X-ray Photoelectron Spectroscopy (XPS)

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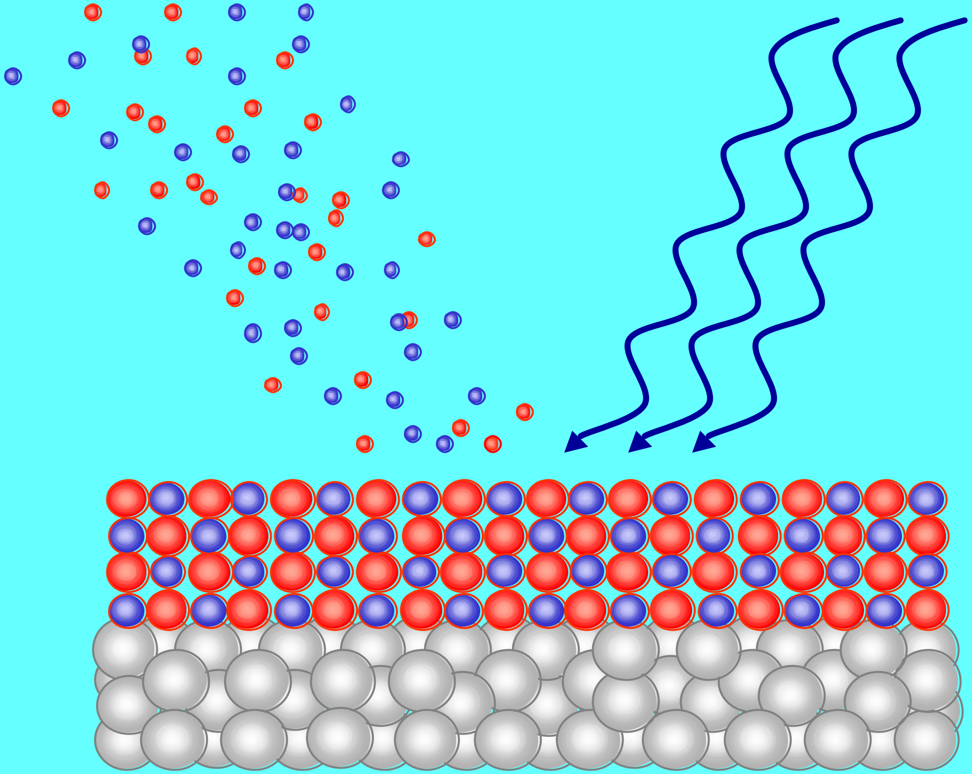


U.S. Department of Energy
Pacific Northwest National Laboratory

Outline

- Introduction (XPS basic principles)
- Quantification.
- Energy resolution and count rates.
- Wide scan data (low energy resolution)
- Narrow scan data (high energy resolution)
- Chemical state analysis.
- Sensitivity.
- Sputter depth profiles.
- Line scans.
- Maps.
- Web sites and references.

Introduction
X-ray Photoelectron Spectroscopy (XPS)

- X-ray photoelectron spectroscopy works by irradiating a sample material with monoenergetic soft x-rays causing electrons to be ejected.

- Identification of the elements in the sample can be made directly from the kinetic energies of these ejected photoelectrons.

- The relative concentrations of elements can be determined from the photoelectron intensities.

Introduction (XPS)
Analysis capabilities

- Elements detected from Li to U.
- None destructive (some damage to x-ray beam sensitive materials)
- Quantitative.
- Chemical state analysis (some exceptions)
- Surface sensitivity from 5 to 75 angstroms.
- Conducting and insulating materials.
- Detection limits that range form 0.01 to 0.5 atom percent.
- Spatial resolution for surface mapping from >10 μm
- Depth profiling capabilities.

Introduction (XPS)
Basic principles

The relationship governing the interaction of a photon with a core level is:

$$KE = hn - BE - e\Phi$$

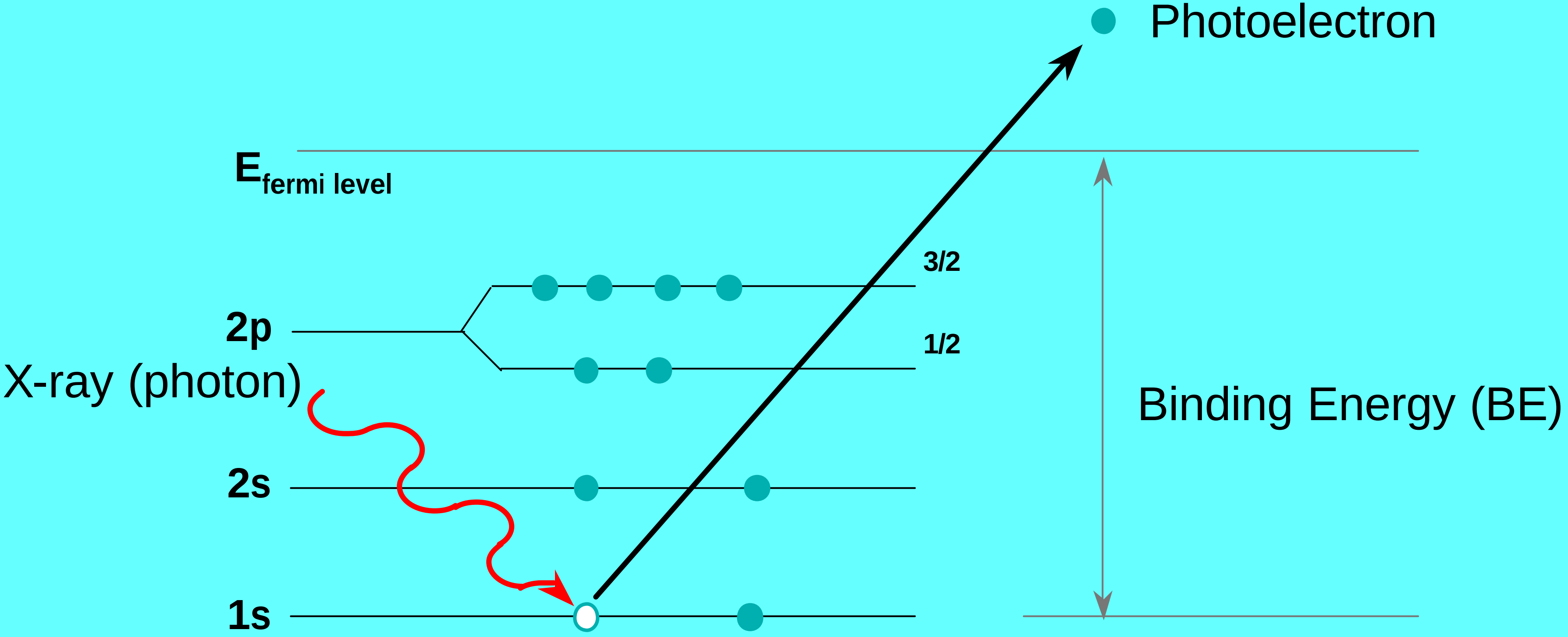
KE = kinetic energy of ejected photoelectron

hn = characteristic energy of X-ray photon

BE = binding energy of of the atomic orbital from which the electron originates.

$e\Phi$ = spectrometer work function

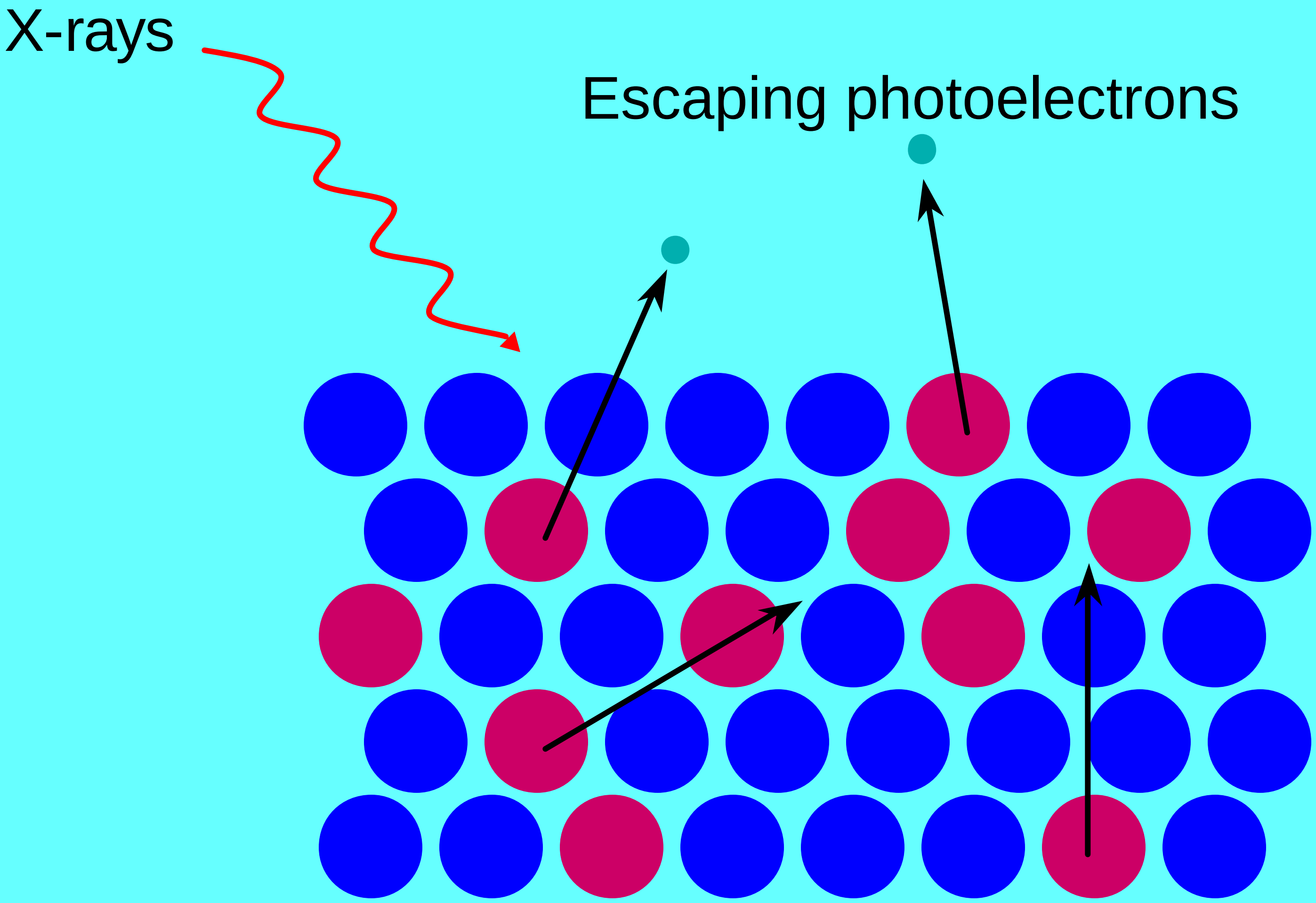
Introduction (XPS)
XPS emission process



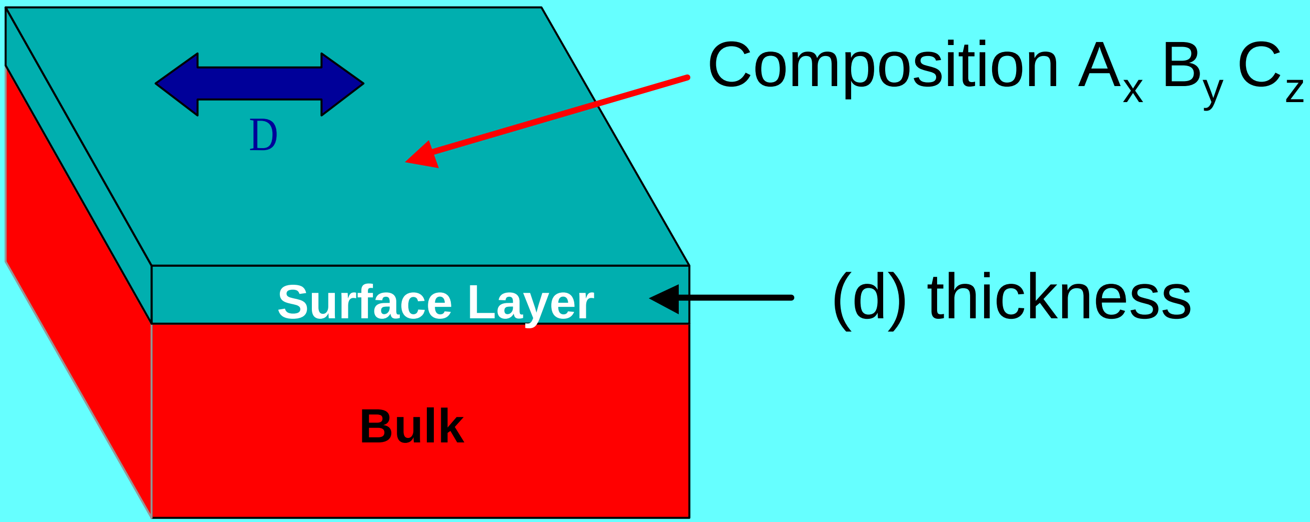
An incoming photon causes the ejection of the photoelectron

BE = X-ray Energy Al Kα (1486.7 eV) - Photoelectron Kinetic Energy

Introduction (XPS)
Surface sensitivity



Introduction (XPS)
Analysis objective



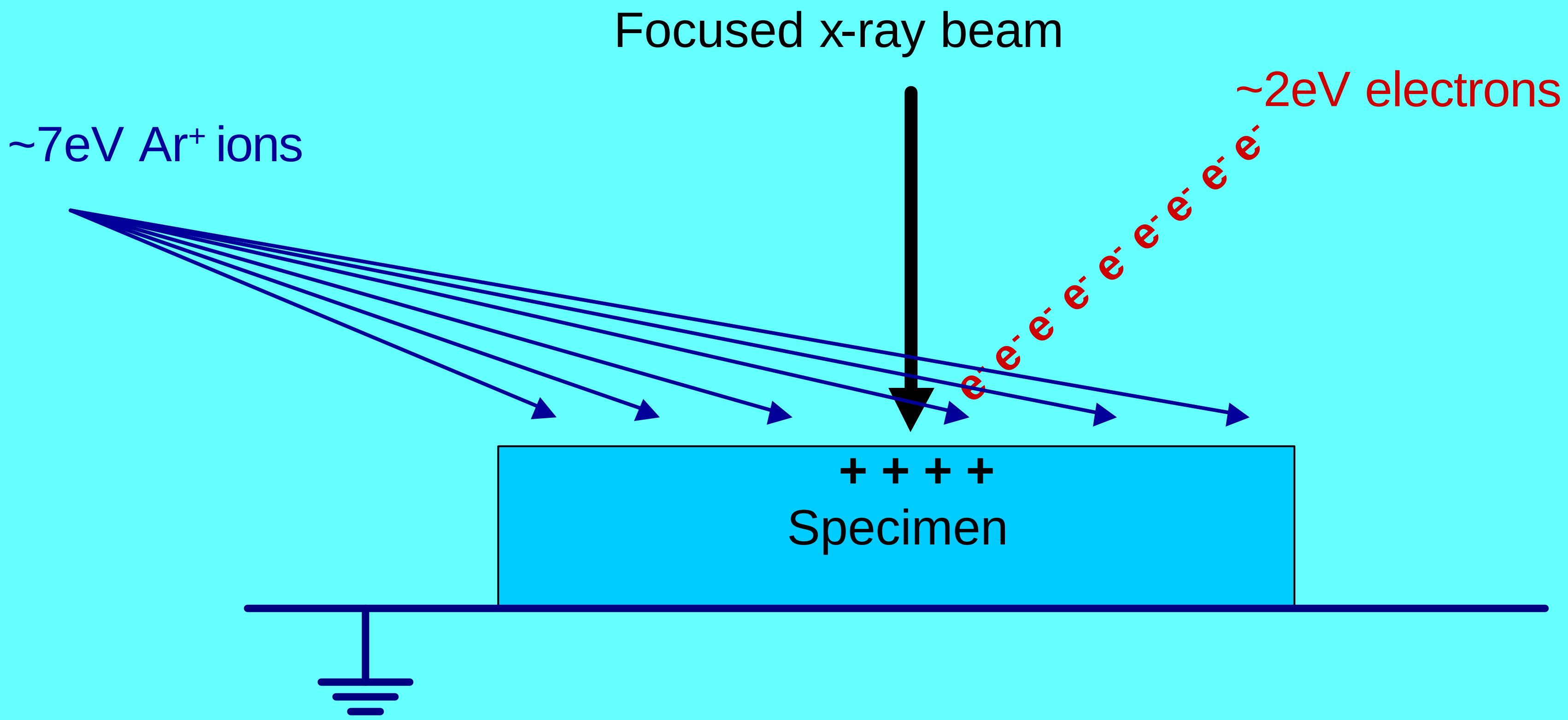
- Composition ($A_x\ B_y\ C_z$)
- (d) Thickness (depth resolution)
- Δ Lateral resolution (spatial resolution)

XPS Quantification

- Quantitative data can be obtained from peak heights or peak areas, and identification of chemical states often can be made from exact measurements of peak positions and separations, as well as from certain spectral features.

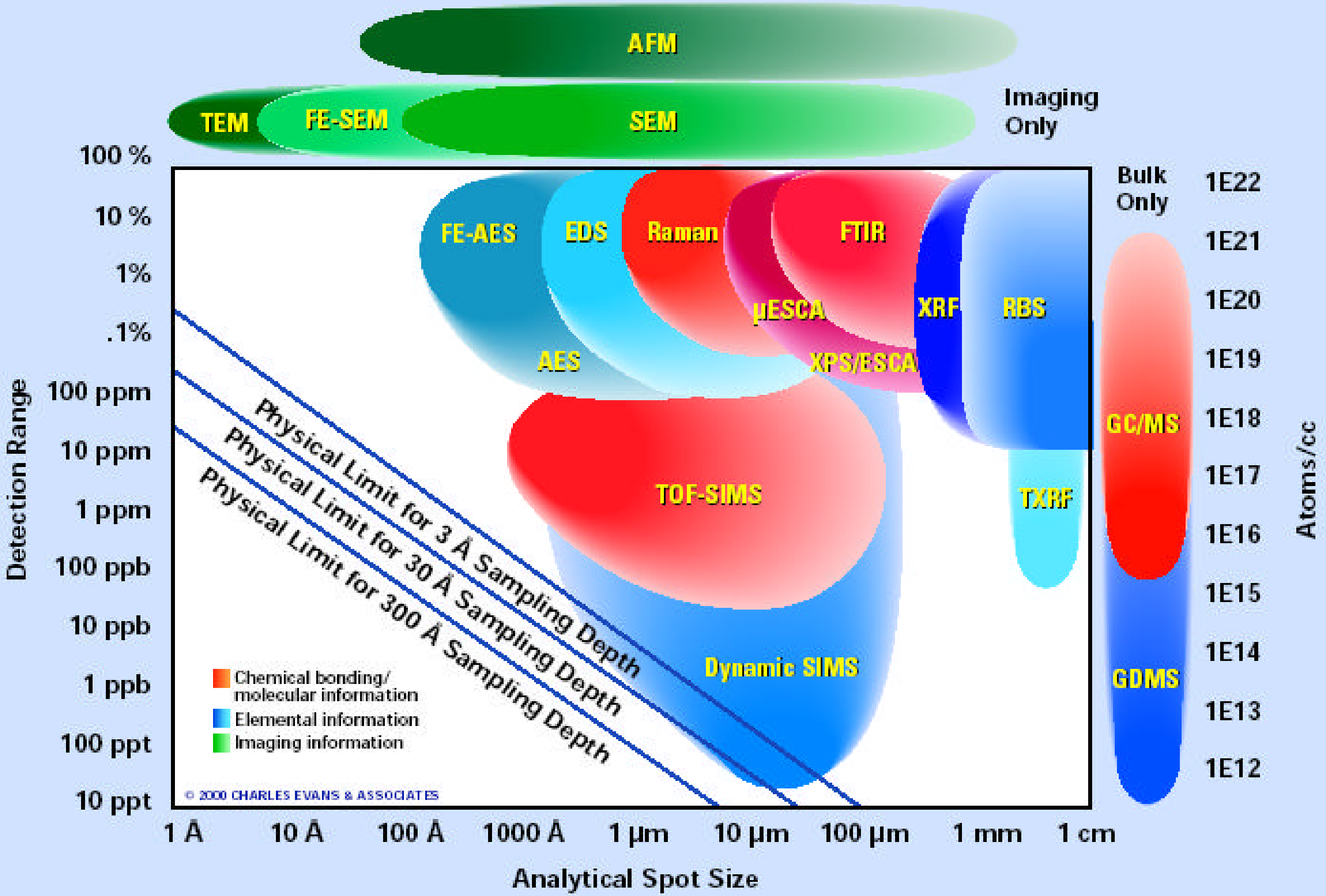
- The following building blocks are used to provide accurate quantification:
  - A standardized set of *sensitivity factors*.
  - The *transmission function* of the spectrometer.
  - Corrections for *geometric asymmetry* related to the angle between the X-ray source and the analyzer input lens.

XPS Instrumentation
Charge neutralization for insulating samples



- Low-energy electrons from a cold cathode flood gun alleviates positive charging
- Low-energy source of positive ions alleviates the surrounding negative charge

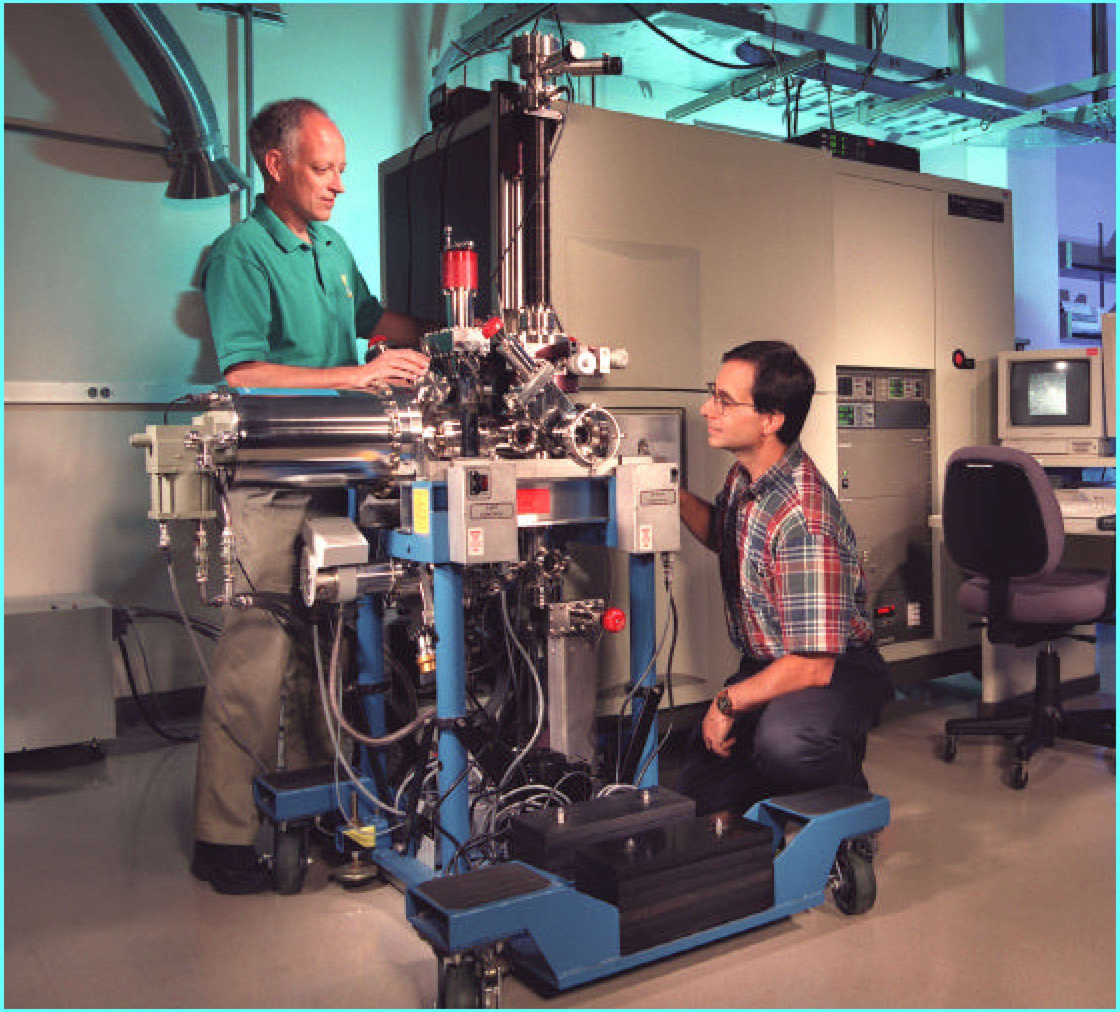
Analytical Resolution versus Detection Limit



CHARLES EVANS & ASSOCIATES

SPECIALISTS IN MATERIALS CHARACTERIZATION

EMSL XPS Instrumentation

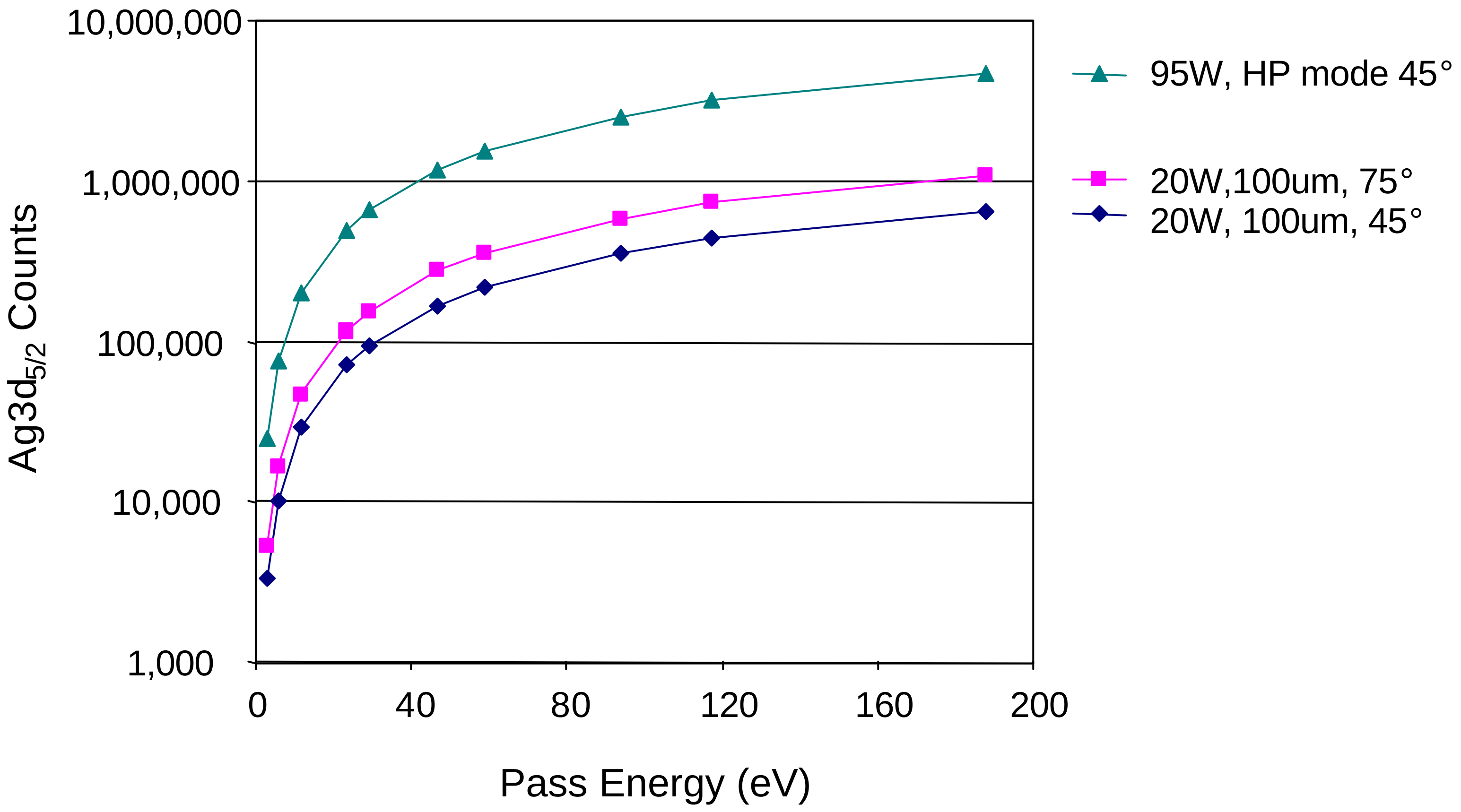


Physical Electronics Quantum 2000 Scanning ESCA Microprobe

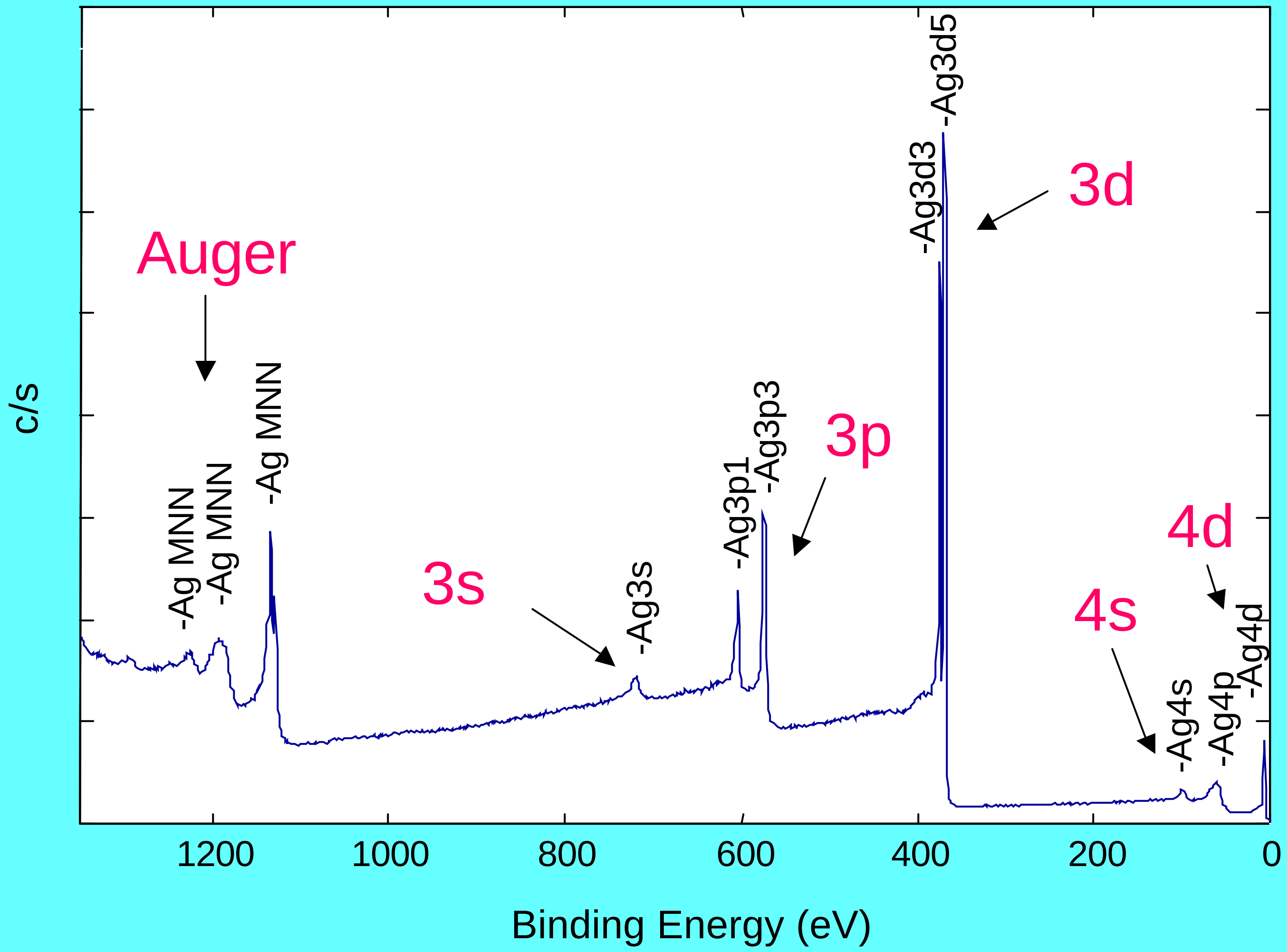
Portable electrochemical experimental station

Portable deposition experimental station (not shown)

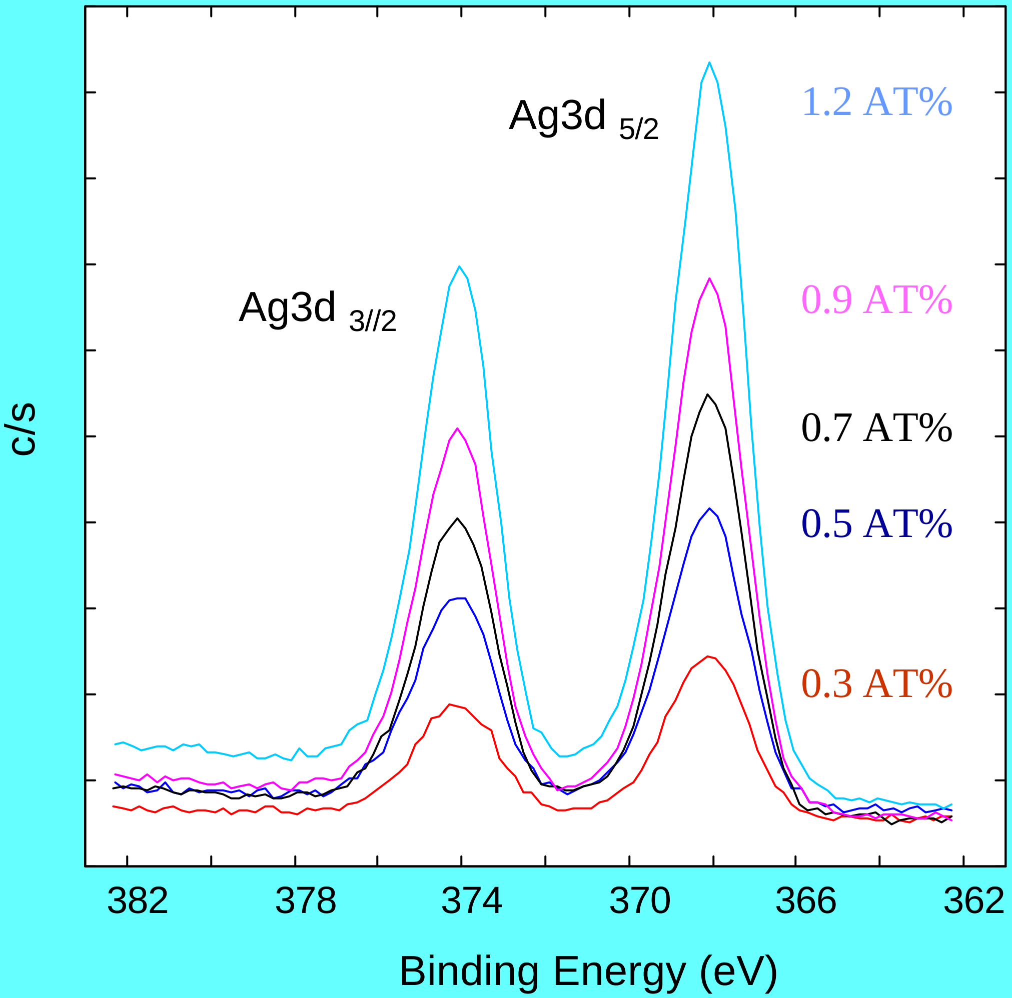
XPS Instrumentation
Count rate as a function of energy resolution



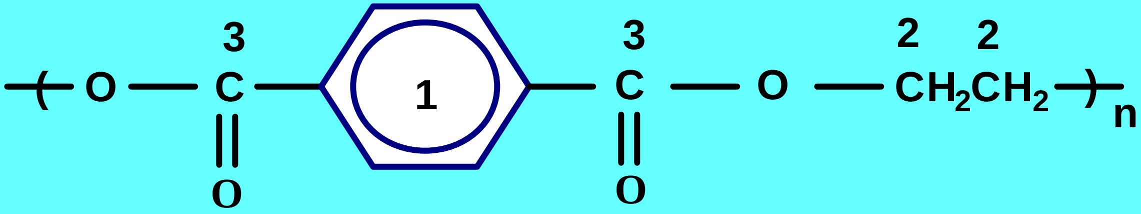
XPS wide scan of clean Ag photoelectron lines and Auger lines

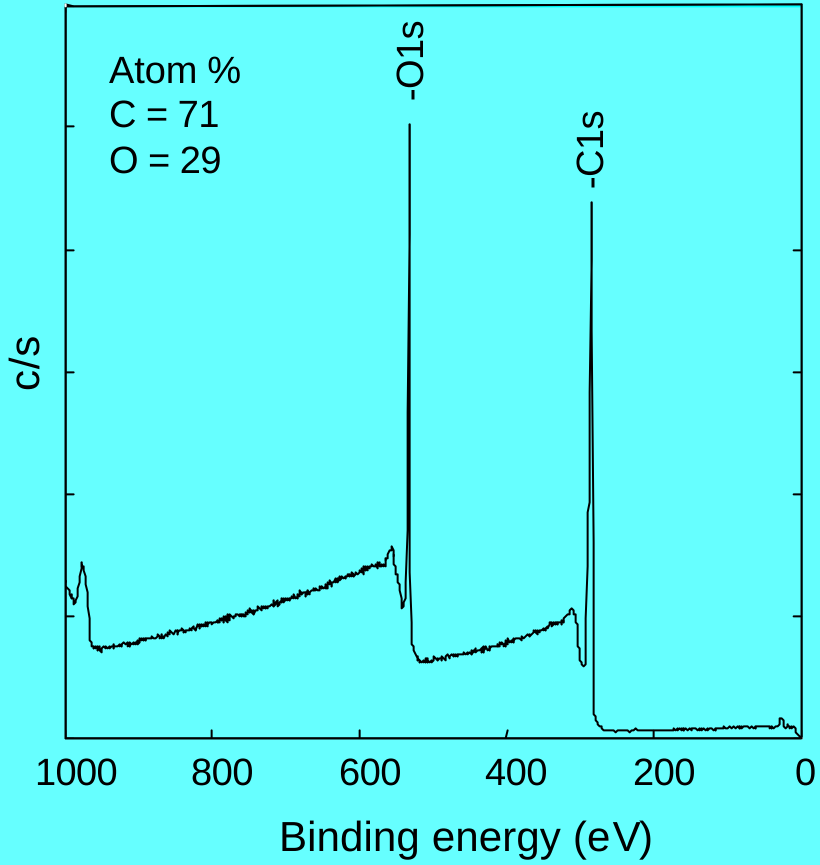


XPS of the Ag3d region
Ag based catalyst on γ-Al_2O_3

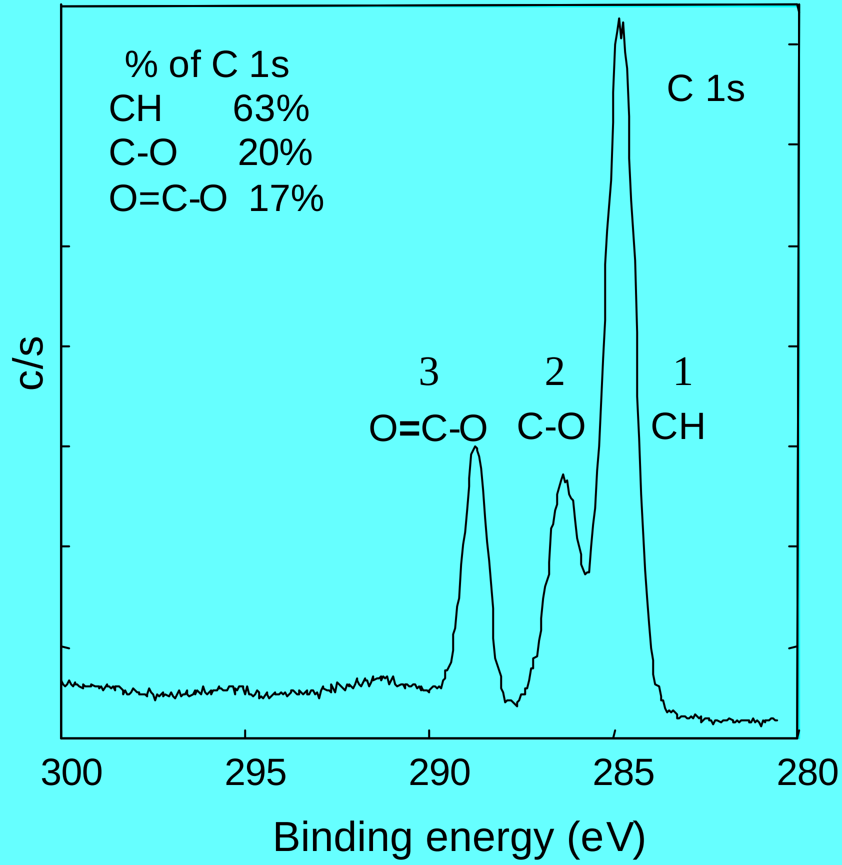


XPS of Poly(ethylene terephthalate)



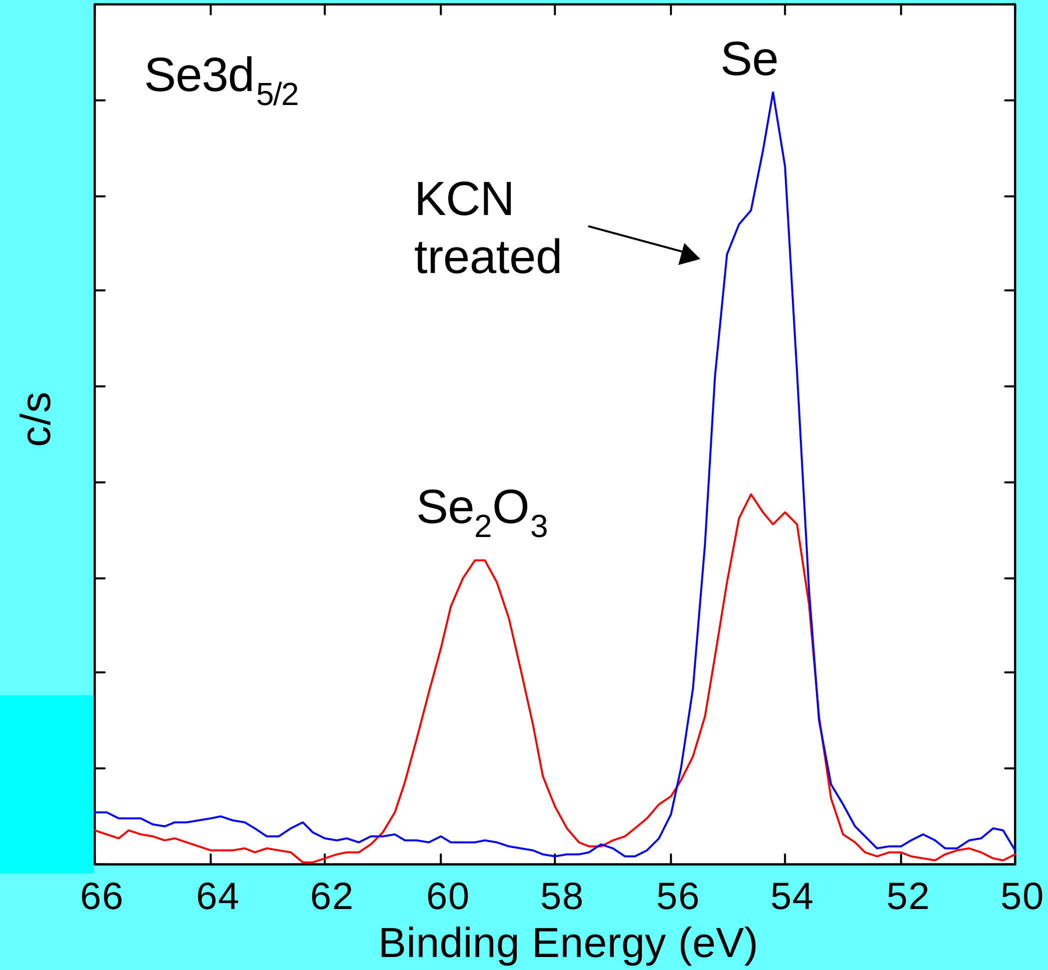


Quantitative elemental information



Chemical state information.

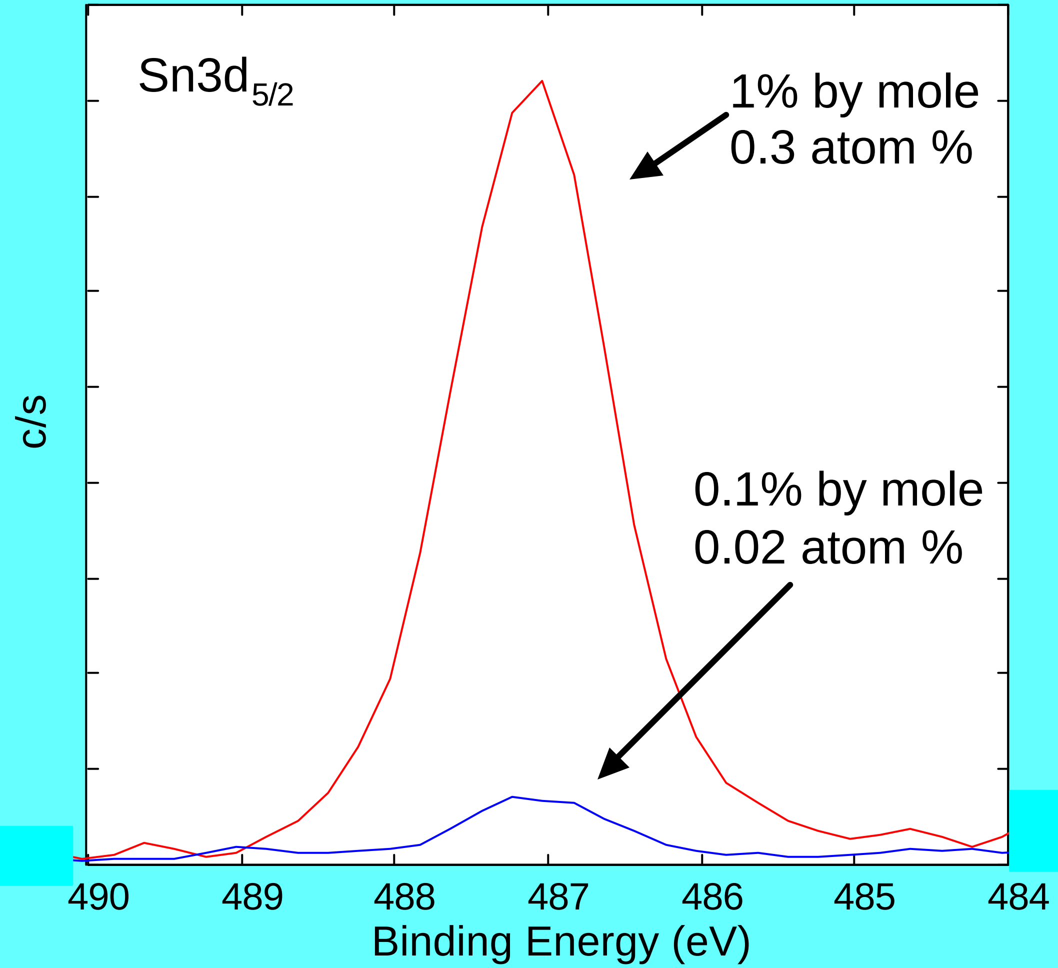
XPS high energy resolution spectra of solar cell before & after KCN treatment



Work in collaboration with Peter Eschbach and Larry Olsen from Washington State University

Thesis by Peter Eschbach “Investigation of Buffer Layers in Copper Indium Gallium Selenium Solar Cells” (2002)

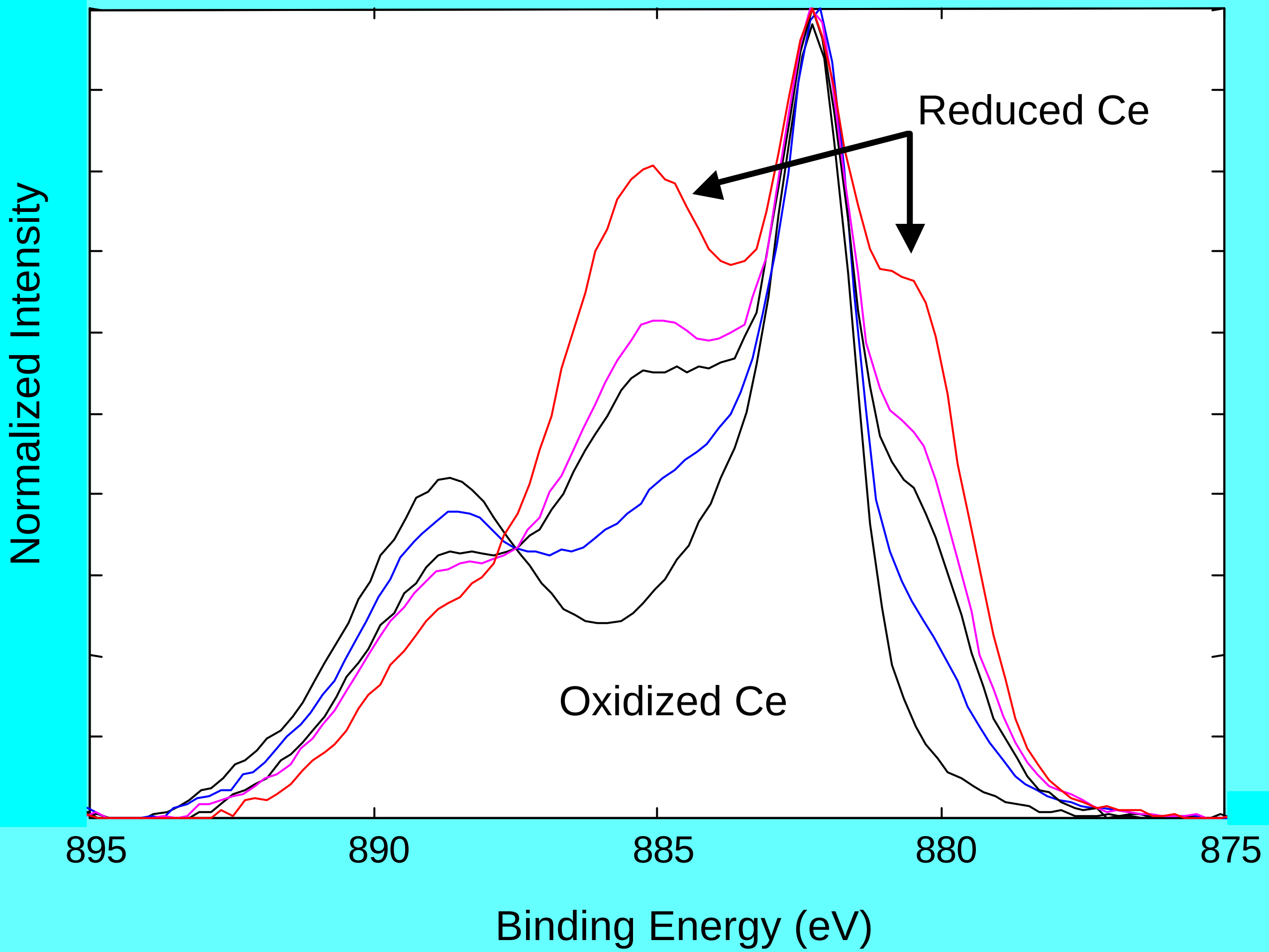
XPS high energy resolution spectra SnO$_2$ doped hematite



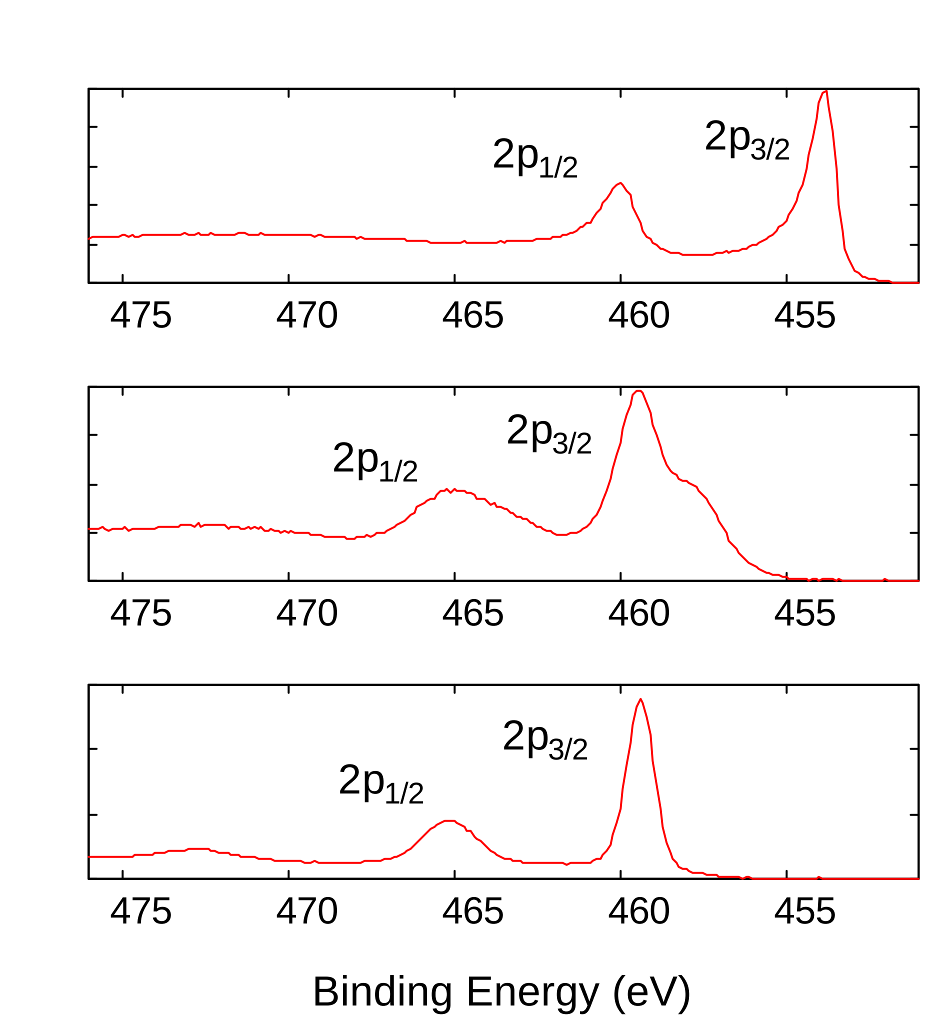
Work in collaboration with Barbara Balko & Kathleen Clarkson from Lewis & Clark College

“The Effect of Doping with Ti(IV) and SN(IV) on Oxygen Reduction at Hematite Electrodes” *J. of Electrochemical Society*, **148** (2001)

XPS high energy resolution spectra oxidized and reduced CeO_2



XPS spectra of Ti2p peaks for Ti and TiO_2

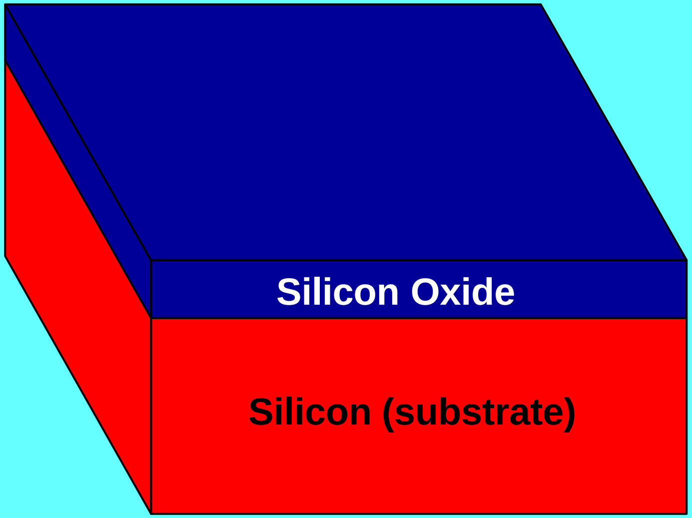


Ti metal peak (454 eV)

TiO_2 (110)
with some
reduced states

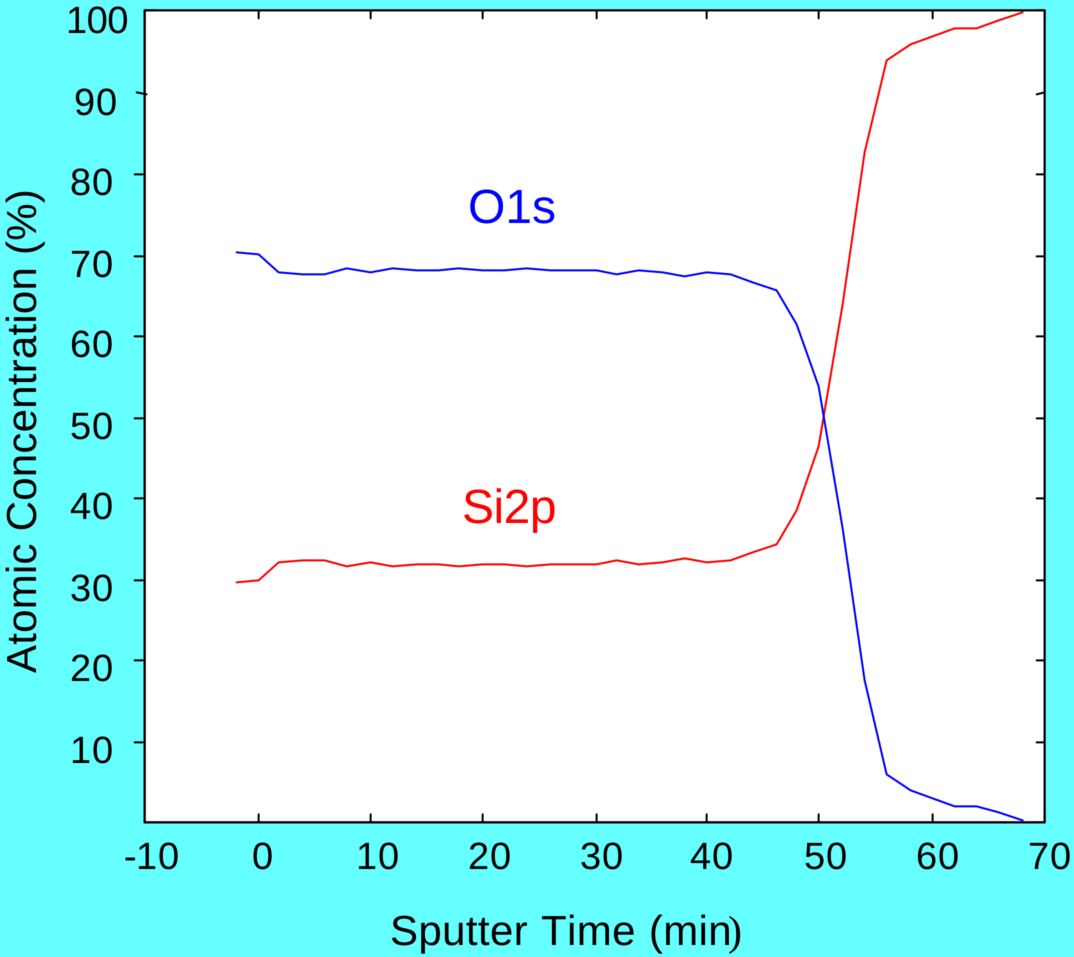
TiO_2 peak (459 eV)

XPS depth profile of SiO_2 on Si

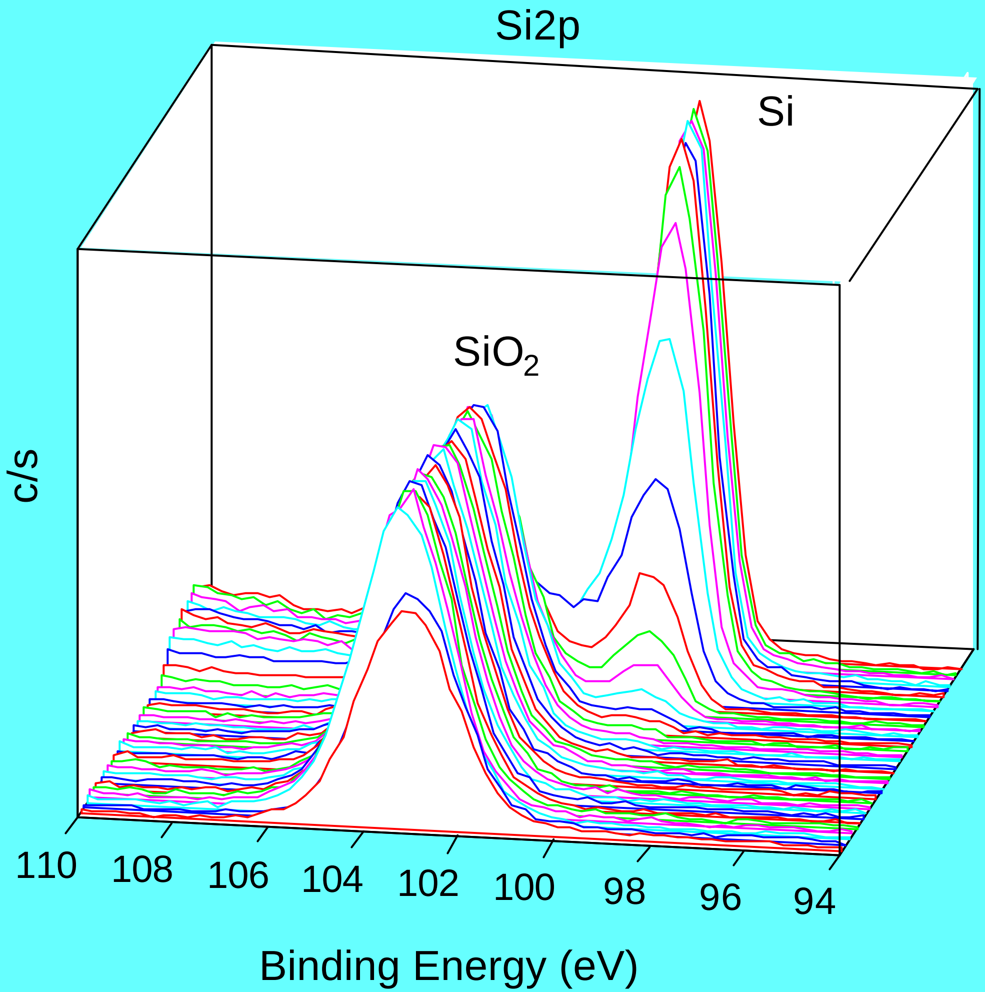


Silicon Oxide

Silicon (substrate)

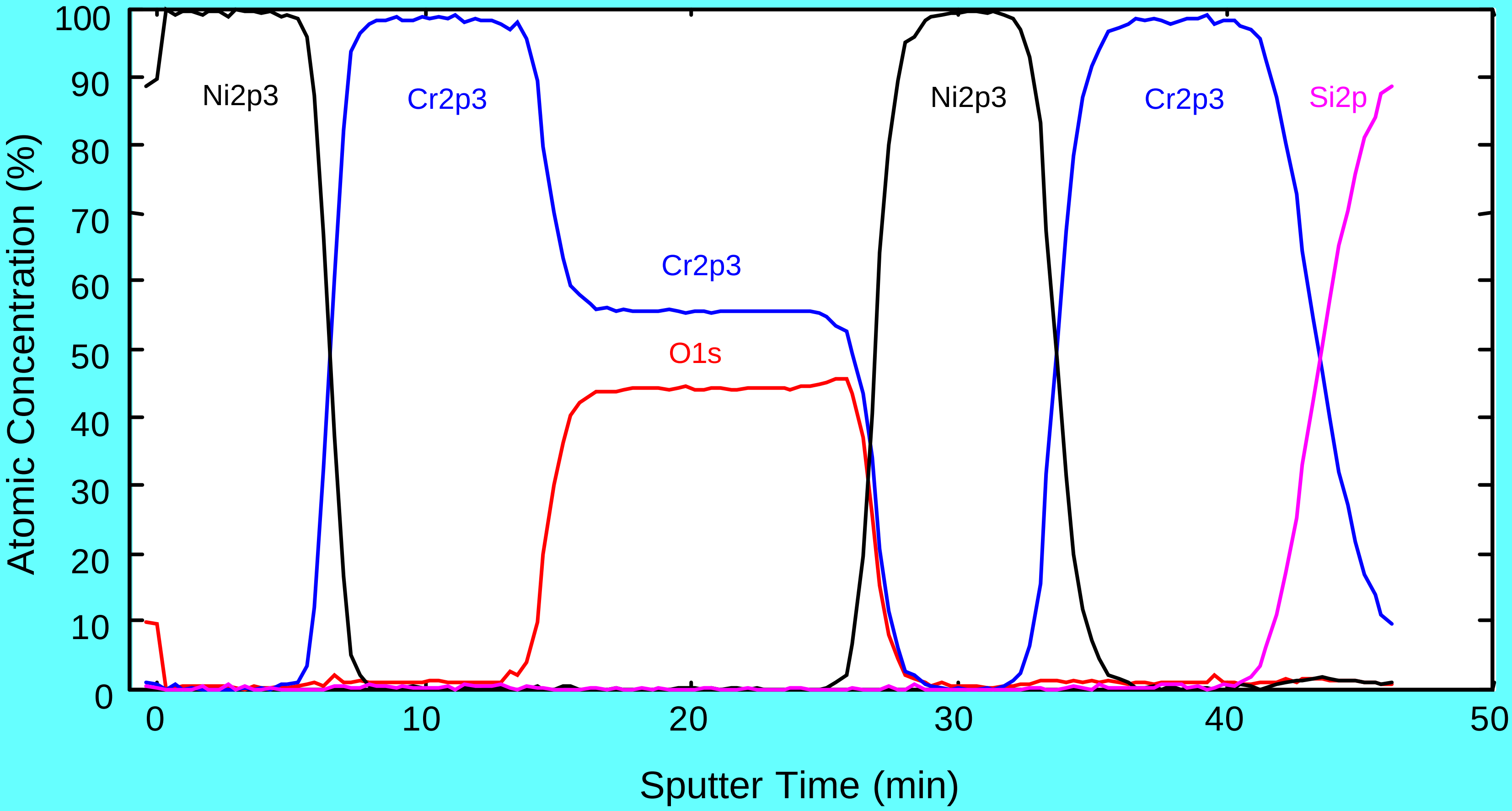


XPS depth profile of SiO_2 on Si

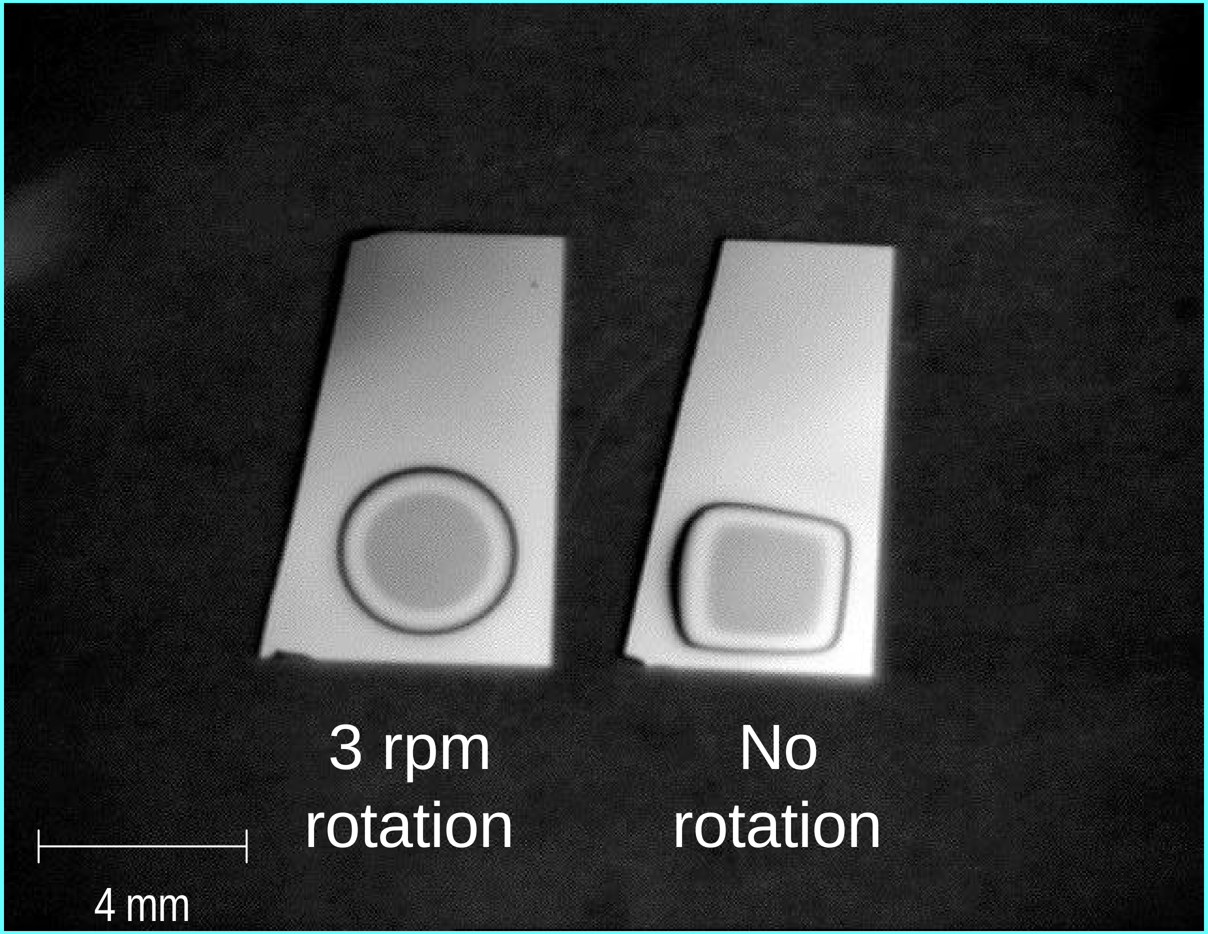


Si = 99.3 eV
SiO_2 = 103.3 eV

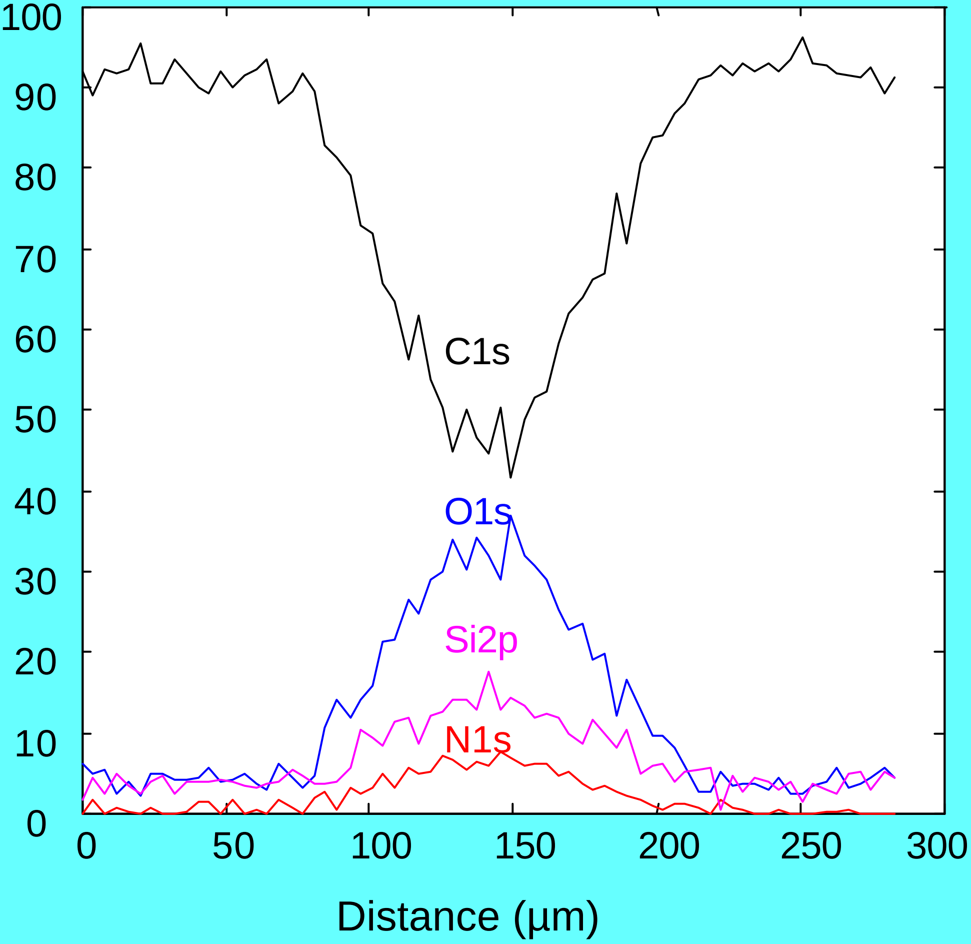
XPS depth profile of multilayer Ni/Cr/CrO/Ni/Cr/Si

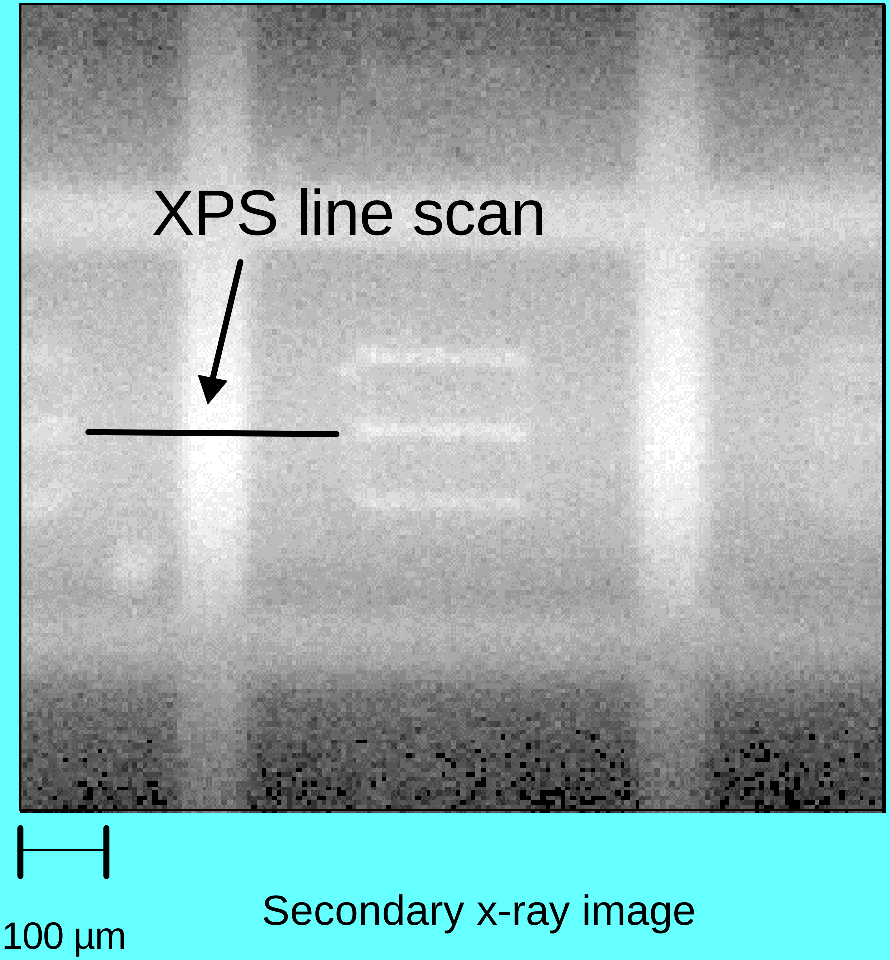


Sputter depth profile craters in Multilayer Films using Ar+ ions with and without sample rotation



XPS line scan of patterned polymer film using a 20 um diameter Al Kα X-ray beam



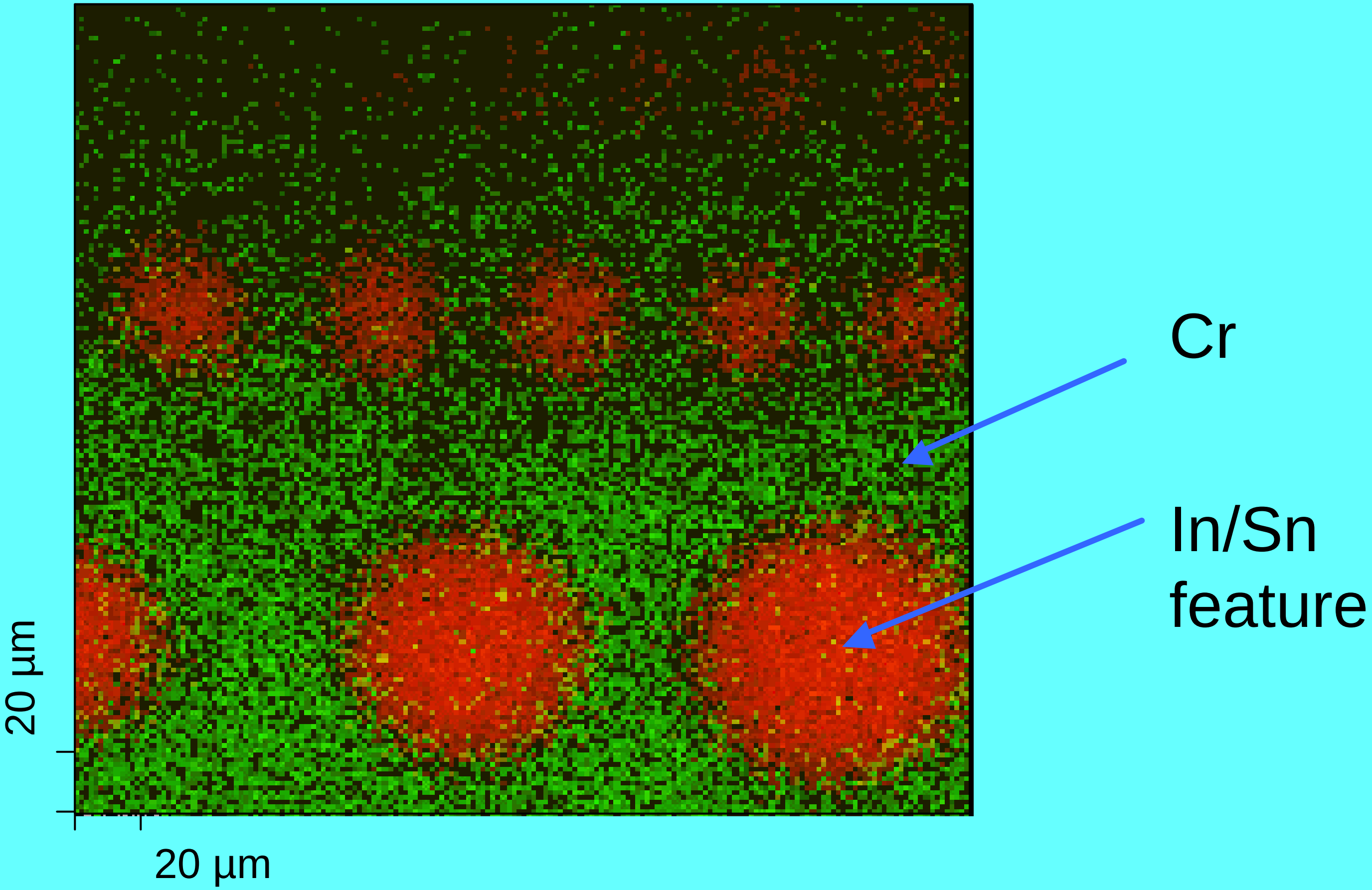


Secondary x-ray image

Work in collaboration with Mingdi Yan and Michele Bartlett from Portland State University

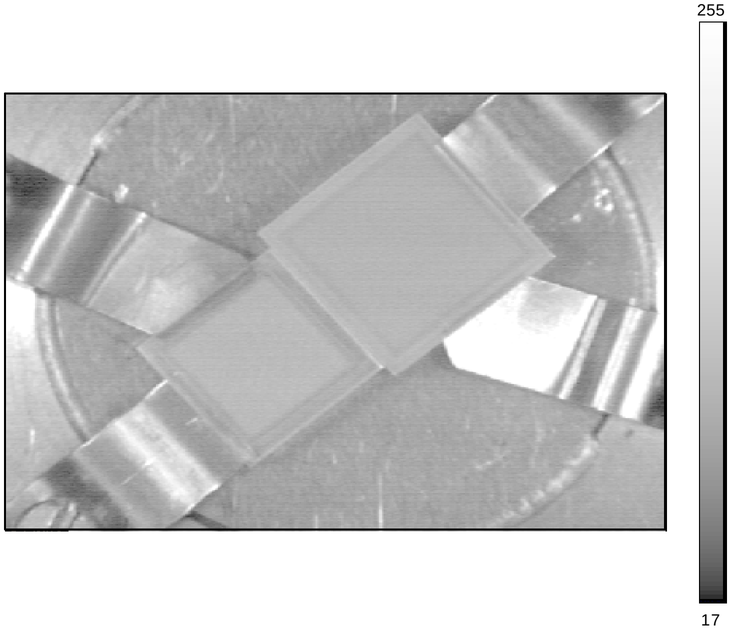
“Micro/Nanowell Arrays Fabricated from Covalently Immobilized Polymer Thin Films on Flat Substarte” *Nano Letters* V2, N4 (2002)

XPS Elemental Map of ITO circular patterns

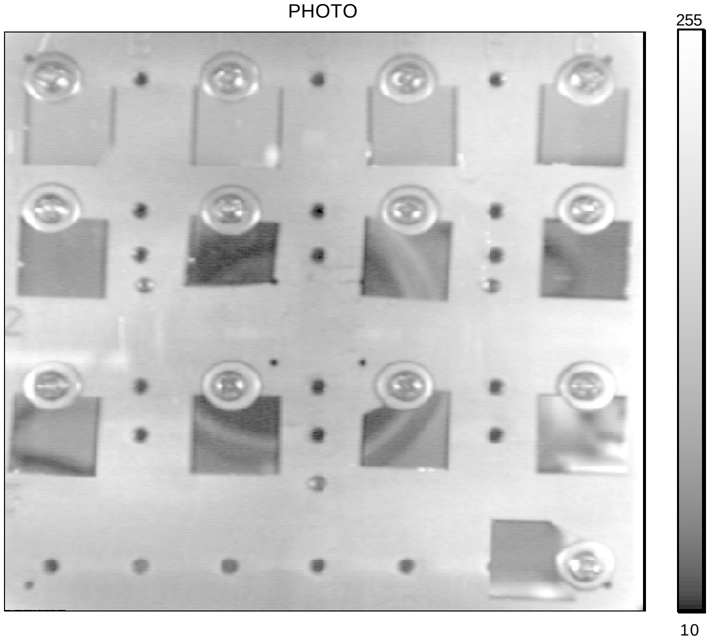


Examples of sample holders

TiO_2 and $SrTiO_3$ crystals



Self-assembled monolayers on Au/Si



Web sites

- EMSL: www.emsl.pnl.gov
- AVS Science & Technology Society: www.avs.org
- Evans Analytical Group: www.cea.com

References

Practical Surface Analysis (second edition) V1 edited by D. Briggs and M. P. Seah.

Encyclopedia of Materials Characterization, editors C. R. Brundle, C. A. Evans, S. Wilson and L. E. Fitzpatrick.

Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, www.phi.com

The XPS of Polymers, edited by G. Beamson & D. Briggs, SurfaceSpectra Limited. (CD rom version)