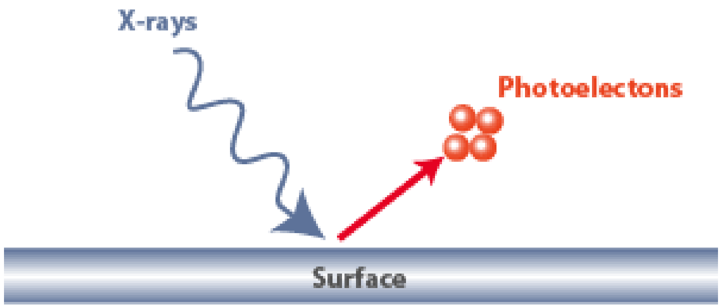
Principles and Practical Techniques of XPS

Xinqi Chen



ESCALAB 250Xi

K Alpha

Outline

1. Brief introduction of the shared instruments in Keck-II
2. XPS basic principles and instrumentation
3. Various characterization techniques with XPS

Questions → Using Chat

FT-IR

Mode:

- Transmission
- ATR
- DRIFT

Sample:

- Powder
- Film
- Solution
- Gel
- Micrometer spot

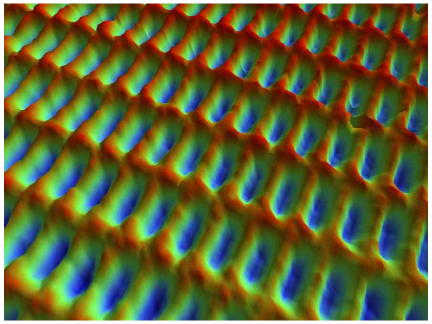
Bruker Lumos IR Microscope

Thermo Nicolet iS50 FT-IR spectrometer

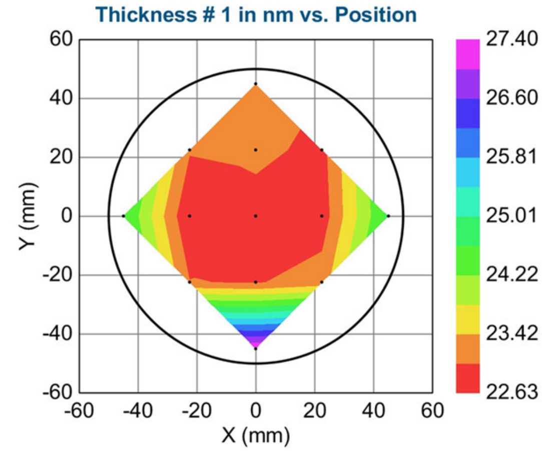
Surface Profiler

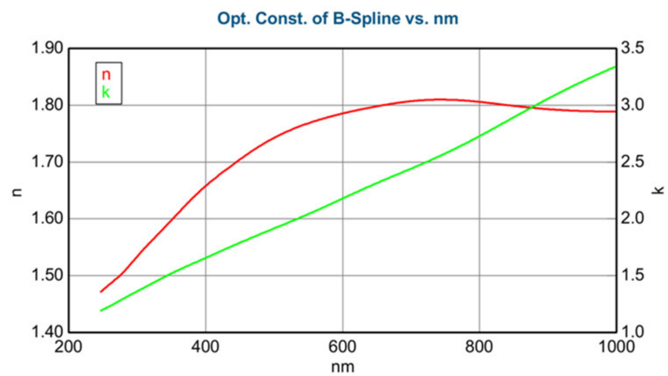
Optical profilometer
(3D optical microscope)

Stylus profilometer



Ellipsometer





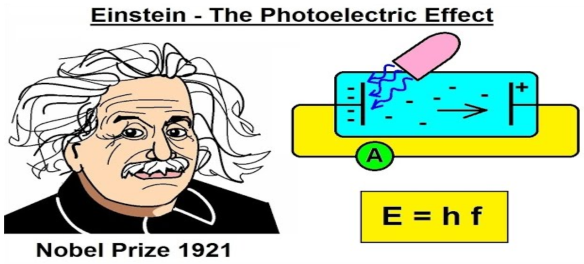
ION TOF M6 TOF SIMS

- High lateral resolution (< 50 nm) with the new Nanoprobe 50.
- From nm to µm – DSC, the high-performance work horse for inorganic depth profiling with O_2 and Cs.
- Quantitative depth profiling in MCs^+ Mode
- Gas Cluster Ion Source - The best solution for organic depth profiling
- Focused ion beam (FIB) – cross section analysis
- Sample Heating and Cooling

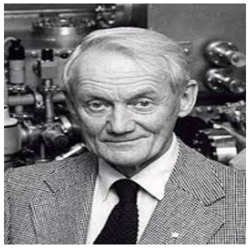
XPS Background

XPS technique is based on **Einstein**'s discovery of the photoelectric effect in1905

- The concept of photons was used to describe the ejection of electrons from a surface when photons were impinged upon it.
- 1921 Nobel Prize in Physics "for his discovery of the law of the photoelectric effect"



During the mid 1960's Dr. Kai Siegbahn and his research group developed the XPS technique.

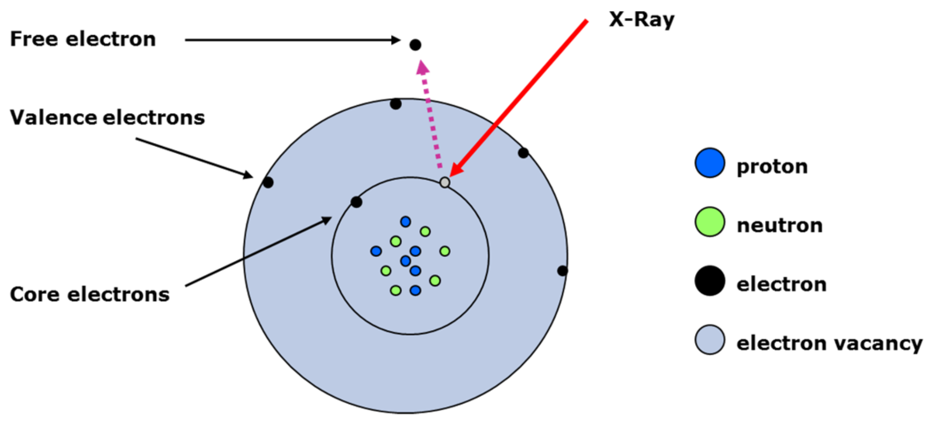


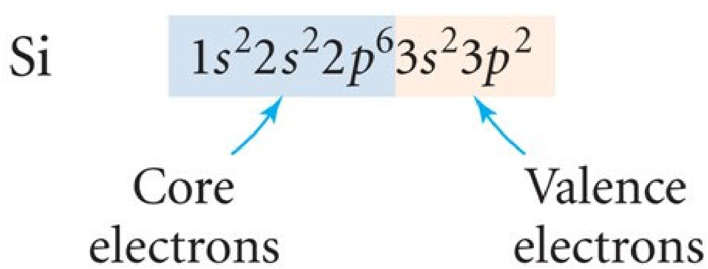
– **Electron Spectroscopy** for Chemical Analysis (ESCA)

– In 1981, Dr. Siegbahn was awarded the Nobel Prize in Physics for the development of the XPS technique

– Manne Siegbahn (Kai's father) was awarded the Nobel Prize in Physics in 1924 "for his discoveries and research in the field of **X-ray spectroscopy**".

Core Electron





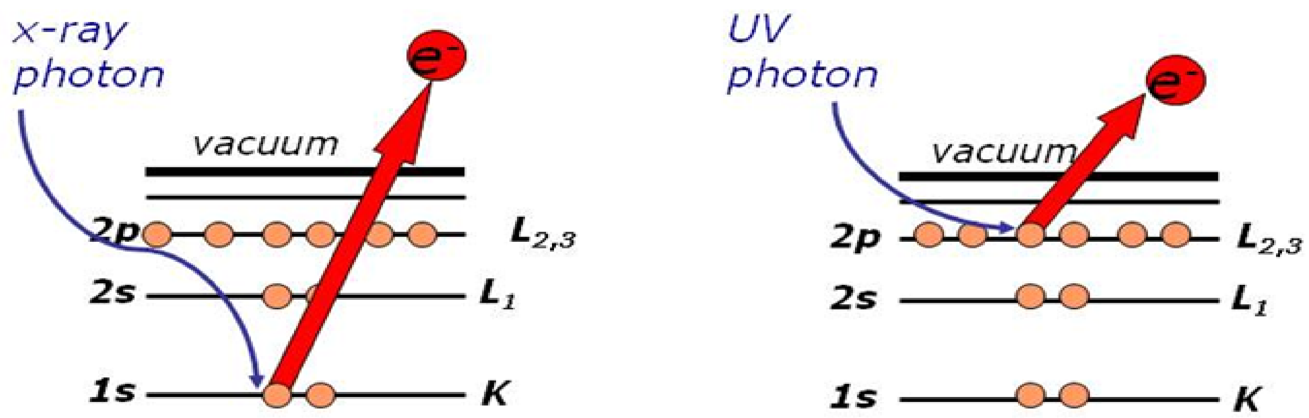
Equation

KE=h*v*-BE-Ø

BE=h*v*-KE-Ø

KE	Kinetic Energy (measure in the XPS spectrometer)
hv	photon energy from the X-Ray source (controlled)
Ø	spectrometer work function. It is a few eV, it gets more complicated because the materials in the instrument will affect it. Found by calibration.
BE	is the unknown variable

Surface electron spectroscopies

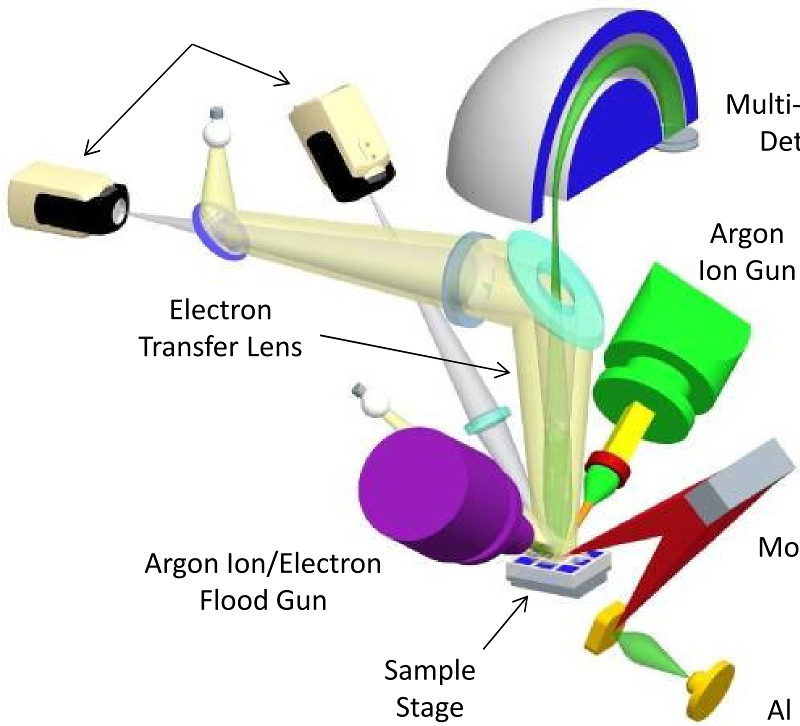


e^- = electron detected in experiment

XPS	UPS
-core electrons ejected -gives elemental composition -provides some info about "environment" of atoms	-valence electrons ejected -provides estimates for "density of states", frontier orbital energies (HOMO), work function

Basic Components of XPS Instrumentation

- UHV system (i.e., ~10^{-9} torr):
  - Ultra-high vacuum keeps surfaces clean
  - Allows longer photoelectron path length
- X-ray source:
  - Typically Al Kα radiation (1486.6 eV)
  - Monochromated using quartz crystal
- Lens, energy analyser & detector
- Low energy electron flood gun:
  - Low energy e^- (plus Ar^+)
  - Analysis of insulating samples
- Ion gun:
  - Typically noble gas ions (monatomic or clusters)
  - Sample cleaning
  - Depth profiling

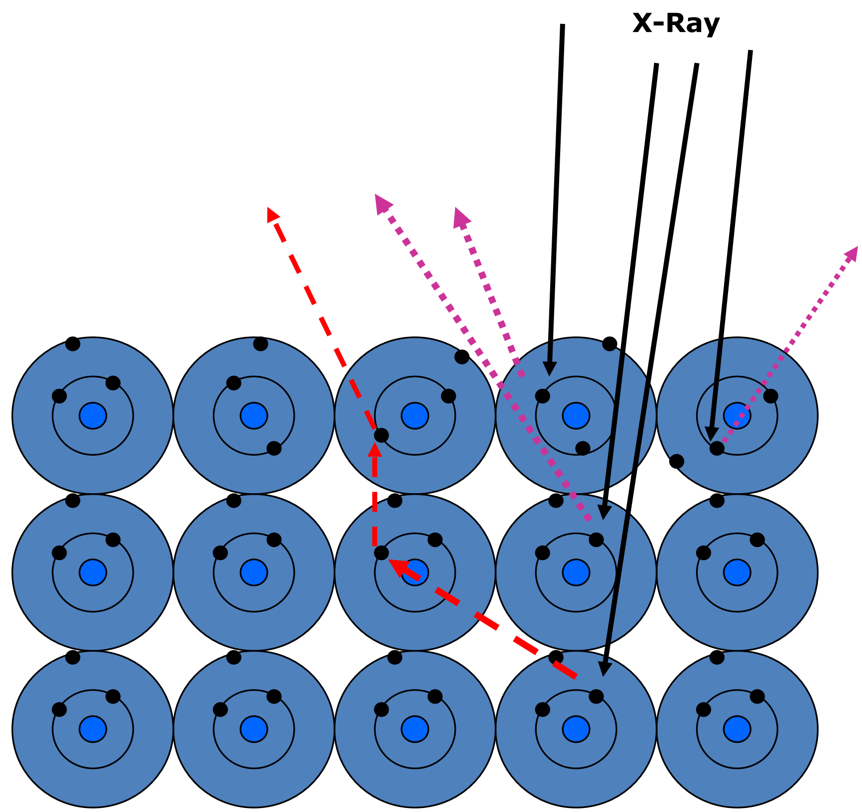


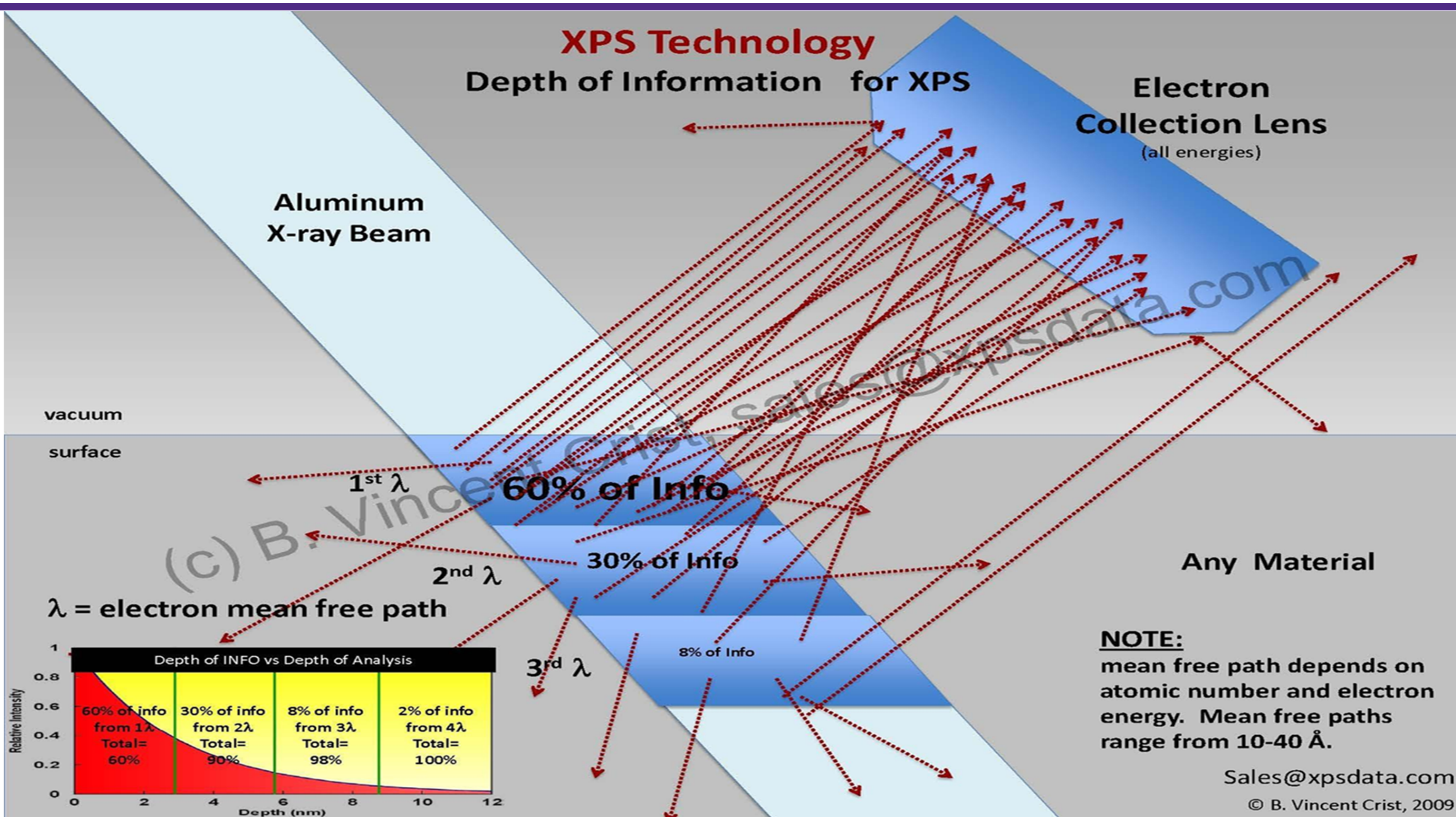
X-Rays and the Electrons

Electron without collision

Electron with collision

The noise signal comes from the electrons that collide with other electrons of different layers. The collisions cause a decrease in energy of the electron and it no longer will contribute to the characteristic energy of the element.




XPS Technology
Depth of Information for XPS
Electron
Collection Lens
(all energies)
Aluminum
X-ray Beam
vacuum
surface
1st λ
60% of Info
2nd λ
30% of Info
3rd λ
8% of Info
λ = electron mean free path
Any Material
Depth of INFO vs Depth of Analysis
60% of info from 1λ Total= 60%
30% of info from 2λ Total= 90%
8% of info from 3λ Total= 98%
2% of info from 4λ Total= 100%
Relative Intensity
Depth (nm)
NOTE:
mean free path depends on atomic number and electron energy. Mean free paths range from 10-40 Å.
Sales@xpsdata.com
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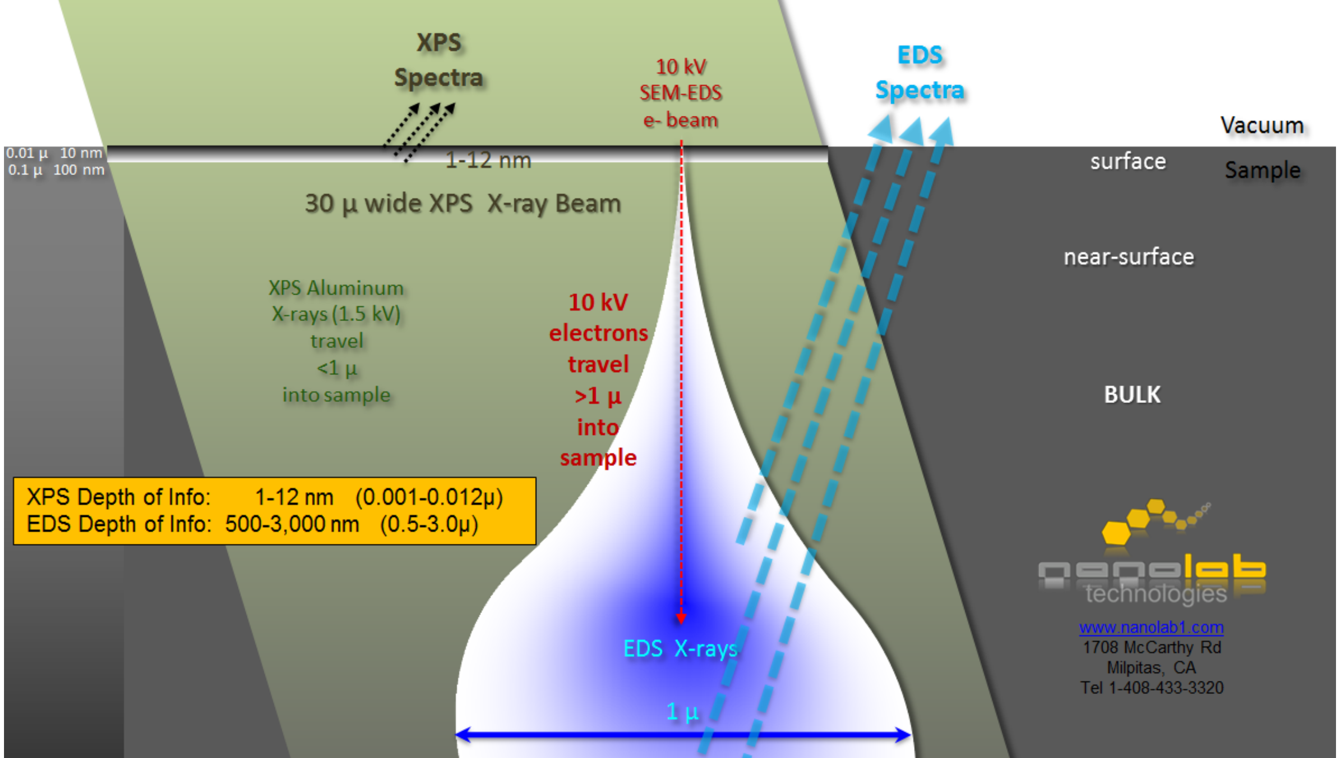
ASK Customer: **Do you need chemical states ?** **Do you want atom% from top 1-12 nm?** **Do you want atom% from bulk?**

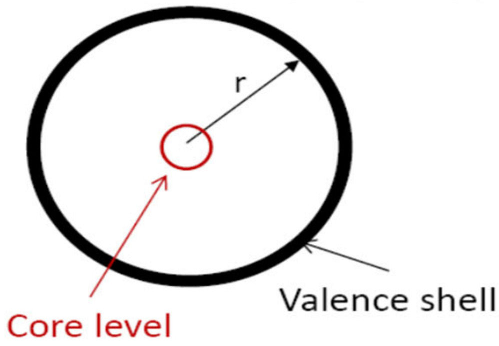


	Insulator Survey*	Atom%	Chemical States	Insulators	Info Depth (Z)	Smallest XY Size	Damage during analysis
EDS (SEM)	11-17 min	+/-15%	none	Need to coat w *20 nm Au*	>500 nm (0.5µ)	800 nm (0.80 µ)	Possible (5-25 kV electrons)
XPS	8-15 min	+/-5%	many	Easy	1-12 nm (0.01µ)	30,000 nm (30.0 µ)	Rare (1.5 kV X-rays)

1 µ
1,000 nm

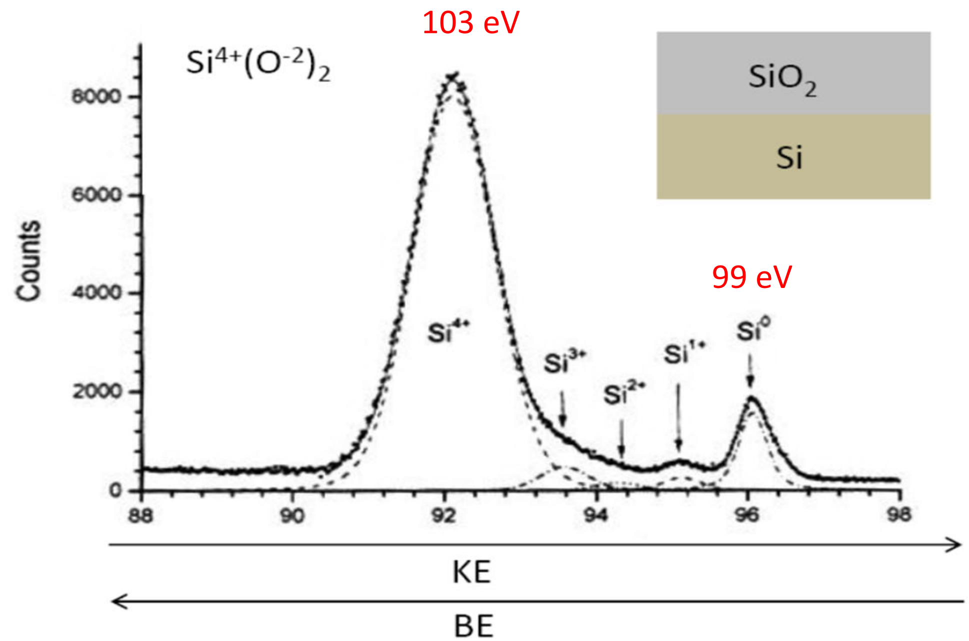
*Time needed to cut sample, (gold coat 4 SEM = 5 min), mount, pump down, locate defect, setup, collect, analyze, remove sample

Chemical information in core levels XPS



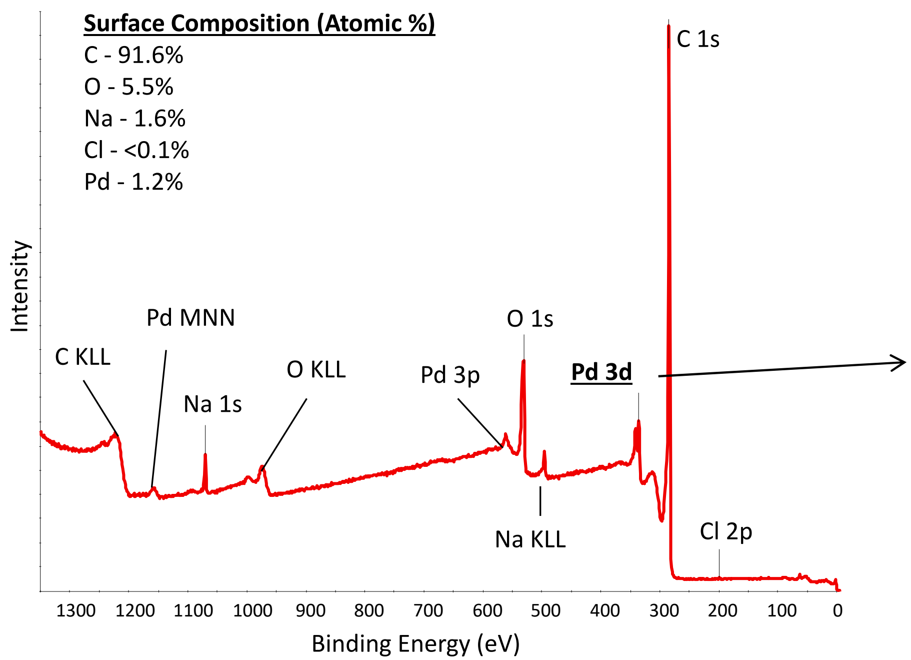
If a charge q is added to (or removed from) the valence shell due to chemical bond formation, the electrostatic potential felt by the electron inside the atom is changed. $\Delta E \sim q/r \sim \Delta BE$

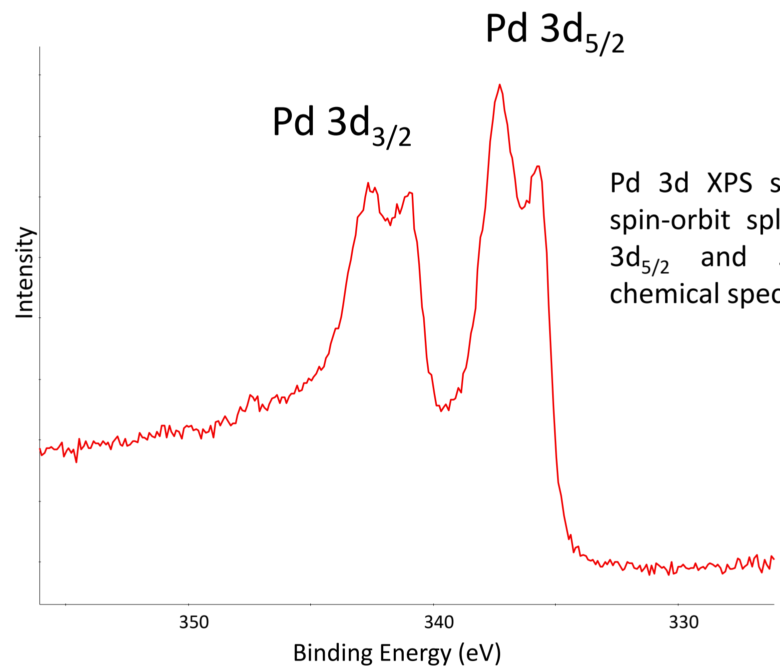
- When atom loses valence charge ($Si^0 \rightarrow Si^{4+}$): BE increases.
- When atom gains valence charge ($O \rightarrow O^{2-}$) BE decreases.



XPS Spectra: 10% Pd/Activated Carbon Catalyst

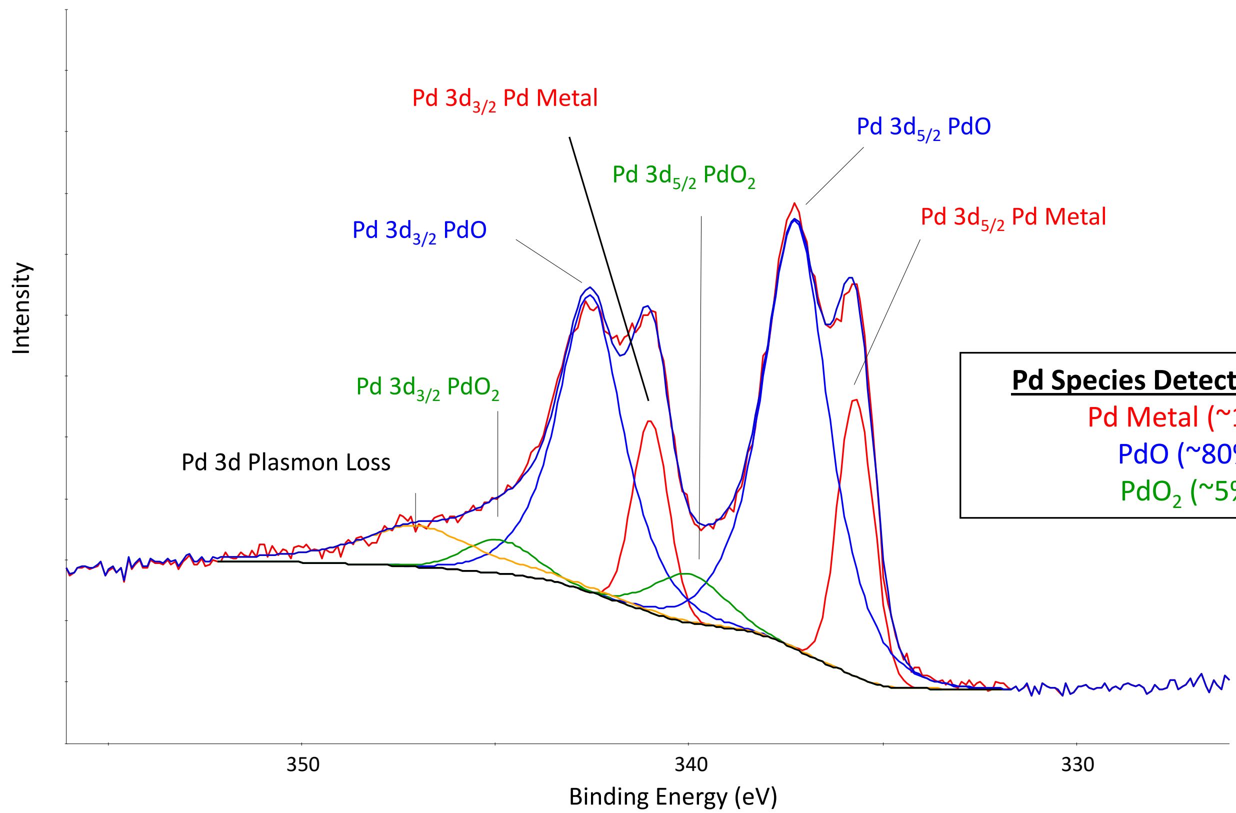
- XPS survey spectra (left) provide qualitative and quantitative elemental surface information.
- High resolution XPS spectra (right) provide chemical state surface information.





Pd 3d XPS spectra have two spin-orbit split peaks (i.e., Pd $3d_{5/2}$ and $3d_{3/2}$) for each chemical species present.

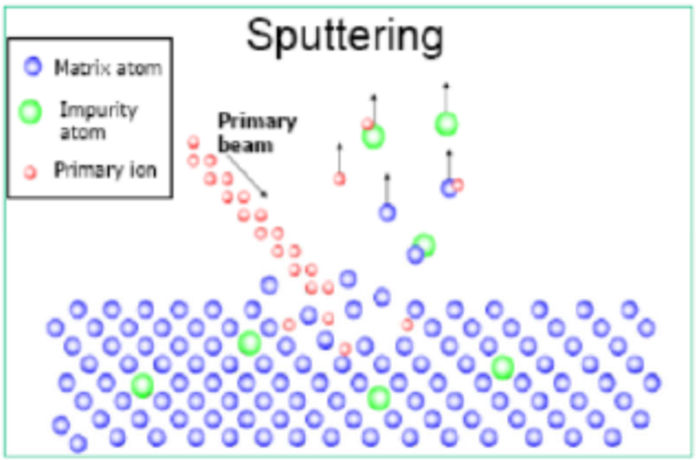
Peak Fit for the Pd 3d XPS Spectrum: 10% Pd/Activated Carbon Catalyst

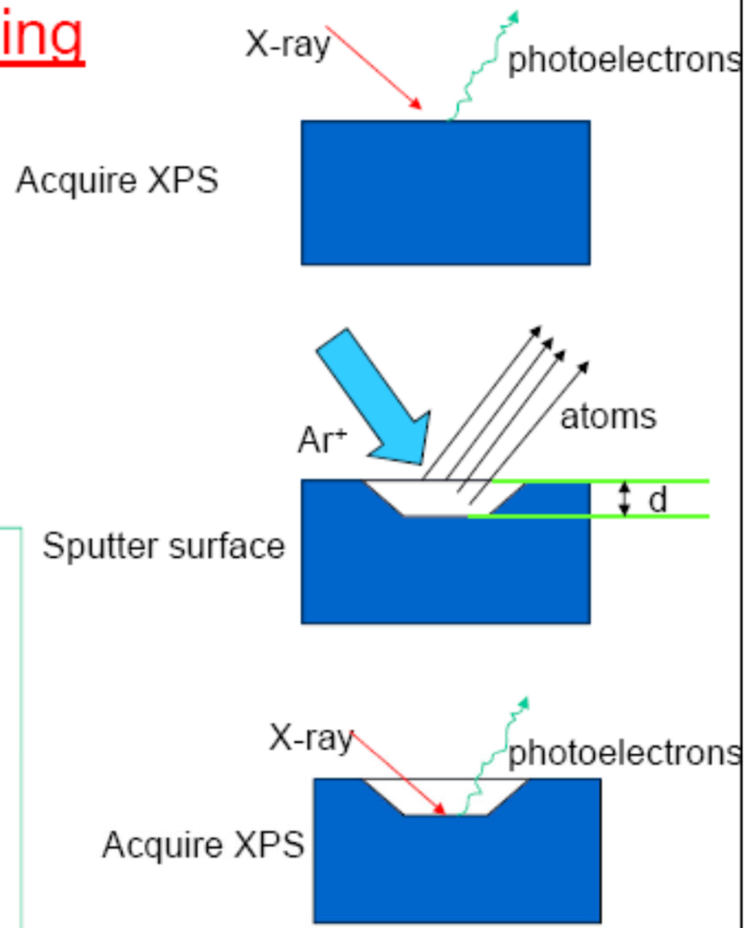


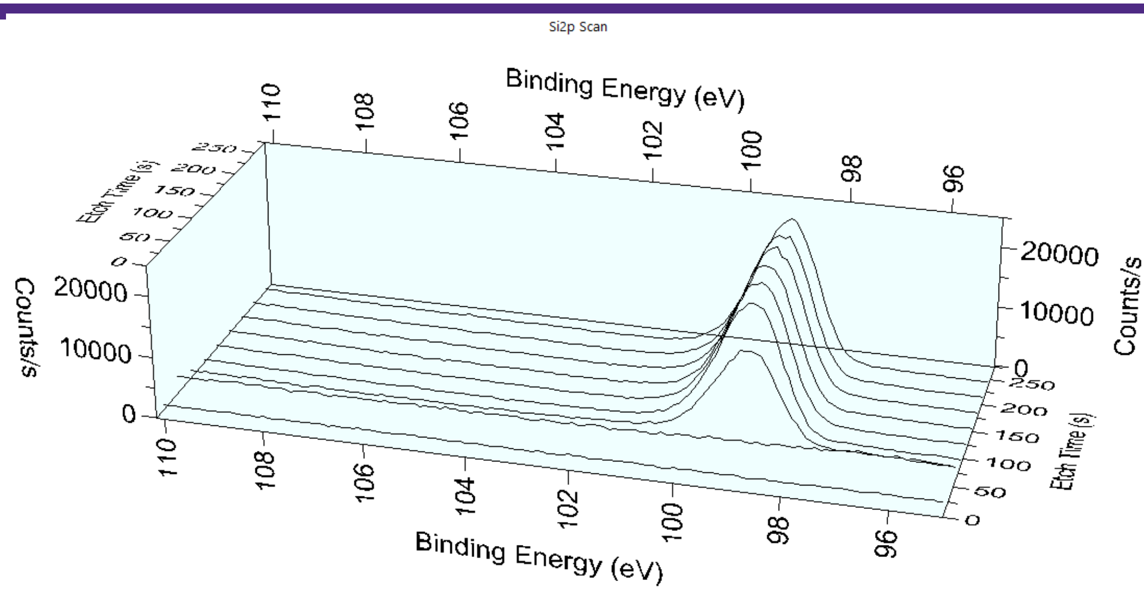
Pd Species Detected by XPS:
Pd Metal (~15%)
PdO (~80%)
PdO_2 (~5%)

Destructive depth profiling

- Acquire XPS spectrum
- Ar ion sputtering
- Acquire XPS spectrum
- Ar ion sputtering
- Acquire XPS spectrum

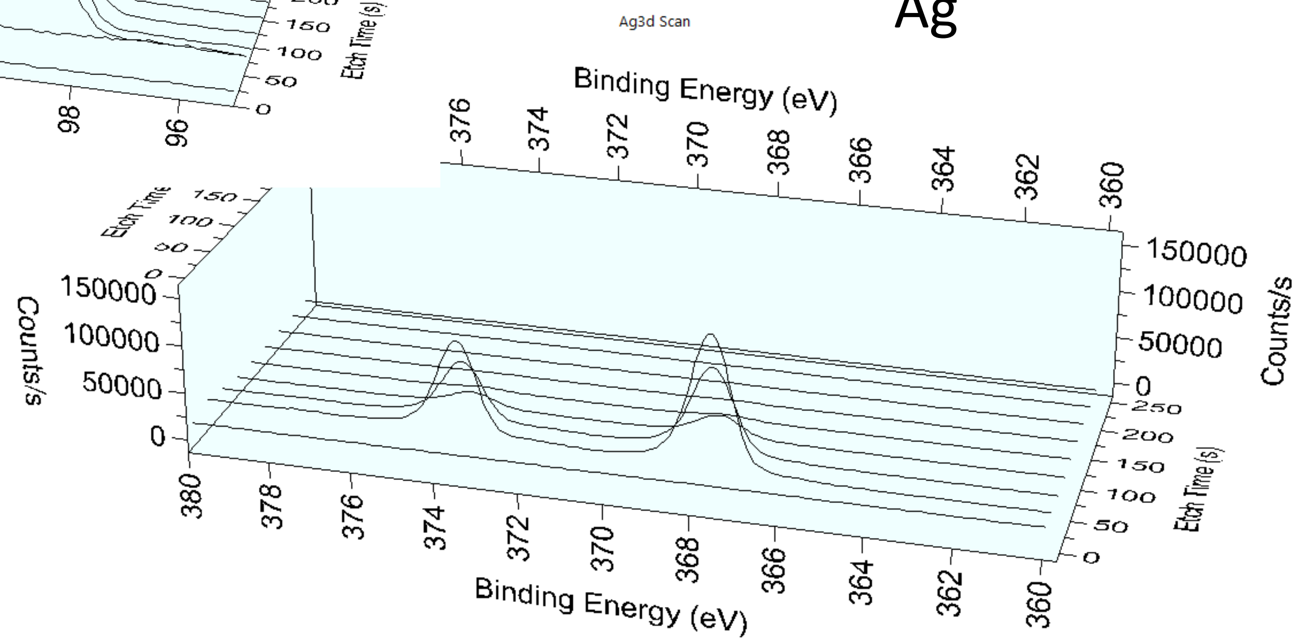




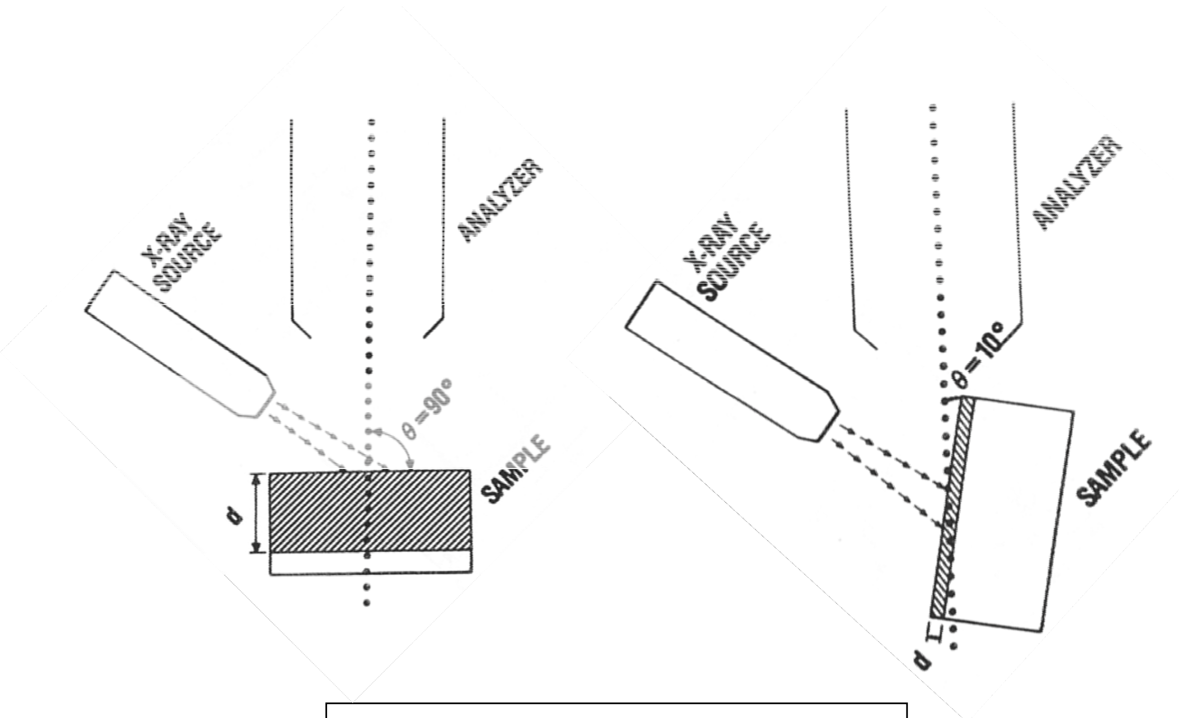

Si2p Scan
Binding Energy (eV)
110
108
106
104
102
100
98
96
Etch Time (s)
250
200
150
100
50
0
Counts/s
20000
10000
0

Si

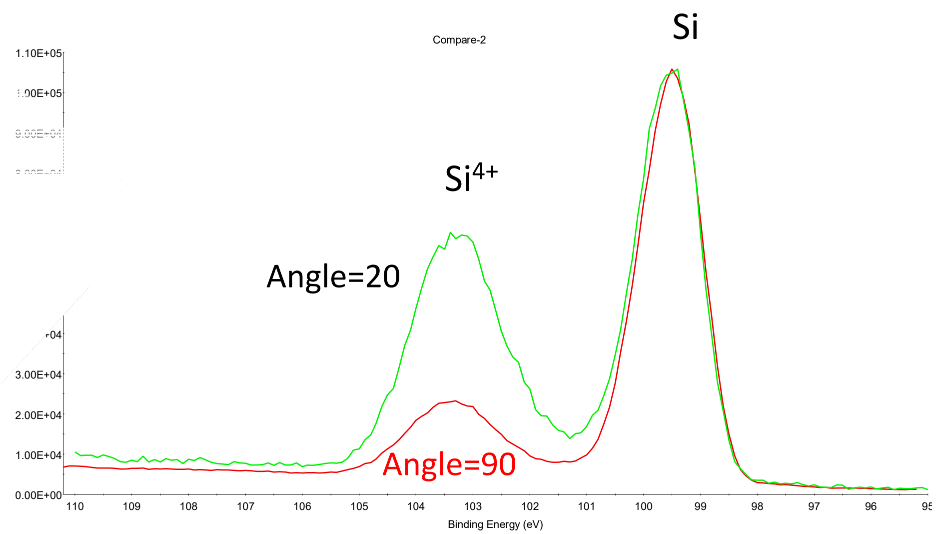
Ag


Ag3d Scan
Binding Energy (eV)
380
378
376
374
372
370
368
366
364
362
360
Etch Time (s)
250
200
150
100
50
0
Counts/s
150000
100000
50000
0

Variation in Sampling Depth with Angle-Resolved XPS (ARXPS)

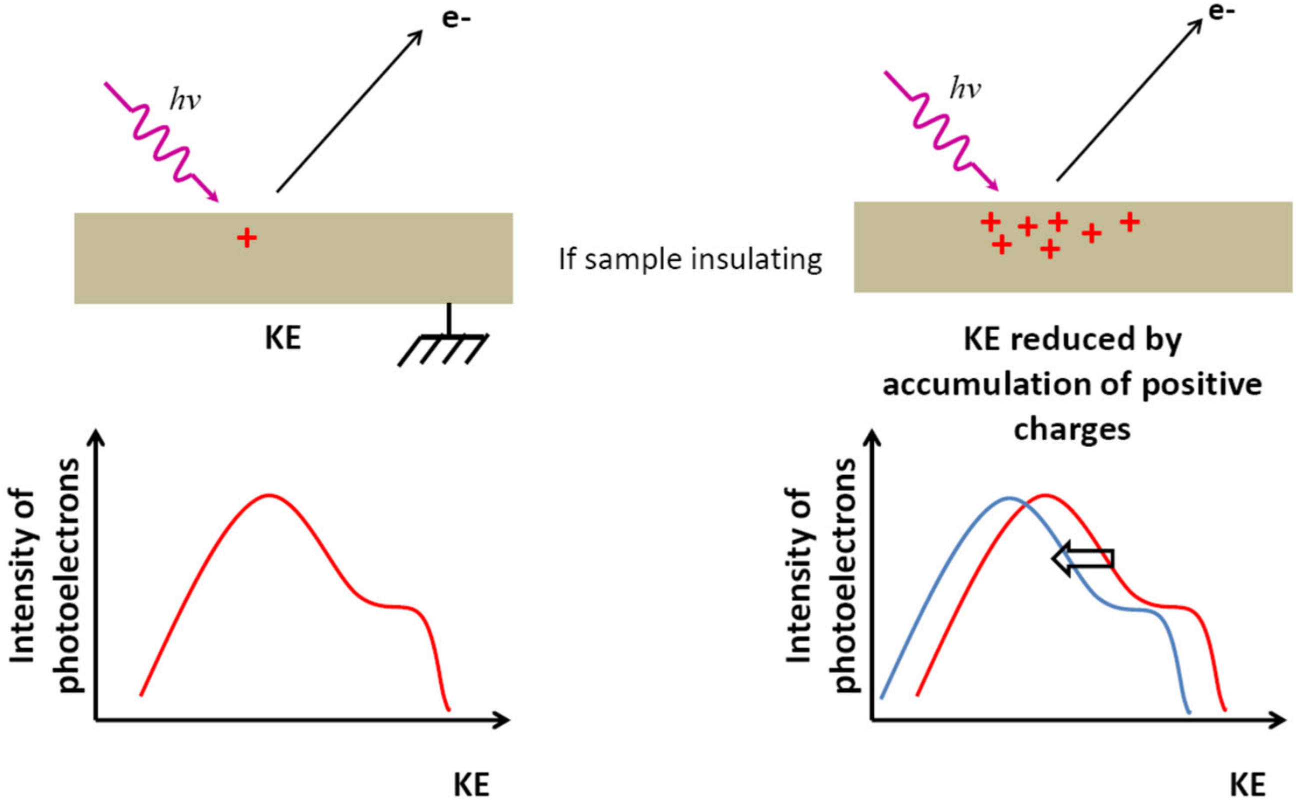


Sampling depth = d = 3λ sinΘ
Θ = electron take-off angle
λ = IMFP



Native SiO_2 on Silicon

Charging effects



Conductive samples are necessary to perform the measurements
Thin films on conductive substrates

Heating and Cooling in Analysis Chamber

Sample plate temperature range: -170C to 300C

Summary of XPS Analysis Capabilities

1. Provides **quantitative** elemental and **chemical state** information for all elements except H and He.
2. Detection limit is ~0.05-0.1 atomic % for most elements.
3. Sampling depth ≤ 10 nm.
4. Can be used for point analysis, line scans, and area analysis (mapping and imaging).
5. Can provide in-depth analysis by AR-XPS (1-10 nm) or ion sputter depth profiling (sputtered depths of 10 µm or more now possible).
6. Can be used for **conductive and insulating solid samples**, e.g., metals, metal oxides, catalysts, ceramics, coatings, multi-layer thin films, polymers etc.
7. Samples can be fibers, foil, particulate, powder, rods, sheet, thin film, etc. In general, no special sample preparation is required.
8. Samples must be compatible with **ultrahigh vacuum** (~10^{-8} torr or lower) and **stable under Al Kα X-ray** bombardment.

Pros

- Quantitative elemental composition
- Chemical bonding information
- Surface sensitive
- All solid materials including insulator, semiconductor, and metals
- Analysis is fast and easy

Cons

- Poor lateral resolution
- UHV compatible

Primary XPS region Ti2p **Overlapping regions** $Ru3p_{3/2}$, $In3d_{3/2}$

Binding energies of common chemical states

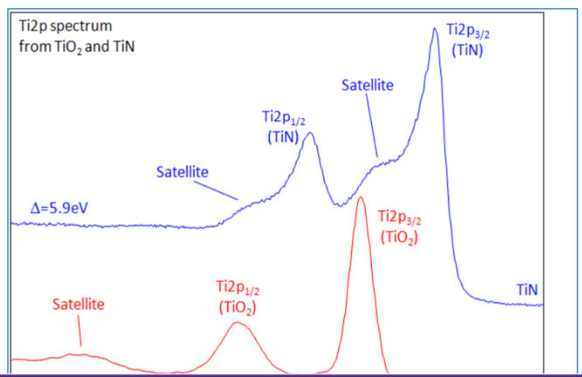
Chemical state	Binding energy $Ti2p_{3/2}$ / eV
Ti metal	454.1
TiN	454.9
TiO_2	458.5
$SrTiO_3$	458.4

Compounds charge referenced to adventitious C1s peak at 284.8eV

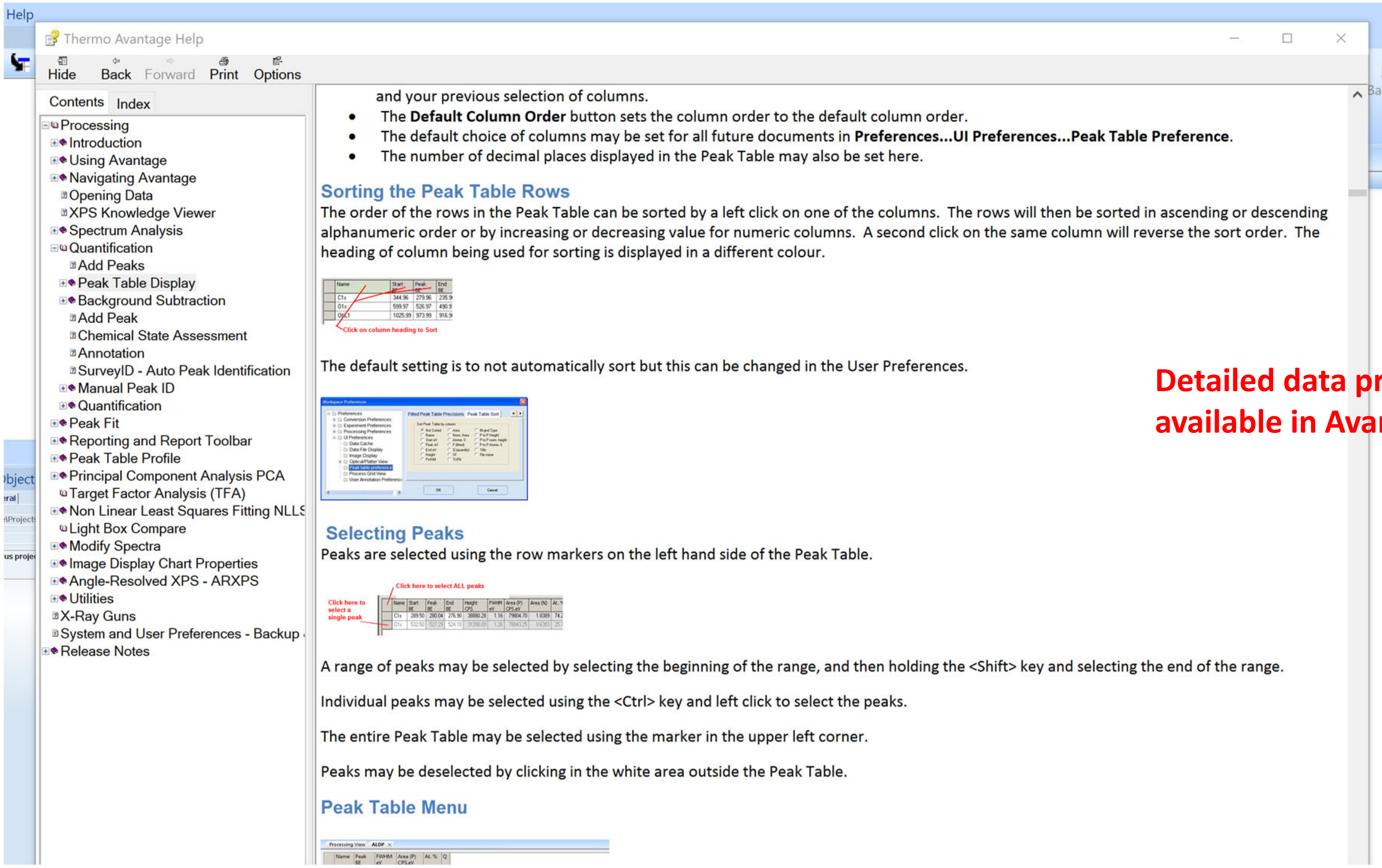
Experimental information

Interpretation of XPS spectra

- Ti metal gives asymmetric Ti2p peaks shapes
  - TiO_2 has symmetric peaks shapes and TiN has a complex peak shape, involving satellite features.



- Avantage software is free downloadable.
- XPS Knowledge View is helpful.



Help

Thermo Avantage Help

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Light Box Compare
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and your previous selection of columns.

- The **Default Column Order** button sets the column order to the default column order.
- The default choice of columns may be set for all future documents in **Preferences...UI Preferences...Peak Table Preference**.
- The number of decimal places displayed in the Peak Table may also be set here.

Sorting the Peak Table Rows

The order of the rows in the Peak Table can be sorted by a left click on one of the columns. The rows will then be sorted in ascending or descending alphanumeric order or by increasing or decreasing value for numeric columns. A second click on the same column will reverse the sort order. The heading of column being used for sorting is displayed in a different colour.

Click on column heading to Sort

The default setting is to not automatically sort but this can be changed in the User Preferences.

Selecting Peaks

Peaks are selected using the row markers on the left hand side of the Peak Table.

Click here to select ALL peaks

Click here to select a single peak

A range of peaks may be selected by selecting the beginning of the range, and then holding the <Shift> key and selecting the end of the range.

Individual peaks may be selected using the <Ctrl> key and left click to select the peaks.

The entire Peak Table may be selected using the marker in the upper left corner.

Peaks may be deselected by clicking in the white area outside the Peak Table.

Peak Table Menu

Detailed data process procedure is available in Avantage help file.