



Photoelectron Spectroscopy Introduction and Application

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Science. Ingenuity. Sustainability.

Introduction to photoelectron spectroscopy (PES)



Photoelectron Spectroscopy

- Photoelectron spectroscopy (PES) measures is the measurement of electrons liberated from a surface of a material using the <u>photoelectric effect</u>
- □ Photoelectrons are measured from core (localised) and valence (delocalised) states:

=> PES is a probe of **occupied** electron states

□ PES is highly surface sensitive, probes the top few nanometres of a material



- Photoelectron energy distribution highlights the occupied density of states (DOS) of the sample.
- Most of the electrons suffer inelastic scattering travelling through the material, resulting in a dominant "secondary electron tail" ~ 0 – 20 eV

Unscattered photoelectrons carry a wealth of information about their initial states



Surface Sensitivity: Electron Mean Free Path

- PES is extremely surface sensitive due to the small inelastic mean free paths (λ) of free electrons in solids
- The photon interaction volume extends *much* deeper than the region from which the electrons escape

 $I = I_0 e^{-d/\lambda}$

d

 I_0

Vacuum

d/λ

1

2

3

4

0.15

0.05

.02

Inelastic Mean Free Path (IMFP) vs electron energy



95% of photoelectrons have scattered within 3λ from the surface



Instrumentation Requirements

1. Photon Source

X-ray anode

- Electron bombardment at high voltage of thin metal film (e.g Al, Mg, Cu, ...)
- □ X-rays of "single" energy produced
- □ Larger spot size than synchrotron

Common Examples:

| Source | Energy (eV) | Linewidth (eV) |
|---------------------|-------------|----------------|
| Mg <i>K</i> α | 1253.6 | 0.7 |
| ΑΙ <i>Κ</i>α | 1486.6 | 0.85 |





Vacuum Ultra Violet (VUV) and laser sources

- Delta Plasma (DC, RF) of He, Ne, Ar, Kr
- □ For UPS and ARPES
- □ Light directed down capillary to sample
- More recently: Ti:Sapphire, Nd:YVO₄ laser sources < 1meV linewidth</p>

Examples:

| Source | Energy (eV) |
|---------------------|--------------|
| He I, He II | 21.2/40.8 eV |
| Ne I | 16.8eV |
| Nd:YVO ₄ | 7 eV |
| Ti:Sapphire | 6 eV |



Synchrotron Radiation

- Continuously tunable energy
- □ Adjustable polarization (linear, circular, elliptical)
- Coherent (undulator)
- High energy resolution
- □ High flux
- $\hfill\square$ Small spot size (100µm to 10's of nm with optics)

Soft X-ray beamline, Australian Synchrotron



Photon Energy / eV



SXR Undulator Source



SXR Beamline, Australian Synchrotron

2. Electron Energy Analyser

- Measures the kinetic energy of photoelectrons (and often emission angle)
- Electrons are energy filtered and focussed through an electron optical lens system
- Electron detection using channeltron, delay line detector (1D or 2D), microchannel plate (MCP) with phosphor screen
- Hemispherical sector, cylindrical mirror, toroidal, retarding grid

Hemispherical Sector Analyser



3. High or Ultra-High Vacuum System

Samples are studied and prepared in vacuum environment of 10⁻⁷ - 10⁻¹¹ mbar

Facilities for:

Sample Preparation

- Ion sputtering/cleaning
- > Thin film growth
- Gas dosing
- Sample heating/cooling
- Crystal cleaving/scraping

Sample Characterisation

- Electron diffraction (LEED, RHEED)
- Scanning probes (STM)
- Residual gas analysis (RGA)





SXR Beamline: Prevac endstation for PES and XAS



X-ray Photoelectron Spectroscopy (XPS)



Core Level Binding Energy: Accessible with PES

• The kinetic energy of the photoelectron E_{kin} is related to the photon energy $h\nu$ and initial state binding energy E_B via the equation:

$$E_b = h\nu - E_{kin} - \phi$$



- Electrons in atomic core shells (1s, 2s, 2p,etc) are bound to the nucleus with *element specific* binding energies
- PES allows us to measure the binding energy of core level electrons => elemental composition of a sample



http://www.ifw-dresden.de/institutes/ikm/organisation/dep-31/methods/x-ray-photoelectron-spectroscopy-xps/xps2.jpg

Application of PES: X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS)

A Surface Sensitive Chemical Probe

XPS can be used to identify:

- Elemental composition
- Chemical environment of element
- Relative concentrations of elements
- Interfacial chemistry



Kai Siegbahn

Nobel Prize in Physics (1981)

Electron Spectroscopy for Chemical Analysis (ESCA)



XPS "Survey Scan" of Au foil in vacuum chamber, hv = 600eV

Overall emission spectrum. Positions of core level BE obtained, no line-shape analysis, only total area considered



XPS Spectra: Chemical Shift

Chemical environment around an atom affects the binding energy of electrons due to different "screening" of the nuclear potential

Chemical "shift" in BE

- <u>Example</u>: The <u>Electronegativity</u> of covalently bonded species affects BE
- Higher electronegativity => Bonding wavefunction is pulled further away from the C, reducing the screening of the carbon nuclear potential from the C1s electrons



Survey Scan: Quantification

C1s Region Scan: Chemical State Analysis

XPS with Synchrotron Radiation: ADVANTAGES

1. Cross-section Optimization

- Photoionisation cross section for a shell (e.g 1s or K) exhibits a rapid increase, followed by a smooth decrease, at its nominal binding energy
- For lab based X-ray source energies (e.g Al-K α = 1486.6eV), the cross-section is quite low for light, low Z elements





http://ulisse.elettra.trieste.it/services/elements/WebElements.html



XPS with Synchrotron Radiation: ADVANTAGES

2. Vary the photoelectron's kinetic energy

Recall:

Inelastic scattering => most of the signal comes from a few IMFP of the surface.

With SR: one can change the KE of a photoelectron to obtain depth information



Qualitative (Easy) Quantitative (Harder)





Example 1: Oxidation of Black Phosphorus

Single layer black phosphorus: "phosphorene", member of the family of 2D materials

Attractive properties for devices:

- Electronic and optical anisotropy
- Layer dependant band gap (0.3_(bulk) 2.0eV_(ML))
- Good current on/off ratios in FETs
- Charge carrier mobility of up to 1000 cm² V⁻¹ s⁻¹
- <u>Problem</u>: oxidation!!!!





Layered "puckered honeycomb" structure

1. Protection + encapsulation of BP is paramount

2. Can a native oxide protect the pristine BP?



X-ray Photoelectron Spectroscopy (XPS) : => Ideal for topmost chemistry of layered materials



Evolution of the surface oxide

□ XPS of the P 2p core level for the as cleaved surface shows a single P environment (P1) as expected: P 2p_{1/2}, _{3/2} spin orbit-split core level

Exposure to air : additional oxide-related components (P2,3,4)

DFT : Calculate core level shifts of P_xO_y structures

- \blacktriangleright P4 corresponds to layered phosphorus pentoxide P₂O₅
- P2 and P3 are bridging and terminal sites in the stable suboxide p-P₄O₂



P 2p (hv = 180eV)



Photon Energy Dependent XPS

- Photon energy dependant spectra : yield surface vs bulk components
- As hv increases, components P2, P3 and P4 all decrease with respect to P1.

These oxide species are therefore only associated with the surface of the BP

Overlayer thickness model:

$$d = \lambda \log_e \left(\frac{I_{Oxide}}{I_{BP}} + 1 \right) \sim 0.4 \ nm$$

Good agreement with a DFT value of 0.46 nm for a single layer of planar P₂O₅



Example 2: Metal-mediated graphene growth on SiC



Røst et al., JPPC 125(7), 4243-4252 (2021)

Example 3: Diamond surface passivation for near surface NV centres

Silicon terminated (100) diamond: LEED



Angle-Resolved Photoelectron Spectroscopy (ARPES)



Electronic bandstructure

- Fundamental property of periodic condensed matter (single crystals)
- Critical for understanding electronic/transport properties in quantum materials



ARPES: The premier technique for electronic bandstructure

Topological Insulators





M. Bianchi et al, Nat. Comm. 1, 128 (2010)

Transition metal dichalcogenides

Superconductors





2D materials





Zhang et al, Nature Nanotech. 9, 111 (2014)

Li et. al, Nature Nanotechnology 9, 372 (2014)

Direct Transitions in crystalline materials

- For ordered, periodic solids featuring an electronic bandstructure, photoexcitation causes electron transitions from occupied to unoccupied bands: so-called "Direct transitions"
- Momentum is conserved modulo bulk reciprocal lattice vectors *G* such that for the transition:

$$\boldsymbol{k}_f = \boldsymbol{k}_i + \boldsymbol{G}$$

Transition "assisted" by a G vector



How to determine initial state **k** inside the solid from the photoelectrons *outside* the sample??



Vacuum wave-vector K

Photoelectrons are free electrons, with an energy-momentum relationship given by the free electron model:

 $E_{kin} = \frac{\hbar^2 |\boldsymbol{K}|^2}{2m_c}$

Inverting this relationship, we obtain the magnitude of the electron wave-vector in units of Å⁻¹

 $|\textbf{\textit{K}}| = 0.511 \sqrt{E_{kin}} \, (\text{\AA}^{-1})$

□ Normally, polar emission angle θ is referred to the surface normal, one resolves *K* into in-plane (*K*_{||}) and out of plane (*K*_⊥) components



Fundamental of ARPES: Conservation of k_{ll}

Due surface translational order, the component of final state wave-vector parallel to the surface $k_{f||}$ is <u>conserved</u> across the solid-vacuum interface

i.e:
$$K_{\parallel} = k_{f\parallel} = k_{i\parallel} + G_{\parallel}$$

Where:

$$|\mathbf{k}|_{f\parallel} = |\mathbf{K}|_{\parallel} = 0.511 \sqrt{E_{kin}} \operatorname{sin}(\theta_p) \,(\text{\AA}^{-1})$$

(*G* is a bulk reciprocal lattice vector, easily accounted for)

> Thus we can recover $k_{i\parallel}$ absolutely



ARPES: Key to revealing electronic bandstructure



1. Measure photoelectron emission angle and kinetic energy OUTSIDE sample

2. Use energy and momentum conservation rules to obtain initial state energy vs. wavevector INSIDE the sample ("bandstructure")

Require detection of photoelectron kinetic energy <u>and</u> emission angle



Experimental Requirements

Angle resolving electron spectrometer

- □ Spectrometer capable of measuring emission angle from the surface
- □ Must feature high energy and angle resolution for good *k* space resolution



Hemispherical analyser *Most popular and highest resolution*



"Momentum Microscopes" Real and *k* space modes





Region 1 E-E_F=28.8eV, FoV=4.1Å⁻¹



SXR Toroidal Analyser

Offline (VUV lamp) Online (SXR beamline)



Example 1: Monolayer graphene on SiC

Real space lattice (*left*), reciprocal (*right*)



"Dirac Cone" of graphene bandstructure



Hydrogen intercalation: 1 to 2 layers of graphene

BE (eV)



Quasi free standing bilayer graphene on SiC



ARPES => carrier velocity, and sign and magnitude of the carrier density

Molecular surface transfer p-type doping



Reidel et al, J. Phys. D: Appl. Phys. 43, 374009 (2010)



Tadich et. al, Appl. Phys. Lett, 102(24), 241601 (2013)



Doping from intercalation: fluorine



Walter et al, Appl. Phys. Lett. 98, 184102 (2011)

Example 2: Transition metal dichalcogenide MoSe₂

- MoSe₂ grown on 6H-SiC(0001) via MBE in ARPES capable system ٠
- Predicted transition from *direct* to *indirect* band gap as function of thickness ٠ experimentally confirmed



8ML MoSe₂

ANSTO

Zhang et al, Nature Nanotech. 9, 111 (2014)

SUMMARY

Photoelectron Spectroscopy

Measurement of occupied electron states emitted from a solid using the photoelectric effect

1. XPS

- Characterization of surface chemistry via excitation of core level electrons using VUV to SXR x-ray energies
- □ SR-XPS advantages: Adjustable photon energy => Depth tuning, cross section

2. ARPES

- □ Angle resolved photoemission from the valence band of single crystalline materials
- Reveals the electronic bandstructure, an important property of condensed matter governing transport properties



Thank You

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3. Near Edge X-ray Absorption Fine Structure (NEXAFS)



ANSTO

-CH2-CH2-



- NEXAFS measures transitions from occupied core states to unoccupied states
- Molecular orbitals (molecular systems), band states (crystals), etc

Rydberg

 It is a fingerprinting technique in the sense that resonances depend on local bond configurations around the absorbing element.

Comparison to reference systems important!

Courtesy J. Stohr SSRL

How is NEXAFS measured?

LIII

LI

κ

10-

10-7

10-3

Ξ

- We cannot *directly* measure the electrons participating in bound state transitions. Instead we measure *secondary processes associated with the core hole de-excitation*
- Relaxation of the core-hole results in either the emission of an Auger electron, or a fluorescence photon

($\omega_a >> \omega_f$ for low Z elements)

Both Auger electron and x-ray fluorescence yields are proportional to x-ray absorption

 Electron-yield NEXAFS is very surface sensitive. Soft X-ray NEXAFS a complement to PES



http://physics.anu.edu.au/ampl/images/AESprocess.gif

Electron Yield Detection modes

- 1. Electron energy analyser: Monitor the Auger electron intensity directly ("Auger Electron Yield", AEY)
- 2. Retarding grid detector: High pass energy filter which captures the Auger electrons ("Partial Electron Yield", PEY), rejecting the large secondary electron background
- 3. Total photocurrent leaving sample ("Total Electron Yield", TEY, also called drain current). All electrons!



Orbital directions using SXR NEXAFS

The Search Light Effect

 NEXAFS resonance intensity **Benzene Molecular Orbitals** Lying-down benzene on Ag (110) depends on alignment of electric 8 in-plane field vector *E* of the radiation and π1 the wavefunction of the unoccupied state (dipole operator) Normalized Intensity π_{2} out-of-plane Polarised soft x-rays act as a π "search" light for unoccupied states aligned with the *E* vector 8 Ē **NEXAFS** is a powerful tool for determining the real space 4 σ_1^* σ_2^* directionality/orientation of molecular orbitals in the surface region of a material 0 C_{1s} 295 305 275 285 315 325 Photon Energy (eV)

Courtesy J. Stohr SSRL



Early Demonstration of NEXAFS to Determine Molecular Orientation

- CO on Ni(100): How does it absorb on the surface ?
- <u>E</u> // to surface stimulated the π* transition.
- <u>E</u> \perp to surface stimulated the σ^* transition
- With the well known MO structure of CO, it was concluded the CO molecules stick up from the surface



J Stöhr and R Jaeger. Phys. Rev. B, 26, p4111 1982

Geometry Of Melamine Adsorption On Graphene





Context: Using graphene as small molecule sensor

- C K- edge and N K- edge NEXAFS data suggest a flat adsorption geometry up to 3.6ML
- Amino π* angle dependence indicates 8° tilt angle from plane of graphene



J. Cervenka et. al. Nanoscale 7 (4), 1471-1478 (2014)

Thank You

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