CHAPTER - 2
Surface Analytical Techniques

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 unsaturation and configurational variations can be seen only in these layers. It is usual to list out the available techniques in some of the tabulations and since this will not give the whole picture, we wish to adopt a method based on input/output probes. There are generally four particle beams, namely electrons, ions, neutrals and photons and there are four other fields, namely thermal, electrical, magnetic, surface sonic waves that can be used as input probes. When one employs any one of these eight 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 to 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 forms 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 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** for this chapter. 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.

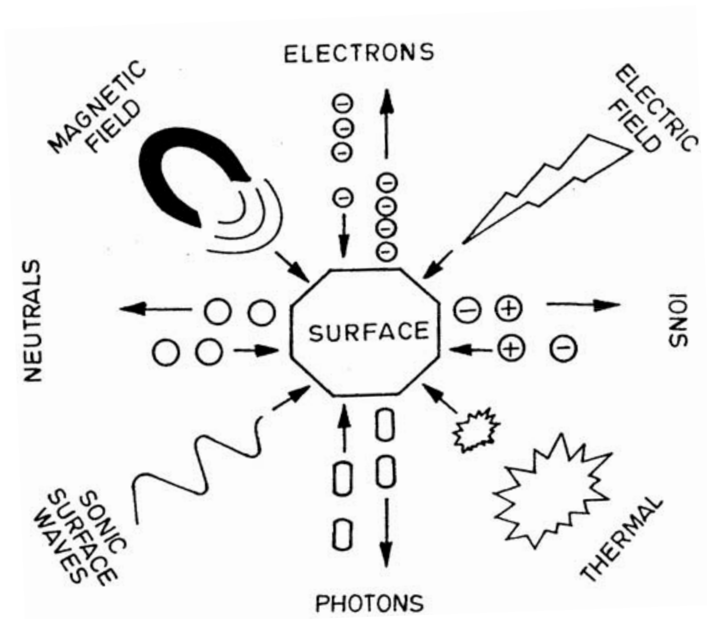

Fig.2.1.A pictorial representation of generating the possible techniques in terms of input and out put probes.

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 out put 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. We shall only focus on the applications of some of these techniques in handling the problems in catalysis on the basis of situation and show what technique is suitable for a given situation and why? This is done with illustrative examples wherever possible.

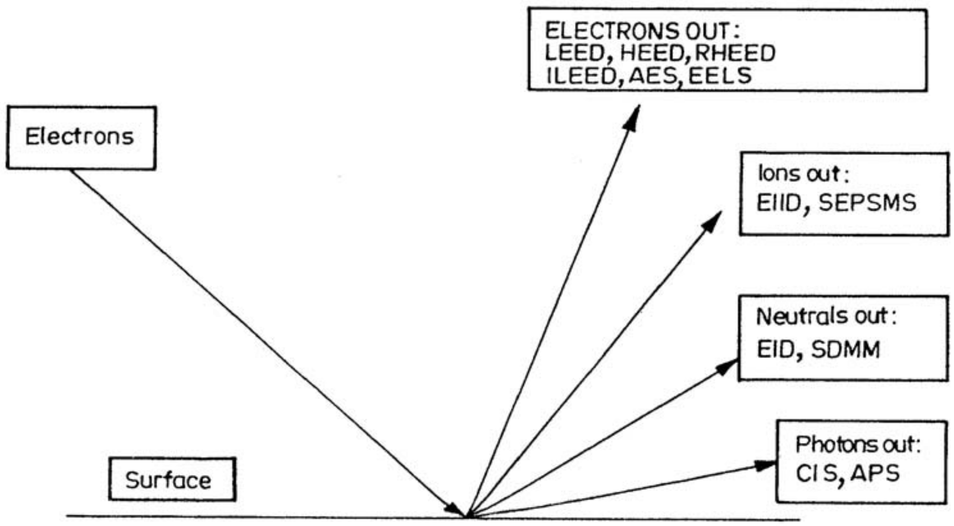

Fig. 2.2 Representation of the techniques based on Electrons in – electron, ion, neutral and photon out LEED: Low Energy Electron Diffraction; HEED: High Energy Electron diffraction; **RHHED:** Reflected High Energy Electron Diffraction**; ILEED:** Ineleastic Low Energy Electron Diffraction**; AES:**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

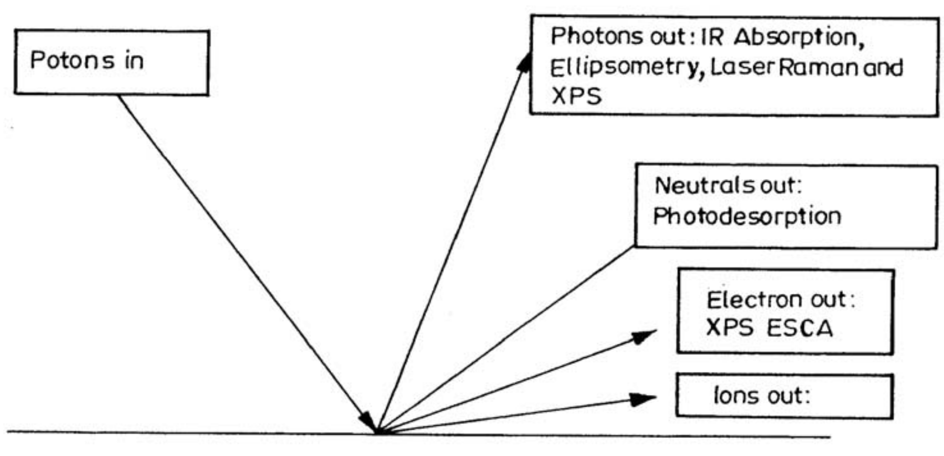

Fig. 2.3 Schematic representation of the techniques that can be generated from Photon- in photon, neutral, electron or ion-out methodology**. XPS**: X ray Photoelectron Spectrroscopy; **ESCA:** Electrons Spectroscopy for Chemical Analysis.

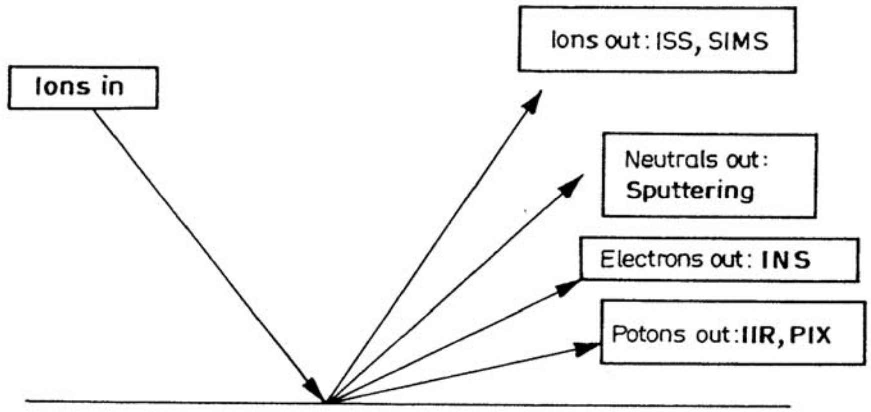

Fig. 2.4 Schematic representation of the techniques that can be generated from Ions-in ion-, neutral-, electron- or photon-out methodology. **ISS:** Ion Scattering Spectroscopy, **SIMS:** Secondary Ion Mass Spectrometry, **INS:** Ion Neutralization Spectroscopy, **PIX:** Proton Induced X ray emission.

Table 2.1 Typical information on some of the surface analytical techniques, the information that can be obtained employing these techniques and the limitations of these techniques. (data not yet complete)

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	-				
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					
Infra red absorption spectroscopy	Structure and bonding of adsorbates	Vibrational excitation of surface bonds					
Ion Scattering Spectroscopy	Atomic structure composition	Elastic reflection of inert gas ions					
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.					
Thermal Desorption Spectroscopy	Adsorption energy	Thermally induced desorption or decomposition of adsorbates					

Appendix 2.1

Listing of the Surface Science Techniques (list not yet complete will be added)

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
CHA	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
	Ellipsometry
EMS	Electron Momentum Spectroscopy
EPMA	Electron Probe Micro-Analysis
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 tunneling spectroscopy
KRIPES	k-Resolved Inverse Photoemission Spectroscopy
ILS	Ionisation Loss Spectroscopy
INS	Ion Neutralisation Spectroscopy
IPES	Inverse Photoemission Spectroscopy
IRAS	Infra-Red Absorbtion 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
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
PIXE	Proton Induced X-ray Emission
PSD	Photon Stimulated Desorption
RAIRS	Reflection Absorbtion 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
TDS	Thermal Desorption Spectroscopy
TEAS	Thermal Energy Atom Scattering
TIRF	Total Internal Reflectance Fluorescence
TPD	Temperature Programmed Desorption

TPO	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
XANES	X-ray Absorption Near-Edge Structure
XPD	X-ray Photoelectron Diffraction
XPS	X-ray Photoemission Spectroscopy
XRR	X-ray Reflectometry
XSW	X-ray Standing Wave
