Chapter 2

Characterization Techniques

2.1 Ion Scattering Techniques

2.1.1 Rutherford Backscattering Spectrometry

2.1.1.1 Introduction

In Rutherford backscattering spectrometry (RBS), one is concerned with energetic projectiles that traverse through a target material, lose energy along their path, and are scattered by collision with target atoms. There are four basic factors that are involved in this process [1]:

- (a) The energy of the projectile after the collision can be related to its energy before the collision by means of a *kinematic factor*.

- (b) The interaction between the projectile and the target atom that can be described as an elastic collision between two isolated particles and expressed in terms of a *scattering cross section, σ*.

- (c) The energy loss of the energetic projectile as it traverses the path leads to the concept of the *stopping cross section*.

- (d) The energy loss process is a statistical process. Thus mono-energetic projectiles assume an energy distribution after penetrating a given depth of the
Fig. 2.1. Schematic diagram showing the scattering process.

target. This is known as straggling

The scattering cross section provides RBS with a quantitative capability, the stopping cross section results in the capability for the depth analysis and energy straggling sets limits on mass and depth resolution

(a) Kinematic Factor, K:

In an RBS experiment, a projectile of mass $M_1$ and energy $E_0$ gets scattered at an angle $\theta$ by a target atom of mass $M_2$. After the scattering the energy of the projectile becomes $E$ (See Fig 2.1)

The kinematic factor, $K$ for a target mass $M_2$ is defined by

$$K_{M_2} = \frac{E}{E_0}$$

(2.1)

By applying the energy and the momentum conservation, the kinematical factor can be obtained as [1]

$$K_{M_2} = \left( \frac{M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_2 + M_1} \right)^2$$

(2.2)

$K$ depends on masses $M_1$, $M_2$ and the scattering angle $\theta$. If a projectile of known mass $M_1$ and known energy $E_0$ is directed at the target of an unknown mass $M_2$, by
measuring the energy \( E \) of the scattered particles at an angle \( \theta \), the unknown mass \( M_2 \) can be determined.

In deriving Eqn (2.2), it has been assumed that the interaction between the two atoms can be described by a simple elastic collision. This is true under two conditions:

- (i) The projectile energy \( E_0 \) must be much larger than the binding energy of the atoms in the target.
- (ii) Nuclear reactions and resonances must be absent.

Nuclear processes depend on the specific choice of the projectile and target atoms. With a \( H^+ \) beam, nuclear effects can appear even below 1 MeV, with \( He^+ \), they begin to appear at 2 to 3 MeV for light-elemental targets.

As we are dealing with MeV ions, the first condition is satisfied for all cases.

If a target contains two masses that differ by a small amount \( \Delta M_2 \) the difference in the energy \( E \) of the projectile after the collision is given by

\[
\Delta E = E_0 \frac{dK}{dM_2} \Delta M_2
\]  

(2.3)

The largest change in \( K \) for a given change \( \Delta M_2 \) occurs when \( \theta = 180^\circ \) and is given by [1]

\[
\delta M_2 = \frac{\delta E}{E_0} \frac{(M_2 + M_1)^3}{4M_1(M_2 - M_1)}
\]  

(2.4)

with the use of a detector with a reasonable energy resolution \( \delta E \), isotopic mass resolution is possible up to about chlorine but the mass resolution degrades with increasing target mass. Heavy elements (say, around gold) cannot be distinguished unless they differ by \( \sim 20 \) amu.

In the vicinity of \( \theta = 180^\circ \), i.e., \( \theta = \pi - \delta \), and for \( M_2 > M_1 \),

\[
\Delta E = E_0 (4 - \delta^2)(M_1/M_2^2) \Delta M_2
\]

(2.5)

If \( \Delta E \) is less than the resolution of the detector, then the masses in the target, \( M_2^A \) and \( M_2^B \) (\( \Delta M_2 = M_2^A - M_2^B \)) cannot be separated. To obtain good mass resolution, it is therefore desirable that the coefficient of \( \Delta M_2 \) be as large as possible. Thus is possible for higher \( E_0 \), larger projectile mass \( M_1 \) (\( M_1 < M_2 \)) and smaller \( \delta \) (i.e., \( \theta \))
approximately 180°)

(b) **Scattering cross section** $\left(\frac{d\sigma}{d\Omega}\right)$ and the scattering yield:

The mass of the target atoms is established by the energy of the scattered particle after an elastic collision. The number of target atoms per unit area ($N_s$, areal density) is determined by the probability of a collision between an incident particle and a target atom and measured through the total number of the detected particles for a given number of incident particles. For a thin target of thickness $t$ with $N$ atoms/cm$^2$, $N_s = Nt$. The differential cross section, $\frac{d\sigma}{d\Omega}$, of a target atom for scattering an incident particle through an angle $\theta$ into a differential solid angle $d\Omega$ centered about $\theta$ is defined by:

$$\frac{d\sigma}{d\Omega} N_s = \frac{\text{Number of particles scattered into } d\Omega}{\text{Total number of incident particles}}$$

In other words, the number of particles detected by a solid state detector of 100% efficiency and subtending a solid angle $d\Omega$, $Y$, is given by:

$$Y = QN_s \frac{d\sigma}{d\Omega} d\Omega$$  \hspace{1cm} (2.6)

where $Q$ is the total number of particles that strike the target. The average differential scattering cross section $\sigma$ can be defined as:

$$\sigma = \frac{1}{\Omega} \int \frac{d\sigma}{d\Omega} d\Omega$$  \hspace{1cm} (2.7)

For small values of $\Omega$, $\sigma \rightarrow d\sigma/d\Omega$ $\sigma$ is usually known as *scattering cross section*. Thus the yield can be written as:

$$Y = \sigma(\theta)\Omega Q N_s$$  \hspace{1cm} (2.8)

In an RBS experiment the number of incident particles $Q$ and the number of detected particles $Y$ and the solid angle $\Omega$ are usually known quantities and hence with known values of $\sigma(\theta)$, the number of atoms per unit area in the target can be determined. The differential cross section for an elastic collision between two atoms is given by Rutherford’s formula, which in the laboratory frame of reference is given by [1]

$$\frac{d\sigma}{d\Omega} = \frac{Z_1 Z_2 e^2}{4E} \frac{4}{\sin^4 \theta} \left\{ [1 - ((M_1/M_2)\sin\theta)^2]^{1/2} + \cos\theta \right\}^2$$  \hspace{1cm} (2.9)
where $E$ is the energy of the projectile immediately before scattering and $Z_1, Z_2$ are the atomic numbers of the projectile and the target atom respectively. A beam of 10 MeV $He^+$ scattering from silicon at $\theta = 170^\circ$ has a cross section $\sigma = 1$ barn ($1.0 \times 10^{-24} cm^2$). The same beam scattering from gold has a cross section $\sigma = 32.8$ barns. The ratio of the scattering yield from the heavier element (e.g., Au) to that from a lighter one (e.g., Si) is approximately given by

$$\frac{Y_{Au}}{Y_{Si}} = \left( \frac{Z_{Au}}{Z_{Si}} \right)^2 \approx 32$$

(2.10)

and illustrates the enhanced sensitivity of RBS to heavy elements. Note also that the cross section for scattering is inversely proportional to $E^2$. Thus, the yield for a 20 MeV $He^+$ beam is one-quarter of that for a 1 MeV $He^+$ incident beam.

(c) Stopping cross section ($\epsilon$)

As an energetic particle passes through a solid it loses energy. For the light particles and for the energies used in RBS the two dominant energy loss processes are:

- (i) interactions with bound or free electrons in the target i.e., electronic stopping (cross section $\epsilon_e$) and
- (ii) interactions with the screened or unscreened nuclei of the target atoms i.e., nuclear stopping (cross section $\epsilon_n$)

In the total stopping cross section ($\epsilon$) for beams of $H^+$ and $He^+$ the nuclear stopping is negligible ($\epsilon_n \ll \epsilon_e$) except at the lowest energies (i.e., at the deepest penetration of the probe beam). For example, for 1 MeV $He^+$ in silicon the rate of energy loss $dE/dx$, due to the electronic and nuclear stopping are 31.7 eV/Å and 0.04 eV/Å, respectively. The rate $dE/dx$ at which a particle loses energy is typically 10-100 eV/Å for $He^+$ and $dE/dx$ depends on the energy, $E_x$, of the projectile at a depth $x$. $E_x$ is given by

$$E_x = E_0 - \int_0^x (dE/dx)dx$$

(2.11)
The stopping cross section $\epsilon$ is given by

$$\epsilon = \frac{1}{N} \frac{dE}{dx}$$ \hspace{1cm} (2.12)

$\epsilon$ or $dE/dx$ is a function of projectile energy and their values can be obtained from Ref [2, 3] $dE/dx$ for compound targets can also be easily evaluated With the knowledge of $dE/dx$, the thickness $\Delta x$ of a thin film sample can be determined from the energy width $\Delta E$ of the RBS spectrum

$$\Delta x = \frac{\Delta E}{[S_0]}$$ \hspace{1cm} (2.13)

where

$$[S_0] = [K(dE/dx)_{E_0} + \frac{1}{\cos \theta}(dE/dx)_{KE_0}]$$ \hspace{1cm} (2.14)

for normal incidence The energy loss in the first term is calculated at the incident energy $E_0$ and that in the second term at $KE_0$ This is called ‘surface energy approximation’ The quantity $[S_0]/N = [\epsilon_0]$ is called the stopping cross section factor.

(d) Energy Straggling (Bohr’s theory)

An energetic particle that moves through a medium, loses energy via many individual encounters Such a quantized process is subject to statistical fluctuations As a result, identical energetic particles do not have exactly the same energy after passing through a thickness $\Delta x$ of a homogeneous medium. The energy loss $\Delta E$ is subject to fluctuation This phenomenon is called energy straggling Energy straggling places a finite limit for the precision with which energy losses, and hence depths can be resolved by backscattering spectrometry Bohr’s theory predicts that energy straggling does not depend on the energy of the projectile and that the rms value of the energy variation increases with the square root of the electron density per unit area $NZ^2t$ in the target For a layer thickness $t$, Bohr straggling has a variance

$$\Omega_B^2 = 4\pi (Z_1e^2)^2 NZ^2t$$ \hspace{1cm} (2.15)

Using the above concepts (a), (b), (c) and (d), schematic Rutherford backscattering spectra are shown in Fig 2.2
Fig. 2.2. Schematic RBS spectra for MeV He$^+$ ions incident on (a) 500 Å Au films on Si and (b) after reaction to form 1000 Å Au-Si layers on Si are shown. Scattering yield from Au ($H_{Au}$) is smaller in (b) mainly because of lower concentration of Au in AuSi compared to pure Au [as in (a)]. Scattering yield from Si ($H_{Si}$) in Au-Si is shown in (b) by dashed lines.
2.1.1.2 Deviations from Rutherford scattering at low and high energy

The derivation of the Rutherford scattering cross section is based on a coulomb interaction potential $V(r)$, between the particle with nuclear charges $Z_1$ and $Z_2$ of a projectile and a target, respectively. This assumes that the particle is energetic enough to penetrate well inside the orbitals of the atomic electrons. Then scattering is due to the repulsion of two positively charged nuclei of atomic number $Z_1$ and $Z_2$. At large impact parameters found in small-angle scattering of MeV He ions or low-energy, heavy ion collisions, the incident particle does not completely penetrate through the electron shells and hence the innermost electrons screen the charge of the target nucleus.

For the Coulomb potential to be valid for backscattering we require that the distance of closest approach (or impact parameter, $d = (Z_1 Z_2 e^2)/E$) should be smaller than the K shell electron radius, which can be estimated from the Bohr radius ($a_0/Z_2$, $a_0 = 0.53 \, \text{Å}$). That is, the distance of closest approach, $d$ sets the lower limit on the energy of the analysis beam and requires that

$$E > \frac{Z_1 Z_2^2 e^2}{a_0}$$

This energy value corresponds to $\sim 10 \, \text{keV}$ for He scattering from silicon and $\sim 340 \, \text{keV}$ for He scattering from gold.

For sufficiently high energies $E$, the distance of closest approach between the projectile and the target nuclei reduces to the dimensions of nuclear sizes. The short-range nuclear forces then begin to influence the scattering process, and the deviations from the Rutherford scattering cross section can appear.

For $\theta \to 0$, the Rutherford cross section tends to infinity (refer to Eqn (2.9)), which violates the assumption that the target nuclei should be so small that they do not overlap. Small scattering angles correspond to large fly-by distances between the projectile and the target nuclei, that is, distance greater than the radius of the innermost electron shell of the target atom. At these distances the electrostatic interaction does not take place between bare nuclei as Rutherford formula assumes.
**2.1.2 Ion channeling**

**2.1.2.1 Introduction**

When the incident direction of an ion beam is aligned with a crystallographic axis or plane of a single crystal sample the majority of the ions penetrate (channel) into the crystal (Fig 2.3). Channeled particles cannot get close enough to the atomic nucleus to undergo large angle Rutherford scattering and hence the backscattering is drastically reduced — in many cases by a factor of about 100 [4]. The channeling phenomenon and RBS spectra under channeling condition are schematically shown in Figures 2.3, 2.4 and 2.5 respectively.

The channeling effect is observed not only when the angle of ion incidence with respect to atomic strings is zero, as shown in Fig 2.3, but also within an angular range around zero. This angular range depends on the type of ion, the incident energy of the ion, the type of the sample (elements) and is specific to a crystallographic axis or plane along which the beam is incident, and finally on the thermal vibrational amplitude of the constituent atoms in the sample crystal. This angular range is
expressed in terms of a critical angle $\psi_{1/2}$,

$$\psi_{1/2} = 0.8 F_{RS}(\psi) \psi_l$$

(2.17)

where, for axial channeling

$$\psi_l = 0.307 \left[ \frac{Z_1 Z_2}{E d} \right]^{1/2} \text{ (degrees)}$$

(2.18)

and $F_{RS}$ is the square root of the continuum Moliere potential, evaluated at $\psi$. $E$ is expressed in MeV. $d$ is the average inter atomic distance (in Å) along the channeling axis. When there are different types of atoms in a row along the channeling axis, $Z_2$ is replaced by the average $Z_2$, $\psi = 1.2 u_1/\alpha$, where $\alpha$ is the Thomas-Fermi screening radius given by

$$\alpha = \frac{0.4685}{(Z_1^{1/2} + Z_2^{1/2})^{2/3}}$$

(2.19)

and $u_1$ is the one dimensional rms vibrational amplitude. The ratio of the backscattering yield for the aligned condition to that for the random incidence is denoted by $\chi_{mn}$ and is called the minimum yield. The $\chi_{mn}$ is a measure of the crystalline quality of the sample and is given by

$$\chi_{mn} = N_a d \pi (2 u_1^2 + \alpha^2)$$

(2.20)

where $N_a$ is the no of atoms/Å$^3$. For a good crystal at room temperature $\chi_{mn}$ is typically 0.01-0.03. Thus, 97–99% of the ions is channeled. The first monolayer of atoms on the crystal are not affected by the correlated sequence of collisions. This is evident from the surface peaks [Fig 2.5] which represent the interaction of the ion beam with the first monolayer of the solid. The scattering from atoms at larger depths are drastically reduced. This improves the ion scattering sensitivity to light impurities on the surface [4]. For example, an small (sub monolayer) amount of C or O impurity on a Si surface can be easily detected under the channeling condition. This is seen in typical RBS spectra shown in Fig 2.4
Fig. 2.4. A typical RBS/channeling spectra with He$^+$ ion beam of 2.5 MeV energy is seen. Light ion impurities like C or O present in small (sub monolayer) amount on the substrate surface can be easily detected in the channeling condition.

In Fig. 2.5, examples of channeling conditions on various surfaces are illustrated. The dashed spectra represent channeling from the ideal crystal surface. In Fig. 2.5(a), the yield from both channeling (aligned) condition and random incidence is shown. In the case (b) the channeling from the reconstructed surface is shown. Here the surface atoms are displaced in the plane of the surface, representing a situation where the second atom is not shadowed. The surface peak intensity in this case is almost twice of the ideal crystal. In the case of surface relaxation, where the surface atoms are displaced normal to the surface plane (c), one must use off-normal incidence, so that the shadow cone established by the surface atoms is not aligned with the atomic rows in the bulk. This would additional backscattering yield from the second, third, ..., atoms along the string. Here in normal incidence the atoms under the surface atom would be shadowed and the yield would be predominantly from the surface atoms only. These two measurements, then, at normal and oblique incidence reveal the...
Fig. 2.5. A schematic representation of scattering under (a) random and channeling conditions from an ideal single crystal materials, (b) channeling condition on a reconstructed surface, where surface atoms have moved laterally from their ideal position, (c) channeling condition in a relaxed system, where the surface atoms are displaced normal to the surface plane (d) channeling condition when the surface is covered with a monolayer of an adsorbate (e) channeling condition ( ) when the substrate surface is covered with a thick epitaxial layer, along with the backscattering yield under random incidence ( ) The dashed curves in each case indicates the backscattering yield from an ideal crystal with an ideal surface under the channeling condition
presence of relaxation. Actual determination of structure in both cases (b,c), can be obtained by comparing the measured surface peak yield to the theoretical yield obtained from Monte-Carlo simulations for various possible structures. A surface adsorbate atom can shadow the atoms of the substrate if $R_{\text{adsorbate}} > \rho_{\text{substrate}}$, where $R_{\text{adsorbate}}$ and $\rho_{\text{substrate}}$ are the shadow cone radius of the adsorbate and thermal vibration amplitude of the substrate atoms respectively. The atomic mass sensitivity of RBS enables discrimination between substrate and adsorbate. In Fig 2.5(d) the channeling conditions of adsorbate situated exactly over the surface atoms and hence reduction in the substrate surface peak is shown. The channeling conditions for a thick epitaxial layer on the substrate is shown in Fig 2.5(e). Due to the registry of the atoms in the epilayer with the substrate surface atoms, the later are shadowed by the epilayer, and hence the substrate surface peak is reduced considerably. Also the reduction in the yield from the epilayer is seen.

Rutherford backscattering technique under the ion channeling condition is used to characterize crystalline materials like single crystals, epitaxial layers, etc. Among the many applications, determination of the crystalline quality, determination of strain, determination of orientation of epilayers, study of surface structure and lattice location of impurities are common. Some of these uses have been exemplified in subsequent chapters.

2.1.3 Standard RBS/channeling experiments (with ion beam size $\sim 1$ mm diameter)

For RBS/channeling experiments we have used the 3 MV tandem Pelletron Accelerator (9SDH2, NEC, USA) facility at our institute [5, 6]. Details of this accelerator facility will be described in the next chapter. Here we will briefly discuss the standard RBS/channeling experimental facilities using a mm dia ion beam. There are three types of ion sources with the accelerator. One (Alphatross) is for providing He, H or other inert gas ions. The others are SNICS sources (single and multi-cathode), for almost all elements in the periodic table except inert gas ions. For the RBS/channeling
experiments (with a mm dia beam) He ions of 1 0 — 4 0 MeV energy and beam currents of 1—15 nA have been used A multipurpose scattering chamber (schematically shown in the Fig 2 6), equipped with a sample goniometer with five degrees of freedom \( (x,y,z,\theta,\phi) \), has been used to carry out RBS/channeling experiments For RBS analysis the total no of incident ions on the sample is determined by integrating the current on the sample around which there is an electron suppressor

2.1.4 Ion scattering techniques using an ion microprobe (ion beam size \( \sim 1 \mu m \) diameter)

For the characterization of micro-structures we have developed an ion microprobe along one of the beamlines of the 3MV Pelletron accelerator facility The technical details of the development of this facility will be be described in chapter 3 Here we briefly discuss some of the ion scattering techniques, emerged world wide due to the
improvements in the spatial resolutions of the probing ion beam and the analyzing techniques. The various techniques used for elemental analysis and microscopy are demonstrated schematically in Fig. 2.7. The interaction of the focused ion beam results in the ejection of several reaction products, nearly all of them provide useful information regarding the sample area under investigation.

The optical photons, emitted from the surface of the target, during the interaction of MeV ion beam can be used by an optical microscope to focus and locate the beam on the target surface.

The intensity of the secondary electrons emitted from the surfaces of the sample can be recorded together with the x-y position of a scanned ion beam to reconstruct a surface topographic image of the sample. This secondary electron image is used in addition to the optical microscope to focus and locate the beam on the sample. The use of such images become indispensable when the beam spots are in the ~1 μm regime.

![Fig. 2.7. Schematic representation of various techniques used in an ion microprobe, when a light ion beam (mostly H and He) of a few MeV energy interact with matter](image-url)
RBS and elastic recoil detection analysis (ERDA) allow depth profiling. The measurement of the concentration of an element as a function of depth from the surface can be carried out with resolution well below 10 nm.

One of the widely employed techniques with an ion microprobe has been the trace elemental analysis by means of particle (mostly proton) induced X-ray emission (PIXE). In this method by analysing the energies of characteristic X-rays emitted from the sample, due to the incidence of MeV ions, identification of the elements are possible with greater accuracy (ppm level). The lack of primary particle bremsstrahlung enables the PIXE measurements to be carried out with very little background, and therefore much higher analytical sensitivities can be achieved compared with the analogous technique using electrons [7]. This process involves high scattering cross section (up to kilobarn), allows the analysis of the samples within a very short time. Thus the features which made PIXE a well-established technique are its ability to measure simultaneously all elements with atomic number $Z>12$, its simplicity, the relative high sensitivity down to the ppm level and the accuracy of a few percent for quantitative results.

For the identification of elements with lower atomic numbers ($Z<12$), nuclear reaction analysis (NRA) is employed. This complements PIXE in the sense that, due to their lower Coulomb barriers, low $Z$ elements can be favourably analyzed. Details of the reactions usable for NRA are given in the Refs [8–10].

Ion beam induced luminescence (IBIL) (based on the collection of infrared, ultraviolet, visible photons) technique with an ion microprobe can be used for the identification of chemical phases, as a check for the presence of certain trace elements, and for the monitoring of ion induced defects in luminescent materials. The capability of this technique is improved considerably when used in conjunction with RBS/PIXE measurements. This technique has emerged to have wide range of applications in optoelectronic devices.

All these techniques discussed above are of high current processes in the sense that their capabilities mainly depend on the detection of a fraction of the scattering/emission yield in the backscattering geometry. The total number of the detected
particles for the analysis depends on the detector solid angles and also on the cross- 
section of those particular processes, which put a minimum limit on the usable beam 
current and hence the minimum beam spot size. These techniques can be termed as 
the classical techniques.

However, in the transmission geometry, techniques like scanning transmission ion 
microscopy (STIM) and ion beam induced charge collection (IBIC) can be performed 
at very low ion currents (femto Amps) and hence termed as low current techniques. In 
these processes, almost all the incident particles or their induced effects are detected, 
thereby allowing the maximum beam focusing. Beam spatial resolutions of about 
~ 100 nm are achieved easily. These low current processes allow useful electrical 
characterization to be carried out with high lateral resolutions. Let us discuss some 
of these processes.

For thin targets, the transmitted particles of a scanned probing beam may be 
recorded along with x-y positions. In this scanning transmission ion microscopy 
(STIM) every particle in the beam is detected. The beam intensity can therefore 
be reduced to about $10^{-16}$ Amp. The energy loss of the ion transmitted through 
thin samples depends on the elemental composition and thickness, i.e., areal density. 
With STIM, the transmitted ion energies and number of ions at each pixel within 
the scanned area are measured using a semiconductor detector located behind the 
sample and used to generate an image showing variations in the areal density. STIM 
was developed primarily as a method of quantitatively imaging the areal density 
distribution of thin biological samples and identifying the features of interest for 
subsequent analysis with PIXE and/or RBS. It has a wide range of applications in 
biological and environmental samples.

When the MeV ion beam is focused on to a solid, it slows down by losing energy, 
creating a cascade of electron-hole pairs on its path. Based on these ideas, the tech­ 
nique of ion beam induced charge collection (IBIC) was developed for the electrical 
characterization of materials with an areal mapping. The effectiveness of this tech­ 
nique depends on the efficiency of the charge collection detectors. It has a wide range of 
applications into diamond and other wide band gap materials, such as GaN or AlN.

Ion channeling process used in conjunction with the above analytical methods
Characterization Techniques

(RBS, PIXE, STIM) for the analysis of crystalline materials is known as channeling contrast microscopy (CCM). Due to very high divergence of the focused ion beam, axial channeling may not be very convenient. However CCM at the planner channeling conditions are more suitable and provide very useful structural information. An alternative method for the CCM has evolved with the development of the beam rocking technique at Oxford [11]. Briefly, the technique involves the use of two sets of opposing scan coils on an ion microprobe system that allows the beam divergence to be scanned instead of the beam positions. Provided the probe forming lens system aberrations are sufficiently small, the beam may be scanned over $\pm 1.5^\circ$ while remaining within a region less than 300 $\mu$m in diameter on the specimen. This allows a very accurate and convenient location of the orientation of planer and axial channeling minima. A summary of these techniques are described in a book [12]. Development of the experimental facilities for the implementation of some of these techniques are described in chapter 3.

2.2 Auger Electron Spectroscopy

2.2.1 Introduction

Auger electron spectroscopy (AES) was developed in the late 1960's, deriving its name from the effect first observed by Pierre Auger, a French physicist, in the mid-1920's. It is a surface sensitive technique utilizing the emission of low energy electrons in the Auger process and is one of the most commonly employed surface analytical techniques for the chemical analysis of the surface layers of a sample. Auger electron spectroscopy can be considered as involving three basic steps:

(a) Atomic ionization (by removal of a core electron)
(b) Electron emission (the Auger process)
(c) Detection and analysis of the emitted Auger electrons

(a) Atomic ionization

The Auger process is initiated by the creation of a core hole. This is typically carried
out by exposing the sample to a beam of high energy electrons (typically having a primary energy in the range 2-10 keV). Such electrons have sufficient energy to ionize all levels of the lighter elements, and higher core levels of the heavier elements.

(b) Auger electron emission

The ionized atom that remains after the removal of a core electron is in a highly excited state and will quickly relax back to a lower energy state by one of the two competing processes (i) X-ray fluorescence, or (ii) Auger emission. Here we will only consider the latter mechanism, an example of which is illustrated schematically in Fig. 2.8(a). In this example, one electron falls from a less tightly bound higher energy level to fill an initial core hole in the K-shell and the energy liberated in this process is simultaneously transferred to a second electron, a fraction of this energy is required to overcome the binding energy of this second electron, and the remaining energy is retained by this emitted Auger electron as kinetic energy (KE). In the Auger process illustrated, the final state is a doubly-ionized atom with core holes in the L\(_1\) and L\(_{2,3}\) shells. A rough estimation of the KE of the Auger electron can be made from the binding energies of the various energy levels involved. In this particular example,

\[ KE = (E_K - E_{L1}) - E_{L23} \]  

(2.21)

The expression for the energy can also be re-written in the form

\[ KE = E_K - (E_{L1} + E_{L23}) \]  

(2.22)

as the KE of the Auger electron is independent of the mechanism of initial core hole formation. Besides incident electrons, core holes can also be created by energetic incident ions and X-rays. It is clear from the above expression that the latter two energy terms could be interchanged without any effect, i.e., it is actually impossible to say which electron fills the initial core hole and which is ejected as an Auger electron, they are indistinguishable. An Auger transition is therefore characterized primarily by (i) the location of the initial hole, and (ii) the location of the final two holes.
Fig. 2.8  (a) Schematic diagram showing the Auger electron spectroscopy (AES) processes, (b) Schematic of the KL₁L₂₃ and LV₁V₂ Auger de-excitation processes in Si. Binding energies are indicated in the left. The energy of Auger electron in the KL₁L₂₃ process is approximately 1591 eV and the LV₁V₂ Auger electron has an energy of approximately 92 eV.
When describing the transition, the initial hole location is given first, followed by the locations of the final two holes in order of decreasing binding energy; e.g., the transition illustrated here is a KL\textsubscript{1}L\textsubscript{2,3} transition.

If we just consider these three electronic levels there are clearly several possible Auger transitions specifically, KL\textsubscript{1}L\textsubscript{1}, KL\textsubscript{1}L\textsubscript{2,3} KL\textsubscript{2,3}L\textsubscript{2,3}. In general, since the initial ionization is non-selective and the initial hole may therefore be in various shells, there will be many possible Auger transitions for a given element—some weak, some strong in intensity. Since the electron-electron interactions are strongest between electrons whose orbitals are closest, the strongest Auger transitions are of the type KLL or LMM. Since Auger electrons carry the KE which is the characteristic of the energy levels of that atom, energy analysis enables to identify the elements present on the surface of the sample. Of all the elements in the periodic table, no two elements have the same set of electron energy-levels. Therefore no two elements have the same set of Auger-electron transition energies. Detailed comparisons of the (i) relative strengths of various Auger lines of the same element, (ii) relative strengths of various Auger lines of different elements and (iii) dependence of Auger peaks with the primary electron energy are given in Ref. [13].

For the lighter elements (Z<20) Auger emission is more probable than X-ray emission for a K-shell initial-state hole, and for Z<15 it is almost an exclusive process. For higher Z, Auger process dominates for initial state holes in other shells. A comparison of both these competing processes is given in Ref. [14–16].

In Fig. 28 (b) Si KL\textsubscript{1}L\textsubscript{23} and L\textsubscript{23}V\textsubscript{1}V\textsubscript{2} (LVV) Auger transitions are indicated with V\textsubscript{1} and V\textsubscript{2} located at positions of maxima in the density of states in the valence band. Typically, Auger electron energies are in the range of 50 to 1500 eV. The mean-free paths of these electrons are in the range of 5 to 50 Angstrom. Hence AES is a surface-sensitive technique, because the Auger electrons emitted from a material must have originated in the near-surface region. Unfortunately these are not the only electrons emitted from a solid, when probed by a few keV electrons. Most of the emitted electrons are inelastically-scattered electrons.
(c) Detection and analysis of the Auger electrons
An AES system consists of an electron gun for excitation of the sample and an energy analyzer system for the detection of the Auger electron peaks in the total secondary electron energy distribution. The experimental arrangement for obtaining Auger electron spectra is shown in Fig. 2.9. We have used a reverse view retractable 4-grid SPECTRALEED optics, supplied by OMICRON Vacuum Physics, Germany for the AES measurements. The 4-grid SPECTRALEED optics is used as a retarding field energy analyzer by feeding a retarding voltage to the middle grids and detecting the passing electrons at the LEED screen. The whole system consists of:

1. Electron gun and SPECTRALEED optics
2. Electron gun power supply (NGE35)
3. Spectrometer control unit (ARC)
4. Matching unit (MUL)
5. Lock-in amplifier

The electron gun is controlled by the power supply (NGE35), giving a point focused beam of energies as high as 3.5 kV with beam current up to 50 µA. The retarding voltage to the grids is supplied by the spectrometer control unit (ARC). This unit generates also the DC supplies for the preamplifier of the matching unit. The modular circuit of the matching unit adds a small ac component to the retarding voltage. An electron current detected at the LEED screen can be compared by the lock-in to this modulation signal thus raising the sensitivity of this analyzer. To compensate for the capacitive cross-talk between the modulated grids and the charge collecting LEED screen, a link between modulator circuit and preamplifier is provided. The analyzer can be run by a personal computer using the Auger Control Software (ACS) provided by OMICRON. ACS controls the Spectrometer control unit, lock-in amplifier and the oscillator. Auger spectroscopy is based upon the measurement of the kinetic energies of the emitted electrons. Each element in a sample being studied will give rise to a characteristic spectrum of peaks at various kinetic energies. Auger electron transitions generally appear as small features superimposed on the large background of secondary electrons. So Auger spectroscopy is usually carried out in the derivative mode to get a better sensitivity of these small signals. The
Fig. 2.9. Schematic diagram showing the experimental arrangements for Auger electron spectroscopy with a retarding field SPECTRALEED Optics (OMICRON, Germany) using a PC. The arrows in the figure indicate cables with plugs rather than signal flow.
differentiation is conveniently done electronically by superimposing a small ac voltage and synchronously detecting in-phase signal from the electron energy analyzer with a lock-in amplifier. The derivative spectrum is extracted directly. In this method a perturbing voltage $\Delta V = k \sin \omega t$ is superimposed on the analyzer voltage so that the collected electron current $I(V)$ is modulated. $I(V+\Delta V)$ can be written in a Taylor expansion

$$I(V + k\sin \omega t) = I_0 + I'k\sin \omega t + \frac{k^2}{2!}\sin^2 \omega t + \cdots$$

where the primes denote differentiation with respect to $V$. Including the higher order terms in the expansion

$$I = I_0 + [kI' + \frac{k^3}{8}I'''\sin \omega t] - \frac{k^2}{4}I'' + \frac{k^4}{48}I''''\cos 2\omega t$$

where $I_0$ contains all non-time dependent terms. Here we assumed $k << V$ so that the terms of order $k^3$ and higher can be neglected. Using a lock-in amplifier, for phase sensitive detection, we select the component of the signal associated with the frequency $\omega$, which is the desired quantity $I'$ or $dN(E)/dE$.

In Fig. 2.10 an elastic backscattered (primary peak) spectra of the incident electron with 1.2 keV energy in the f-mode and its differential are shown. From the peak-to-dip width, the system resolution was found to be 0.66%. Fig. 2.11 shows Si(LVV) Auger electron signal in the differential (2f) mode using an electron beam of 3.0 keV primary energy. Without differentiating, it would have been difficult to extract the small Auger Si(LVV) signal from the high secondary electron background.

2.2.2 Elemental quantification

Auger electron peaks are proportional to elemental concentrations. However, it is seldom possible to measure concentrations from first principles. Several instrumental factors influence Auger peak heights. These include primary beam energy, sample orientation, and the energy resolution and acceptance angle of the analyzer. The chemical states of elements in the sample also influence the process of the elemental
Fig. 2.10. An elastic backscattered (primary peak) spectra of the incident electron with 1.2 keV energy in the f-mode and its differentiation are shown. From the peak-to-dip width the system resolution was found to be 0.66%.

Fig. 2.11. Si(LVV) Auger electron spectra is shown in the differential (2f) mode.
Both peak intensity and peak shape vary, especially as a function of oxidation states. Sample heterogeneity must be considered for the quantitative analysis. The sample should be homogeneous in the lateral directions relative to the primary beam diameter for the measurements to be accurate. In spite of the above considerations, quantitative analysis can be accomplished with varying degrees of accuracy by comparing the peak heights obtained from an unknown specimen with those from pure elemental standards or from compounds of known composition. More detailed expressions for the elemental quantifications may be found in the Ref [13,15–17].

### 2.2.3 Summary

AES is a surface-sensitive spectroscopic technique used for elemental analysis of surfaces, it has unique advantages such as

- High sensitivity (typically ~ 1% monolayer) for all elements except H and He
- Quantitative compositional analysis (up to 0.1 atomic %) of the surface region of specimens, by comparison with standard samples of known composition. Without the standard samples the compositional analysis can be carried out for major elements up to ±10 atomic percents

The typical applications of AES are

- A means of monitoring surface cleanliness of samples. Analysis of surface contamination of materials to investigate its role in such properties as oxidation, corrosion, wear, electrical and optical properties, and catalysis
- In-depth compositional profile via sputtering to evaluate the surface coatings, surface treatment and modifications of various metallurgical processes and thin films and multilayer structures used in microelectronics applications
- Monitoring the various growth modes during deposition of materials
- Scanning Auger Microscopy (SAM). Due to the advent of very small (20 nm) spot size of the probing electron beam, high degrees of spatially-resolved compositional information on heterogeneous samples can be extracted

AES in combination of RBS is quite useful in these depth profile analyses. More details of these applications are described in the Ref [16,17]. Some of these applications
2.3 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is extensively used in fundamental research, technology and bio-medical field by devoted researchers. AFM does not require the sample to be electrically conductive unlike scanning tunneling microscopy (STM). So the AFM is applicable to any type of material – metal, semi-metal, semiconductor, or insulator. The Fig 2.12 shows a schematic diagram of an atomic force microscope. Here the laser beam deflection method is depicted. As the cantilever bends, the path of the laser beam directed onto it changes (it is reflected at different angle) and this deviation is detected by the photodiode. The cantilever bends because of force between the tip and the sample. This force, \( F \), can be calculated using the equation

\[
F = ks
\]

where \( s \) is the distance by which the cantilever bends and \( k \) is its spring constant.

There are mainly three scanning modes used in AFM. These are the following...
(i) **Contact or repulsion mode**: In this mode, the tip touches the sample surface where the repulsion forces dominate. The force maintained during the scanning is usually $1 - 10 \text{nN}$ depending on the circumstances. This scanning force is necessary to trace the topography of the sample surface. This mode is applied on hard crystalline surfaces with atomic or molecular resolution, but it is not suitable for biological samples where this force is still strong enough to cause their deformations.

(ii) **Non-contact or attractive mode**: In this mode, the tip is at a distance from the sample surface where the attractive Van der Waals forces dominate. The major advantage of the non-contact mode AFM is its truly non-invasive character. This mode is suitable for biological samples or soft samples.

(iii) **Tapping mode**: This mode is a compromise between the contact and non-contact modes— the cantilever is made to oscillate so the tip is very close to the sample for a brief time and then far away for a brief time. The compromise between the two mode allows one to scan soft adsorbate on a substrate with better resolution than in the non-contact mode but with less interaction (and, consequently, less modification of the sample) between the tip and adsorbate as in the non-contact mode.

AFM has achieved atomic resolution while imaging the surface of solid materials. On soft materials on a solid surface AFM can resolve features of few nm or less.

Sometimes the AFM image of a given structure depends on the scan direction which is not expected [18]. When the cantilever is pushed relatively to the surface, the defects are detected as hollows, whereas when the cantilever is pulled, these defects are visualized as hillocks. The scan direction-dependent image indicates the presence of friction forces acting on the tip. By pushing the cantilever into the defect region, the tip slows down and the end of the lever with the tip bends downwards, simulating a hole in the surface. In the opposite scan direction, the end of the lever is forced away from the surface as one would expect from a hill. Due to the fact that the direction of the cantilever in the AFM is measured with a laser system, it is not possible to distinguish between the friction forces and the real topography. Only in combination with a lateral-force microscopy (LFM) it is possible to clarify this problem.

In this thesis, some AFM results have been presented in chapter 4, 5 and 6. Details of AFM analysis may be found in Ref [19, 20].
Bibliography


