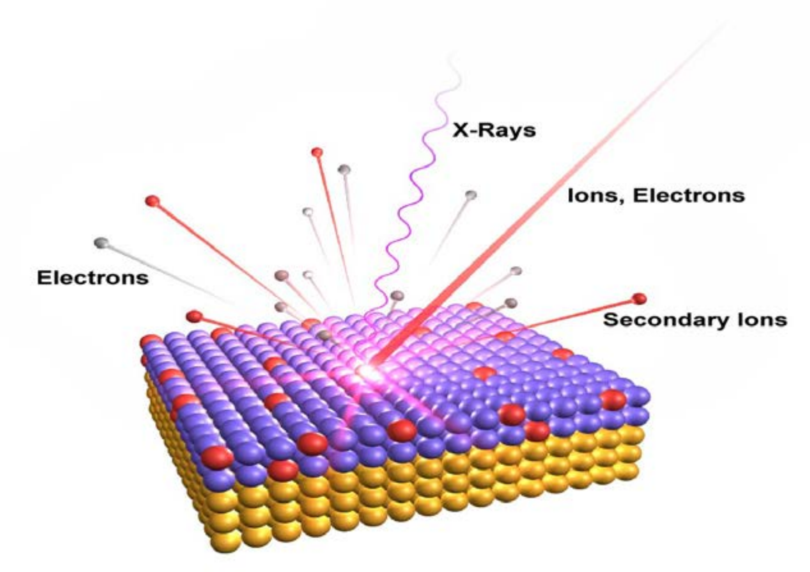
X-Ray Photoelectron Spectroscopy XPS

Mark Engelhard



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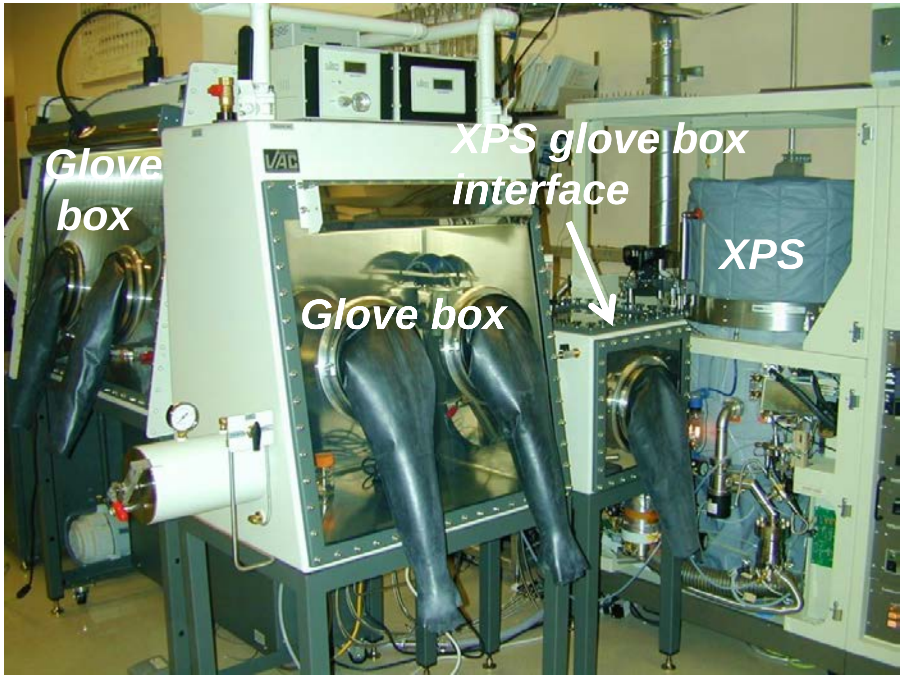
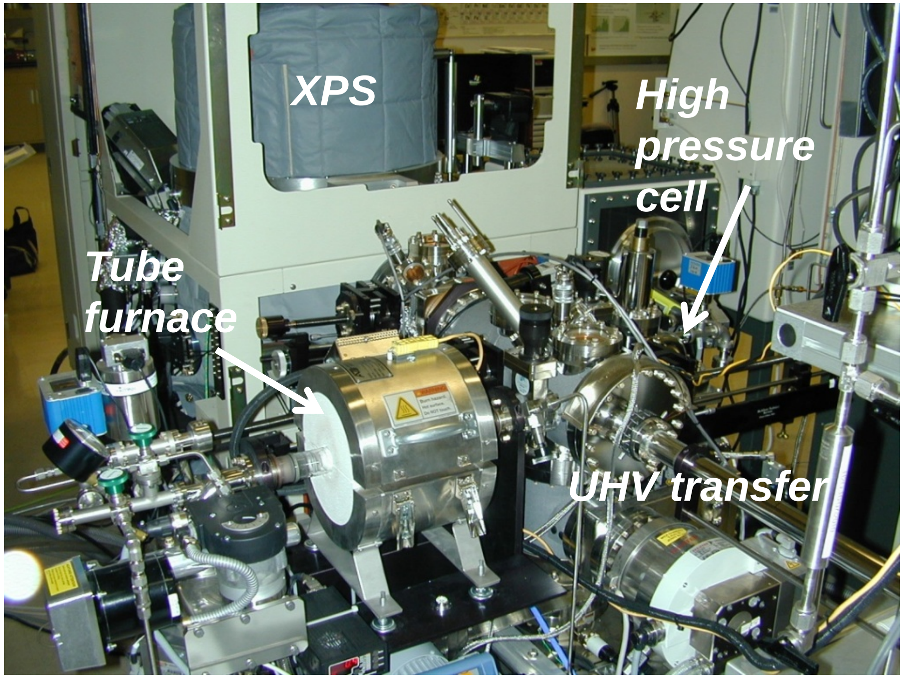
Physical Electronics Quantera XPS
High Energy Resolution Focused X-ray Beam Capability





Catalysis reaction and processing chamber with inert atmosphere glove box connected to a PHI Quantera Scanning X-ray Microprobe system.

- *High pressure reactor with heating up to 800°C*
- *Vacuum/Atmosphere tube furnace with heating up to 1K°C*
- *Currently six gases including: H_2, O_2, He, N_2, NO and CO.*
- *Gas with liquid vapor exposure capabilities.*
- *Pfeiffer OMNI star gas analysis system.*

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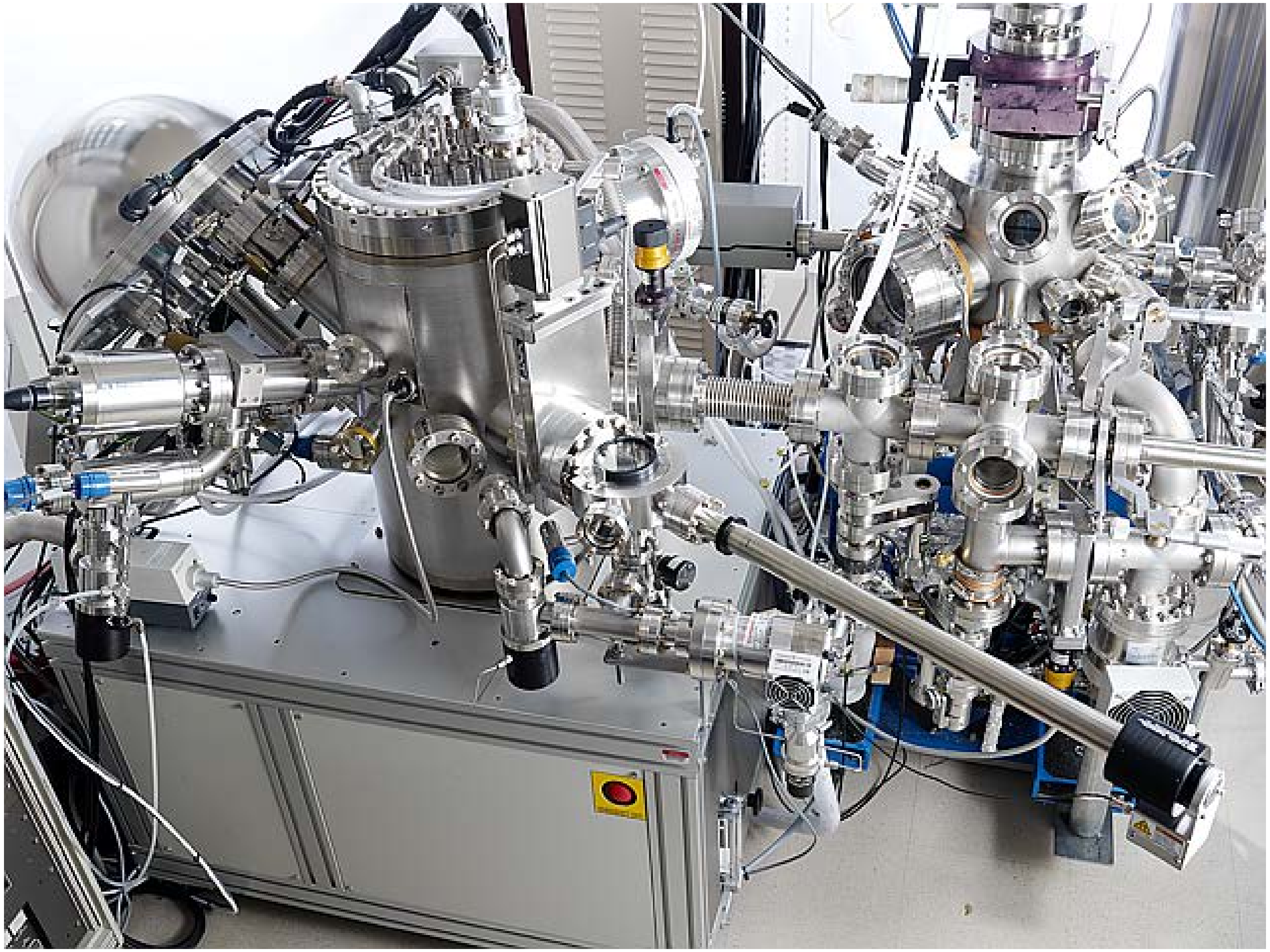
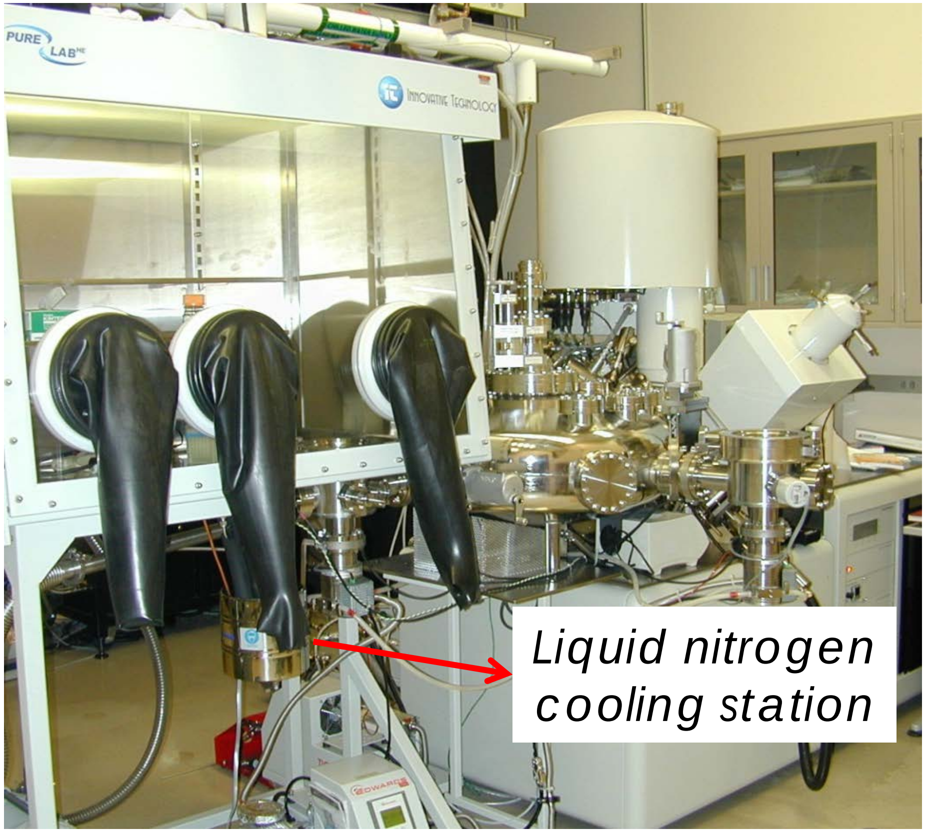
PHI 5000 VersaProbe XPS

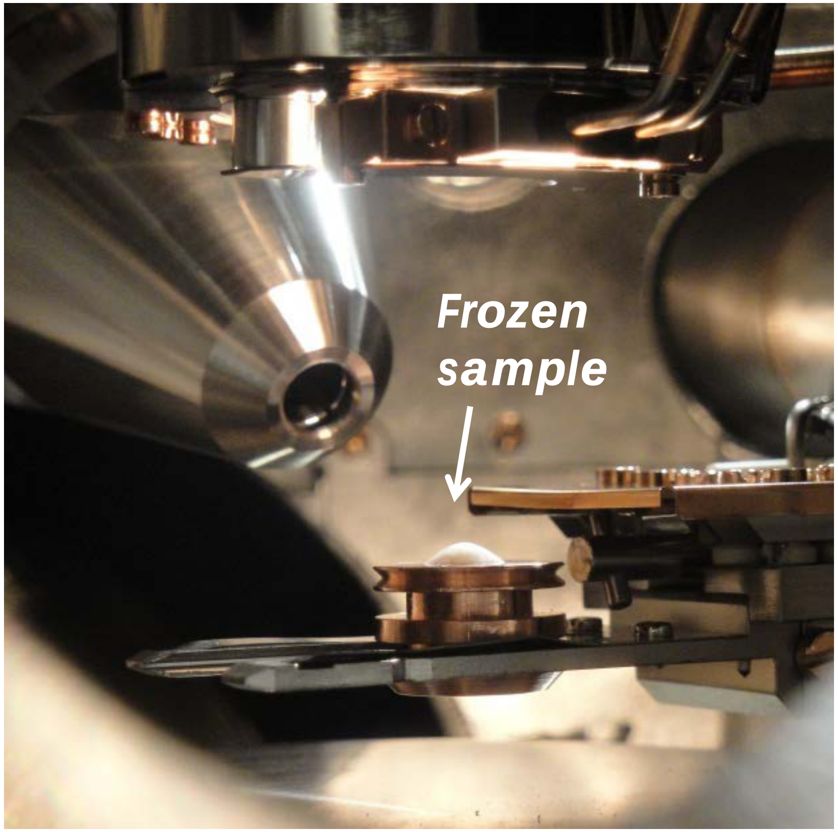
- PHI VersaProbe
  - monochromatic Al Kα
  - non-monochromatic
  - UPS capability
  - C60 ion gun
  - Side chamber



Kratos Axis DLD X-ray Photoelectron Spectrometer



Liquid nitrogen cooling station



Frozen sample

- Sample preparation in glove box
- Frozen from room temperature to liquid nitrogen temperature within 10 minutes
- Maintained at liquid nitrogen temperature during XPS measurements

History (XPS)

X-ray Photoelectron Spectroscopy (XPS) was developed in the mid-1960s by Kai Siegbahn and his research group at the University of Uppsala, Sweden. The technique was first known by the acronym ESCA (Electron Spectroscopy for Chemical Analysis). The variation of photopeak energy with chemistry allowed the development of this surface sensitive chemical analysis method.

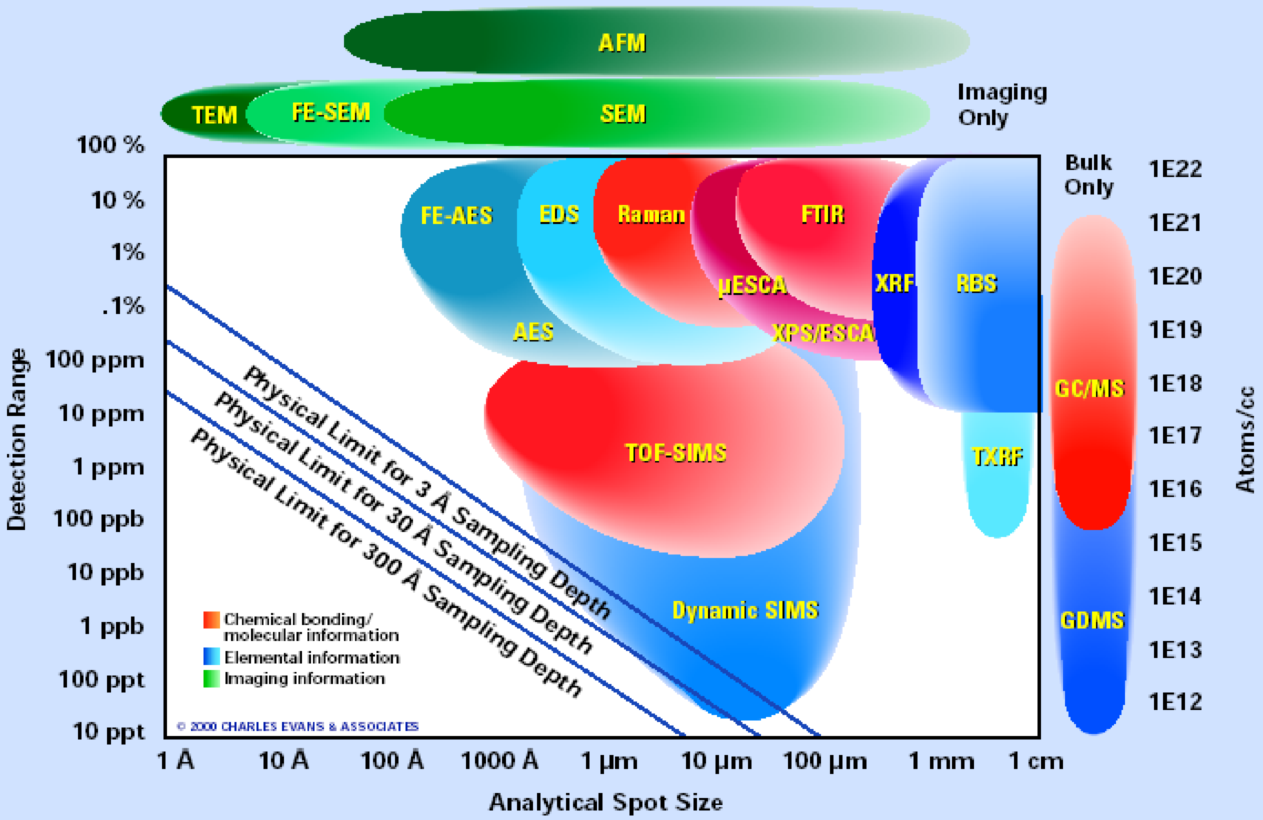
The advent of commercial manufacturing of surface analysis equipment in the early 1970s enabled the placement of equipment in laboratories throughout the world. In 1981, Siegbahn was awarded the Nobel Prize for Physics for his work with XPS.

Outline

- Introduction to XPS (basic principles)
- Quantification
- Energy resolution and count rates
- Wide scan data (low energy resolution spectra)
- Narrow scan data (high energy resolution spectra)
- Chemical state analysis
- Detection sensitivity
- Depth profiles, Line scans, and Elemental Maps
- Sample neutralization
- Sample holders
- Useful web sites and references

Introduction to XPS

Analytical Resolution versus Detection Limit



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Introduction to 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.
- An important advantage of XPS is its ability to obtain information on chemical states from the variations in binding energies, or chemical shifts, of the photoelectron lines.

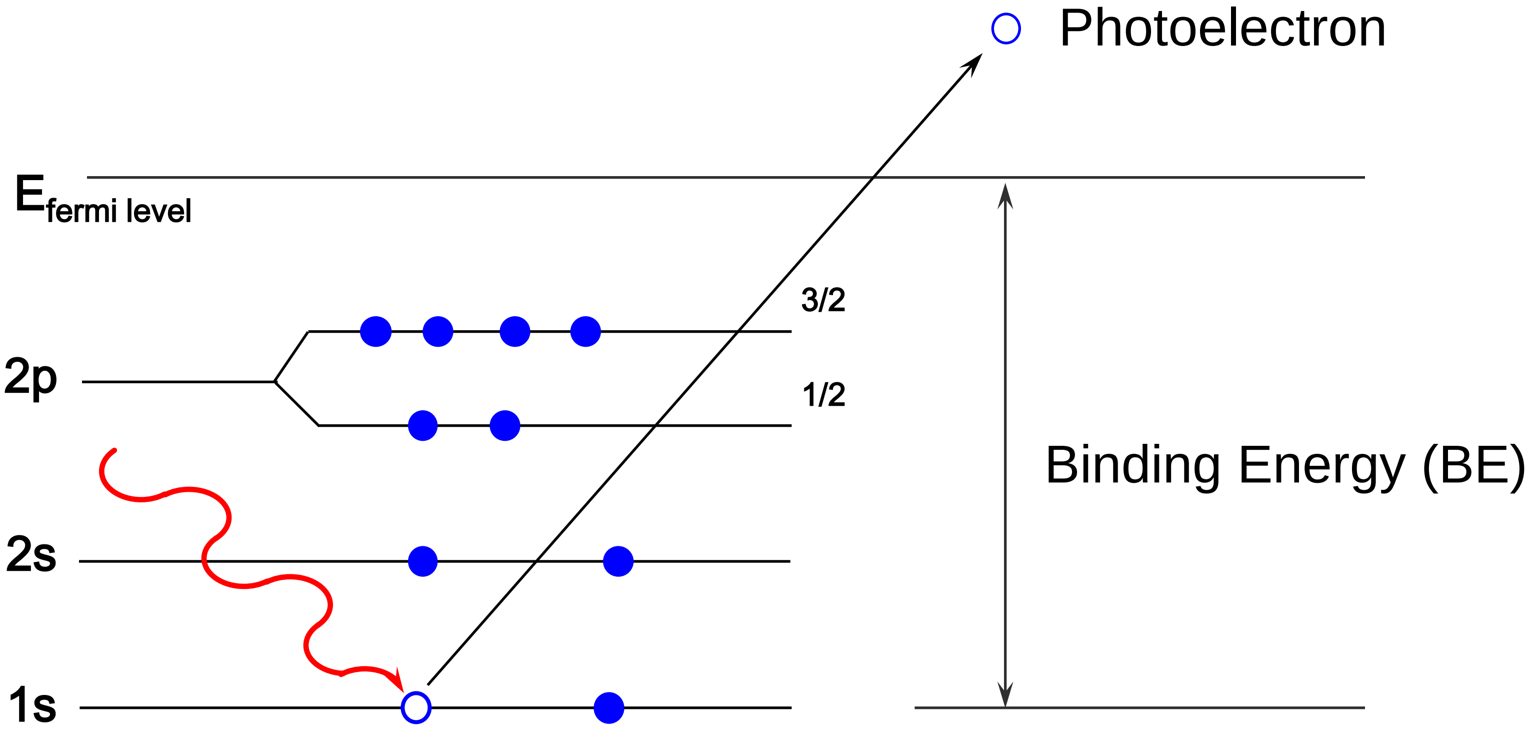
Introduction to XPS -- Analysis capabilities

- ► Elements detected from Li to U
- ► Quantitative
- ► Chemical state identification
- ► Valence band electronic structure
- ► Conducting and insulating materials
- ► Surface sensitivity from 5 to 75 angstroms
- ► Detection limits that range form 0.01 to 0.5 atom percent
- ► Chemical/Chemical state distributions
  - ● Mapping (x,y) with <10 μm resolution
  - ● Depth (z)
    - \- Sputter depth profiling
    - \- Angle dependent depth profiling
    - \- Layer information from electron energy loss

Introduction to XPS --
XPS emission process

EMSL

An incoming photon causes the ejection of the photoelectron



$$KE = h\nu - BE - e\Phi$$

Kinetic Energy = $h\nu$ (Al Kα 1486.7 eV) – Binding Energy

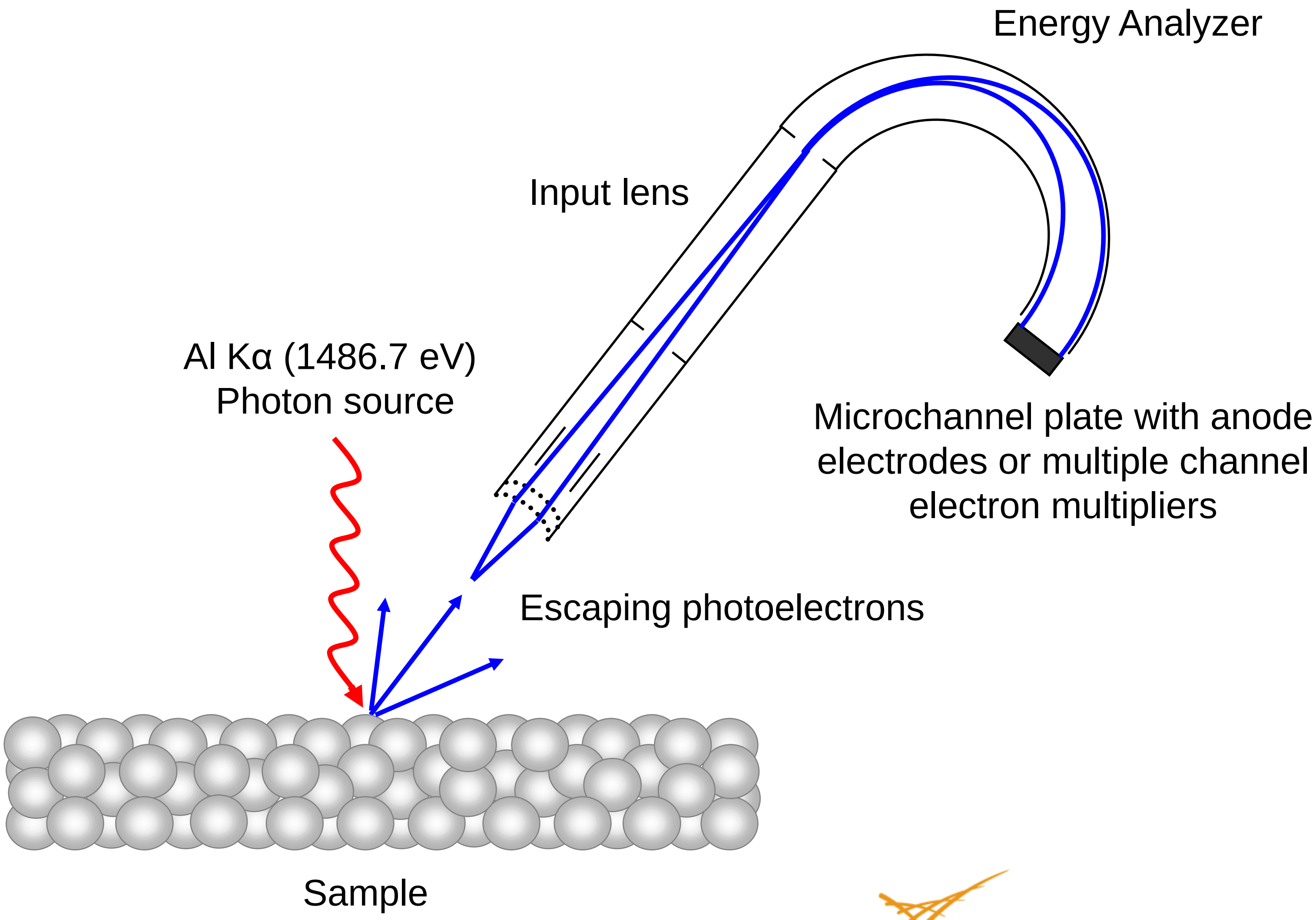
Introduction to XPS -- Basic principles

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

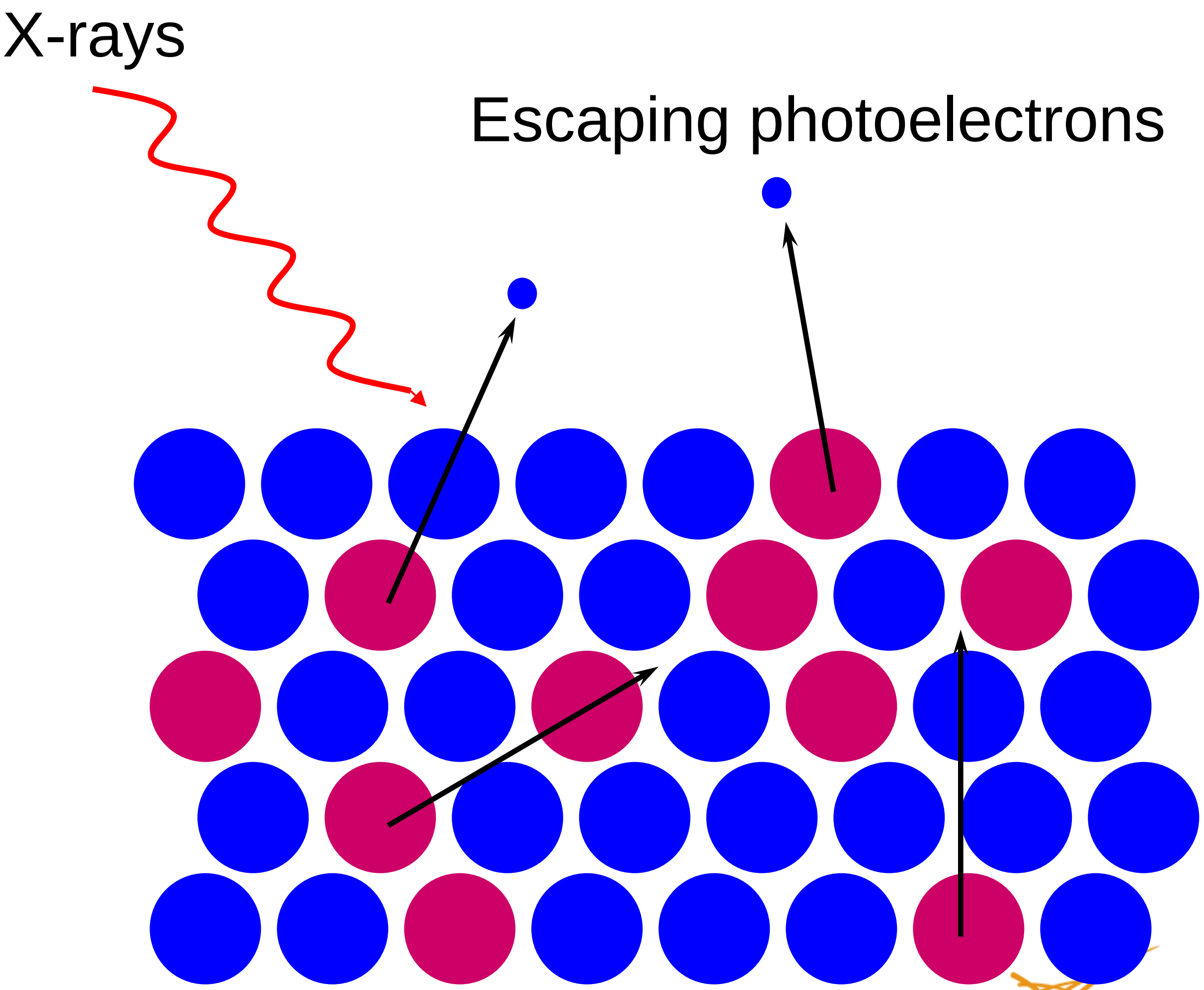
$$KE = h\nu - BE - e\Phi$$

KE	Kinetic Energy of ejected photoelectron
$h\nu$	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 to XPS -- Hemispherical Analyzer

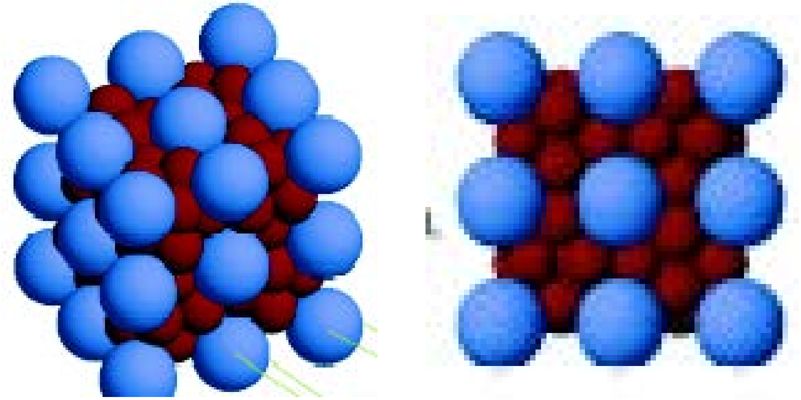


Introduction to XPS -- Surface sensitivity



Introduction to XPS -- Surface sensitivity

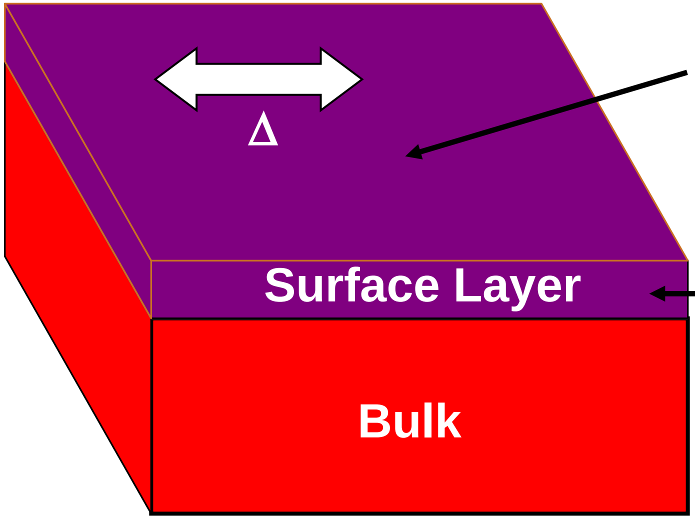
X-ray Photoelectron Spectroscopy
Auger Electron Spectroscopy
Secondary Ion Mass Spectrometry
Surface Enhanced Raman Spectroscopy
Ultraviolet Photoelectron Spectroscopy
Low Energy Electron Diffraction



Surface to volume ratio

A **3 nm** iron particle has	**50%** atoms on the surface
A **10 nm** particle has	**20%** on the surface
A **30 nm** particle has	**5%** on the surface

Introduction to XPS -- Analysis objective



Composition $A_x\ B_y\ C_z$

(d) thickness

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

Quantification

- Quantitative data can be obtained from peak heights or peak areas.
- 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.

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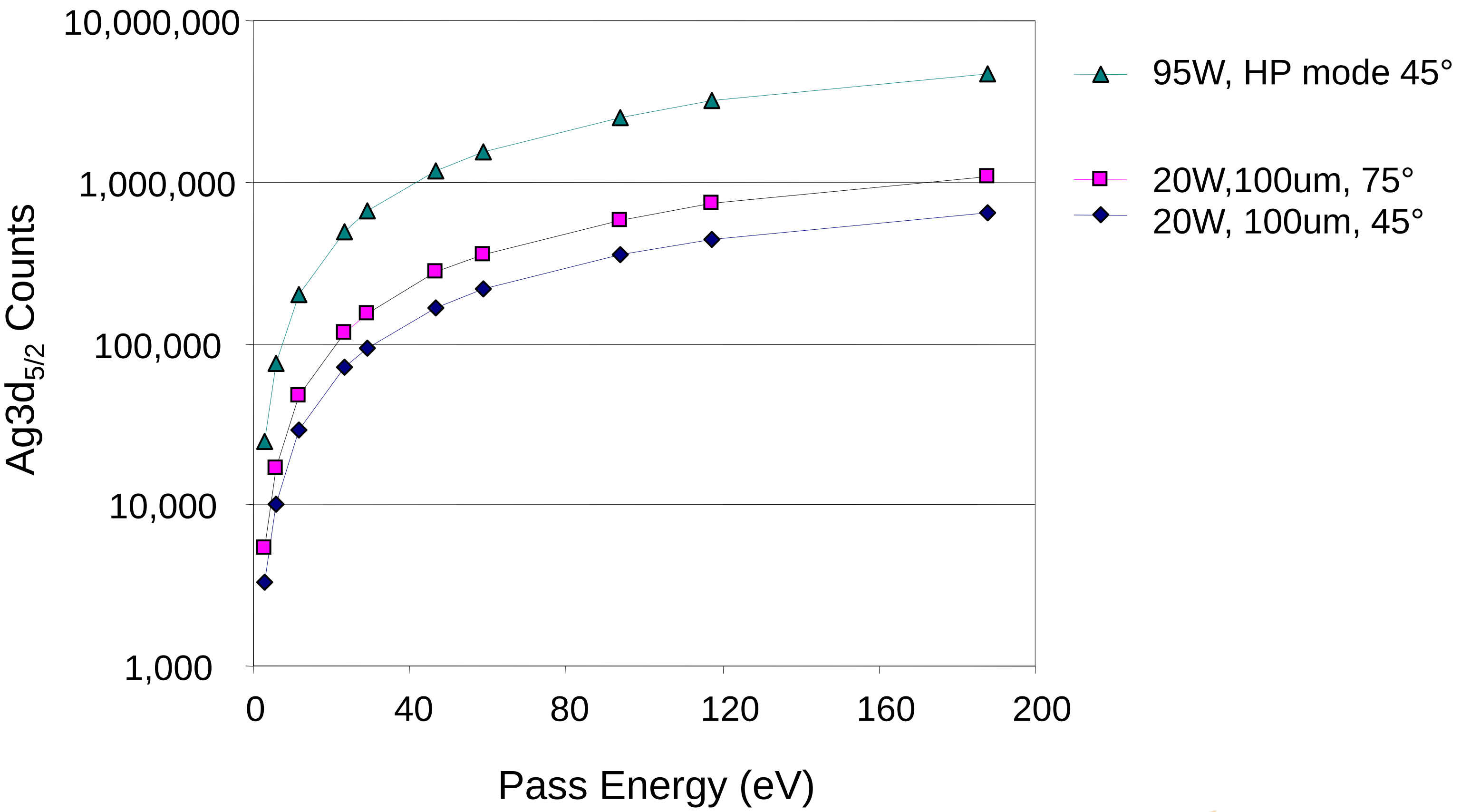
Count rate as function of energy resolution



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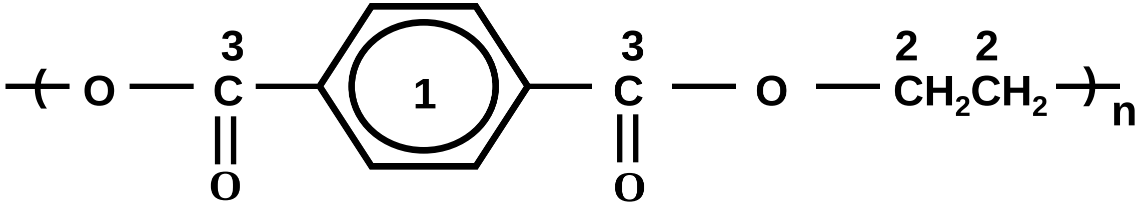
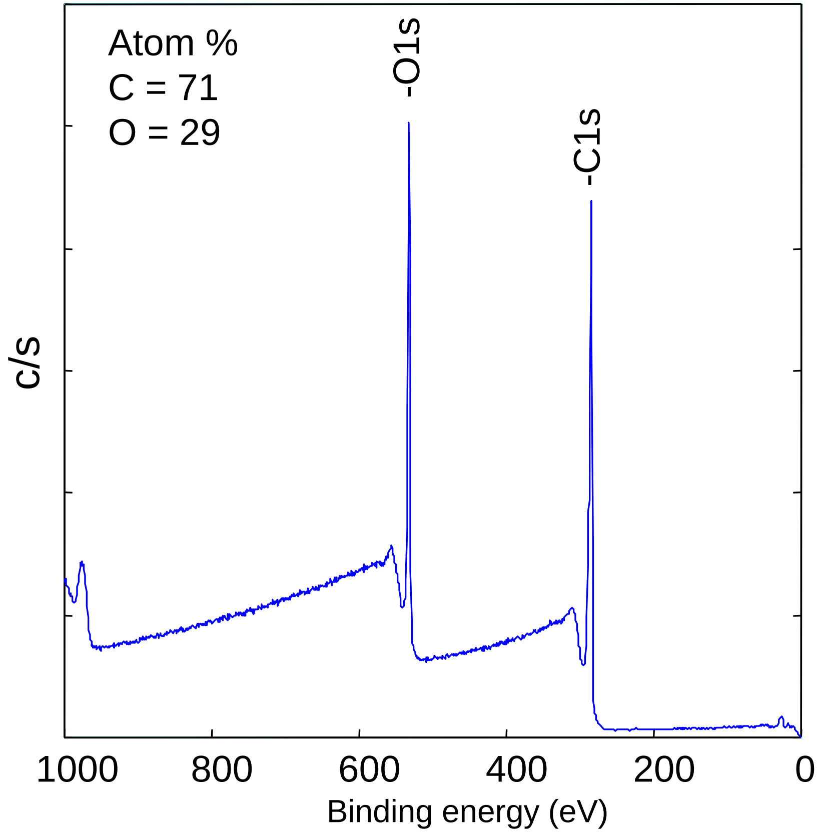
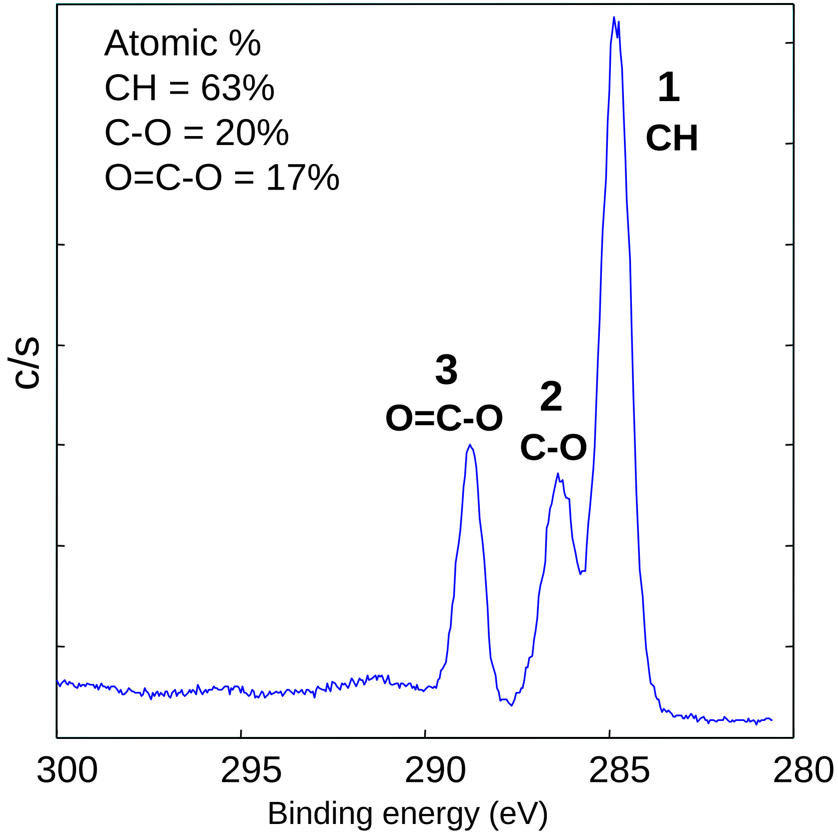
XPS of Poly(ethylene terephthalate)



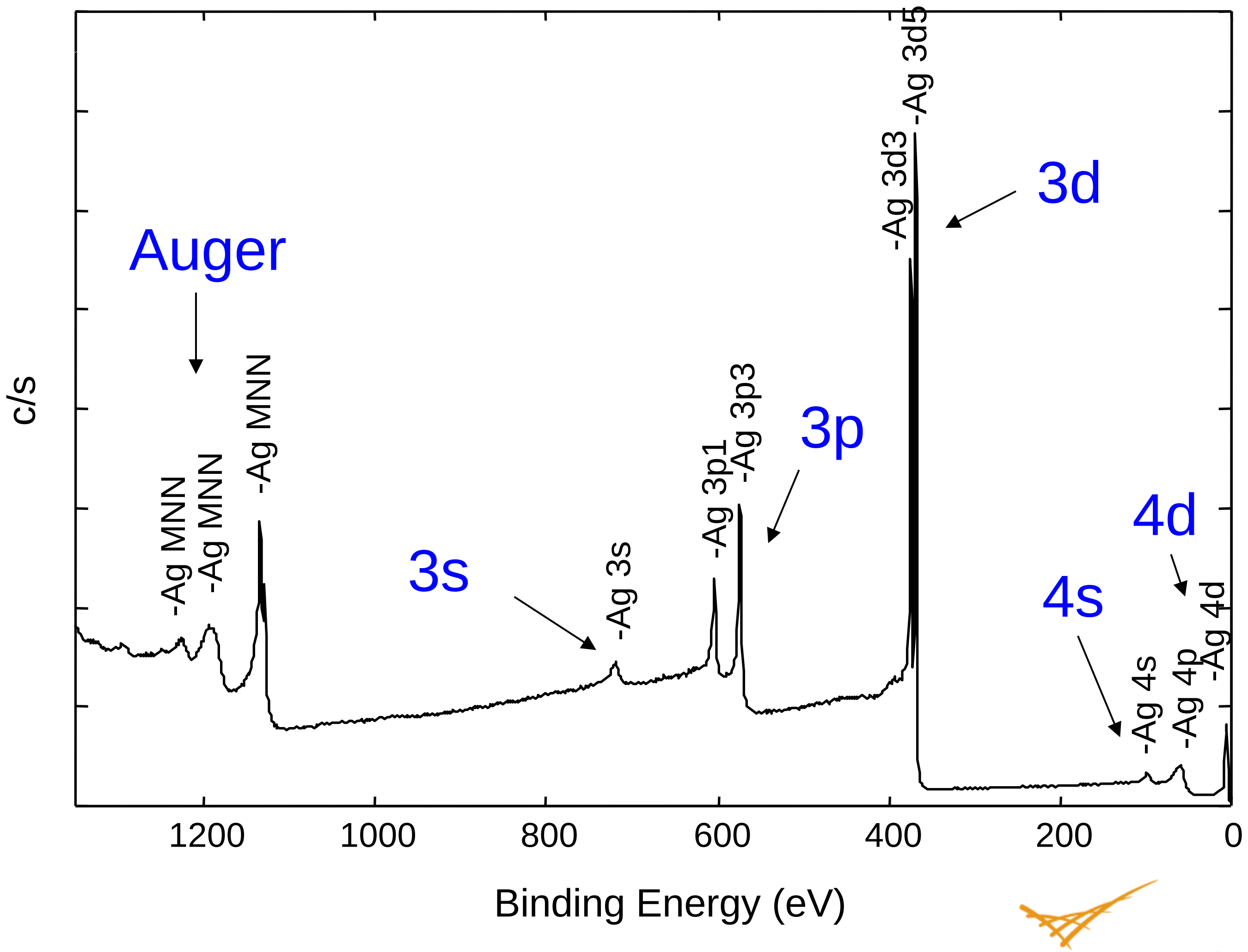


Quantitative elemental information



Chemical state information

Wide scan data (low energy resolution spectra) -- Ag photoelectron and Auger lines



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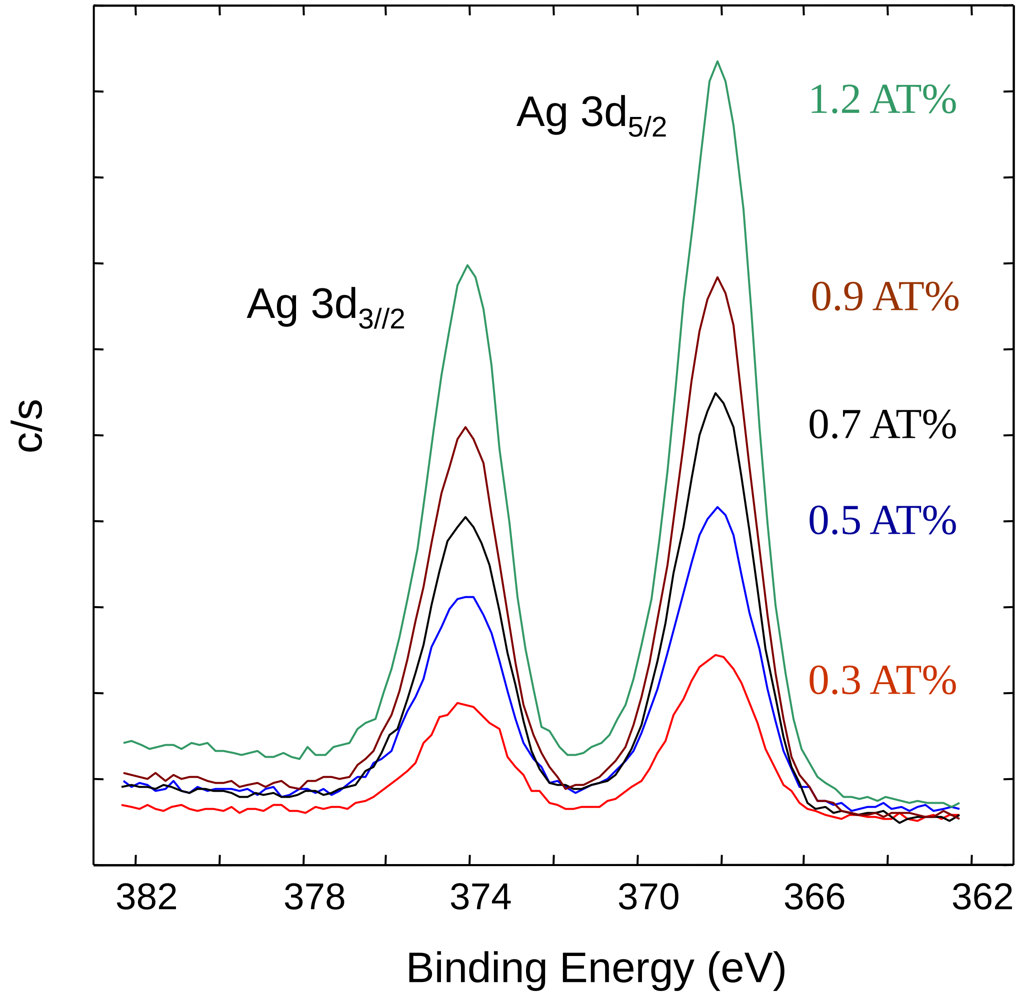
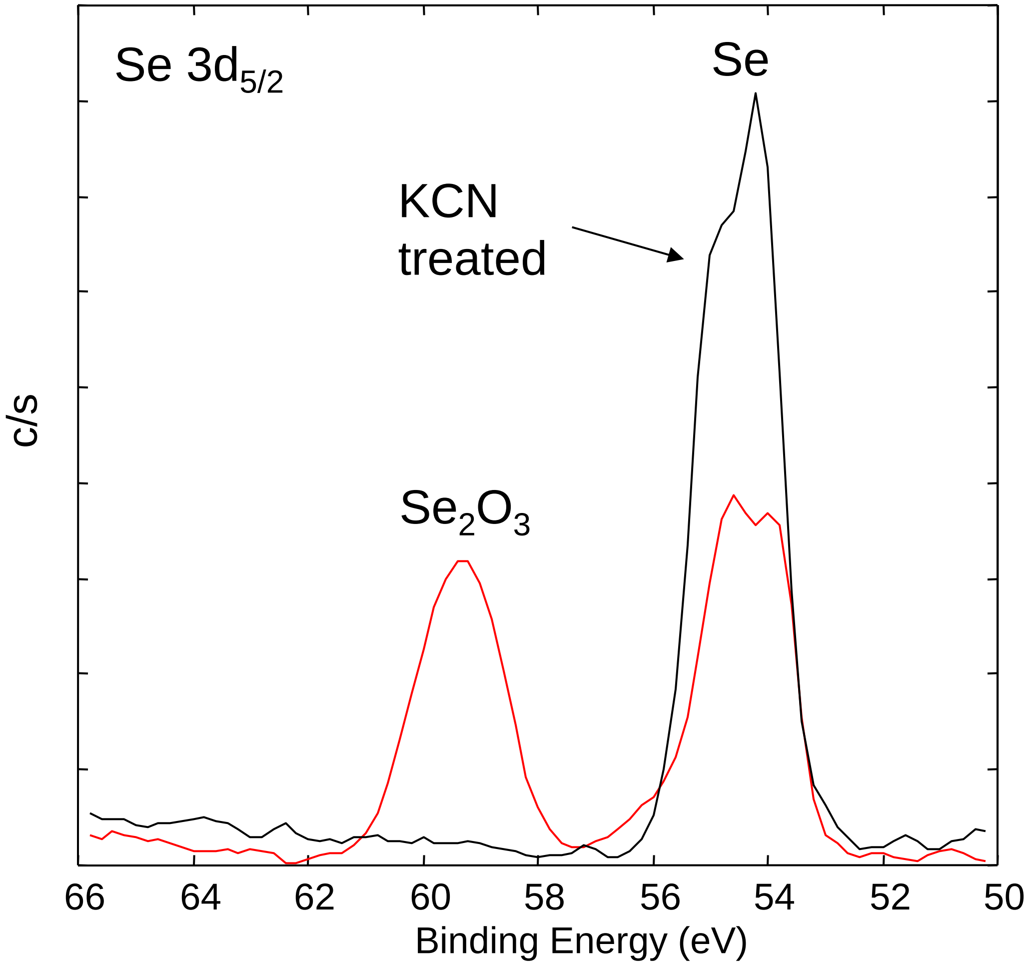
Narrow scan data (high energy resolution spectra) -- Ag 3d region -- Ag catalyst on γ-Al_2O_3



XPS spectra – P type absorber exposed to KCN prior to deposition of an N type partner



Work in collaboration with Peter Eschbach from Washington State University

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

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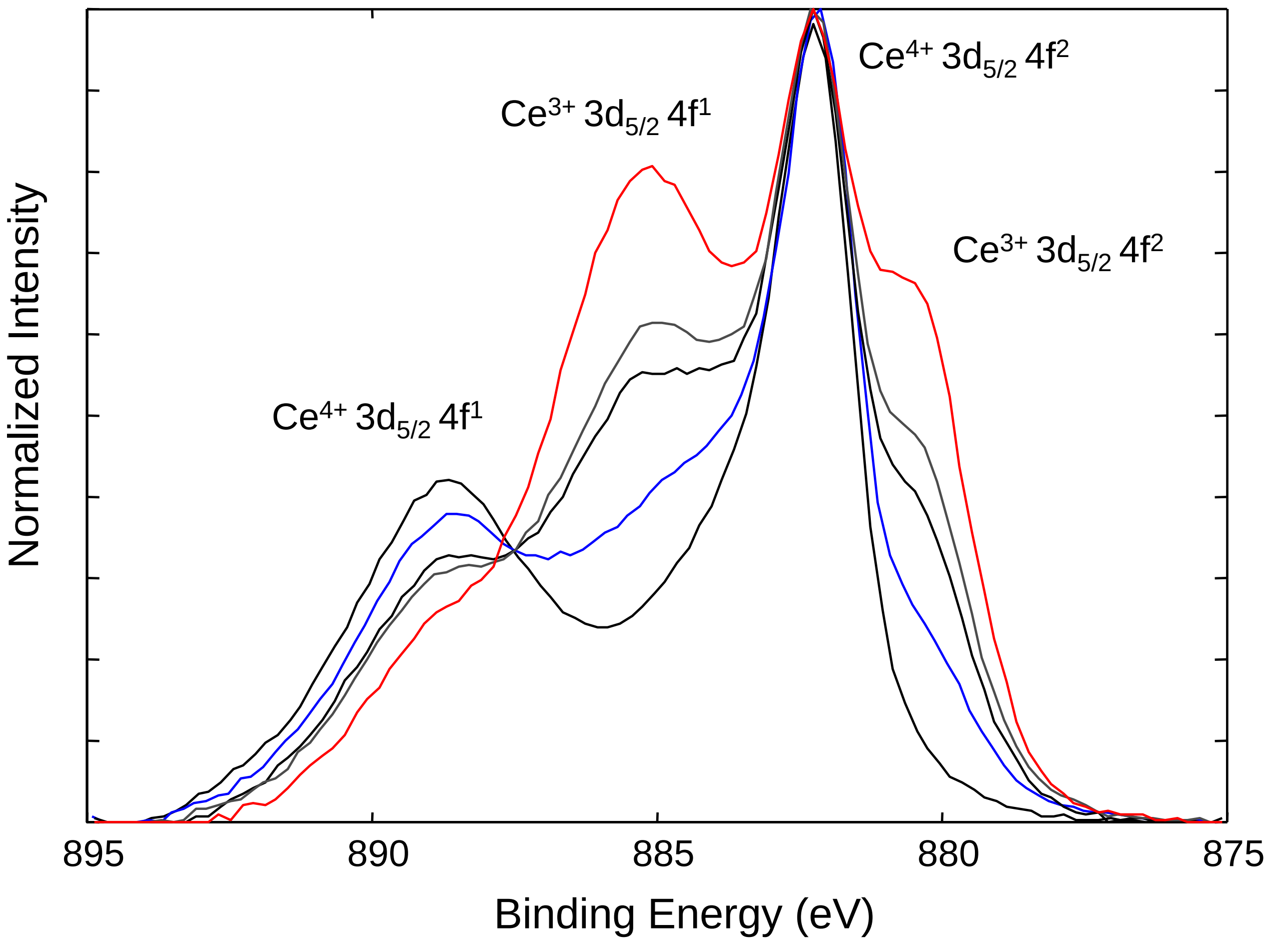
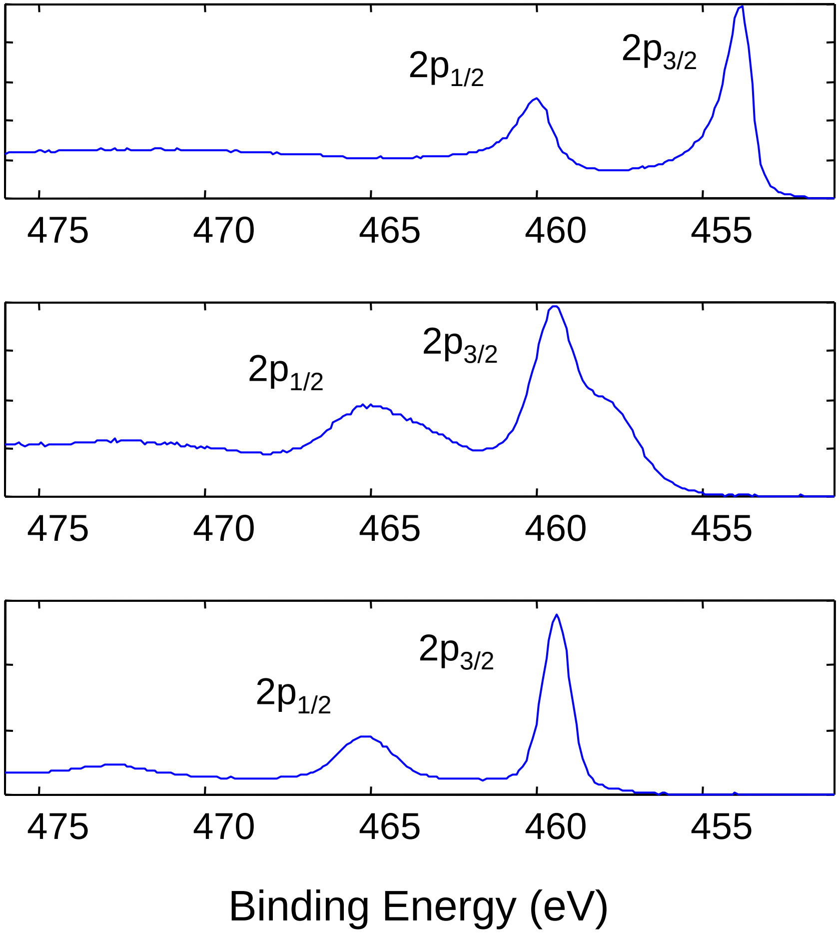
High energy resolution spectra -- Oxidized and reduced CeO_2



M. A. Henderson, C. L. Perkins, M. H. Engelhard, S. Thevuthasan, and C.H.F. Peden,
“Redox Properties of Water on the Oxidized and Reduced Surfaces of CeO2(111)”
Surface Science, 526:1-2 (2003) 1-18.

Ti 2p XPS spectra for Ti and TiO_2

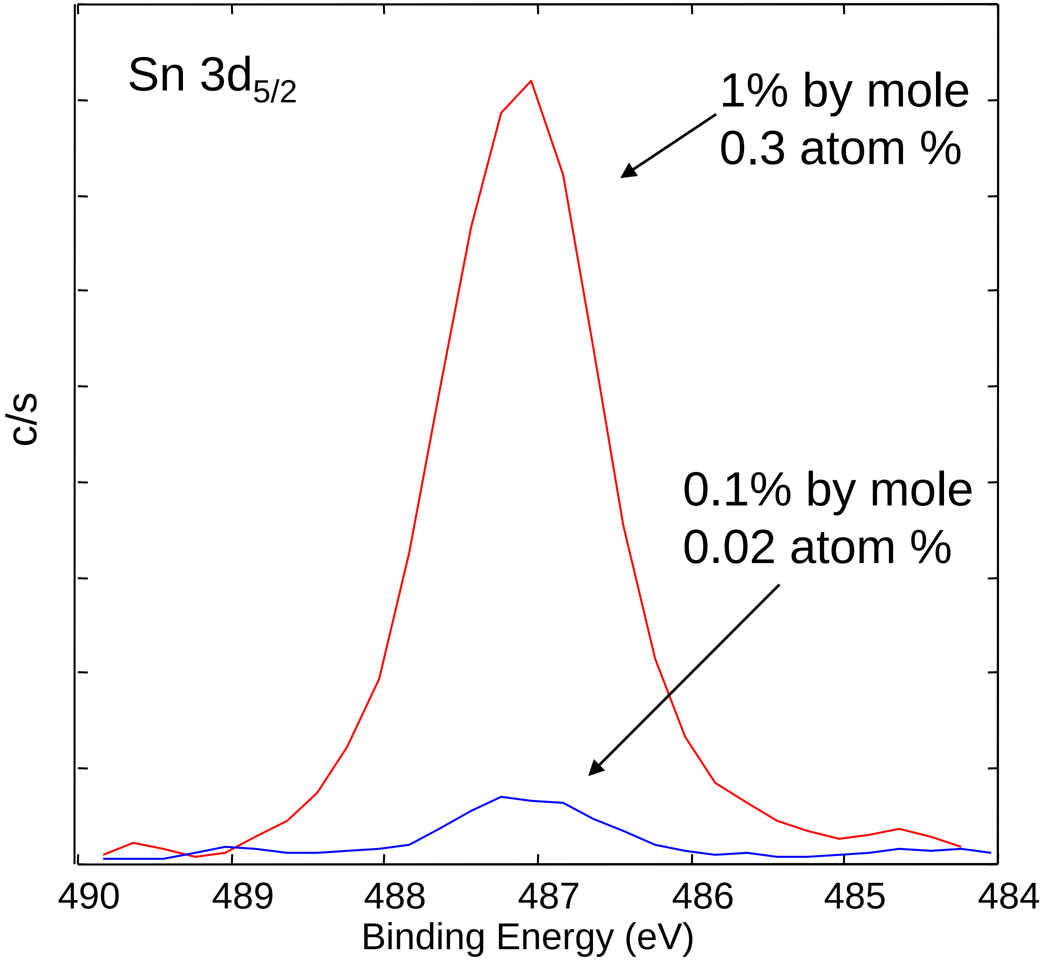


Ti metal peak @ 454 eV

TiO_2 with some reduced Ti^{+3}

TiO_2 peak @ 458.8 eV

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)

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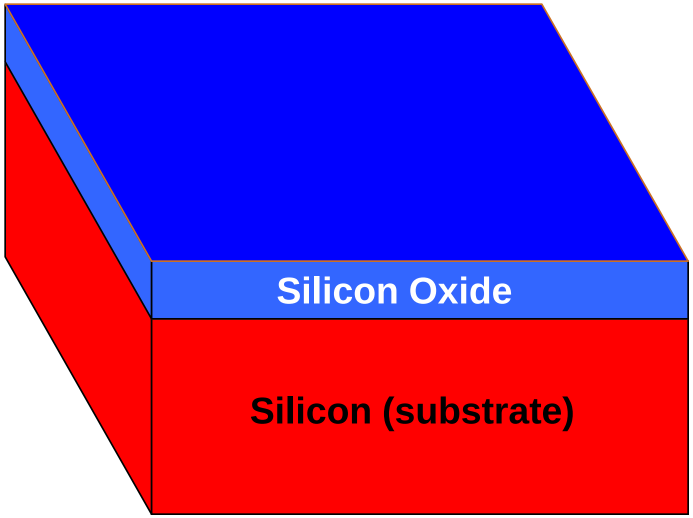
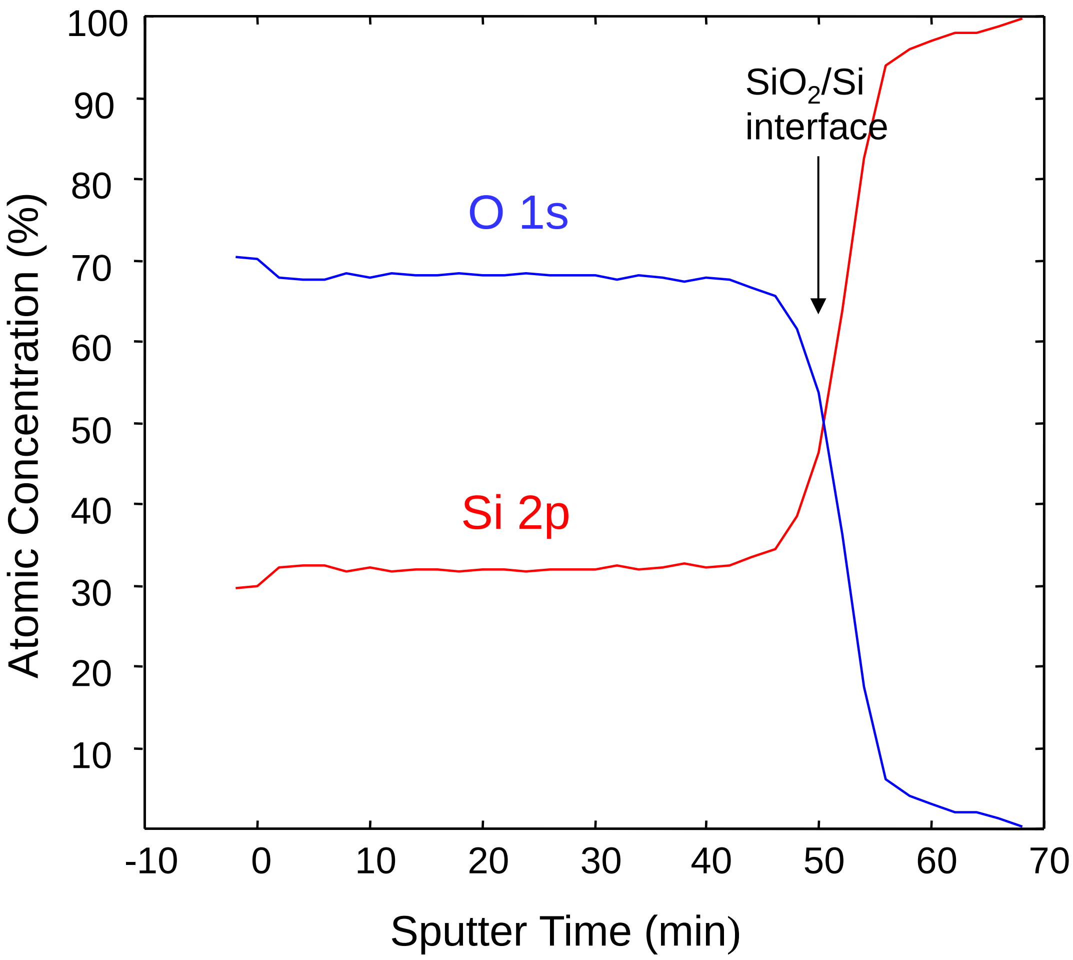
XPS depth profile – SiO_2 on Si





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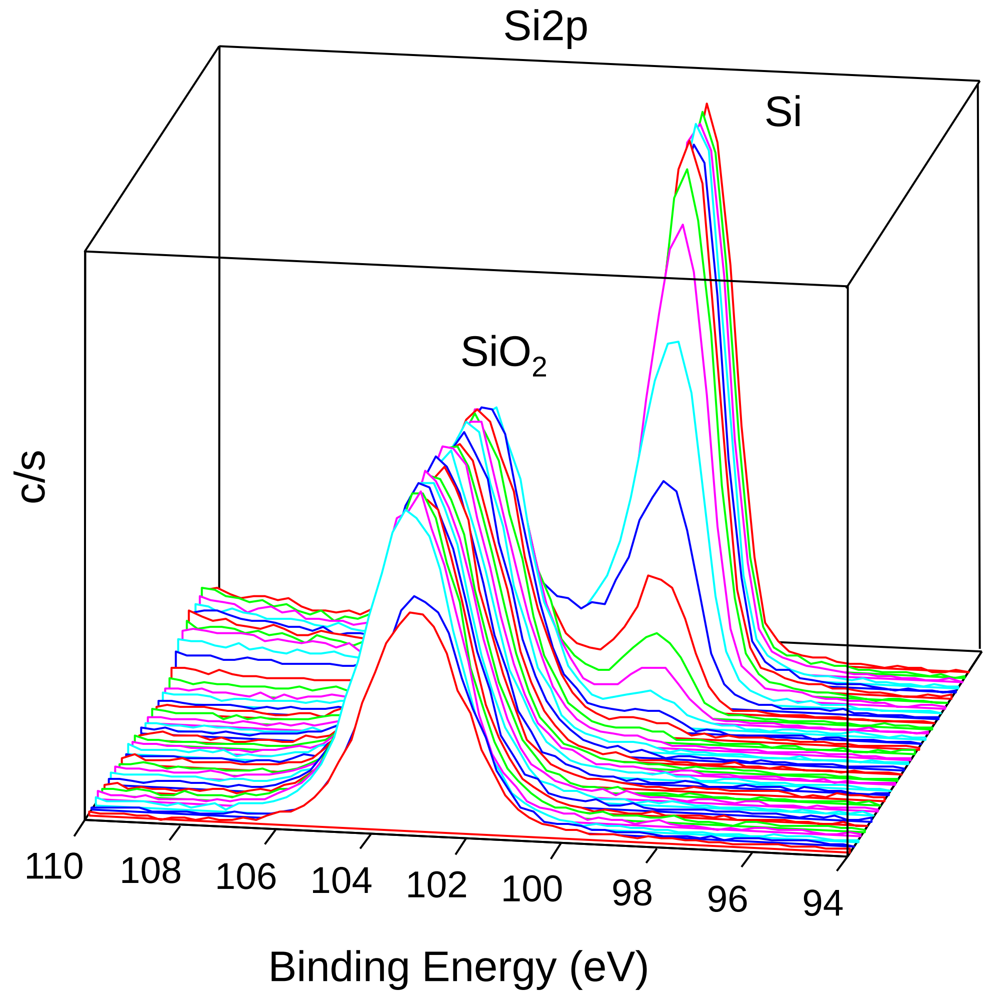
XPS depth profile – SiO_2 on Si



Si = 99.3 eV
SiO_2 = 103.3 eV

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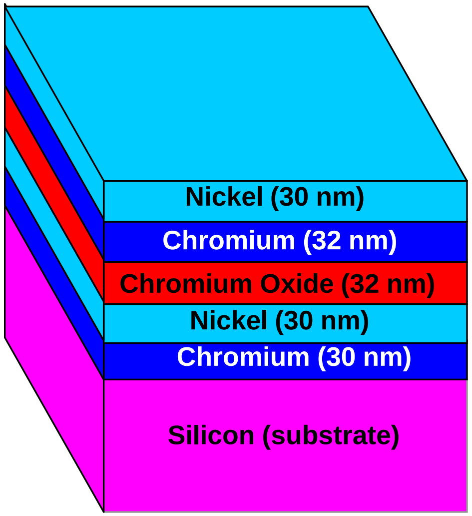
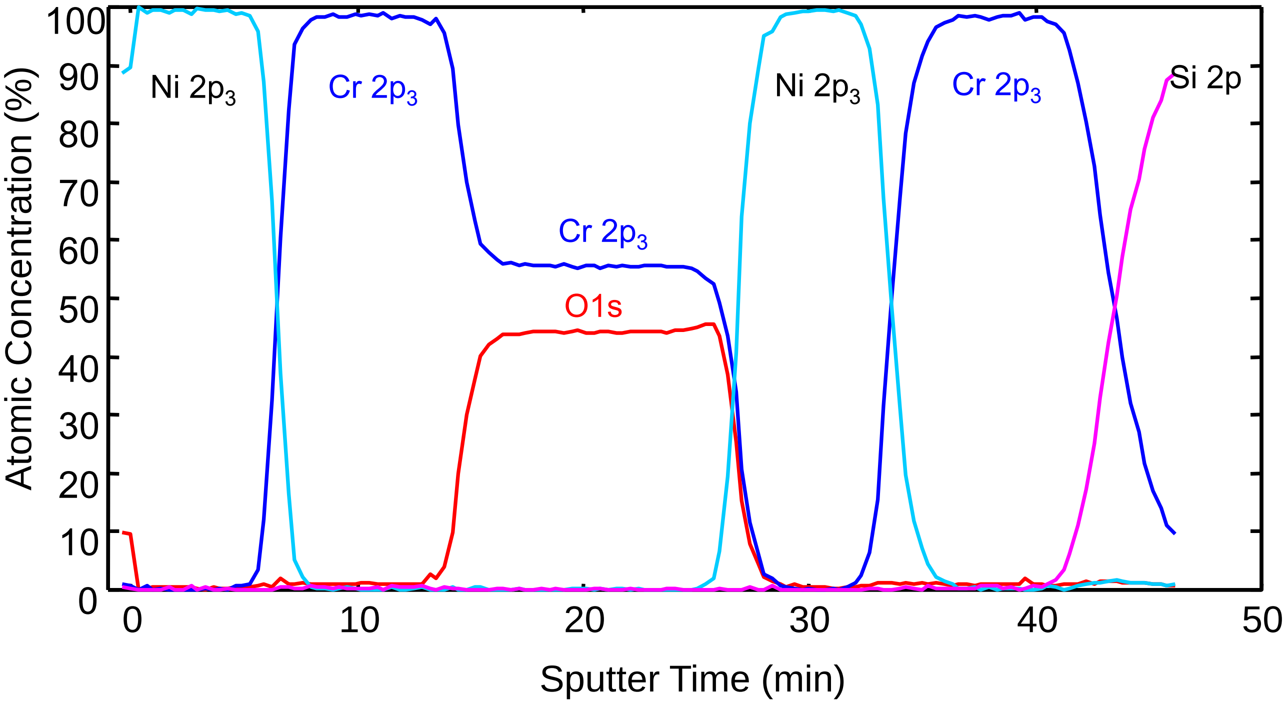
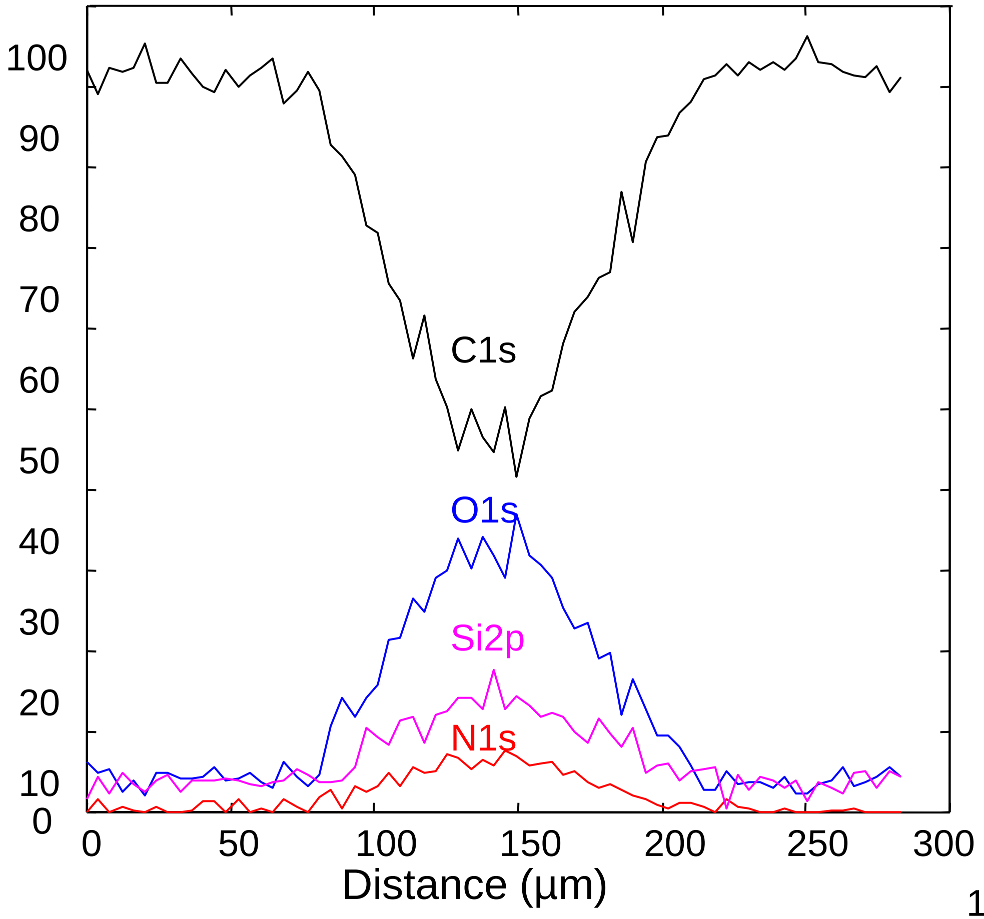
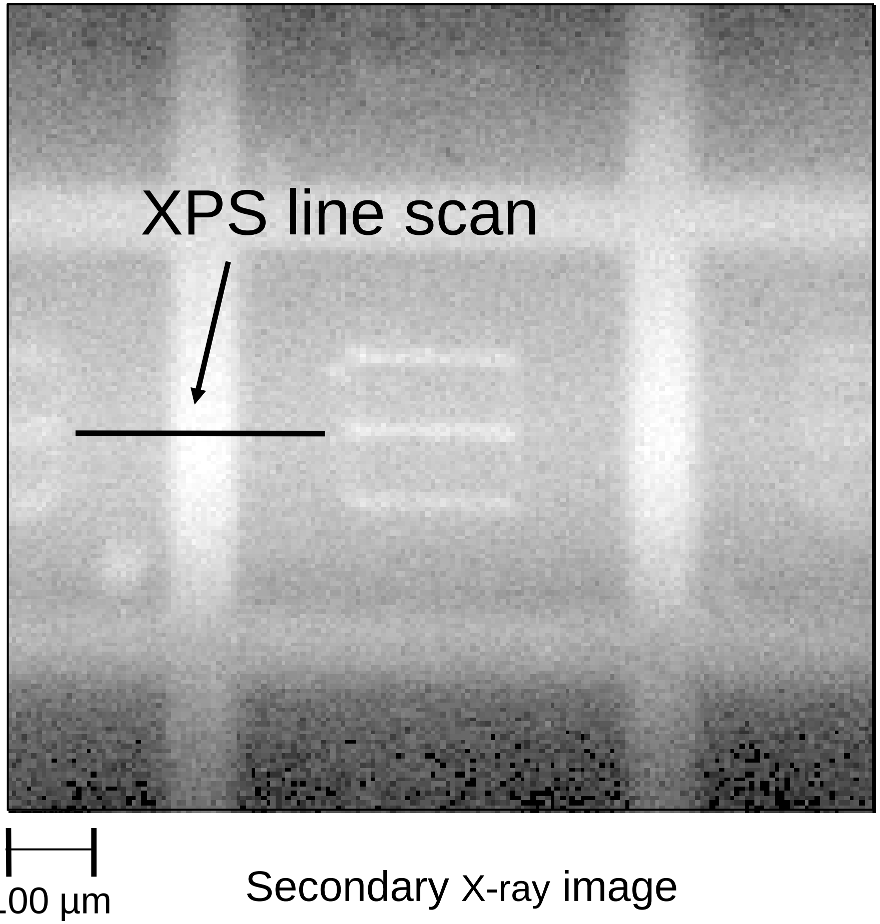
XPS depth profile -- Multilayer Ni/Cr/CrO/Ni/Cr on Si sample





XPS line scan – Patterned polymer film using 20 um diameter Al Kα X-ray beam



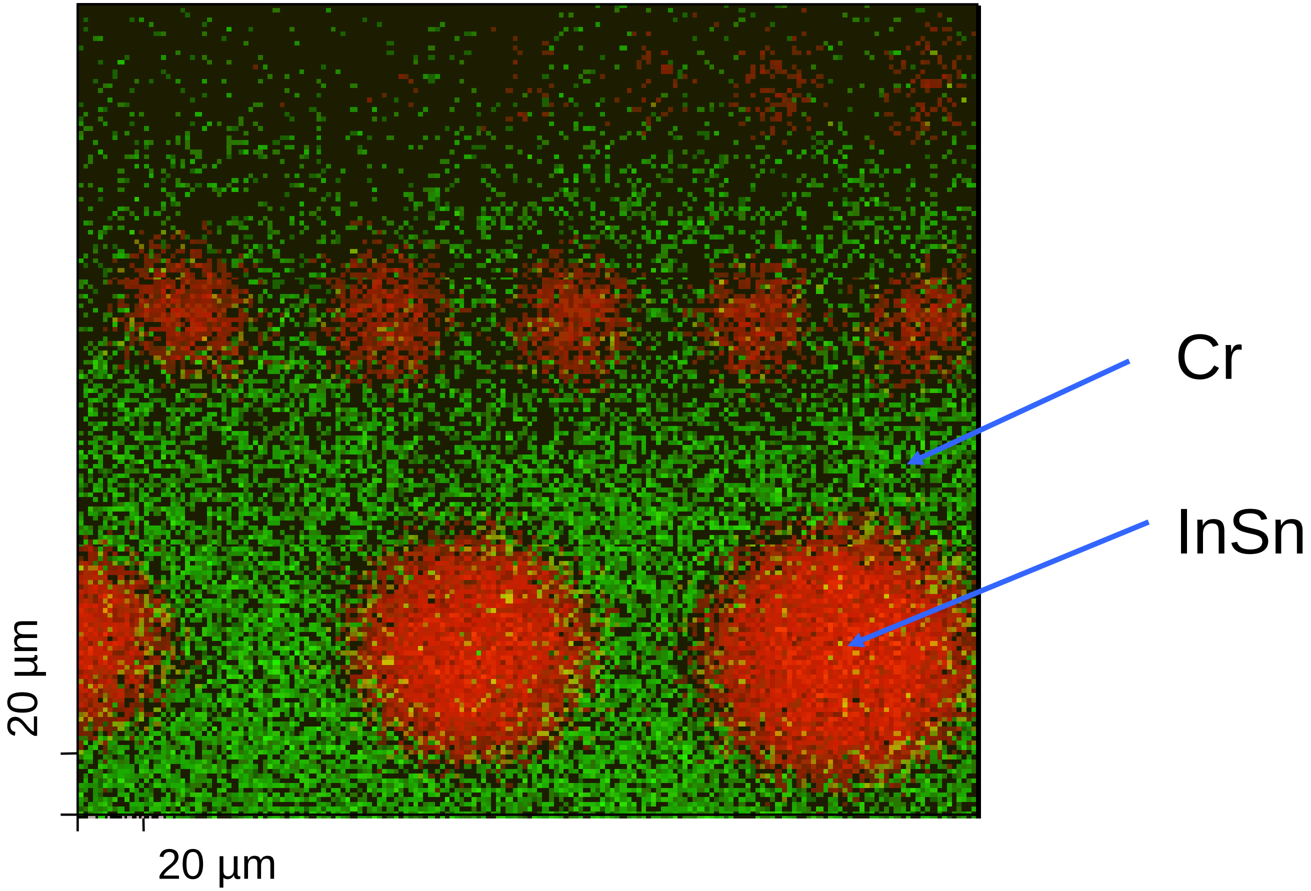


Secondary X-ray image

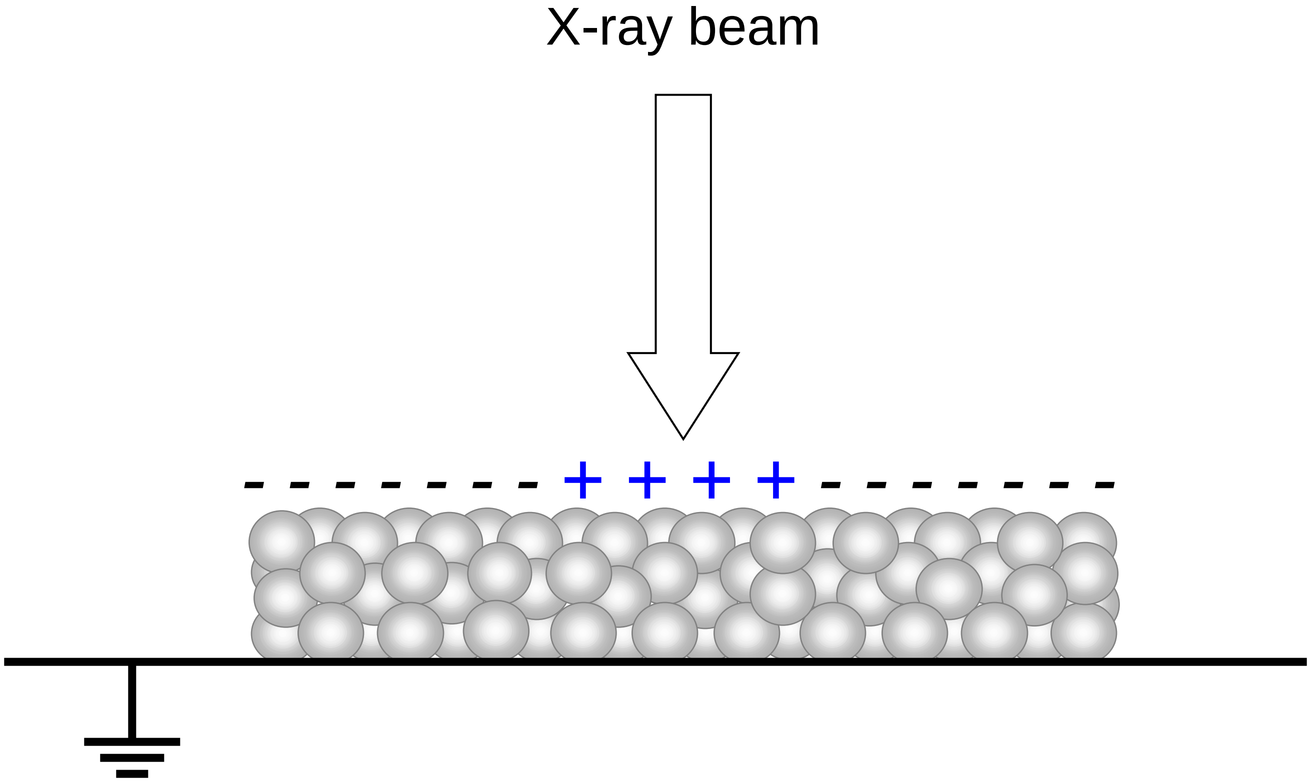
Work in collaboration with Mingdi Yan and Michele Bartlett from Portland State University

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

XPS Elemental Map – ITO circular patterns

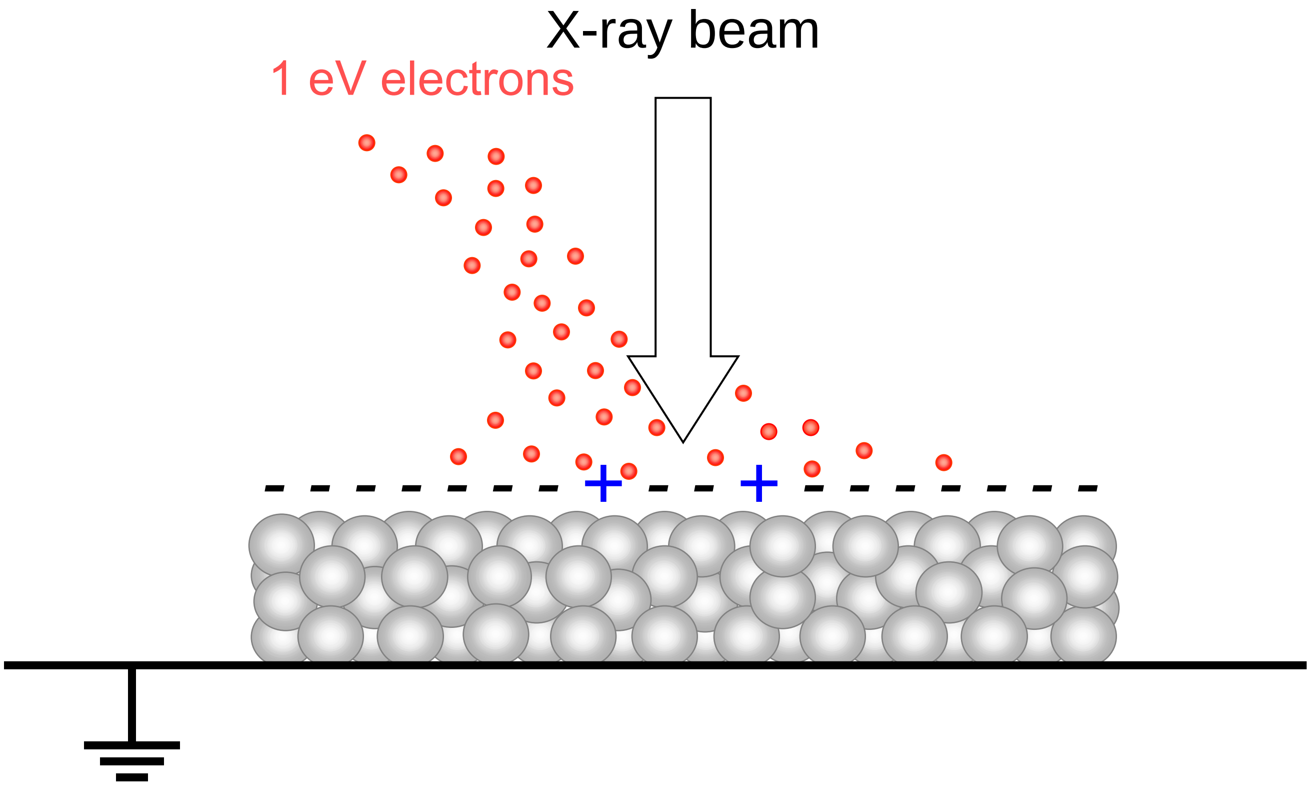


Charge neutralization for insulating samples



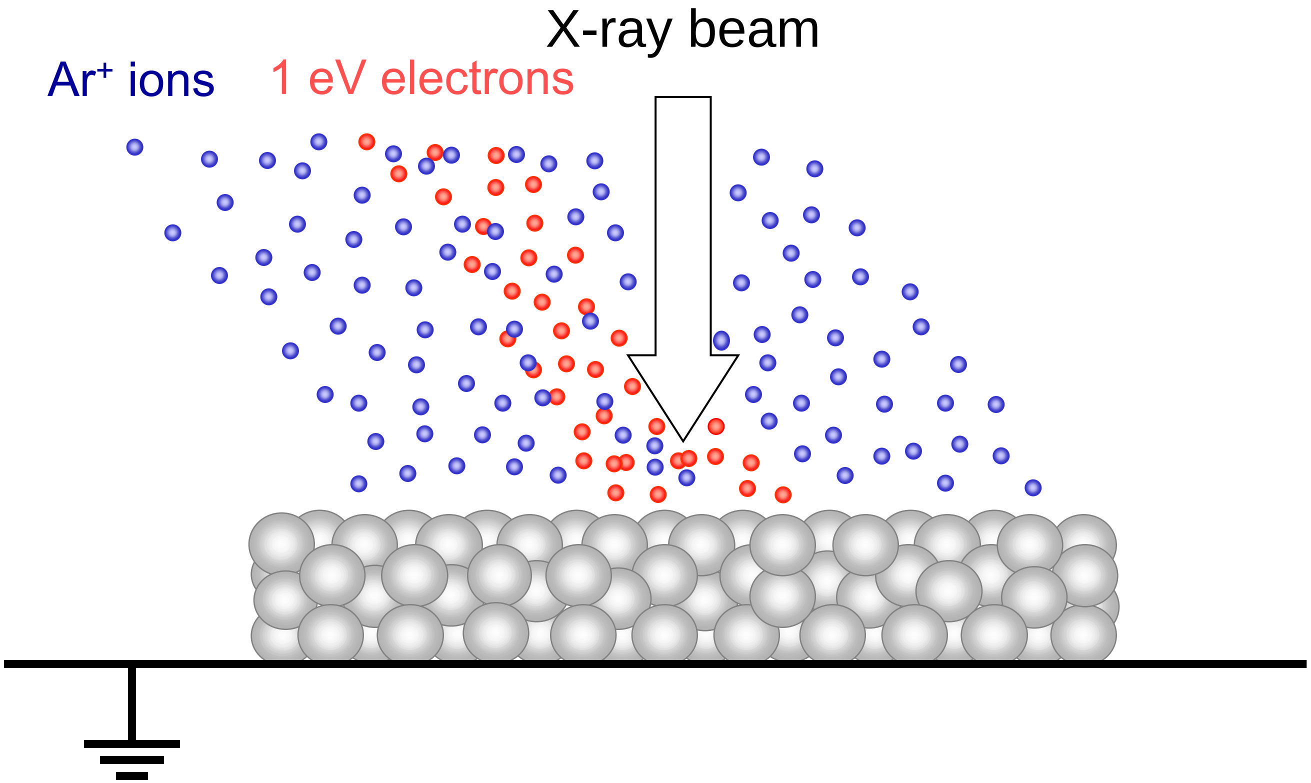
Photoemitted electrons leave local positive charges on the surface

Charge neutralization for insulating samples



Low-energy electrons from a cold cathode flood gun alleviates most positive charges

Charge neutralization for insulating samples

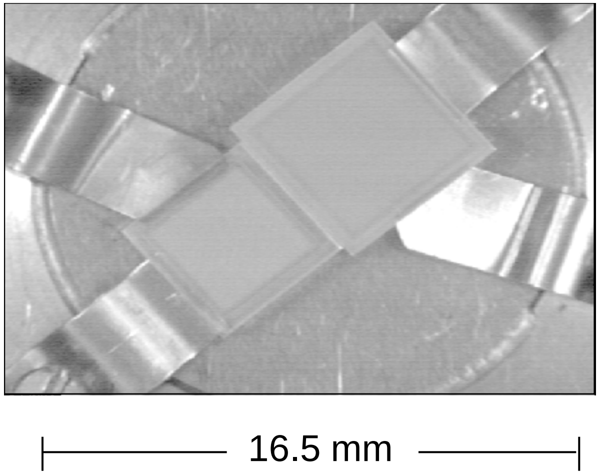


Flooding the surface with both positive ions and negative electrons provide a uniform surface potential

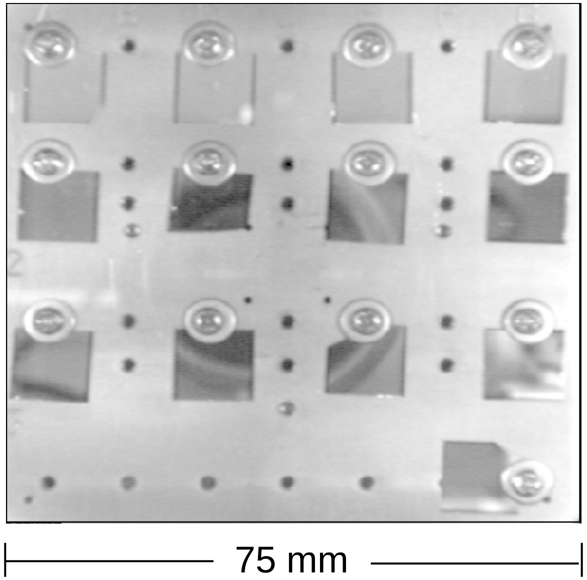
Examples of sample holders

TiO_2 and $SrTiO_3$ crystals

Self-assembled monolayers on Au/Si



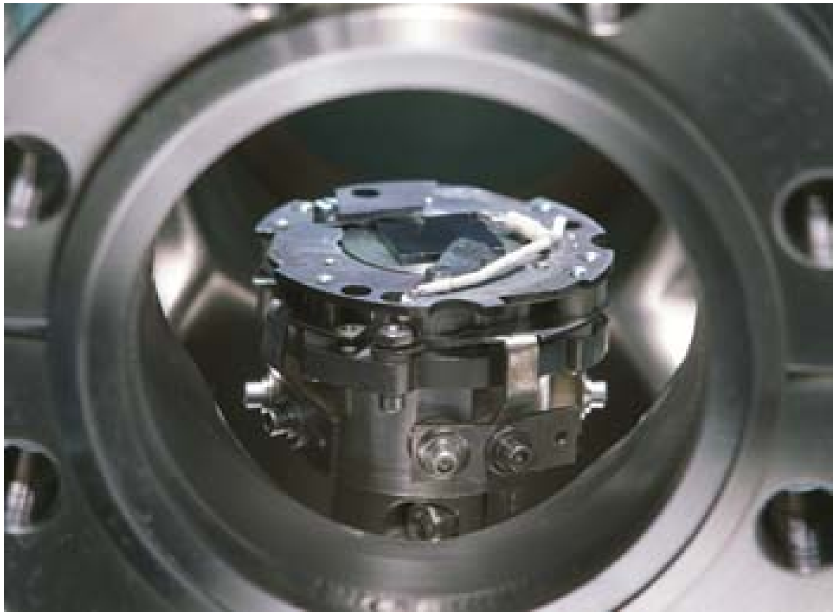
High temperature sample platen



Standard sample platen

Examples of sample handling

sample vacuum transfer chamber



High temperature sample platen

Examples of sample holders

Useful web sites

- PNNL EMSL: www.emsl.gov
- AVS Science & Technology Society: www.avs.org
- AVS Surface Science Spectra: www.avs.org/literature.sss.aspx
- Evans Analytical Group: www.cea.com
- NIST X-ray Photoelectron Spectroscopy Database: www.srdata.nist.gov/sps/
- NIST Electron Inelastic-Mean-Free-Path Database: www.nist.gov/srd/nist71.htm
- QUASES-IMFP-TPP2M QUASES-Tougaard Inc.: www.quases.com
- Surfaces & Interfaces Section, National Physical Lab. www.npl.co.uk/npl/cmmt/sis
- XPS MultiQuant www.chemres.hu/aki/XMQpages/XMQhome.htm
- ASTM International: www.astm.org

Useful XPS references

1. *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy,* edited by D. Briggs and J.T. Grant. IM Publications and SurfaceSpectra Limited (2003).

2. *Practical Surface Analysis (second edition)* V1, edited by D. Briggs and M. P. Seah. John Wiley and Sons Ltd. (1990).

3. J.F. Moulder, W.F. Stickle, P.E. Sobol and K.D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*. Physical Electronics Inc., Eden Prairie (1995).

4. G. Beamson and D. Briggs, *High Resolution XPS of Organic Polymers-The Scientia ESCA 300 Database*. John Wiley & Sons, Chichester (1992).

5. B.V. Crist, *Handbooks of Monochroamtic XPS Spectra,* 5 Volume Series. XPS International, Kawasaki (1997).

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