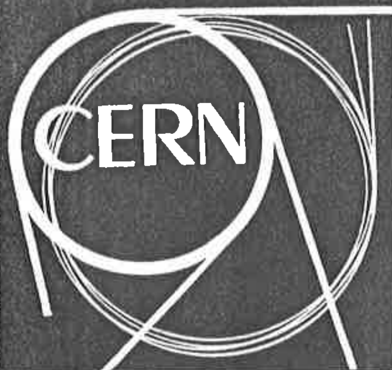

(106)

Cours/Lecture Series

1981-1982 ACADEMIC TRAINING PROGRAMME

Title	"Surface analytical techniques"
Lecturer	J.C. RIVIERE (AERE Harwell)
Dates	February 1, 2, 3, 4 & 5, 1982
Time	11h to 12h
Place	TH Division Conference Room, 3rd floor, Building 4

Abstract

The proliferation of physical techniques used to characterise the chemical properties of solid surfaces has led to some confusion as to the differences between them, and the information that each one provides.

The series of lectures about these techniques will therefore discuss and compare their operating conditions, mechanisms, spatial and depth resolution, relative elemental sensitivities, nature of information, and fields of application.

They will be grouped according to the method of initial excitation, i.e. electron, photon, or ion, and where appropriate comparisons of advantages and disadvantages will be made.

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LECTURE NOTES

Surface Analytical Techniques

CERN, February 1st-5th, 1982

J C Rivière (AERE, Harwell, GB)

Definitions

1. Surface: The first atom layer, and all subsequent layers affected by the discontinuity at the surface. In practice this corresponds to a depth of 3-5 nm.

2. Surface-specific techniques: Those physical techniques whose analytical information is only about the surface, and that are incapable of analysing the bulk.

3. Surface-sensitive techniques: Those physical techniques that have sufficient sensitivity to analyse material if present on a surface, but cannot distinguish between surface and bulk.

A. SURFACE-SPECIFIC TECHNIQUES

A1. Electron Excitation

(a) AES - Auger Electron Spectroscopy

Incident probe:- Electrons, 5-20 keV, 10^{-8} - 10^{-5} A.
Analysed particles:- Auger electrons, 0-2000 eV
Depth of analysis:- 0.5-3 nm.
Spatial resolution:- 5 x 10^{-7} - 5 x 10^{-5} mm^2
Sensitivity:- 0.1-1.0 at %
Information:- Elemental composition, some chemical.

(b) SAM - Scanning Auger Microscopy

Incident probe:- Electrons, 10-40 keV, 10^{-9} A
Analysed particles:- Auger electrons, 0-2000 eV
Depth of analysis:- 0.5-3 nm
Spatial resolution:- 2 x 10^{-9} - 5 x 10^{-7} mm^2
Sensitivity:- 0.1-1.0 at %
Information:- Elemental distribution across surface.

(c) EELS - Electron Energy Loss Spectroscopy

Incident probe:- Electrons, 2-5 eV, 10^{-10}-10^{-9} A, energy spread 6-10 meV.
Analysed particles:- Loss electrons, 20-2000 meV.
Depth of analysis:- $\sim$ 1 nm
Spatial resolution:- 0.2-2 mm^2
Sensitivity:- 0.1 monolayers of adsorbed species
Information:- Vibrational losses of molecules on surfaces, hence mostly chemical.

(d) APS - Appearance Potential Spectroscopy

Incident probe:- Electrons, 0-1000 ev (varied continuously), 10^{-3} A
Analysed particles:- Soft X-rays (thresholds in range of primary energy)
Depth of analysis:- 0.5-3 nm
Spatial resolution:- 10-100 mm^2
Sensitivity:- 0.1-100 at %
Information:- Densities of unoccupied electronic states above Fermi level of solid.

(e) EIL - Electron Induced Luminescence

Incident probe:- Electrons, 3 keV, 10^{-5} A
Analysed particles:- Photons, visible, from decay of excited atoms or clusters formed on surface by reaction.
Depth of analysis:- 0.5-1.0 nm
Spatial resolution:- 1 mm^2
Sensitivity:- 1-10 at %
Information:- Nature of interaction of both weakly and strongly bound species with a surface.

(f) ESD - Electron Stimulated Desorption

Incident probe:- Electrons, 300-1000 eV, 10^{-7}-10^{-6} A
Analysed particles:- Ions desorbed from the surface
Depth of analysis:- 0.5-1.0 nm
Spatial resolution:- 5 x 10^{-7} - 5 x 10^{-5} mm^2
Sensitivity:- 0.5-5 at %
Information:- Nature of adsorbed species, deduced from mass analysis in the gas phase.

A2. Photon Excitation

(a) XPS - X-Ray Photoelectron Spectroscopy

Incident probe:- Soft X-rays (AlK_α, 1486.6 eV; MgK_α, 1253.6 eV), at power variable from 50-1000 W.
Analysed particles:- Photoelectrons (0-1485 eV using AlK_α, 0-1250 eV using MgK_α), Auger electrons (0-1000 eV).
Depth of analysis:- 0.5-5 nm
Spatial resolution:- 1-14 mm^2
Sensitivity:- 0.1-1.0 at %
Information:- Elemental composition and chemical state.

(b) XAES - X-Ray Excited Auger Electron Spectroscopy

Incident probe:- Soft X-rays as for XPS
Analysed particles:- Auger electrons (0-1000 eV)
Depth of analysis:- 0.5-3 nm
Spatial resolution:- 1-15 mm^2
Sensitivity:- 0.1-1.0 at %
Information:- Elemental composition, fine structure in Auger peak shapes.

(c) SRPS - Synchrotron Radiation Photoelectron Spectroscopy

Incident probe:- Synchrotron Radiation, 40-200 eV, continuously variable.
Analysed particles:- Photoelectrons, energies from zero up to incident energy.

SRPS - cont'd

Depth of analysis:- 0.5-3 nm
Spatial resolution:- 1-3 mm^2
Sensitivity:- 0.1-1.0 at %
Information:- Variation of cross-section of photoionisation of shallow atomic levels and of valence band structure. Assists in interpretation of surface reactions.

(d) UPS - Ultra-Violet Photoelectron Spectroscopy

Incident probe:- UV light (HeI, 21.21 eV; HeII, 40.8 eV; NeI, 16.8 eV; NeII, 26.9 eV; ArI, 11.8 eV; etc).
Analysed particles:- Photoelectrons, energies from zero up to incident energy.
Depth of analysis:- 0.5-4 nm
Spatial resolution:- 5-10 mm^2
Sensitivity:- 0.1-1.0 at %
Information:- Valence band structure and its changes during surface reaction.

(e) PESM - Photo-Electron Spectro-Microscopy

Incident probe:- Photons of any energy
Analysed particles:- Photoelectrons of selected energy
Depth of analysis:- 0.5-5 nm
Spatial resolution:- $5 \times 10^{-8} - 5 \times 10^{-6}$ mm^2
Sensitivity:- 0.1-1.0 at %
Information:- Elemental distribution if using high-energy incident photons (ie soft X-rays), chemical state distribution if using low-energy incident photons (ie UV photons).

(f) ELL - Ellipsometry

Incident probe:- Photons, infra-red or visible, plane polarised.
Analysed particles:- Photons, reflected, whose elliptical polarisation parameters are measured.
Depth of analysis:- 0.5-1.5 nm
Spatial resolution:- 1-10 mm^2
Sensitivity:- 0.2-20 at %
Information:- Changes in film thickness and refractive index as a function of coverage during surface reaction.

A3. Ion Excitation

(a) IAES - Ion-Excited Auger Electron Spectroscopy

Incident probe:- Positive ions, usually Ar^+, 5-60 keV, 10^{-6} A.
Analysed particles:- Auger electrons, 0-200 eV.
Depth of analysis:- 0.5-2 nm
Spatial resolution:- 0.1-10 mm^2
Sensitivity:- 0.1-1.0 at %
Information:- Elemental composition, ion-atom interactions.

(b) PAES - Proton-Excited Auger Electron Spectroscopy

Incident probe:- Protons and α-particles, 0.3-3.0 MeV, $10^{-7} - 10^{-6}$ A.
Analysed particles:- Auger electrons, 0-500 eV.
Depth of analysis:- 0.5-3 nm

PAESAES - cont'd

Spatial resolution:-	3 mm^2
Senstivity:-	0.1-1.0 at %
Information:-	Elemental composition, proton and α-particle ionisation cross-sections.

(c) INS - Ion Neutralisation Spectroscopy

Incident probe:-	Positive ions, usually He^+, ∿ 5 eV, 10^{-6} A.
Analysed particles:-	Auger-type electrons from valence band, 0-10 eV.
Depth of analysis:-	∿ 0.5 nm
Spatial resolution:-	∿ 10 mm^2
Sensitivity:-	0.1 monolayers of adsorbed species
Information:-	Densities of occupied states appropriate to the surface atoms only.

(d) IBSCA - Ion Beam Spectro-Chemical Analysis

Incident probe:-	Positive ions, either inert (Ar^+) or reactive (O_2^+, N_2^+), 5-50 keV, 10^{-6} - 10^{-5} A.
Analysed particles:-	Photons, visible and near UV, produced by de-excitation of sputtered particles in gase phase.
Depth of analysis:-	0.5-3 nm
Spatial resolution:-	0.1-10 mm^2
Sensitivity:-	10^{-4} - 10^{-3} at %
Information:-	Nature of surface species produced by reaction, studied under dynamic conditions.

(e) GDOS - Glow Discharge Optical Spectroscopy

Incident probe:-	Positive ions, usually Ar^+, from glow discharge, at 1 keV and 10^{-5} - 10^{-4} A.
Analysed particles:-	Photons, visible and near UV, produced by de-excitation of neutrals sputtered from surface and then ionised in discharge.
Depth of analysis:-	0.5-3 nm
Spatial resolution:-	30-100 mm^2
Sensitivity:-	10^{-6} - 10^{-4} at %
Information:-	Elemental distribution with depth, high sensitivity analysis for some elements.

(f) SSIMS - Static Secondary Ion Mass Spectrometry

Incident probe:-	Positive ions, usually Ar^+, 1-3 keV, 10^{-9} A.
Analysed particles:-	Positive and negative secondary ions, mass range 1-500 amn.
Depth of analysis:-	0.5-3 nm
Spatial resolution:-	0.1-10 mm^2
Sensitivity:-	10^{-4} - 1.0 at %
Information:-	Chemical composition, nature of surface species during chemical reaction, analysis of some elements with high sensitivity.

(g) ISS - Ion Scattering Spectroscopy

Incident probe:-	Positive ions, usually He^+, Ne^+, or Ar^+, 1-4 keV, 10^{-6} A.
Analysed particles:-	Positive elastically scattered ions, whose energies are analysed up to the primary energy.
Dpeth of analysis:-	0.5-1.0 nm
Spatial resolution:-	0.5-5 mm^2

ISS - cont'd

Sensitivity:-	0.1-10.0 at %
Information:-	Elemental composition. Also some structural information by varying angle of incidence.

(h) GDMS - Glow Discharge Mass Spectrometry

Incident probe:-	Positive ions, usually Ar^+, from glow discharge, at 1 keV and 10^{-5} - 10^{-4} A.
Analysed particles:-	Positive ions, formed by ionisation in the discharge of sputtered neutrals, 1-500 a.m.u.
Depth of analysis:-	0.5-3 nm
Spatial resolution:-	30-100 mm^2
Sensitivity:-	10^{-6} - 10^{-4} at %
Information:-	Elemental distribution with depth as surface is sputtered, high sensitivity analysis for many elements.

A4. Other Techniques

(a) CPD - Contact Potential Difference

Methods:-	Various, including electron and photon excitations, application of electrical field, heating, and measurement of change in capacitance.
Analysed particles:-	Photo-electrons, thermionic electrons, or electrons extracted by field emission.
Depth of analysis:-	0.5-1.0 nm
Spatial resolution:-	Field emission method, 10^{-17} mm^2 Capacitance change, 0.1-1 mm^2 Other methods, several mm^2
Sensitivity:-	0.01 monolayers for species adsorbed on surface
Information:-	Change in work function of surface as result of reaction.

(b) TDS - Thermal Desorption Spectroscopy

Method:-	Linearly programmed heating of specimen.
Analysed particles:-	Ions desorbed from surface, 1-200 a.m.u.
Depth of analysis:-	0.5-1.0 nm
Spatial resolution:-	Area of specimen
Sensitivity:-	10^{-2}-1.0 at %
Information:-	Strength of bonding of adsorbed species to surface.

B. SURFACE-SENSITIVE TECHNIQUES

B1. Electron Excitation

(a) Electron Probe Micro-Analysis

Incident probe:-	Electrons, 2-50 keV, $\sim 10^{-9}$ A.
Analysed particles:-	Characteristic X-ray photons
Depth of analysis:-	50-2×10^3 nm
Spatial resolution:-	10^{-6} - 10^{-4} mm^2
Sensitivity:-	0.1 monolayers of material as thin film on surface
Information:-	Elemental composition.

B2. Ion Excitation

(a) RBS - Rutherford Back-scattering Spectroscopy

Incident probe:-	Positive ions, H^+ or He^+, 0.3-5 MeV, 10^{-10}-10^{-8} A.
Analysed particles:-	Positive elastically scattered ions, whose energies are measured up to the primary energy.
Depth of analysis:-	100-3x10^3 nm
Spatial resolution:-	10^{-6} - 10^{-5} mm^2
Sensitivity:-	10^{-3} - 10 at %
Information:-	Some elemental compositional information, but principally depth distribution of heavy elements on and in light elements.

(b) PIXE - Proton Induced X-Ray Emission

Incident probe:-	Positive ions, H^+, 0.1-10 MeV, 10^{-10} - 10^{-5} A.
Analysed particles:-	Characteristic X-ray photons.
Depth of analysis:-	200-5x10^3 nm
Spatial resolution:-	10^{-2} - 3 x 10^2 mm^2
Sensitivity:-	5x10^{-5} - 10^{-2} at %
Information:-	Elemental composition.

(c) HIIXE - Heavy Ion Induced X-Ray Emission

Incident probe:-	Positive ions, various, 0.02-5 MeV, 10^{-10} - 10^{-8} A.
Analysed particles:-	Characteristic X-ray photons
Depth of analysis:-	10 - 10^3 nm
Spatial resolution:-	10^{-5} - 10^{-1} mm^2
Sensitivity:-	10^{-4} - 1 at %
Information:-	Elemental composition, detection of the element sought being enhanced by selection of ion mass and energy.

(d) SIMS - Secondary Ion Mass Spectrometry

Incident probe:-	Positive ions, either inert (Ar^+) or reactive (O_2^+), 1-30 keV, 10^{-8} - 10^{-6} A.
Analysed particles:-	Positive or negative secondary ions, 1-1000 amu.
Depth of analysis:-	1-20 nm
Spatial resolution:-	10^{-6} - 10^{-2} mm^2
Sensitivity:-	10^{-6} - 10^{-2} at %
Information:-	Elemental composition obtained dynamically during continuous erosion of surface.