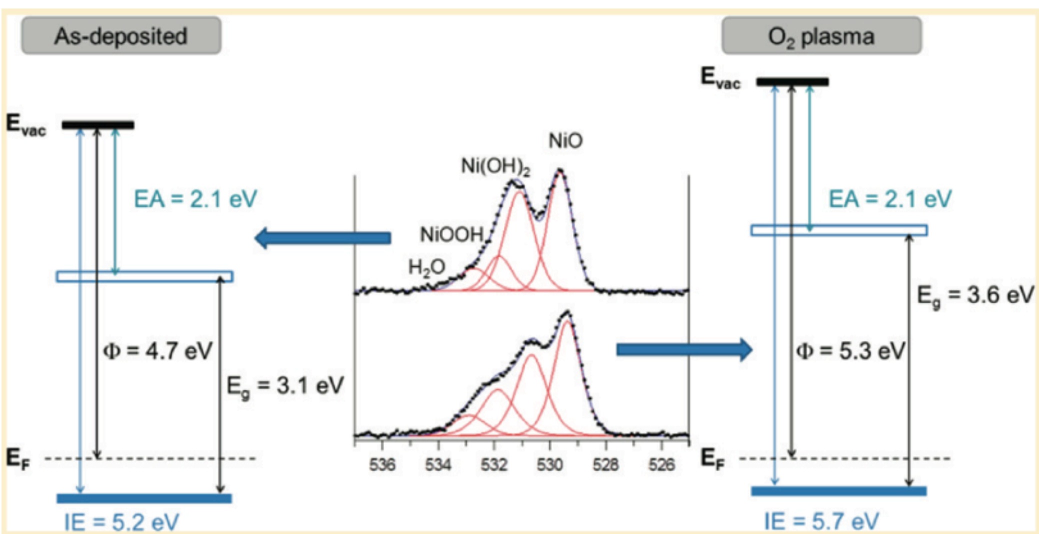
NiOOH Structure-Property-Function



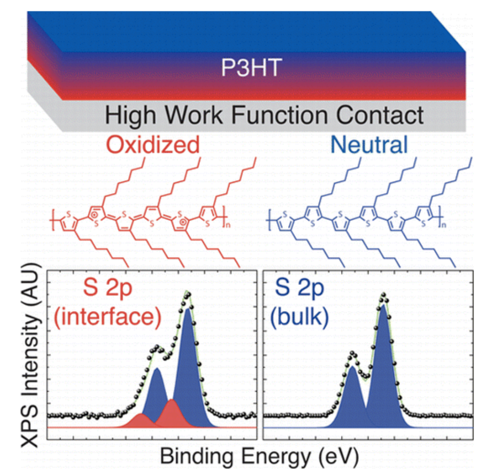
Steirer, Ndione, Widjonarko, Lloyd, Meyer, Ratcliff, Kahn, Armstrong, Curtis, Ginley, Berry, Olson, *Adv. Energy Mater.* **1** 813, (2011)



Ratcliff, Meyer, Steirer, Armstrong, Olson, Kahn, *Organic Electronics*, **13** 744, (2012)

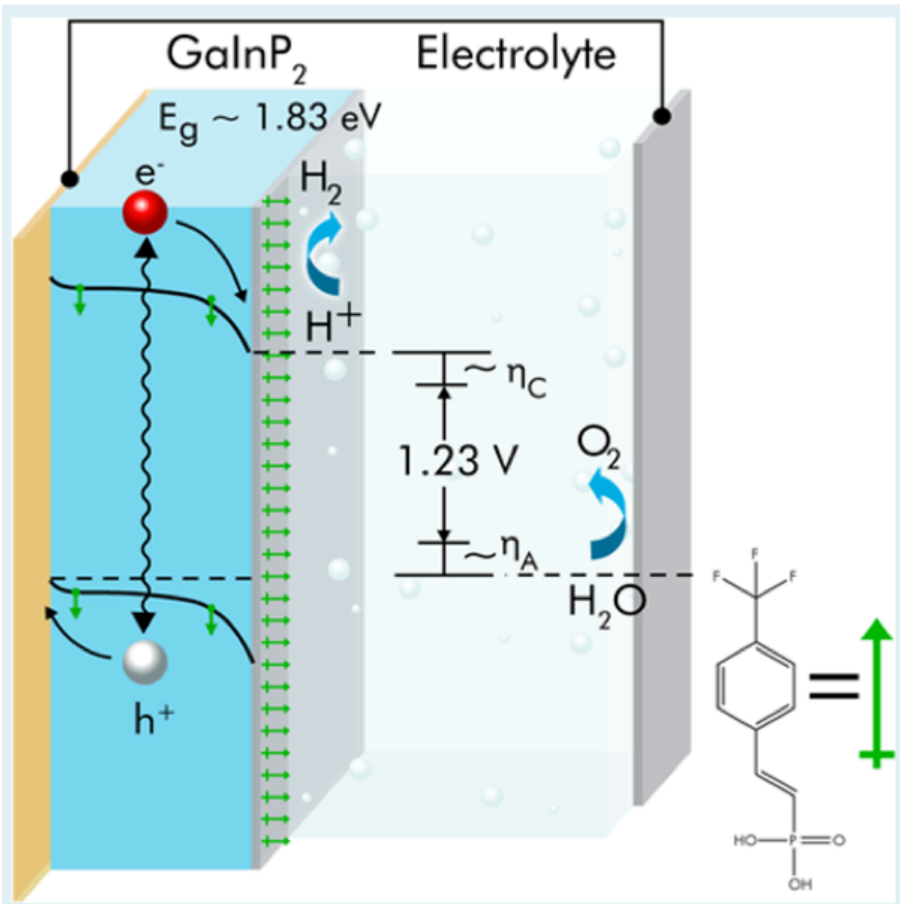


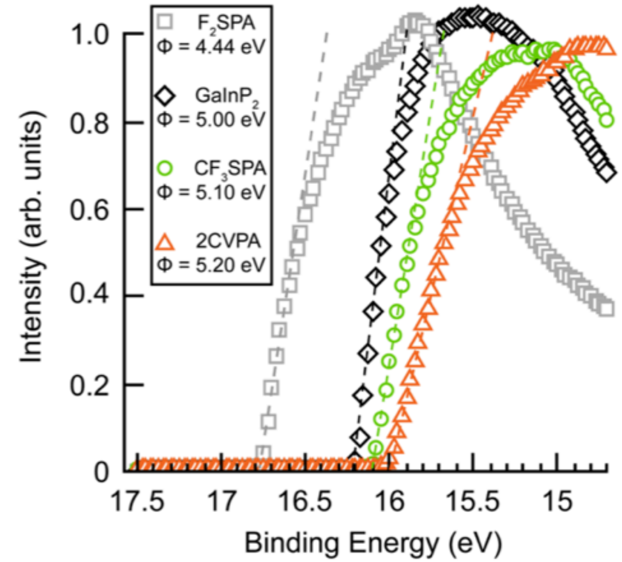
Ratcliff, Meyer, Steirer, Garcia, Berry, Ginley, Olson, Kahn, Armstrong *Chemistry of Materials* **23**, 4988 (2011).

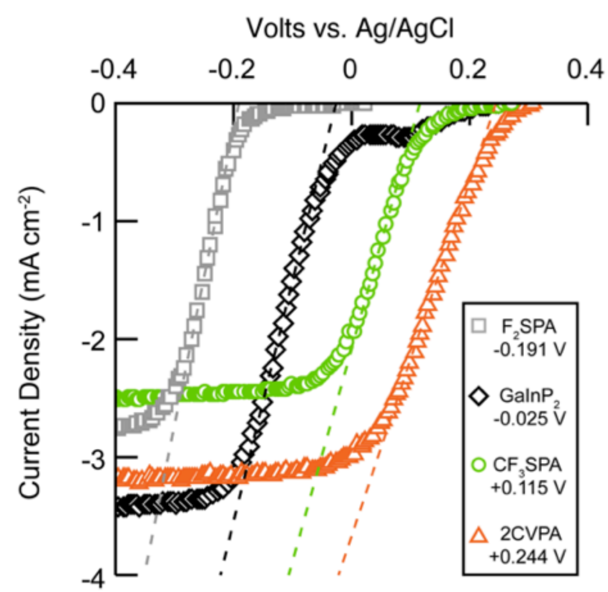


C. Shallcross, et al., *J. Phys. Chem. Lett.*, **6** 1303, (2015)

Dipole effect in photoelectrochemistry



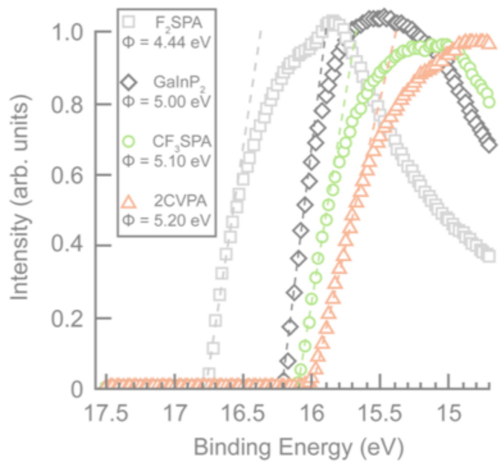




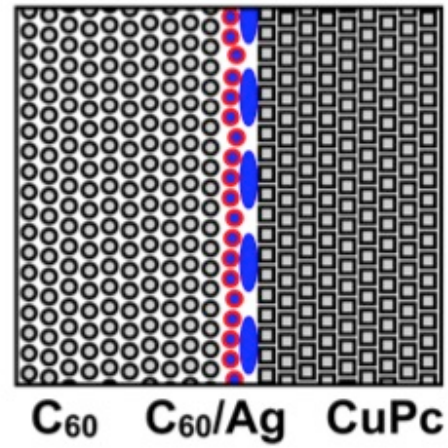
MacLeod, Steirer, Young, Koldemir, Sellinger, Turner, Deutsch, Olson, *ACS Appl. Mater. Interfaces* **7**, 11346–11350 (2015).

PES Research Topics

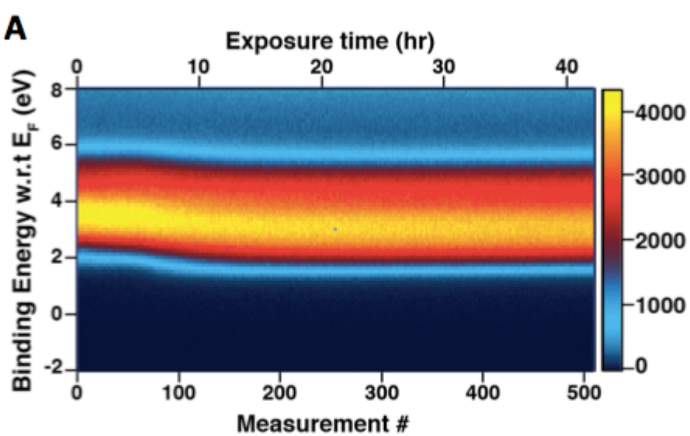
Dipole Studies



Nanostructured Interfaces



Phase Transformations



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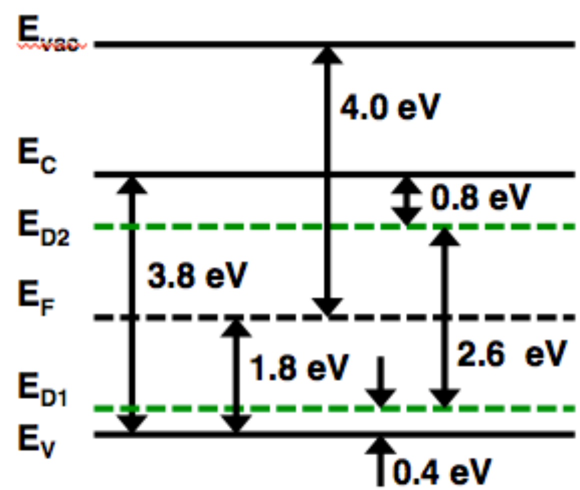
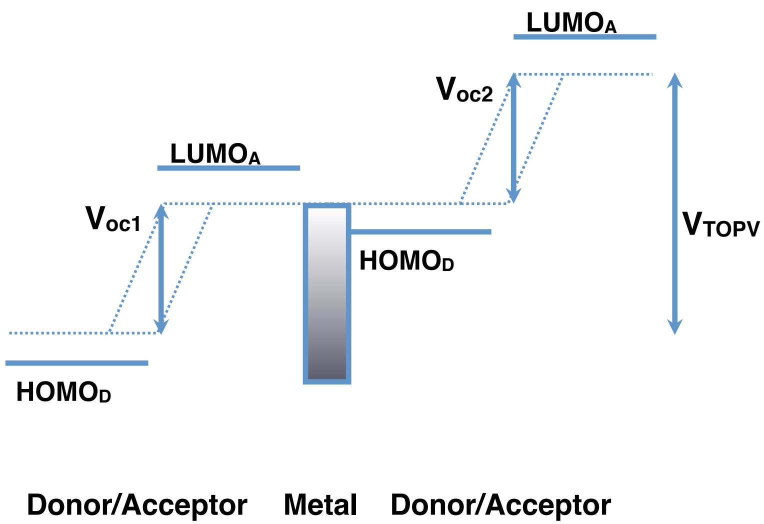
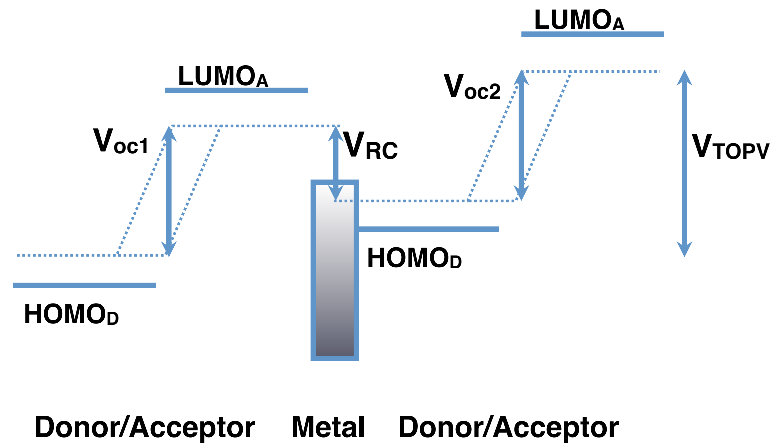
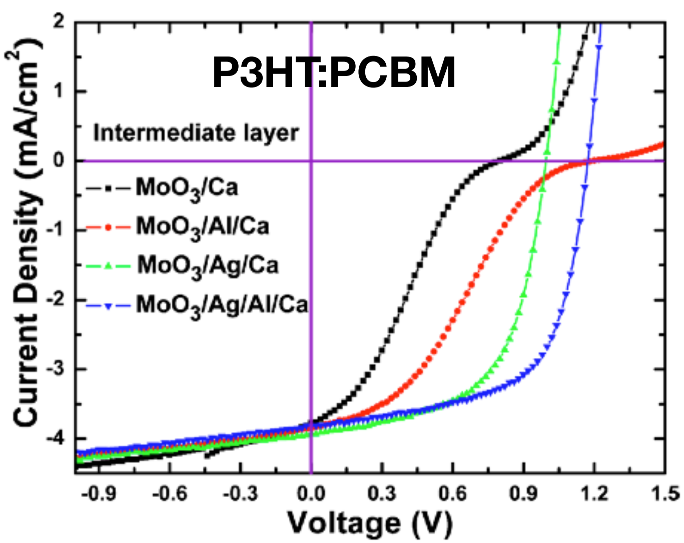


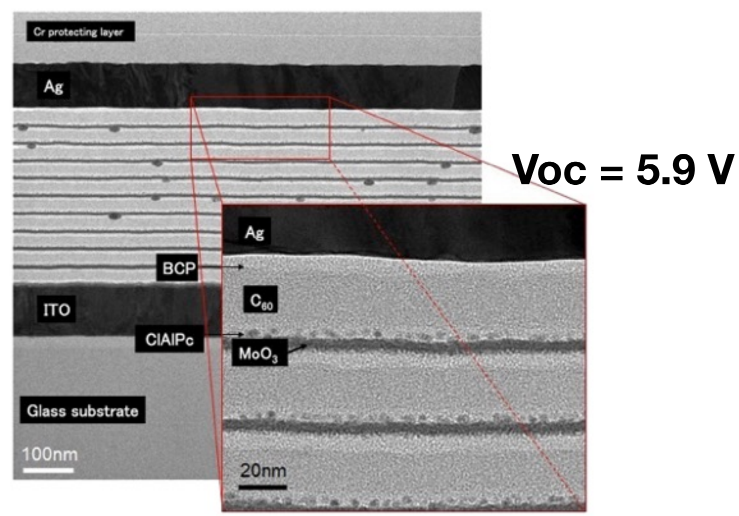
Voltage loss at recombination interface





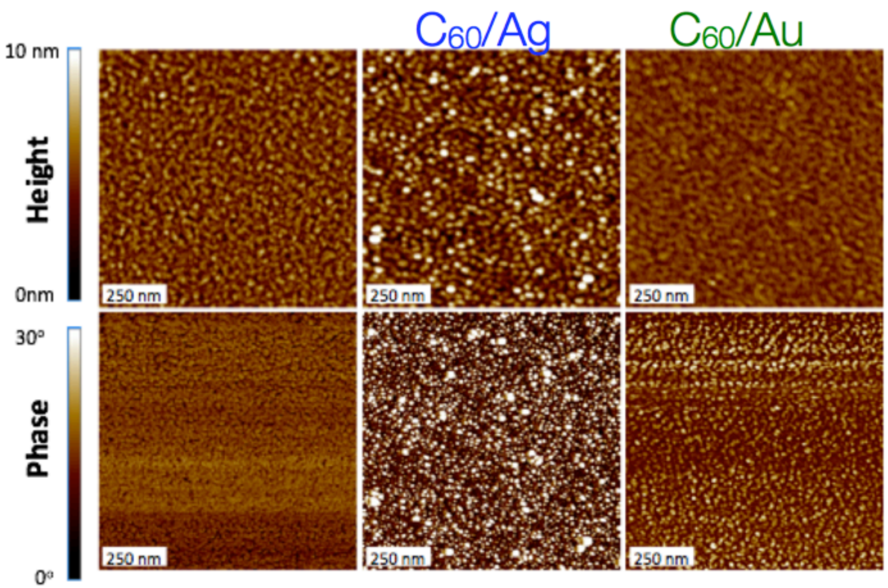


Sun et al. *Applied Physics Letters* (2010) vol. 97 (5) pp. 053303

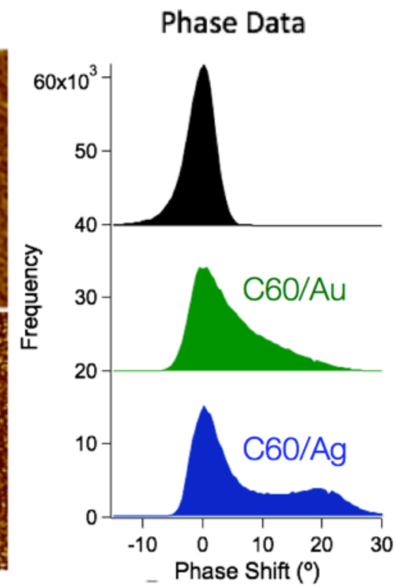


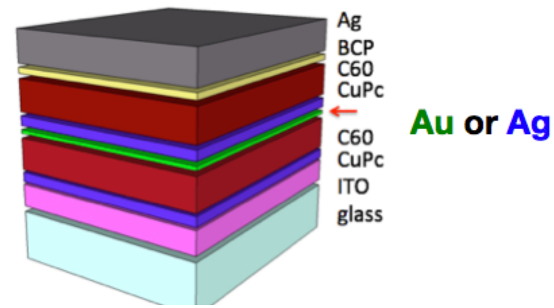
Zou et al. *Applied Physics Letters* (2012) vol. 100 (24) pp. 243302

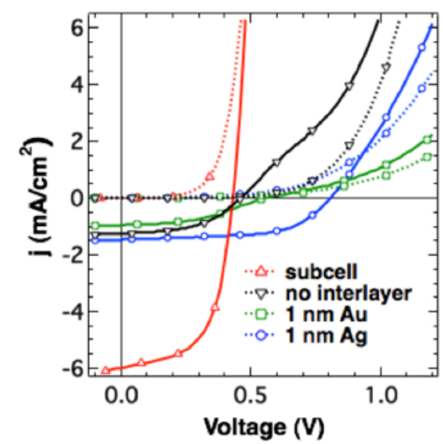
Morphology of Metal/Fullerene

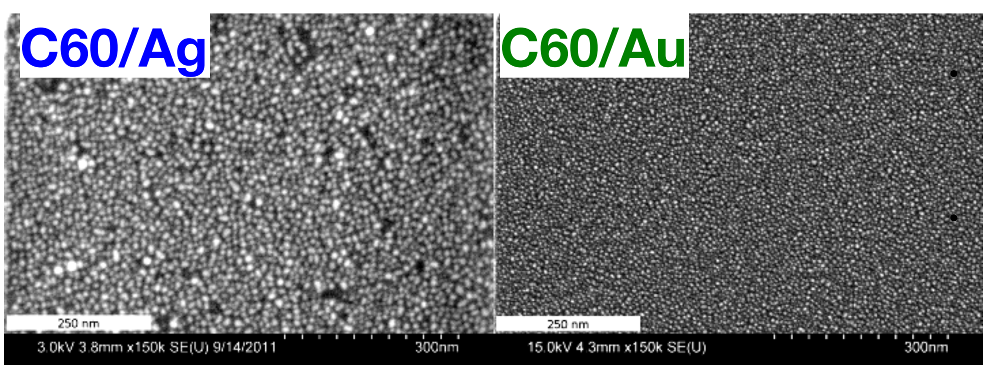


1x1 um tapping mode images









- Diameters: Ag (15 nm) larger than Au (7 nm)
- Au over-layer is more uniformly dispersed

Device	V_{oc} (V)
subcell	0.43
No-interlayer	0.45
1 nm Au	0.56
1 nm Ag	0.81

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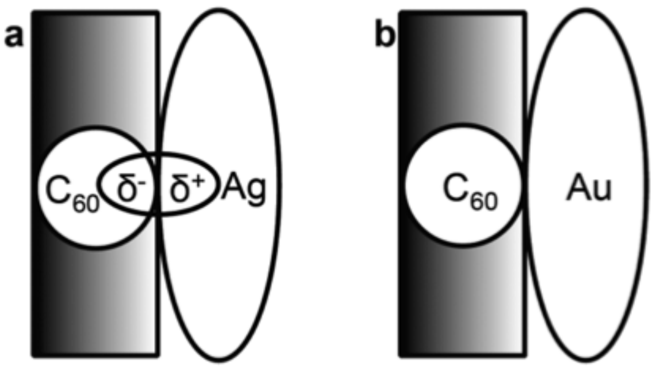
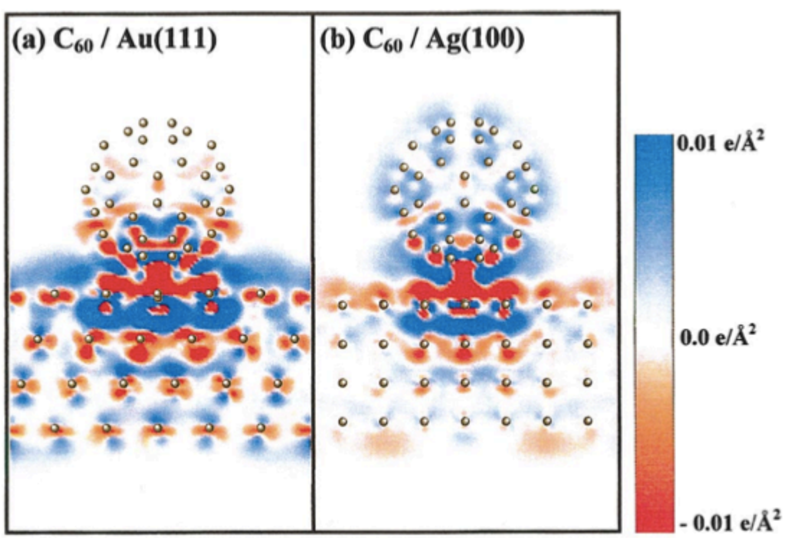
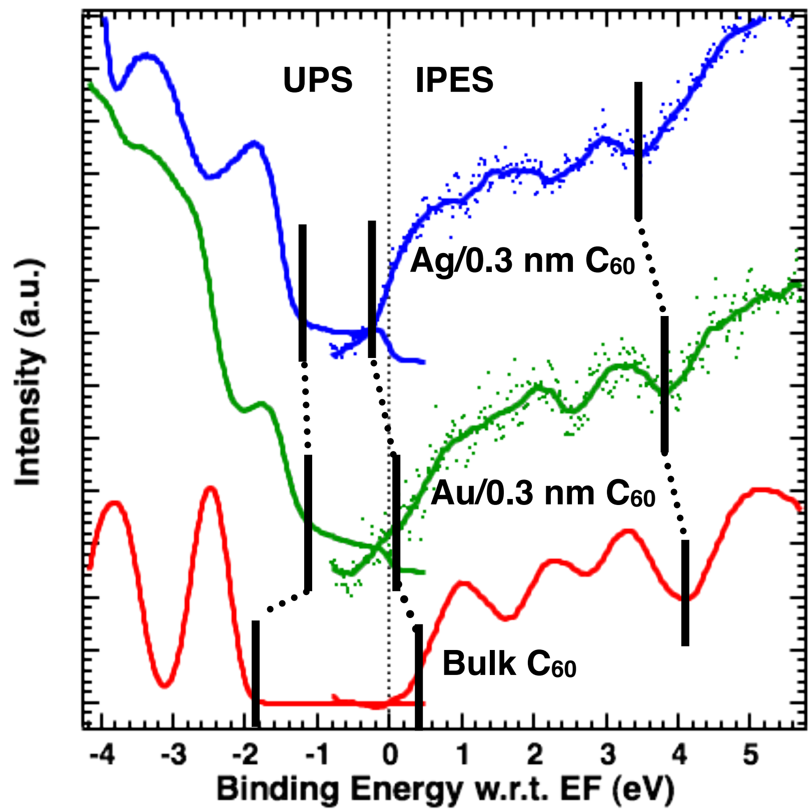
Polarized interfaces



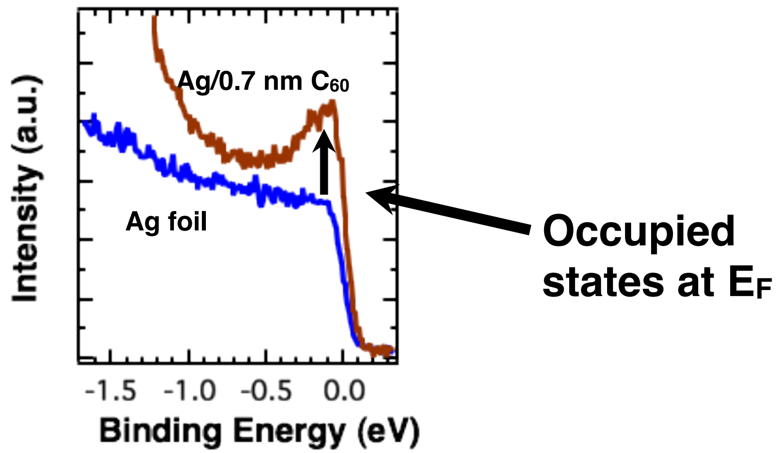


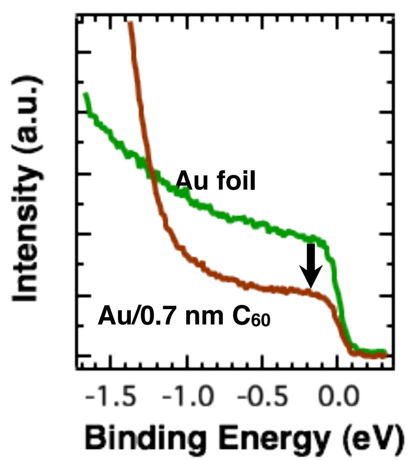
Lu, X., Grobis, M., Khoo, K., Louie, S. & Crommie, M. *Phys. Rev. B* **70,** 115418 (2004).

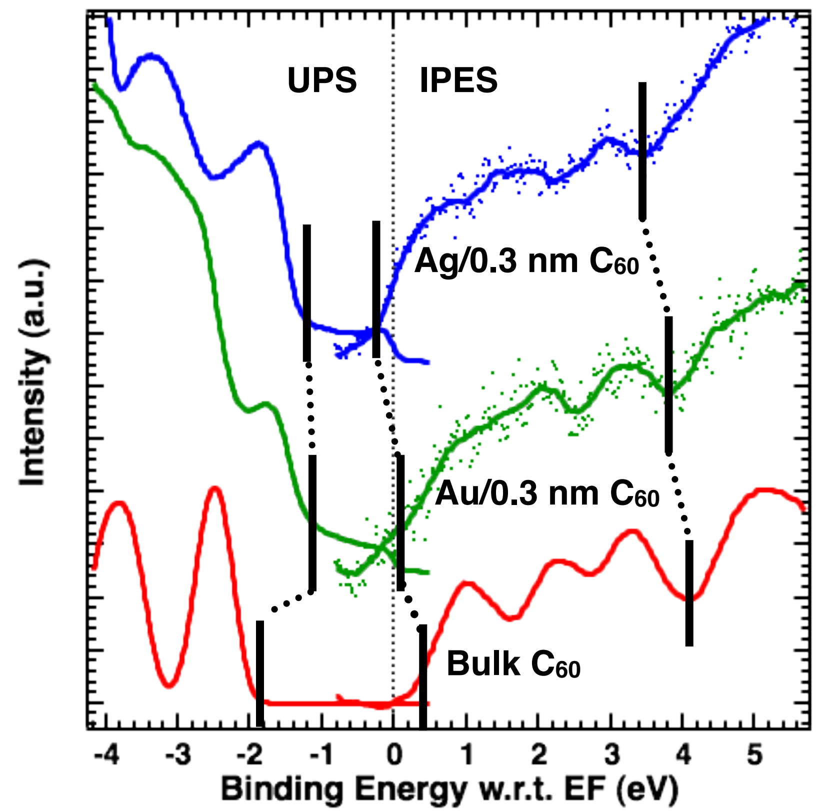


K Steirer, G MacDonald, S Olthof, J Gantz, E Ratcliff, A Kahn, and N Armstrong, *J Phys Chem C* 117(2013)p22331.

Charge redistribution at C_{60}/Metal







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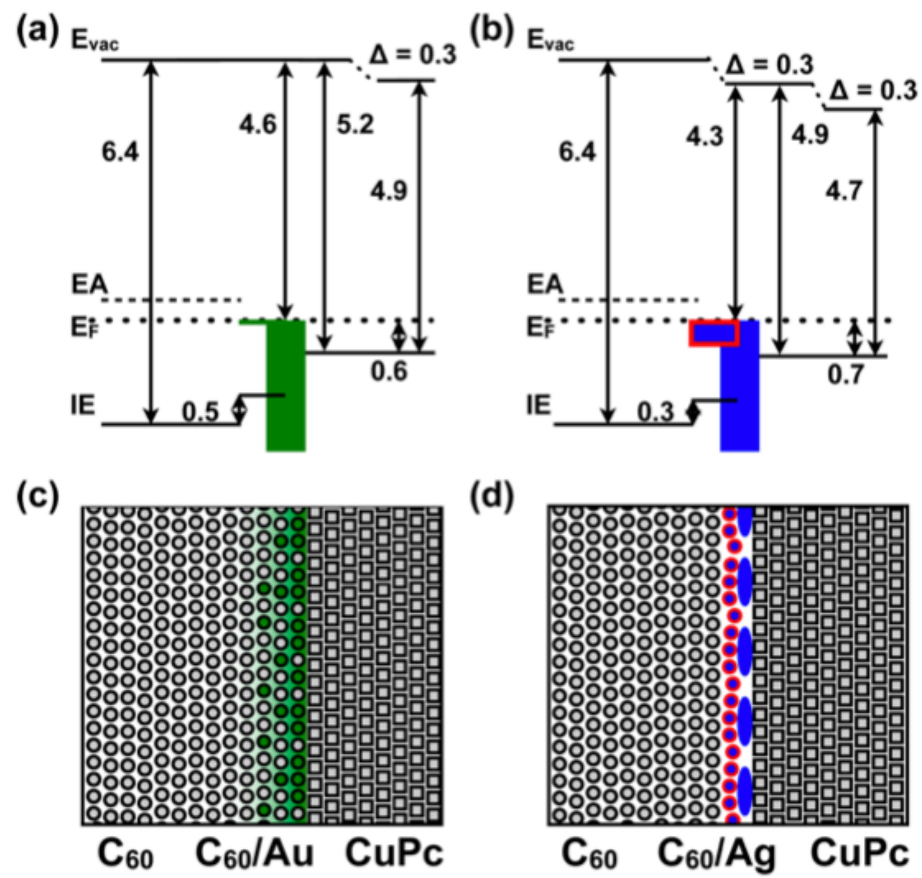
Combined morphology and energetics

Device	V_{oc} (V)
subcell	0.43
No-interlayer	0.45
1 nm Au	0.56
1 nm Ag	0.81

- Reduced electronic gap for C_{60} due to
  - mirror potential
  - rehybridized frontier molecular orbitals
  - delocalized interface state with Ag
- NPs form at both interlayers
  - affected by the nucleation and growth
  - Au is more uniform but less effective
- Voc addition may be result of **exohedral doping/charge redistribution**



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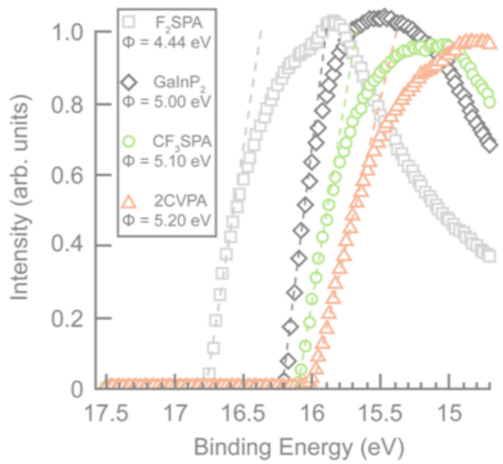
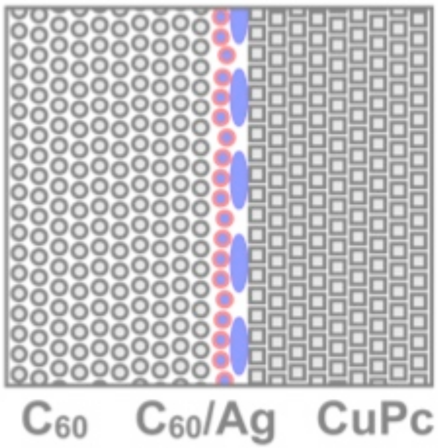
PES Research Topics

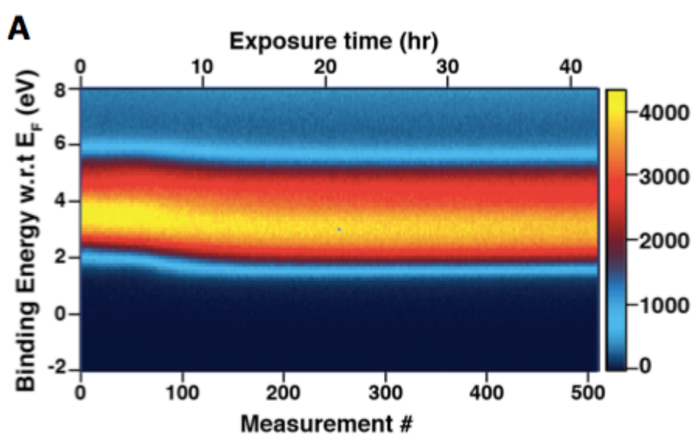
Dipole Studies



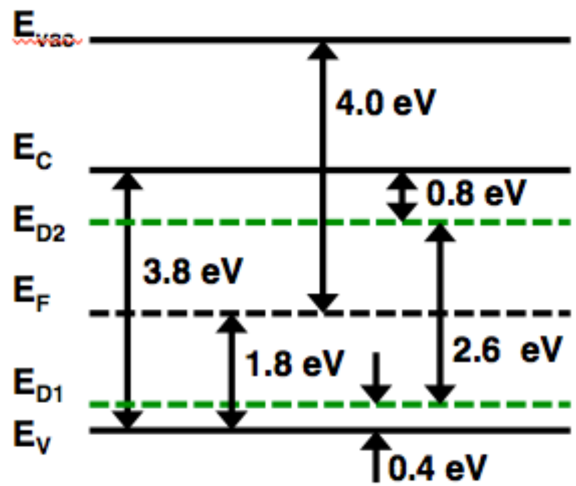
Nanostructured Interfaces



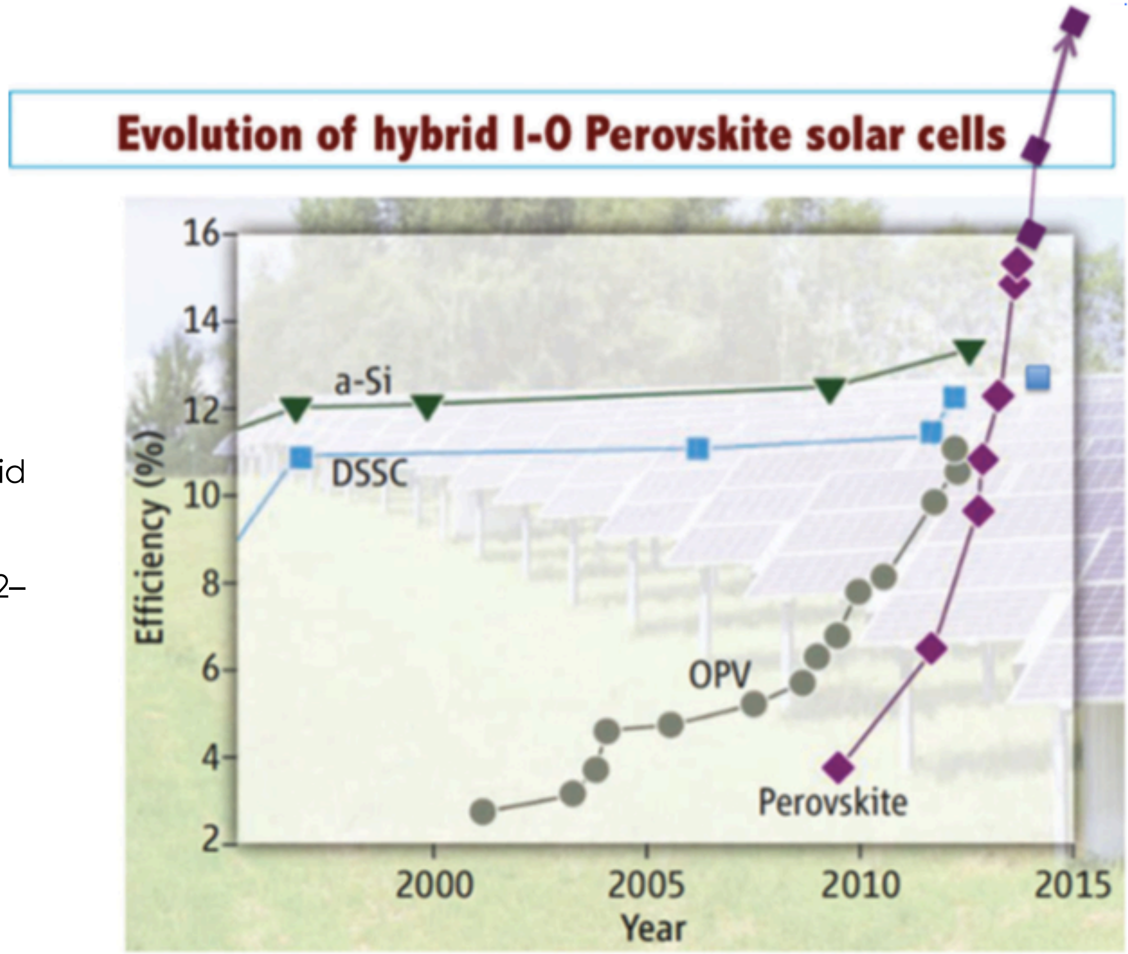
Phase Transformations



Defect Assessments

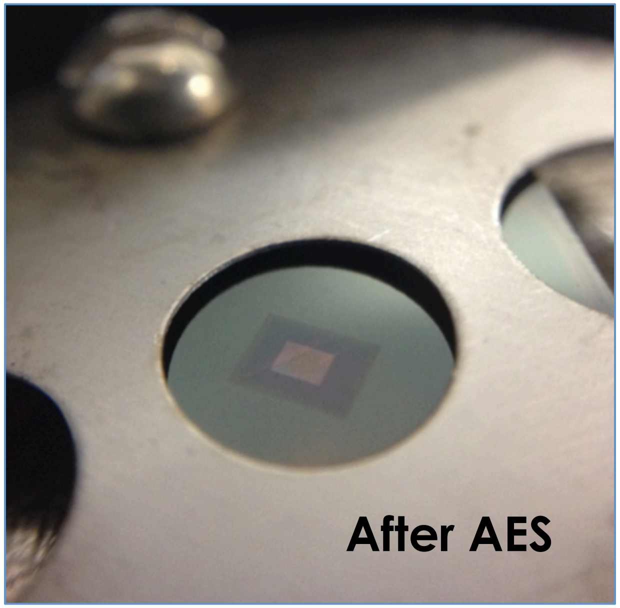


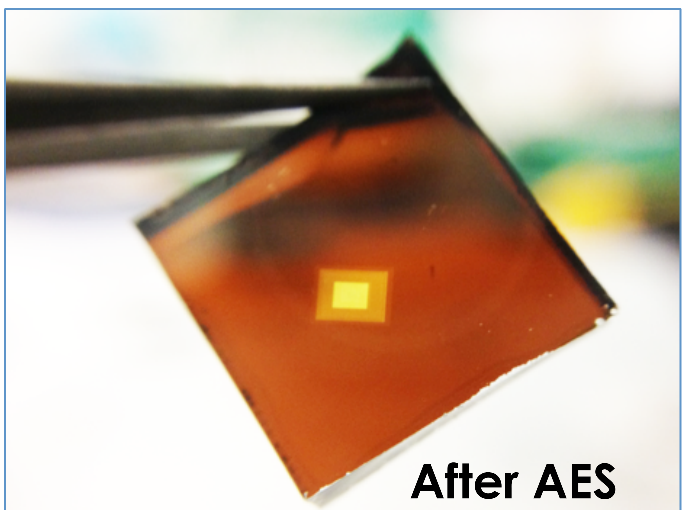
Unprecedented Progress



Berry, J., Buonassisi, T., et al. Hybrid Organic–Inorganic Perovskites (HOIPs): Opportunities and Challenges. *Adv. Mater.* **27**, 5102–5112 (2015).

Electron Degraded $CH_3NH_3PbI_3$



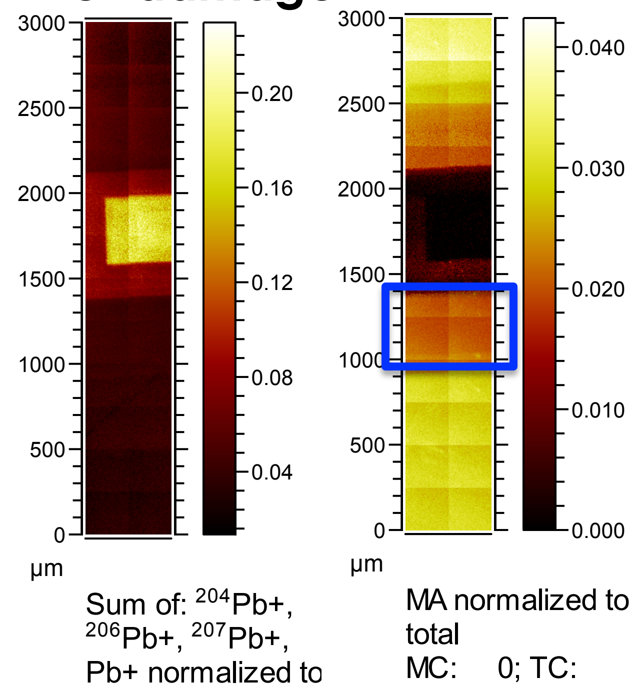


SIMS: 3mm x 0.5mm 2-D surface map

e- damage

Edge of damaged perovskite

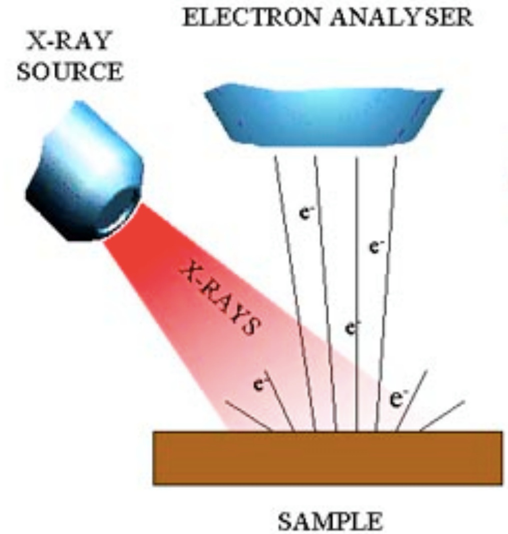
Undamaged perovskite



- Important for XPS, UPS, and e-beam techniques such as IPES, AES, SEM, EBIC, etc.

Approach

- X-ray flux ~ 1.5 x 10^{11}ph/cm^{2}s
  - Can vary by tilting sample, anode choice, changing spectrometers
  - 2 mm Al mono
  - 45° incident
  - Minimum spot
  - 5.4 x 10^{14} ph/cm^{2}hr
- Measure (x510 over 42 hr)
  - elemental %
  - chemical state (BE)
  - valence spectra (E_V)
- Choose vacuum stable MAPI samples (2x10^{-10} torr)
  - Glass/FTO/TiO_2/MAPI
  - Stable in vacuum up to one week

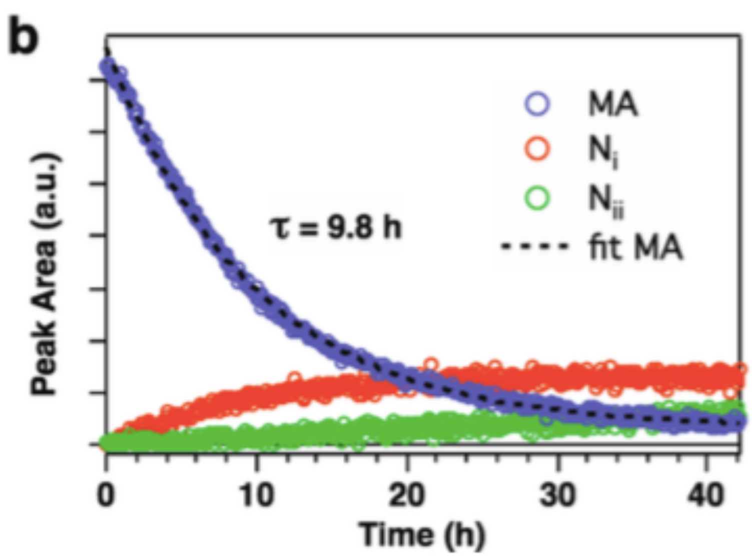


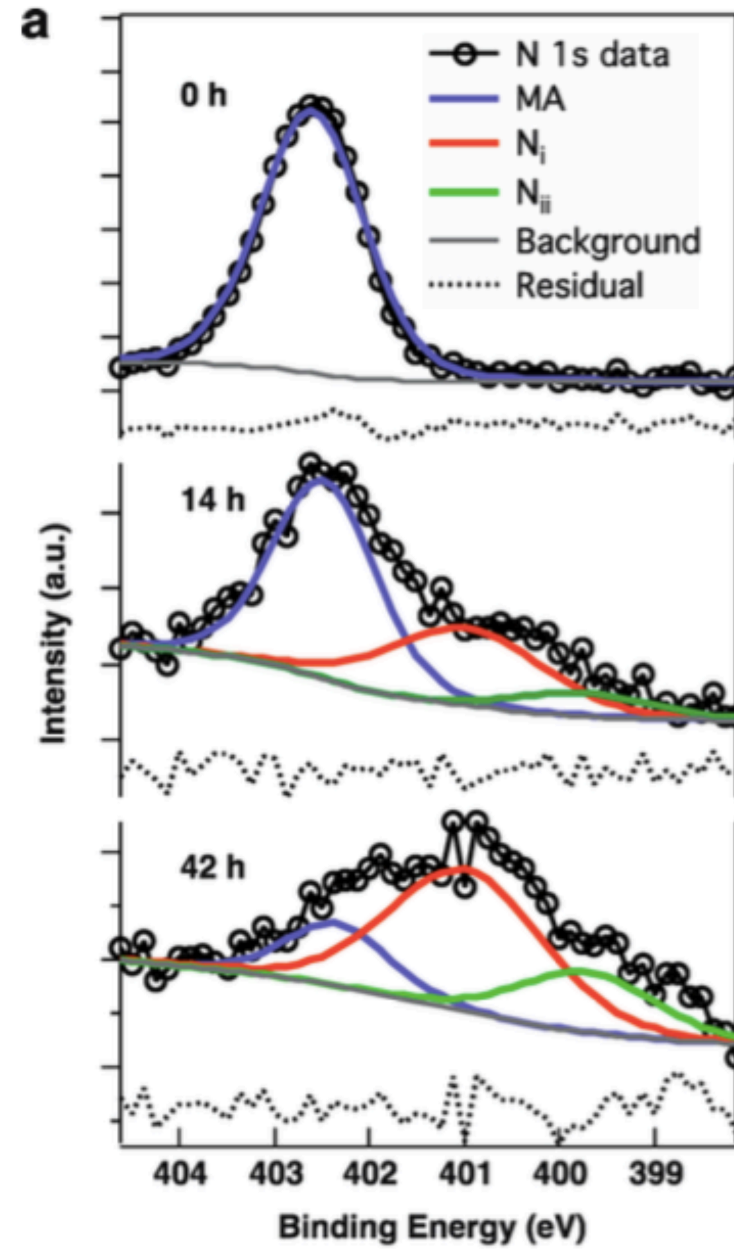
$$I = N \sigma D J L \lambda A T$$

N = atoms/cm^3
σ = photoelectic cross-section, cm^3
D = detector efficiency
J = X-ray flux, photon/cm^2 sec
L = orbital symmetry factor
λ = inelastic electron mean-free path, cm
A = analysis area, cm^2
T = analyzer transmission efficiency

Loss of CH_3NH_3

- N 1s intensity decay follows 1st order kinetics
- Degradation products also observed





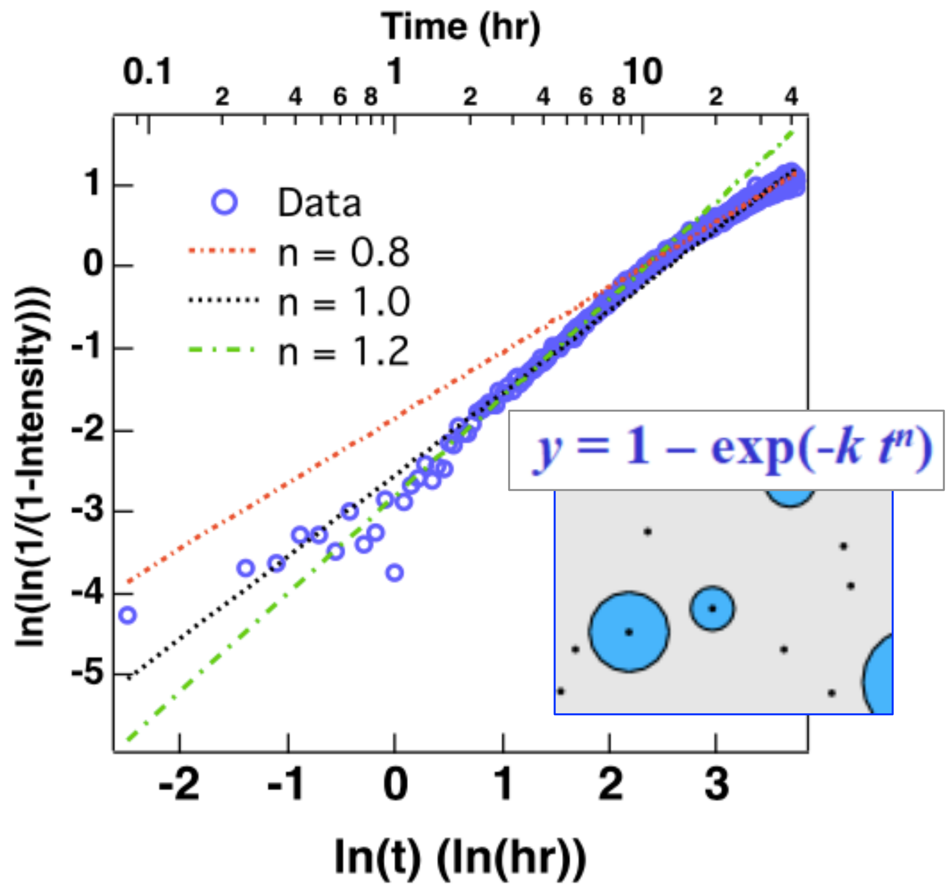
- Steirer, K. X., Schulz, P., et al., *ACS Energy Lett*. **1**, 360–366 (2016).

Uniformly Changing Composition

- Uniform CH_3NH_3 profile
- Slight I surface enrichment
- For n = 3, 3D growth
- For n = 1, constant nucleation rate

ARXPS Atomic Concentration

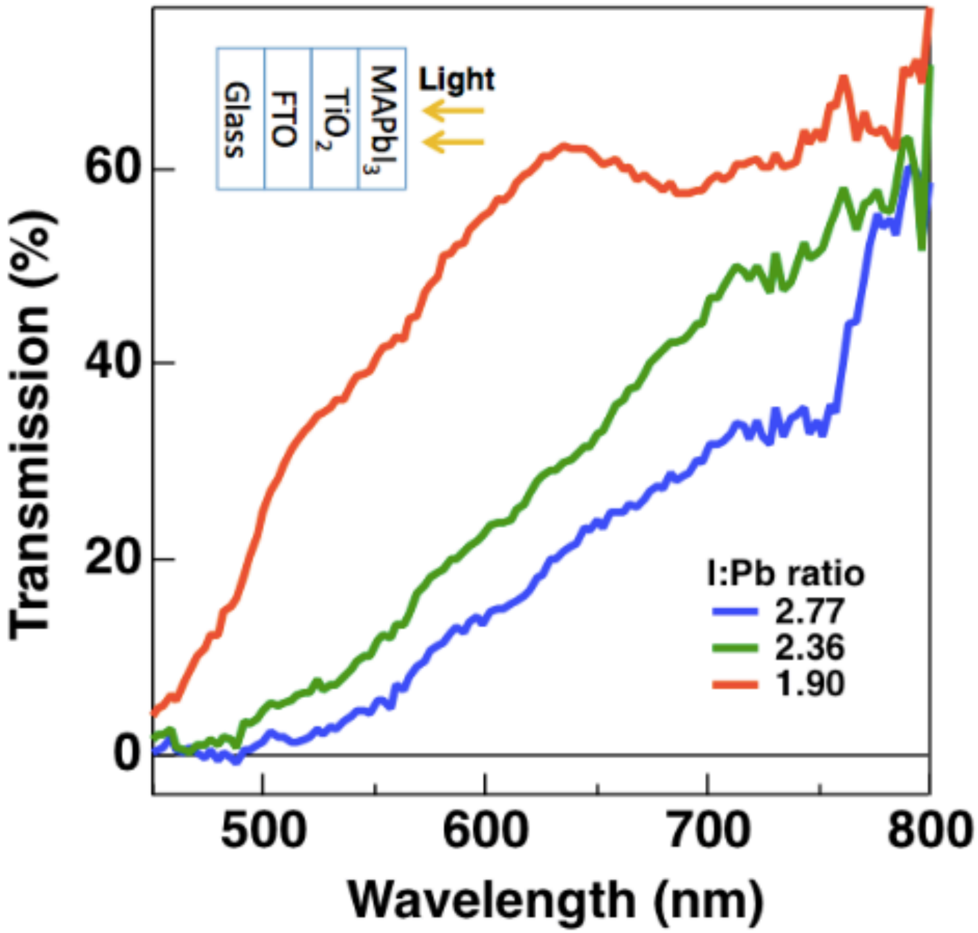
N 1s	I $3d_{5/2}$	Pb $4f_{7/2}$ (RSF Factor)	
(0.499)	(6.302)	(5.172)	
16.9	59.4	23.7	**60º Take Off**
16.7	57.0	26.3	**6º Take Off**



Avrami, M., Granulation, Phase Change, and Microstructure Kinetics of Phase Change. III, Journal of Chemical Physics, 9, 177 (1941)
Du, Z. H., et al., Perovskite crystallization kinetics and dielectric properties of the PMN-PT films …, *J. Mater. Res.* **24,** 1576–1584 (2009).

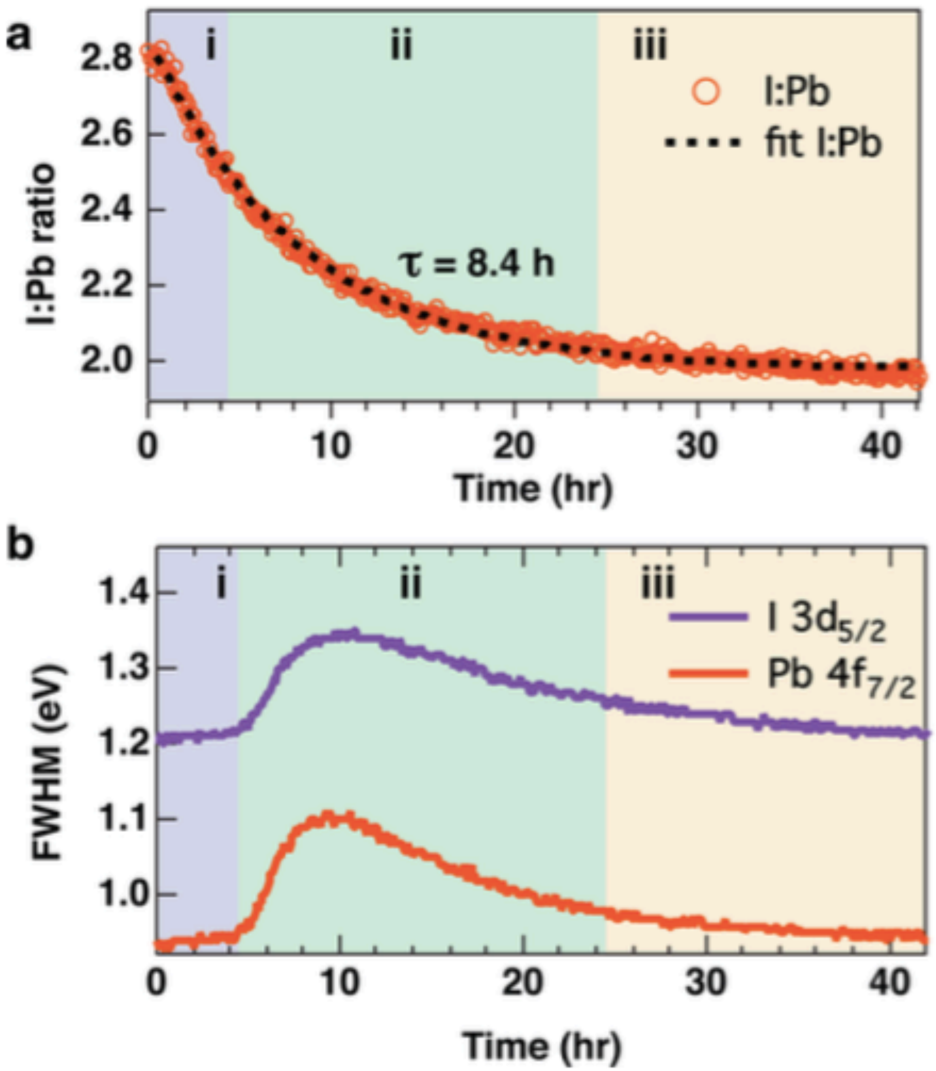
Bulk Transformation to PbI_2

- E_g increases from 1.6 eV to 2.3 eV
- Entire film color changes to yellow



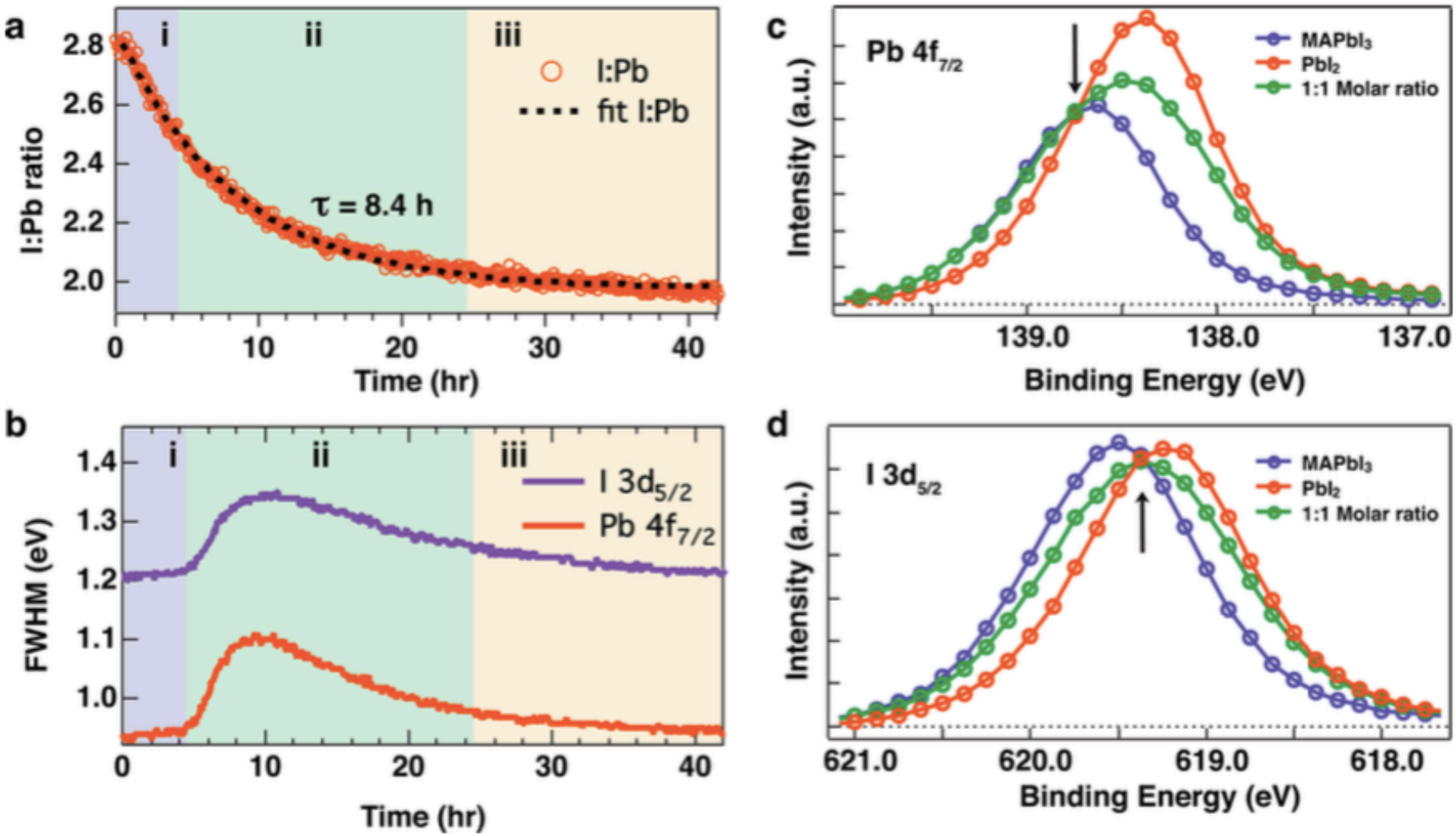
- Steirer, K. X., Schulz, P., et al., *ACS Energy Lett.* **1**, 360–366 (2016).

Delayed Chemical Transformation

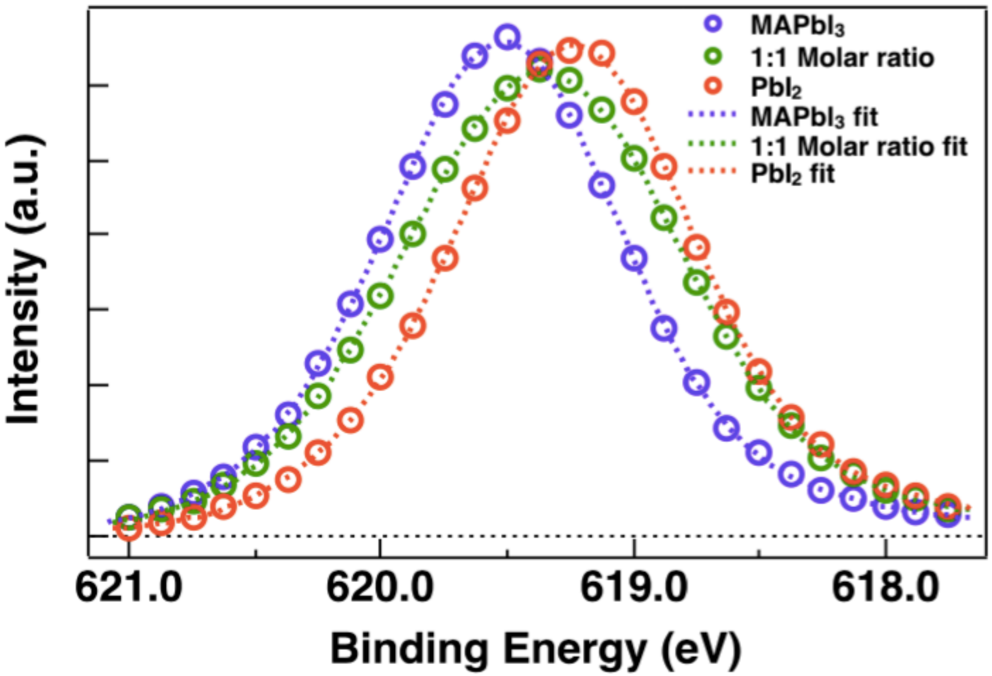


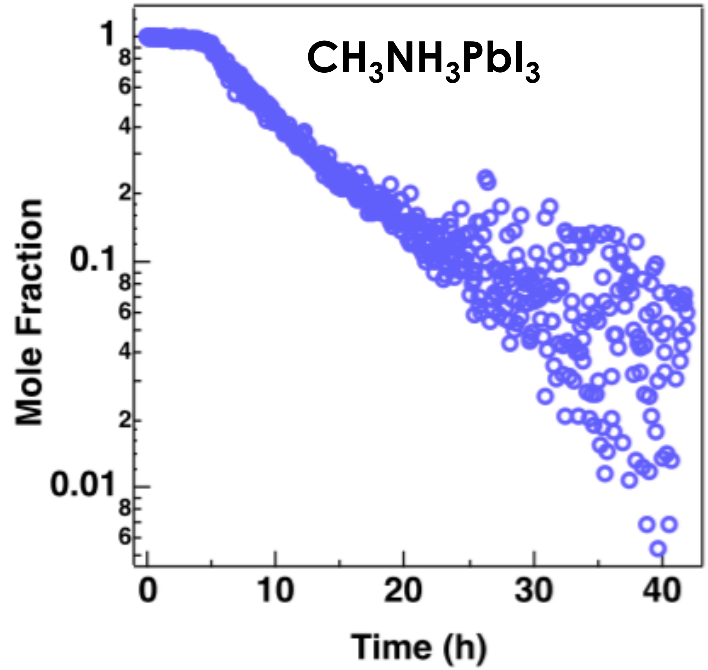
- I/Pb ratio decreases similarly to the N 1s intensity
- No chemical shift or increase FWHM for first 4.5 hr
- FWHM increases then decreases after 9.1 hr
- FWHM returns to original value upon long exposure

Delayed Chemical Transformation

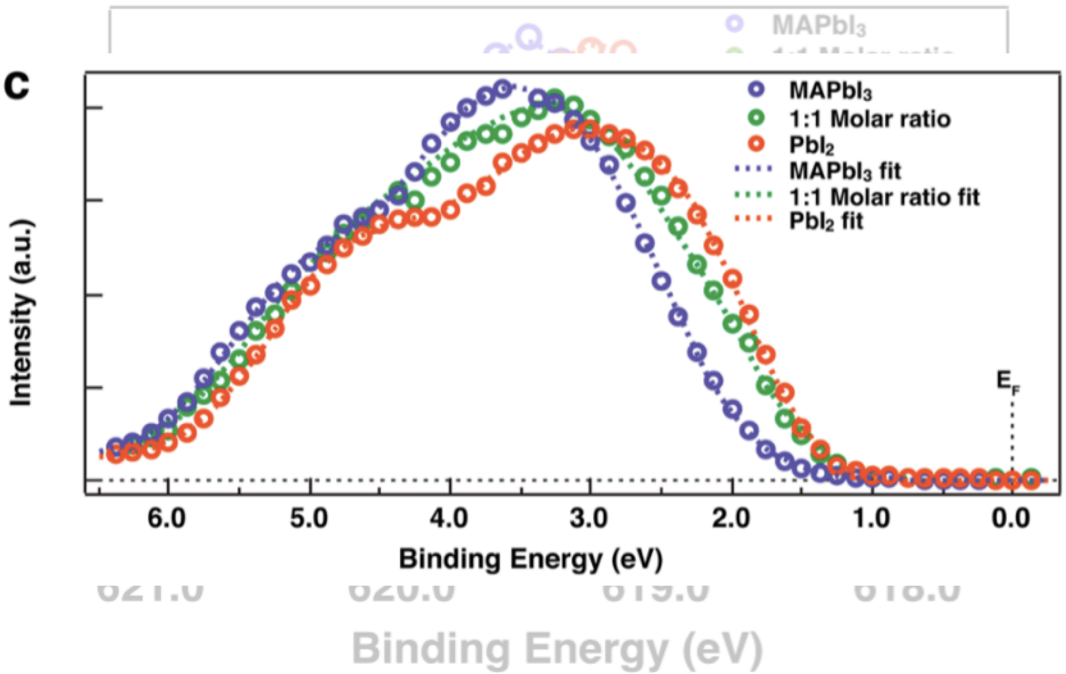


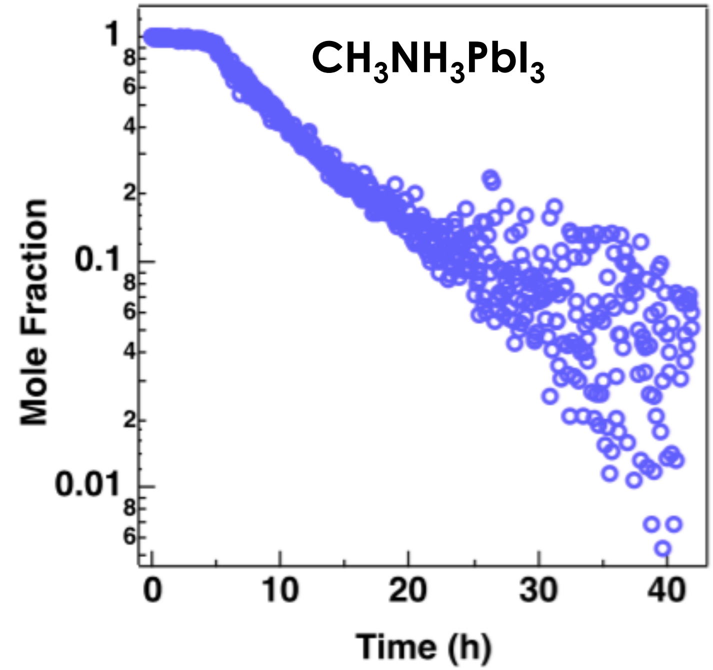
Spectral Decomposition



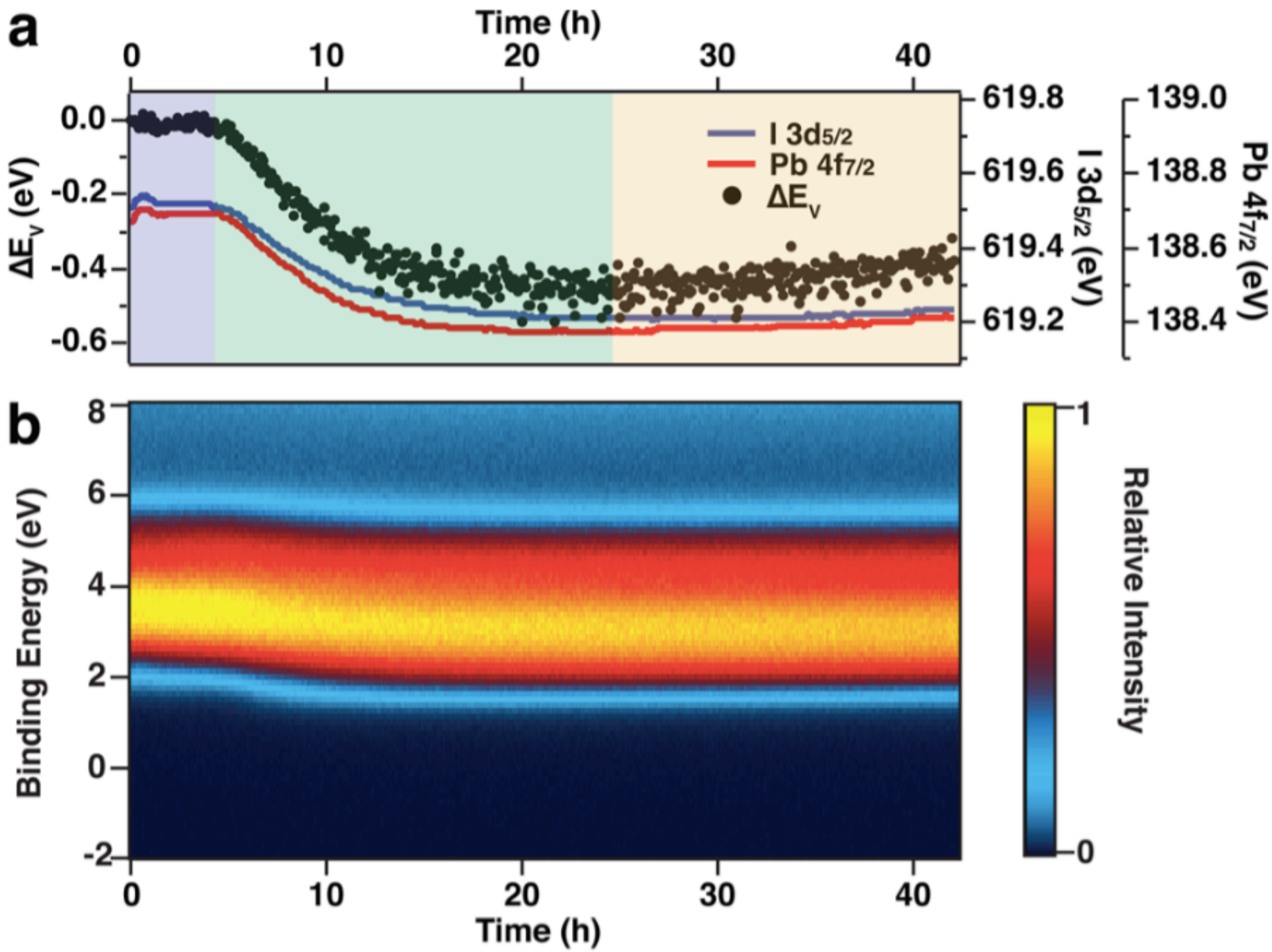


Valence Follows Molar Fraction



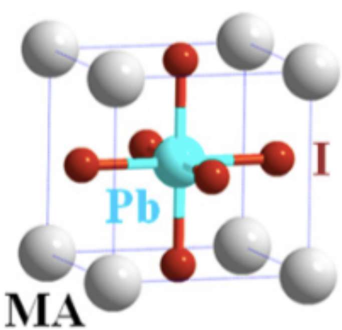


Initially Stable Properties



Neutral Ordered Defects

- XPS indicates CH_3NH_3 and I leaving simultaneously in pairs
- CIS tolerant to 1% defect density



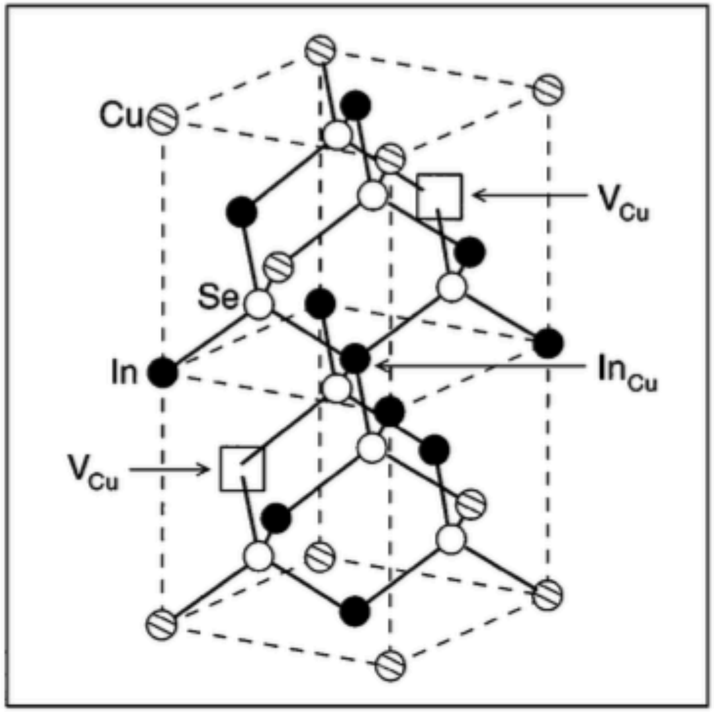
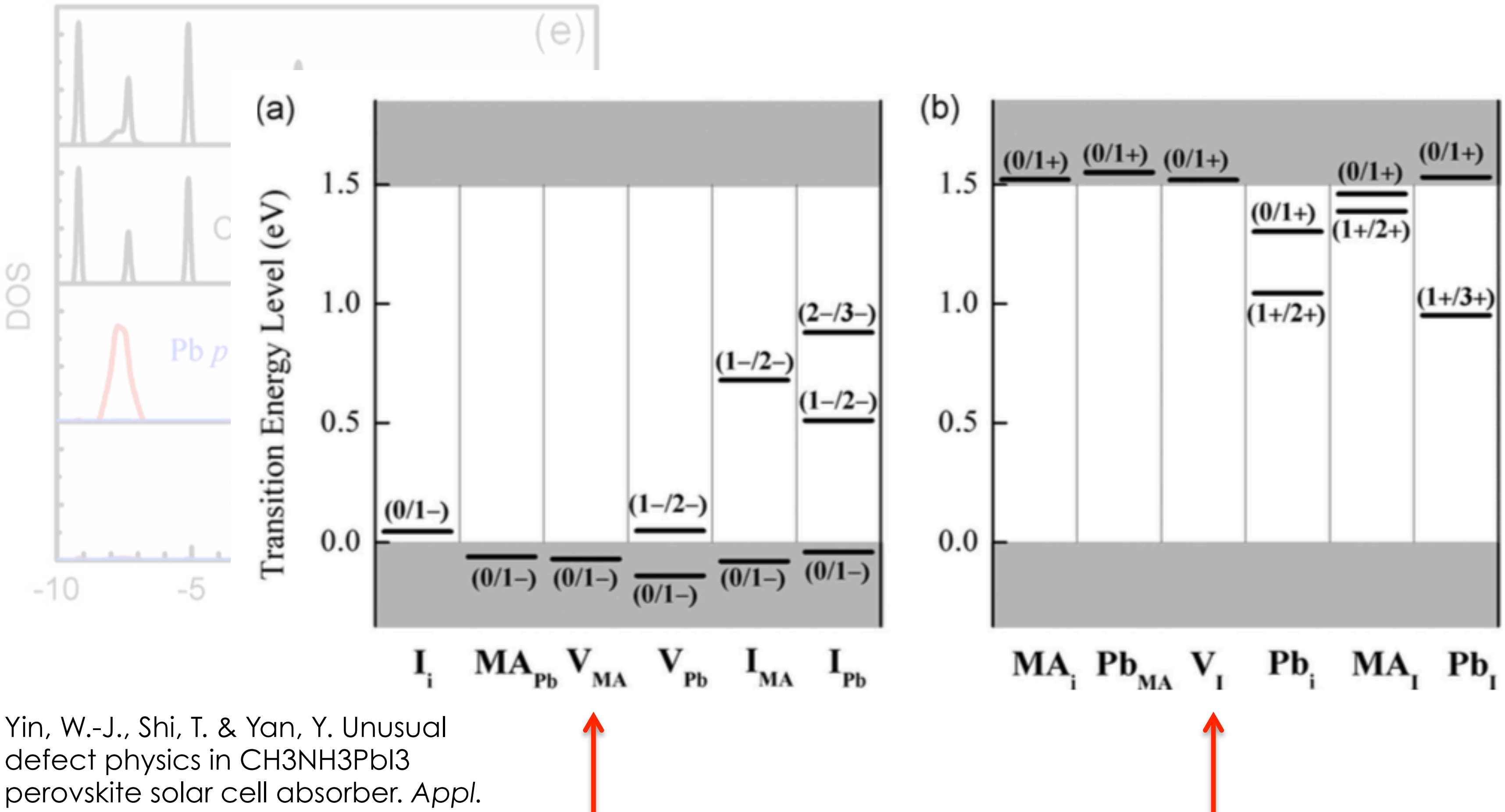


FIG. 3. The calculated structural model for the $(2V_{Cu}^{-} + In_{Cu}^{2+})$ defect pair.

- Zhang, S. B., Wei, S.-H. & Zunger, A. Stabilization of Ternary Compounds via Ordered Arrays of Defect Pairs. *Phys. Rev. Lett.* **78,** 4059–4062 (1997).
- Yin, W.-J., Shi, T. & Yan, Y. Unusual defect physics in CH3NH3PbI3 perovskite solar cell absorber. *Appl. Phys. Lett.* **104,** 063903 (2014).

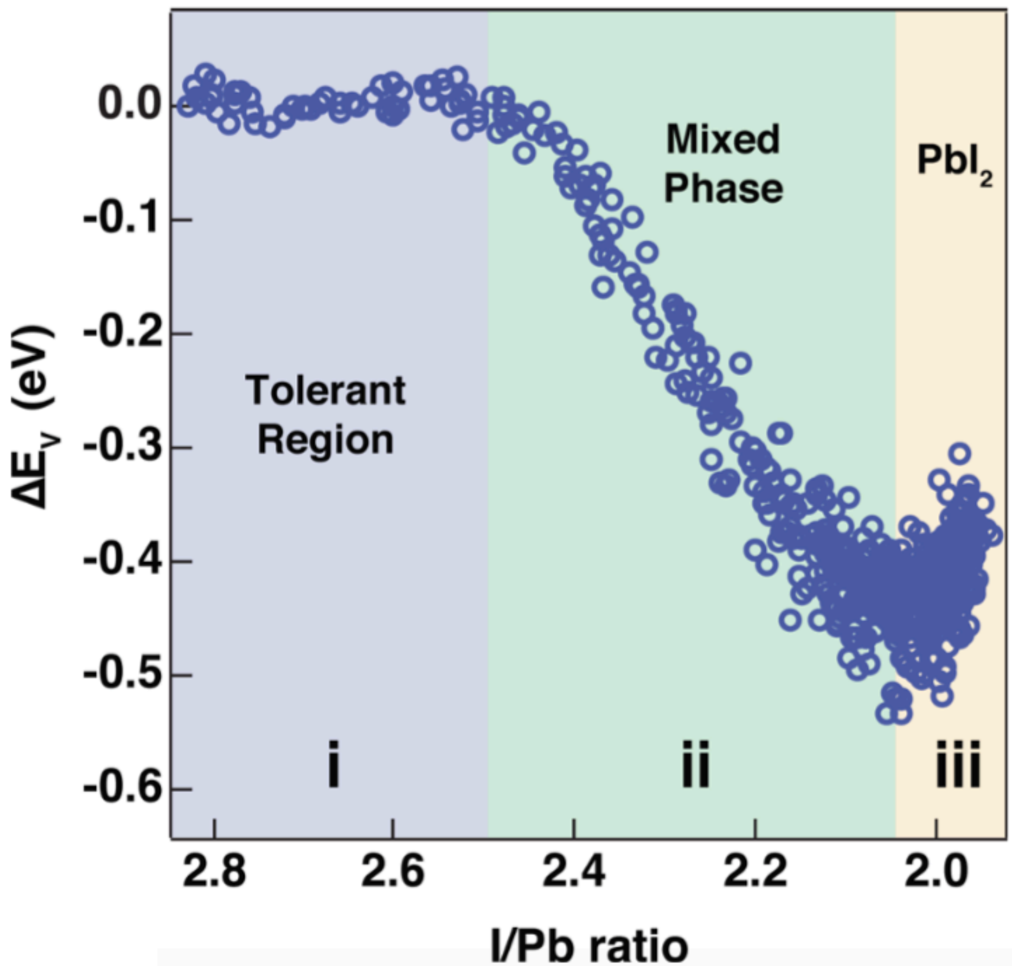
Defect Tolerance Predictions



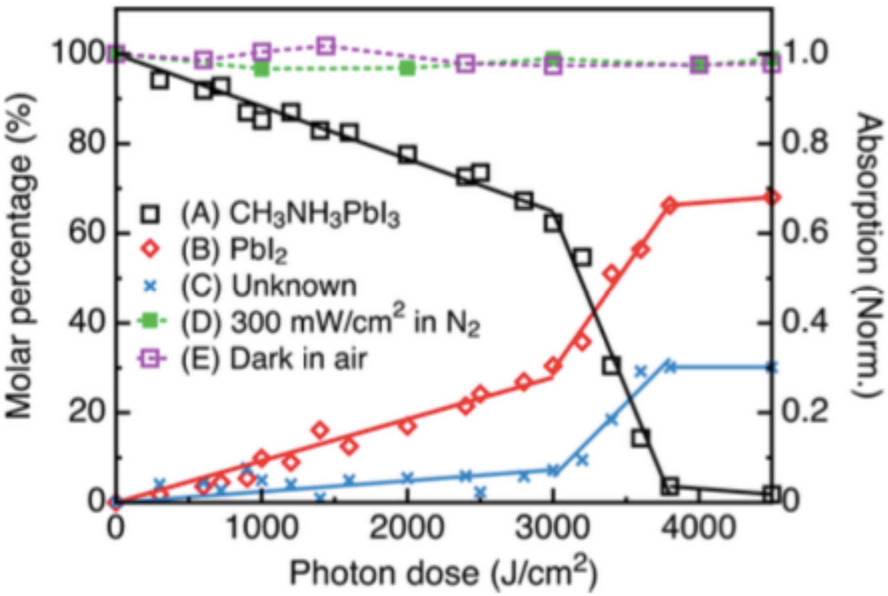
Yin, W.-J., Shi, T. & Yan, Y. Unusual defect physics in CH3NH3PbI3 perovskite solar cell absorber. *Appl. Phys. Lett.* **104**, 063903 (2014).

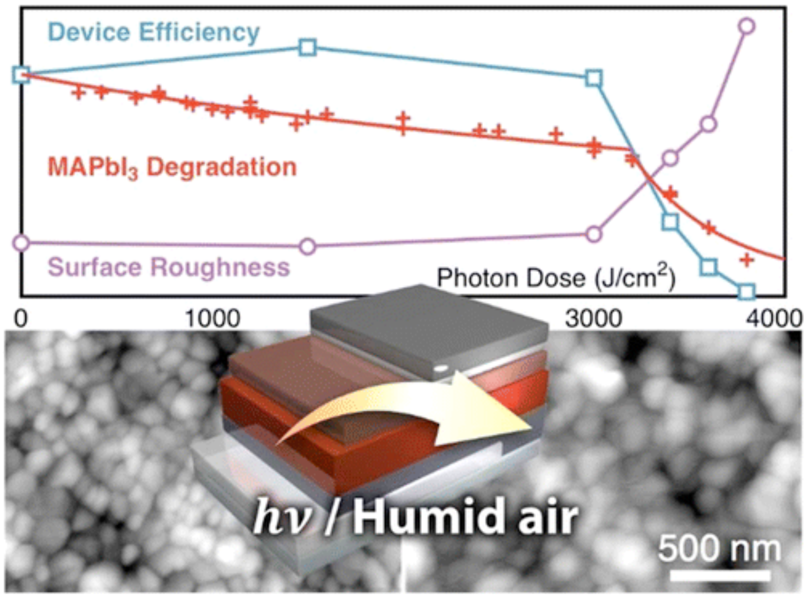
$CH_3NH_3PbI_3$ Defect Tolerance

- Core levels for I and Pb track with E_V
- BE levels stable for I/Pb down to 2.5
- Defect formation appears to be paired $V_{MA} + V_I$
- Defect density corresponds to one defect per octahedron
- Tolerance up to 1/6 of I lattice sites!!!



Helps Explain Device Failure



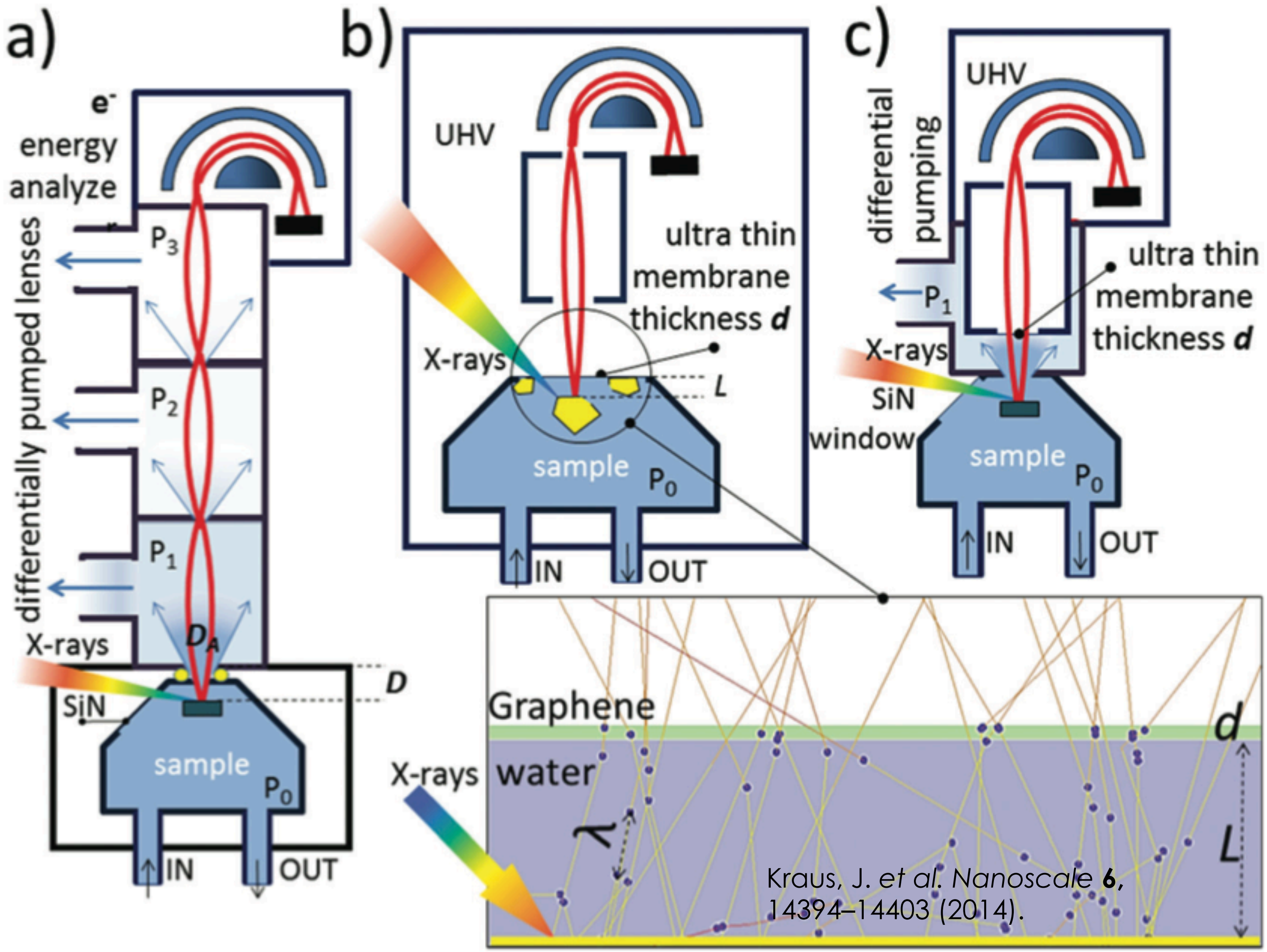


Matsumoto, F., Vorpahl, S. M., Banks, J. Q., Sengupta, E. & Ginger, D. S. Photodecomposition and Morphology Evolution of Organometal Halide Perovskite Solar Cells. *J. Phys. Chem. C* **119,** 20810–20816 (2015).

Emerging Areas in PES

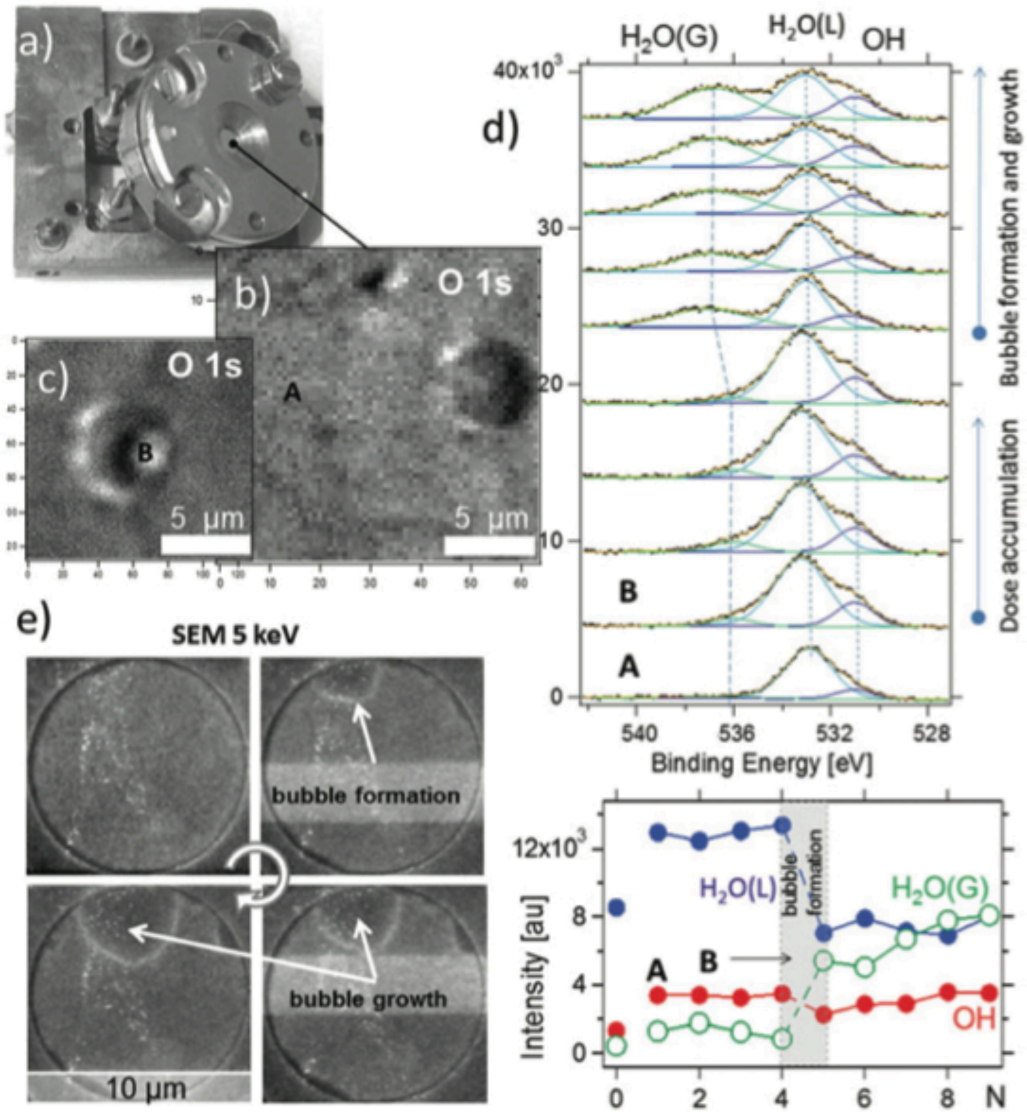
- Ambient Pressure (APXPS)
- Operando
- Chemically Resolved Electrical Measurements (CREM)

Ambient Pressure PES



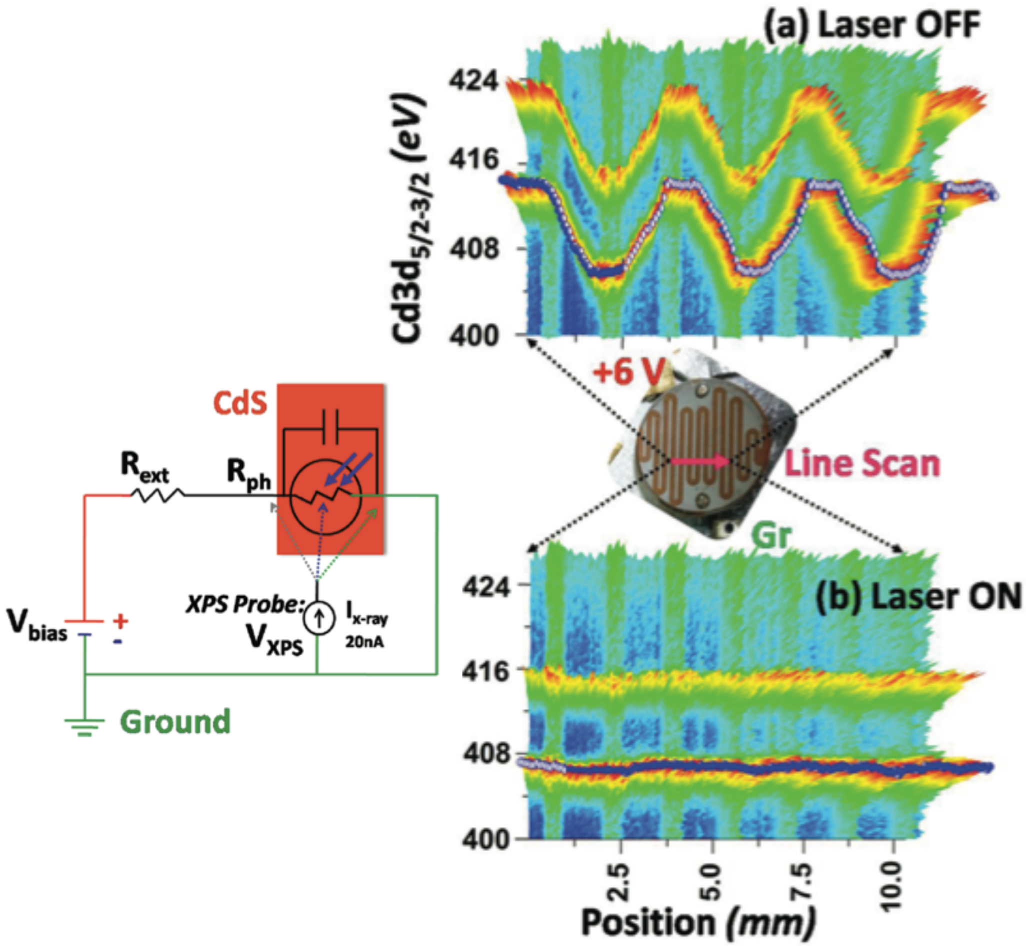
Kraus, J. *et al.* *Nanoscale* **6**, 14394–14403 (2014).

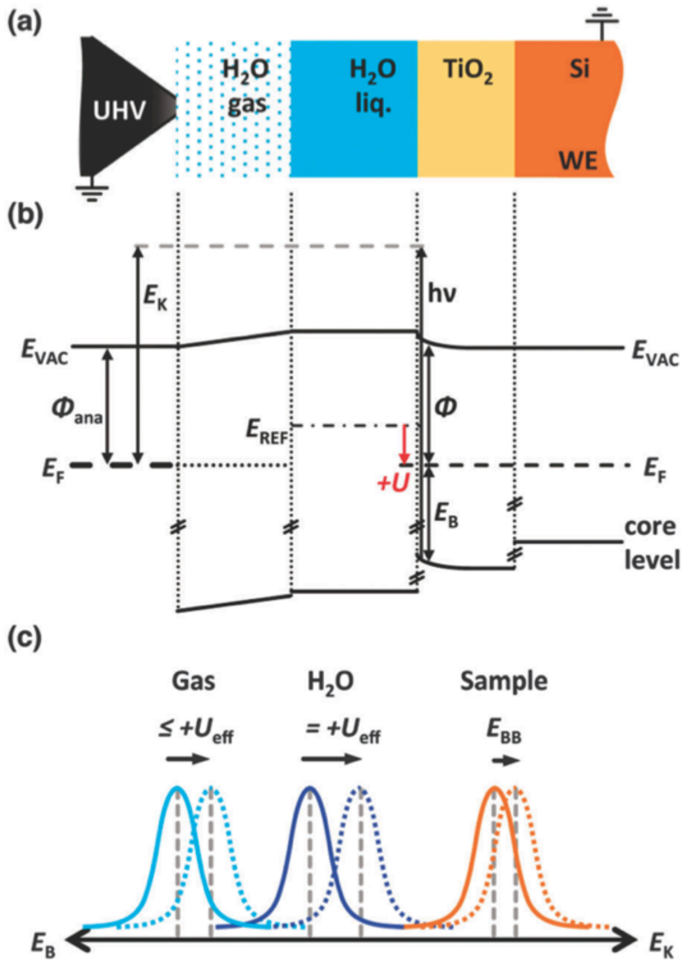
Ambient Pressure PES



Kraus, J. *et al.* *Nanoscale* **6**, 14394–14403 (2014).

Operando PES



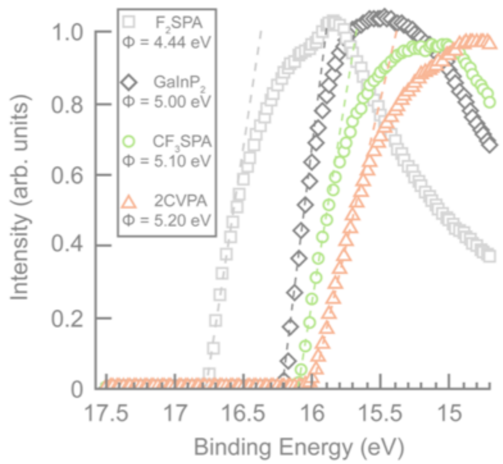


Sezen, H., Rockett, A. A. & Suzer, S. *Anal. Chem.* **84**, 2990–2994 (2012).

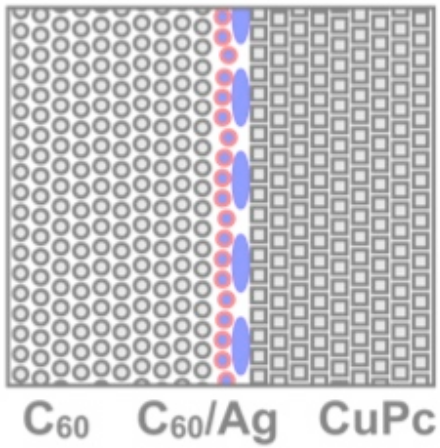
Lichterman, M. F. *et al. Energy Environ. Sci.* **8**, 2409–2416 (2015).

PES Research Topics

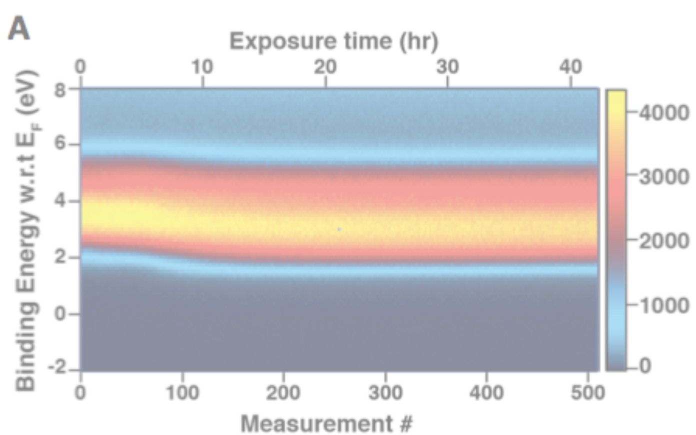
Dipole Studies



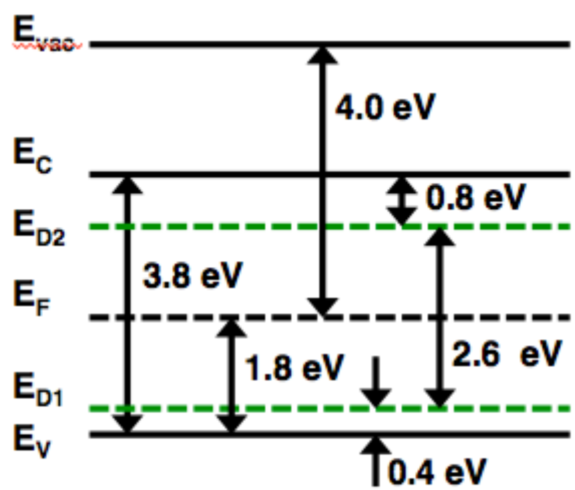
Nanostructured Interfaces



Phase Transformations



Defect Assessments



Chemically Resolved Electrical Measurements

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WEIZMANN INSTITUTE OF SCIENCE

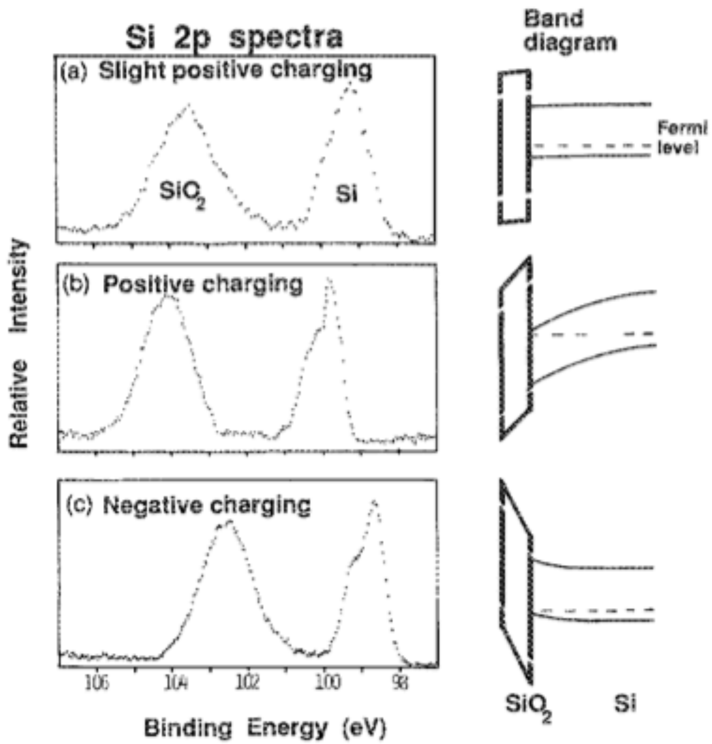
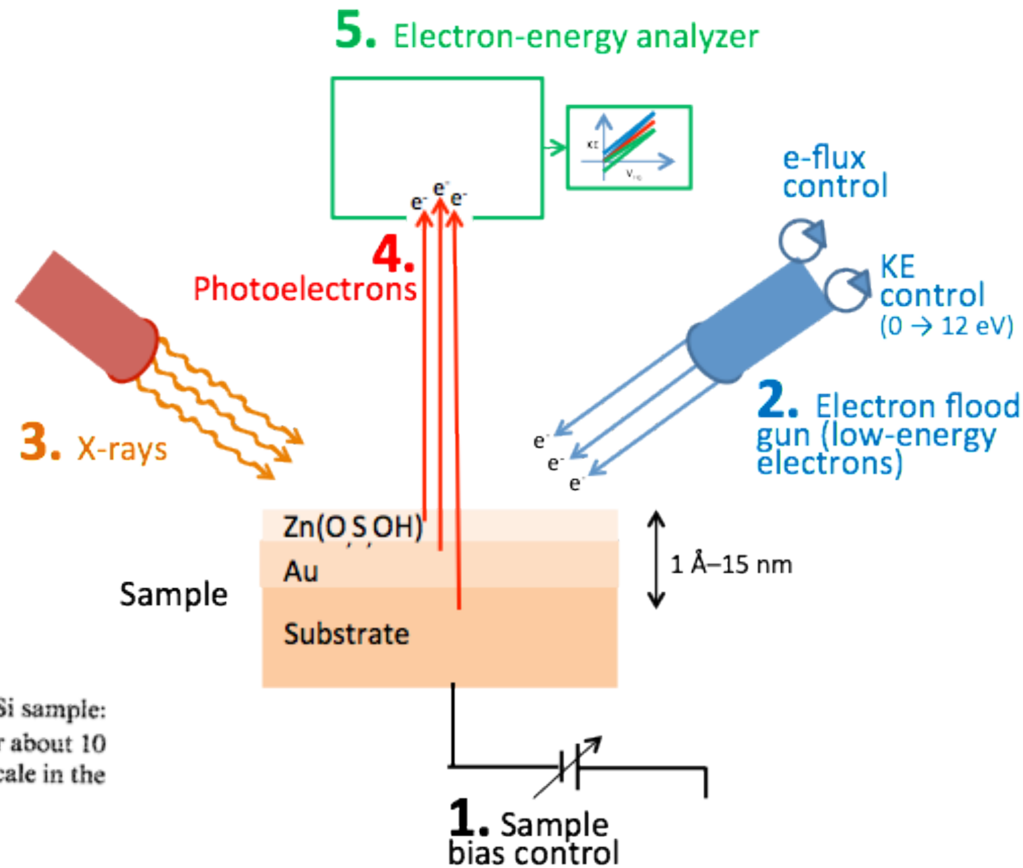


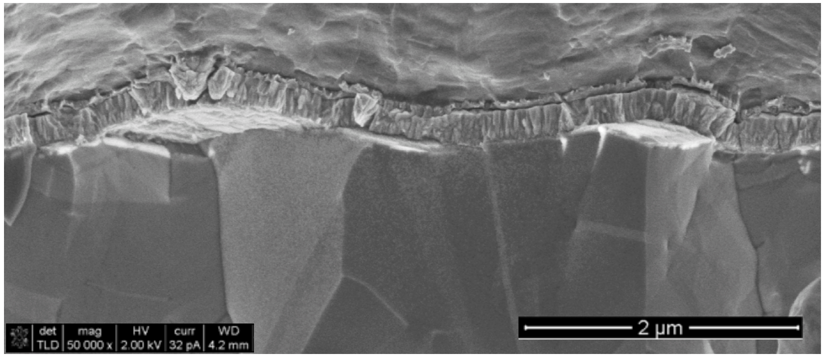
FIG. 1. Si 2*p* spectra and band diagrams of the 1.5 nm SiO_2/*p*-Si sample: (a) irradiated by x ray for about 1 min; (b) irradiated by x ray for about 10 min; and (c) flooded with low-energy electrons. (Depth not to scale in the band diagrams.)



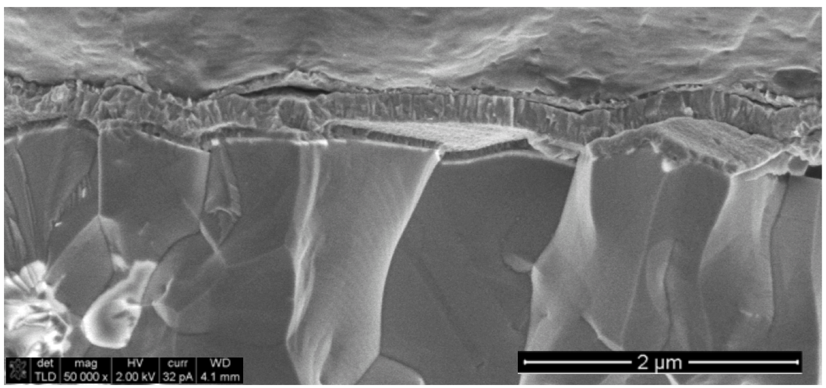
$$E_{k,i} = h\nu - E_B^i + e\phi^i$$

Lau, W. M. *Appl. Phys. Lett.* **54,** 338 (1989).
Cohen, H. *Appl. Phys. Lett.* **85,** 1271–1273 (2004).
Doron-Mor, I. *et al. Nature* **406,** 382–385 (2000).

Defects that enhance performance



CZTSe/ZnOS/i-ZnO/Al:ZnO/metal cleaved from device. CBD-ZnOS is visible and is physically central pn-junction formed between CZTSe and i-ZnO.

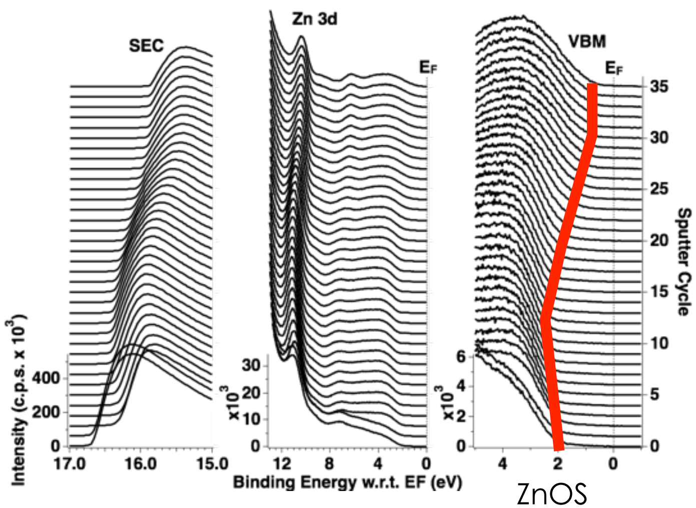


CZTSe/CdS/i-ZnO/Al:ZnO/metal cleaved from device. CBD-CdS operates differently than CBD-ZnOS by place exchange and results in very different electronic structure and solar cell operation.

CIS/ZnOS attained record 20.9% PCE **-** Osborne, Mark. "Solar Frontier produces record 20.9% CIS thin-film solar cell," *PVTech*, 02 April 2014. *Fraunhofer verified*

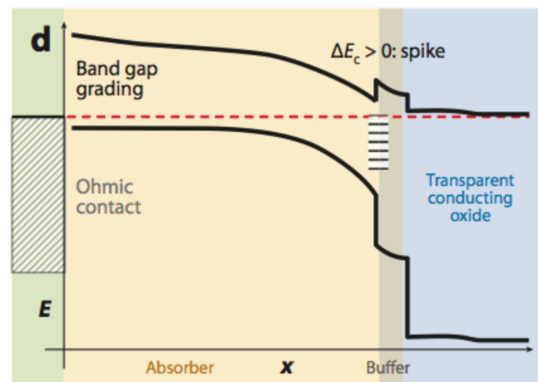
Huge Conduction Band Offset

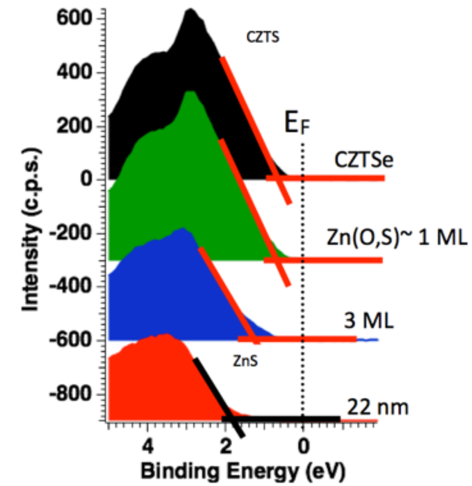
***hv* = 21.2 eV**



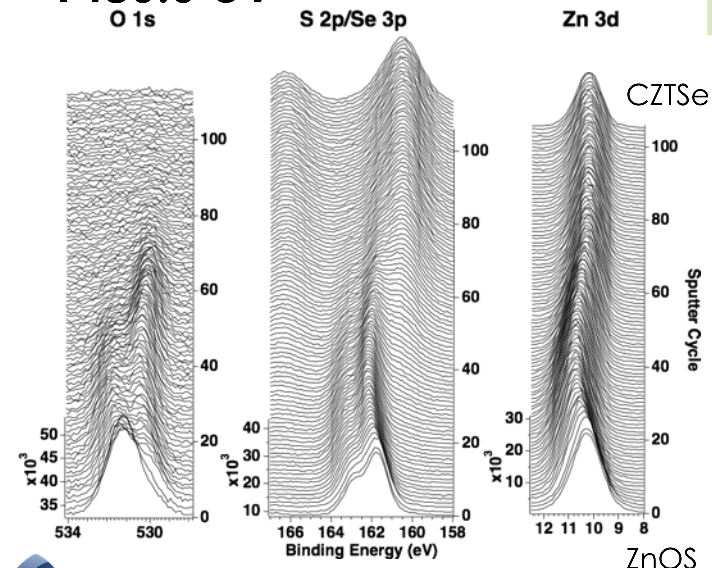
$$\Delta E_V = (E_{CL}^{ZnS} - E_{VBM}^{ZnS}) - (E_{CL}^{CZTS} - E_{VBM}^{CZTS}) - \Delta E_{CL,i}$$ **= -1.0 eV**

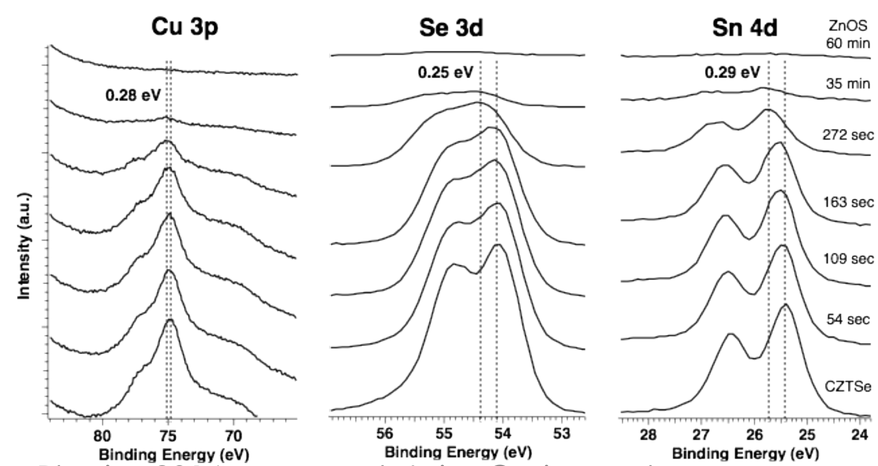
$$\Delta E_C = E_g^{ZnS} - E_g^{CZTS} + \Delta E_V$$ **= 1.6 eV**





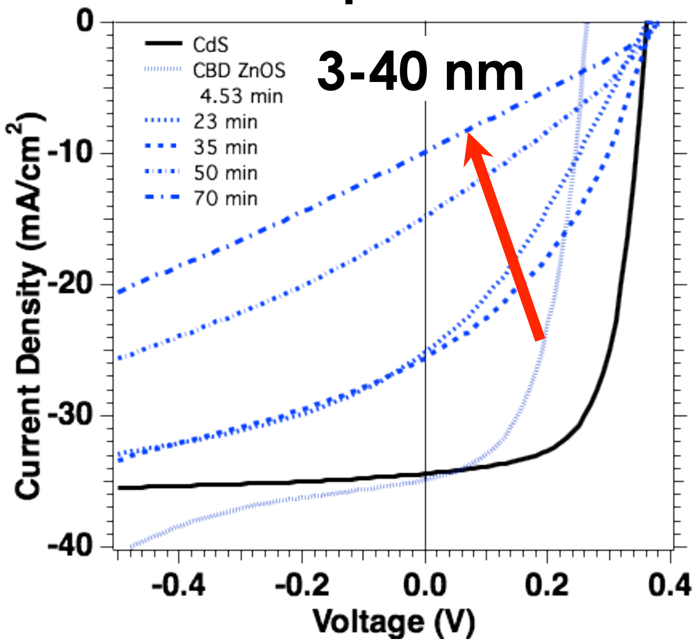
***hv* = 1486.6 eV**



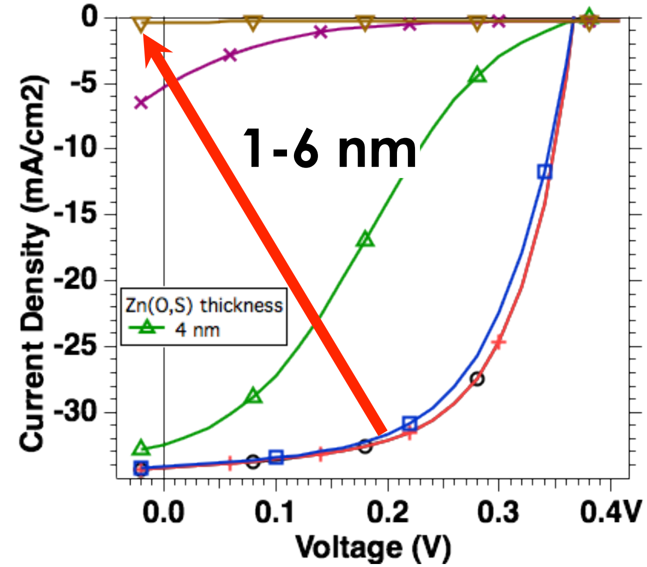


Unexpected Performance

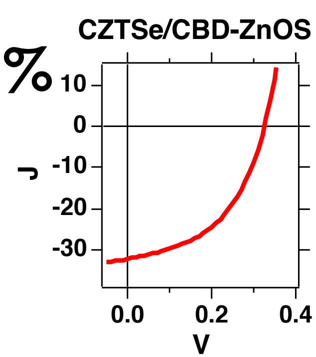
Experiment

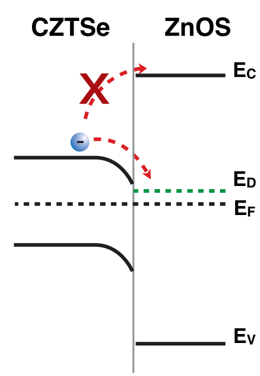


Simulation



PCE$_{max}$ = 5.1%

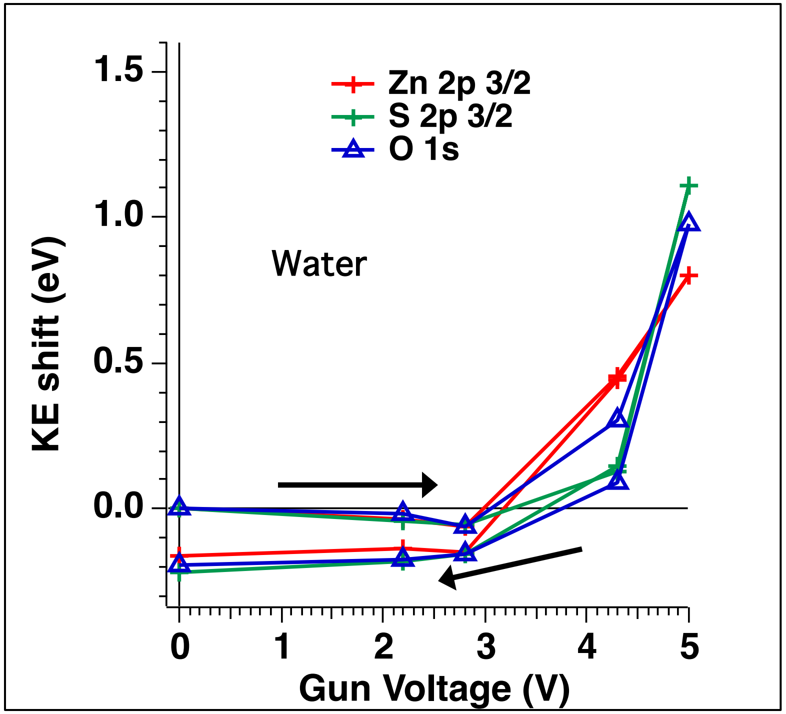




- Buffer Properties
  - Eg = 3.8 eV
  - CBO = 1.6 eV
  - $N_{ZnOS} = 10^{12} - 10^{16}$ cm^{-1}
  - dielectric = 9
  - One sun illumination

Chemically Resolved Electrical Measurements

Electrical Loop



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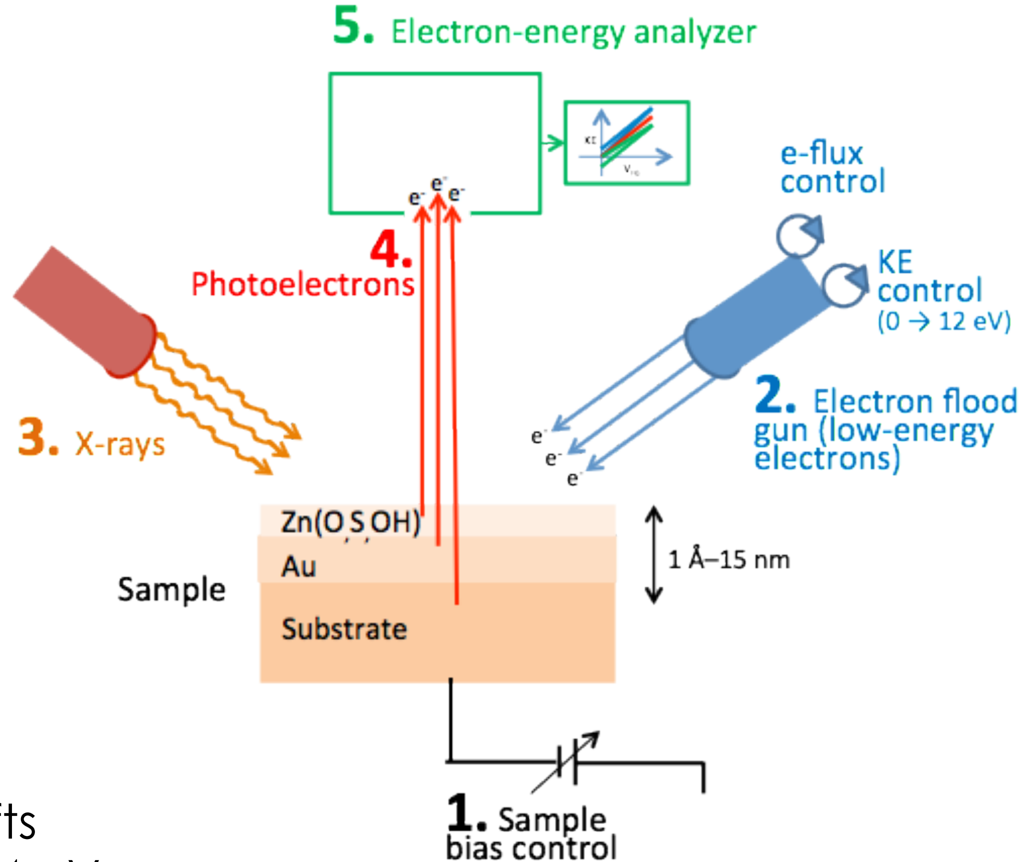
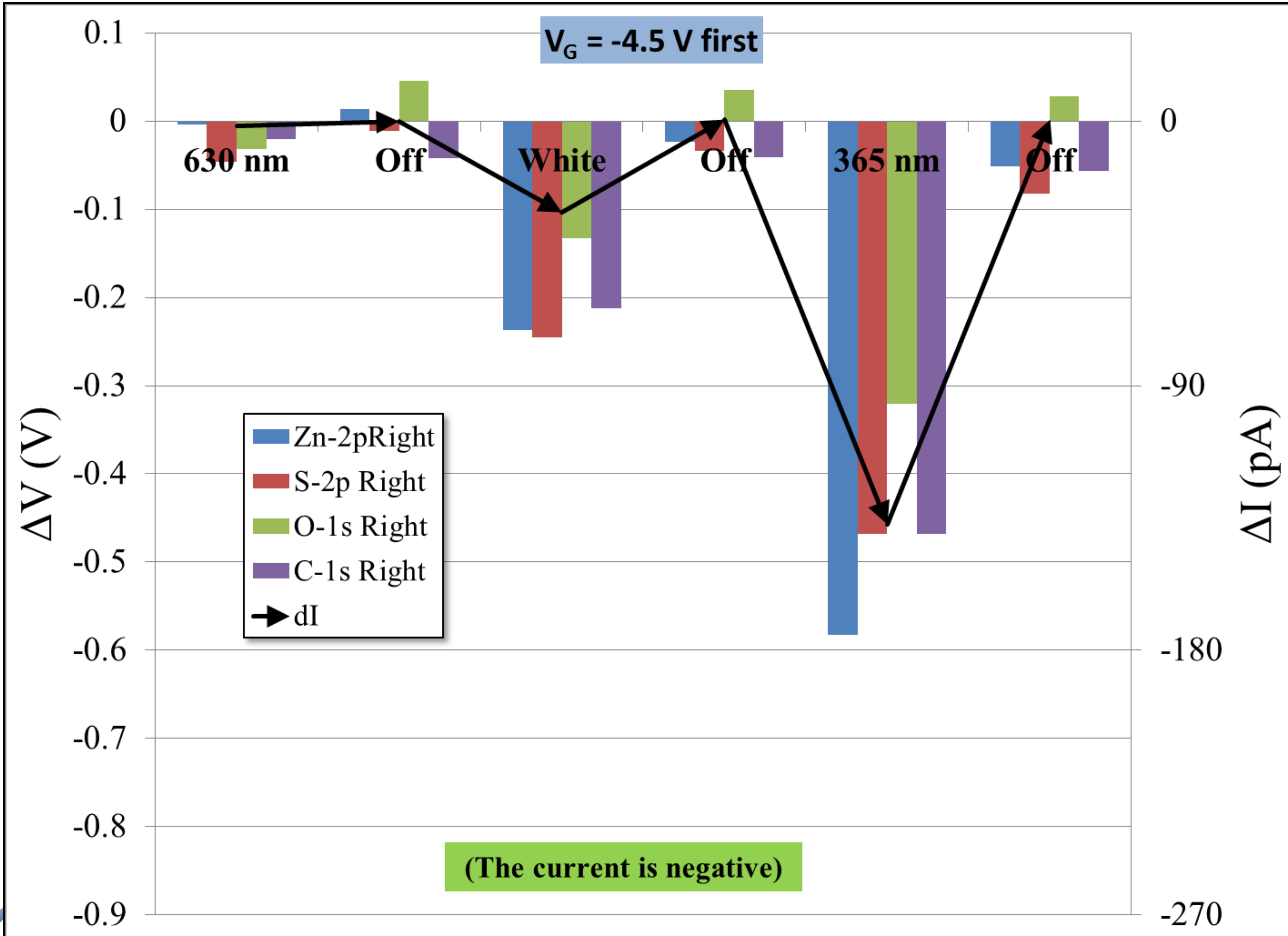


At each point, assess potential shifts with red 2.0 eV/white 2.8 eV/UV 3.4 eV

$$E_{k,i} = h\nu - E_{\mathrm{B}}^{i} + e\phi^{i}$$

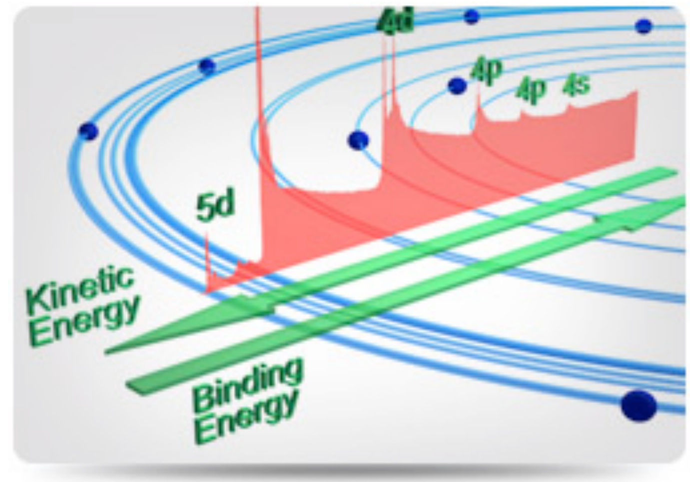
Light-CREM



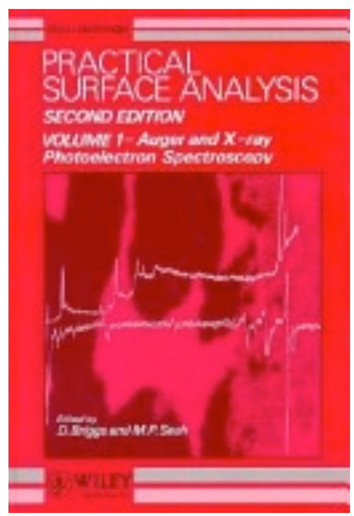
V_G = -4.5 V first
0.1
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
ΔV (V)
0
-90
-180
-270
ΔI (pA)
630 nm
Off
White
Off
365 nm
Off
Zn-2pRight
S-2p Right
O-1s Right
C-1s Right
dI
(The current is negative)

Photoelectron Spectroscopy

- More Resources
  - Prof. Paul Chu Univ. Hong Kong
    - http://slideplayer.com/slide/5052993/
  - Ralph Claessen Univ. Wurzburg
    - http://www.slideshare.net/nirupam12/photoelectron-spectroscopy-for-functional-oxides
  - Textbook
    - Practical Surface Analysis by Briggs and Seah 1990



http://xpssimplified.com/



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Matt Reese
Paul Ndione
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Alex Miedaner
Jordan Chesin
Philip Schulz
Steve Harvey
Craig Perkins
Glenn Teeter
Kai Zhu
Mengjin Yang

Erin Ratcliff
Gordon MacDonald
Kento Ou
Paul Lee
Neal Armstrong

Jens Meyer
Selina Olthof
Antoine Kahn

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Renewable Energy Materials Research Science and Engineering Center
REMRSEC

U.S. Department of Energy

CIS:SEM

Center for Energy Efficient Materials

Colorado School of Mines
Earth • Energy • Environment

NREL
National Renewable Energy Laboratory

Colorado School of Mines
Earth • Energy • Environment