## CHAPTER - 2

## **Surface Analytical Techniques - An Overview**

The analysis of surface starts with defining what a surface is? Generally, it is considered that the top 4 - 5 layers or top 10 Å depth is considered to be the surface, since coordinative un-saturation and variations in configurations can be seen only in these layers. It is usual to list out the available techniques in tabular form. However, since this may not give the whole and true picture, a method based on input/output probes has been adopted There are generally four particle beams, namely electrons, ions, neutrals and photons and there are four other fields, namely thermal, electric, magnetic and surface sonic waves that can be used as input probes. When one employs any one of these eight input probes, they give rise to emission or transmission or scattering of the four particle beams (except the magnetic field) namely electrons, ions, neutrals and photons. These particles carry information of the surface to a suitable detector. The detector assembly can be tuned to count the number of particles emitted (intensity), or it can identify the chemical nature of the species emitted in the case of ions and neutrals or can be made to analyse the energy or angular distribution of the particles emitted. Any or all of these four types of information on the emitted particle are used to develop better understanding of the surface under study.

The combination of the 8 different types of input probes with four different output probes on which four different types of information can be gathered give rise to the multitude of techniques. A pictorial representation of this model of generating all the techniques is given in **Fig. 2.1**. A listing of the possible techniques and their acronyms are given in **Appendix 2.1** 



Fig.2.1.A pictorial representation of generating the possible techniques in terms of input and out put probes.

It can be demonstrated that most of the surface analytical techniques can be rationalized in terms of input and output probes. Consider the of case of electrons in (electrons used as input probe) which can give rise to all the four particle beams. It is generally believed that it is always simple and easily feasible if the same particle is considered as the output probe.

For a conceptual understanding, a simple representation is given in **Fig. 2.2** for the surface analytical techniques that are possible from using electrons as input probes and all the four particle beams as output probes. A similar representation is possible for other combinations as well. Some of these are pictorially shown in **Fig. 2.3 and Fig. 2.4**. A simple compilation of some of the important surface analytical techniques, their basis and the type of information that can be obtained is given in **Table 2.1** 

The purpose of this presentation is not to consider the fundamentals of these techniques as several authoritative compilations are available on them. The focus will be on the applications of some of these techniques in handling the problems in catalysis.



Fig. 2.2 Representation of the techniques based on Electrons in – electron, ion, neutral and photon out LEED: Low Energy Electron Diffraction; HEED: High Energy Electron diffraction; **RHHED**: Reflected High Energy Electron Diffraction; **ILEED**: Ineleastic Low Energy Electron Diffraction; **AES**: Auger Electron Spectroscopy; **EELS**: Electron Energy Loss Spectroscopy; **EIID**: Electron Induced Ion Desorption; **SDMM**: Surface Potential Microscope; **CIS**: Characteristic Isochromat Spectroscopy; **APS**: Appearance Potential Spectroscopy.

It is desirable to deal in detail with the various applications of these surface and bulk analytical techniques and show in which situation, which technique will provide the appropriate information required. However such an exercise will be out of reach for any single volume. Hence in this volume, only a few selected techniques are taken up for consideration. Even in these cases the examples chosen do not cover the entire spectrum of possibilities.



Fig. 2.3 Schematic representation of the techniques that can be generated from Photonin photon, neutral, electron or ion-out methodology. **XPS**: X ray Photoelectron Spectroscopy; **ESCA:** Electrons Spectroscopy for Chemical Analysis.



Fig. 2.4 Schematic representation of the techniques that can be generated from Ions-in ion-, neutral-, electron- or photon-out methodology. **ISS:** Ion Scattering Spectroscopy, **SIMS:** Secondary Ion Mass Spectrometry, **INS:** Ion Neutralization Spectroscopy, **PIX:** Proton Induced X ray emission.

Surface Analytical technique	Typical applications	Signal detected	Elements detected	Detection limits	Depth resolution	Imaging/ Mapping possibility	Lateral resolution (Probe size)
Auger spectroscopy	Elemental analysis, depth profiling	Atomic scale roughness	Li-U	-	206nm	yes	100 nm
Rutherford Back scattering (RBS)	Quantitative think film composition	Backscattered He atoms	Li-U	1-10 at% (for Z<20)0.01-1 at % for X 20-70	2-20 nm	yes	2 mm
Secondary Ion Mass Spectrometry	Dopant and impurity depth profiling, microanalysis	Secondary ions	H-U	ppb/ppm	<5 nm	yes	<5 micron imaging <30 micron depth profiling
X-ray Photoelectron Spectroscopy	Surface analysis both inorganic and organic	Photoelectrons	Li-U	0.01-1 at%	1-10 nm	yes	10μm -2μ
X ray Fluorescence	Thin film thickness composition	X-rays	Na-U	10 ppm	-	no	100µm
Low Energy Electron Diffraction	Surface structure adsorbate structure	Elastic back scattering of low energy electrons	only geometry	Sub-monolayer	-	yes	Atomic dimensions
High Resolution Electron Energy Loss Spectroscopy	Structure and bonding of surface atoms and adsorbates	Vibrational excitation of surface atoms adsorbates by inelastic low energy electrons	All adsorbate molecules	Sub monolayer	-	-	Observation of direct adsorbate- adsorbent bond
Infra red absorption spectroscopy	Structure and bonding of adsorbates	Vibrational excitation of surface bonds	Adsorbates' Internal bonds	Sub monolayer	-	-	-
Ion Scattering Spectroscopy	Atomic structure composition	Elastic reflection of inert gas ions	Any element - mass dependent		possible	possible	Atomic dimensions
Extended X ray Absorption Fine structure	Atomic structure of surface atoms and adsorbates	Interference effects in photo-emitted electron wave function in x-ray absorption.	Mostly all species	Immediate coordniation	-	possible	Atomic dimensions
Thermal Desorption Spectroscopy	Adsorption energy	Thermally induced desorption or decomposition of adsorbates	All species	Sub-monolayer	Not normally done	-	No

## Table 2.1 Typical information that can be obtained employing typical surface analytical techniques and the possible limitations of these techniques.

Appendix 2.1 : Partial	listing of	the	Surface	Analytical	Techniques	with	the
appropriate acronym.							

Acronym	Technique
AEAPS	Auger Electron Appearance Potential Spectroscopy
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
APECS	Auger Photoelectron Coincidence Spectroscopy
APFIM	Atom Probe Field Ion Microscopy
APS	Appearance Potential Spectroscopy
ARPES	Angle Resolved Photoelectron Spectroscopy
ARUPS	Angle Resolved Ultraviolet Photoelectron Spectroscopy
ATR	Attenuated Total Reflection
BEEM	Ballistic Electron Emission Microscopy
BIS	Bremsstrahlung Isochromat Spectroscopy
CFM	Chemical Force Microscopy
СНА	Concentric Hemispherical Analyzer
CMA	Cylindrical Mirror Analyzer
CPD	Contact Potential Difference
CVD	Chemical Vapour Deposition
DAFS	Diffraction Anomalous Fine Structure
DAPS	Disappearance Potential Spectroscopy
DRIFT	Diffuse Reflectance Infra-Red Fourier Transform
EAPFS	Extended Appearance Potential Fine Structure
EDX	Energy Dispersive X-ray Analysis
EELS	Electron Energy Loss Spectroscopy
	Electron induced luminescence
	Ellipsometry
EMS	Electron Momentum Spectroscopy
EPMA	Electron Probe Micro-Analysis
ESDMS	Electron Stimulated Desorption Mass Spectrometry
ESCA	Electron Spectroscopy for Chemical Analysis
ESD	Electron Stimulated Desorption
ESDIAD	Electron Stimulated Desorption Ion Angle Distributions
EXAFS	Extended X-ray Absorption Fine Structure
FEM	Field Emission Microscopy
FIM	Field Ion Microscopy
FTIR	Fourier Transform Infra Red
FTRA-IR	Fourier Transform Reflectance-Absorbtion Infra Red
HAS	Helium Atom Scattering
HDA	Hemispherical Deflection Analyser
HEIS	High Energy Ion Scattering
HREELS	High Resolution Electron Energy Loss Spectroscopy

IETS	Inelastic electron tunnelling spectroscopy
KRIPES	k-Resolved Inverse Photoemission Spectroscopy
ILS	Ionisation Loss Spectroscopy
INS	Ion Neutralisation Spectroscopy
IPES	Inverse Photoemission Spectroscopy
IRAS	Infra-Red Absorption Spectroscopy
	Ion excited Auger Electron spectroscopy
ISS	Ion Scattering Spectroscopy
LEED	Low Energy Electron Diffraction
LEEM	Low Energy Electron Microscopy
LEIS	Low Energy Ion Scattering
LFM	Lateral Force Microscopy
MBE	Molecular Beam Epitaxy
MBS	Molecular Beam Scattering
MCXD	Magnetic Circular X-ray Dichroism
MEIS	Medium Energy Ion Scattering
MFM	Magnetic Force Microscopy
MIES	Metastable Impact Electron Spectroscopy
MIR	Multiple Internal Reflection
MOCVD	Metal Organic Chemical Vapour Deposition
MOKE	Magneto-Optic Kerr Effect
NEOM	Near Field Optical Microscopy
NIXSW	Normal Incidence X-ray Standing Wave
NEXAFS	Near-Edge X-ray Absorption Fine Structure
NSOM	Near Field Scanning Optical Microscopy
PAES	Positron annihilation Auger Electron Spectroscopy
PECVD	Plasma Enhanced Chemical Vapour Deposition
PEEM	Photo Emission Electron Microscopy
PhD	Photoelectron Diffraction
	Proton Excited Auger Electron Spectroscopy
PIXE	Proton Induced X-ray Emission o
	Raman Spectroscopy
PSD	Photon Stimulated Desorption
RAIRS	Reflection Absorption Infra-Red Spectroscopy
RAS	Reflectance Anisotropy Spectroscopy
RBS	Rutherford Back Scattering
RDS	Reflectance Difference Spectroscopy
REFLEXAFS	Reflection Extended X-ray Absorption Fine Structure
RFA	Retarding Field Analyser
RHEED	Reflection High Energy Electron Diffraction
RIFS	Reflectometric Interference Spectroscopy
SAM	Scanning Auger Microscopy
SEM	Scanning Electron Microscopy

SEMPA	Scanning Electron Microscopy with Polarization Analysis
SERS	Surface Enhanced Raman Scattering
SEXAFS	Surface Extended X-ray Absorption Spectroscopy
SHG	Second Harmonic Generation
SH-MOKE	Second Harmonic Magneto-Optic Kerr Effect
SIMS	Secondary Ion Mass Spectrometry
SKS	Scanning Kinetic Spectroscopy
SMOKE	Surface Magneto-Optic Kerr Effect
SNMS	Sputtered Neutral Mass Spectrometry
SNOM	Scanning Near Field Optical Microscopy
SPIPES	Spin Polarised Inverse Photoemission Spectroscopy
SPEELS	Spin Polarised Electron Energy Loss Spectroscopy
SPLEED	Spin Polarised Low Energy Electron Diffraction
SPM	Scanning Probe Microscopy
SPR	Surface Plasmon Resonance
SPURS	Spin Polarised Ultraviolet Photoelectron Spectroscopy
SPXPS	Spin Polarised X-ray Photoelectron Spectroscopy
STM	Scanning Tunnelling Microscopy
SXAPS	Soft X-ray Appearance Potential Spectroscopy
SXRD	Surface X-ray Diffraction
	Synchrotron radiation Photoelectron spectroscopy
TDS	Thermal Desorption Spectroscopy
TEAS	Thermal Energy Atom Scattering
TIRF	Total Internal Reflectance Fluorescence
TPD	Temperature Programmed Desorption
ТРО	Temperature Programmed Oxidation
TPRS	Temperature Programmed Reaction Spectroscopy
TPS	Temperature Programmed Sulphidation
TXRF	Total Reflection X-ray Fluorescence
UHV	Ultra High Vacuum
UPS	Ultraviolet Photoemission Spectroscopy
IR or EELS	Vibrational spectroscopy
XANES	X-ray Absorption Near-Edge Structure
XAES	X-ray induced Auger electron spectroscopy
XPD	X-ray Photoelectron Diffraction
XPS	X-ray Photoemission Spectroscopy
XRR	X-ray Reflectometry
XSW	X-ray Standing Wave

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