Chapter 3

Experimental techniques

3.1 Ion scattering techniques

3.1.1 Rutherford backscattering spectrometry (RBS)

Introduction

Rutherford backscattering spectrometry (RBS) is based on collisions between atomic nuclei and derives its name from Lord Ernest Rutherford, who in 1911 was the first to present the concept of atoms having nuclei. It involves measuring the number and energy of ions in a beam which backscatter after colliding with atoms in a sample at which the beam has been targeted. With this information, it is possible to determine atomic mass and elemental concentrations versus depth below the surface.

RBS has the following characteristics:

• (i) Multi-element depth concentration profiles
• (ii) Fast, non-destructive analysis (no sample preparation or sputtering required)
• (iii) Matrix independent (unaffected by chemical bonding states)
• (iv) Quantitative without standards
• (v) High precision (typically ±3%)
Experimental techniques

• (vi) High sensitivity
• (vii) Depth range (typically 0 - 1mm)
• (viii) Depth resolution ~25 \( \text{Å} \) (typically near surface)

When a sample is bombarded with a beam of high energy particles, the interaction between the projectile and target atom, can be modeled accurately as an elastic collision using classical physics. 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, \( K \).
• (b) The likelihood that the scattering will occur, (i.e., the probability of scattering) depends on the scattering cross section, \( \sigma \).
• (c) The average energy loss \( \frac{dE}{dx} \) 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 target. This is known as straggling.

The kinematic factor leads to the ability of mass analysis, the scattering cross section provides RBS with a quantitative analysis 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, \( K \):

When a projectile of mass \( M_1 \) and energy \( E_0 \) gets scattered elastically at an angle \( \theta \) with a stationary particle of mass \( M_2 \), energy will be transferred from the moving to the stationary particle. After the scattering the energy of the projectile becomes \( E_1 \).

(See Fig. 3.1.)

The assumption that the interaction between the two atoms is properly described by a simple elastic collision of two isolated particles rests on two conditions:
Fig. 3.1. Schematic diagram representing the elastic collision between the projectile and target.

- (i) The projectile energy $E_0$ must be larger than the binding energy of the atoms in the target. Chemical bonds are of the order of 10 eV, so that $E_0$ should be very much larger than that.

- (ii) Nuclear reactions and resonances must be absent. This imposes an upper limit to the projectile energy. Nuclear processes depend on the specific choice of projectile and target atoms, so that the upper limit of $E_0$ varies depending on circumstances.

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

$$K_{M_2} = \frac{E_1}{E_0} \quad (3.1)$$

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

$$K_{M_2} = \left[ \frac{(M_2^2 - M_1^2 \sin^2 \theta)^{1/2} + M_1 \cos \theta}{M_2 + M_1} \right]^2 \quad (3.2)$$

$K$ 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 ($E_1$) of the scattered particles at an angle $\theta$, the unknown mass $M_2$ can be determined.

If a target contains two masses that differ by a small amount $\Delta M_2$ the difference $\Delta E$ in the energy $E$ of the projectile after the collision is given by
\[ \Delta E = E_0 \left( \frac{dK}{dM_2} \right) \Delta M_2 \]  
(3.3)

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

\[ \delta M_2 = \frac{\delta E}{E_0} \frac{(M_2 + M_1)^3}{4M_1(M_2 - M_1)} \]  
(3.4)

To obtain good mass resolution, it is therefore desirable that the coefficient of \( \Delta M_2 \) be as large as possible. To accomplish this, one can

- (i) Increase the incident energy \( E_0 \).

- (ii) Use a projectile of large mass \( M_1 \). (Note: \( M_2 \) masses smaller than \( M_1 \) will not produce any backscattering signal).

- (iii) Measure at scattering angles of approximately 180° (small \( \theta \)).

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

Elemental analysis 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\(^3\), \( N_s = Nt \). 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

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

In the backscattering spectrometry, particles that are scattered at an angle \( \theta \) are detected by a solid state detector that subtends a solid angle that is small (typically less than \( 10^{-2} \) Sr). Thus the number of particles \( Y \), detected by a detector of 100% efficiency and subtending a solid angle \( d\Omega \), is given by

\[ Y = QN_s \frac{d\sigma}{d\Omega} d\Omega \]  
(3.5)
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} (3.6)

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} (3.7)

In an RBS experiment, the number of incident particles $Q$, 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].

$$\frac{d\sigma}{d\Omega} = \left[ \frac{Z_1 Z_2 e^2}{4E} \right]^2 \frac{4}{\sin^4 \theta} \left\{ 1 - \frac{(M_1/M_2)\sin \theta)^2}{1 - \frac{(M_1/M_2)\sin \theta)^2}{1/2} + \cos \theta \right\}^2$$  \hspace{1cm} (3.8)

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. For $M_1 \ll M_2$, this expression for the cross-section can be rewritten as

$$\frac{d\sigma}{d\Omega} = \left[ \frac{Z_1 Z_2 e^2}{4E} \right]^2 \frac{1}{\sin^4 (\theta/2)}$$  \hspace{1cm} (3.9)

The magnitude of the Rutherford cross-section is dominated by the term $(Z_1 Z_2 e^2 / 4E)^2$.

**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 particles with nuclear charges i.e., between a projectile $Z_1$ and a target $Z_2$. This assumes that the particle is energetic enough to penetrate well inside the orbitals of the atomic electrons. Thus, scattering is due to the repulsion between 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, \( d = (Z_1Z_2e^2)/E \)) should be smaller than the K shell electron radius, which can be estimated from the Bohr radius \((a_0/Z_2, a_0 = 0.53 \text{ Å})\). Thus, the distance of closest approach, \( d \) sets the lower limit on the energy of the analysis beam and requires that

\[
E > \frac{Z_1Z_2^2e^2}{a_0}
\]  

(3.10)

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.(3.8)], 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, i.e., 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.

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

An energetic particle passing through a solid loses energy through interaction with electrons and nuclei of the target atoms. For the light particles and the energy ranges 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 it depends on the energy, $E_x$, of the projectile at a depth $x$. $E_x$ is given by

$$E_x = E_0 - \int_0^x (dE/dx) dx \quad (3.11)$$

The stopping cross section $\epsilon$ is given by

$$\epsilon = \frac{1}{N} \frac{dE}{dx} \quad (3.12)$$

$\epsilon$ or $dE/dx$ is a function of projectile energy and their values can be obtained from Ref. [2]. $dE/dx$ for compound targets can also be easily evaluated by using the linear additivity of stopping cross-sections (Bragg’s rule). 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:

$$\Delta x = \frac{\Delta E}{[S_0]} \quad (3.13)$$

where

$$[S_0] = \left[ K \left( \frac{dE}{dx} \right)_{E_0} + \frac{1}{\cos \theta} \left( \frac{dE}{dx} \right)_{KE_0} \right] \quad (3.14)$$

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 while moving 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
Experimental techniques

Introduction

When a well collimated beam of fast ions enters a single crystal along a low index crystal axis, the penetrating (channeled) ions experience strong steering by the (repulsive) potentials of the atom rows along this axis (Fig. 3.3). Channeled particles cannot get close enough to the atomic nucleus to undergo large angle Rutherford scattering and 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 of thickness \(t\), Bohr straggling has a variance

\[
\Omega_B^2 = 4\pi(Z_1e^2)^2NZ^2t
\]  

(3.15)

Using the above concepts (a), (b), (c) and (d), a schematic Rutherford backscattering spectrum is shown in Fig. 3.2.

3.1.2 Ion channeling

Introduction

When a well collimated beam of fast ions incident on MeV implanted Sb in Si(100) single crystal.
Experimental techniques

40

Fig. 3.3. Schematic diagram showing trajectories of particles undergoing scattering at the surface and channeling within the crystal. The shadow cone, which defines a region below the surface atom on each atomic string, is shown by dashed line. The incident ions, cannot enter this shadow cone region. Hence the backscattering is drastically reduced — in many cases by a factor of about 100 [3]. The channeling phenomenon and RBS spectra under channeling condition are schematically shown in Figures 3.3 and 3.4 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. 3.3, 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 $\psi_{1/2}$,

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

(3.16)

where, for axial channeling

$$\psi = 0.307\left[\frac{Z_1Z_2}{Ed}\right]^{1/2} \text{ (degrees)}$$

(3.17)

and $F_{RS}$ is the square root of the continuum Moliere potential, evaluated at $\psi$. $E$ is expressed in MeV and $d$ 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...
Fig. 3.4. A typical RBS/channeling spectra with He$^+$ ion beam of 2.5 MeV energy on Si(100). Light ion impurities like C or O present in small (sub-monolayer) amount on the substrate can be easily detected under channeling condition.

axis, $Z_2$ is replaced by the average $Z_2$, $\psi = 1.2u_i/a$, where $a$ is the Thomas-Fermi screening radius and $u_i$ 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 $\chi_{\text{min}}$ and is called the *minimum yield*. The $\chi_{\text{min}}$ is a measure of the crystalline quality of the sample and is given by

$$\chi_{\text{min}} = N d \pi (2u_i^2 + a^2)$$

where $N$ is the number of atoms/A$^2$. For a good crystal at room temperature $\chi_{\text{min}}$ 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. The scattering from atoms at larger depths are drastically reduced. This improves the ion scattering sensitivity to light impurities on the surface [3]. For example, a small (sub monolayer) amount of C or O impurity on a Si surface can be detected under the channeling condition as is evident from Fig. 3.4.

**Applications**

RBS 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, and of orientation of epilayers, study of surface structures and lattice location of impurities are common. Some of these uses have been exemplified in subsequent chapters.

### 3.1.3 Experimental Set-up

The ion scattering experiments for this thesis have been done using the 3 MV tandem Pelletron Accelerator (9SDH2, NEC, USA) facility at our institute which has been schematically shown in Fig. 3.5. The machine is equipped with three ion sources - one RF ion source (Alphatross) used for providing He, H or other inert gas ions and two Cs sputter ion sources (SNICS) (single and multi-cathode), for almost all
elements in the periodic table except inert gas ions. 15 keV negative ions focused by an Einzel lens are accelerated to an initial energy of about 60 keV before entering the machine through a 45° injector magnet. On the high energy side there is a 60° analyzing magnet for selecting the desired ions with right energy. A switching magnet finally puts the ions into the desired beamlines. There are six beamlines developed with the accelerator. The first one (45°) is a general purpose beamline for carrying out RBS/channeling, PIXE, NRA experiments. The second one developed in +15° beamline is for carrying out $^{14}$C AMS measurements. The zero degree beamline is used for low energy atomic and nuclear physics experiments. The $-15^\circ$ beamline is dedicated for ion implantation. At the $-30^\circ$ beamline, facilities for carrying out surface physics experiments have been developed. The micro-beam facility has been developed at the $-45^\circ$ beamline.

**RBS/Channeling**

For the RBS/channeling experiments He ions of 1.0 — 2.5 MeV energy and beam currents of 1—15 nA have been used. A multipurpose scattering chamber (schematically shown in the Fig. 3.6 (A)), equipped with a sample goniometer with five degrees of freedom ($x,y,z,\theta,\phi$), has been used to carry out RBS/channeling experiments. On the goniometer the $\theta$ rotation has a precision of 0.1° and the $\phi$ rotation has a precision of 0.3°. The vacuum obtained inside the experimental chamber is in the mid $10^{-6}$ Torr range. This chamber is coupled to one of the beam lines of the accelerator (45°). The beam is collimated by a pair of collimators of dia 1.5 mm separated by a distance of about 0.5 meter. This reduces the divergence of the beam which is essential for the channeling measurements.

A schematic diagram of the RBS/channeling experimental set-up is shown in Fig. 3.6 (B). A surface barrier detector is used to detect the backscattered particles from the target over a scattering angle range of $0^\circ$ — 170°. The solid angle subtended by the detector is around 1 $msr$. It operates by the collection of the electron-hole pairs created by the energetic incident ion in the depletion region of the reverse-biased Schottky barrier diode. The electron-hole pairs produce a current (signal) proportional to the energy of the charged particle. The detector signal is first amplified by a
**Experimental techniques**

3. Nal DETECTOR
4. TARGET HOLDER
5. FARADAY CUP
6. SURFACE BARRIER DETECTOR (SBD)

A - The scattering chamber

![Schematic diagram of the scattering chamber](image1)

B - RBS/C experimental set-up

![Block diagram of a typical backscattering experimental set-up](image2)

**Fig. 3.6.** (A) Schematic diagram of the scattering chamber. (B) Block diagram of a typical backscattering experimental set-up.

Pre-amplifier and then shaped and amplified by a spectroscopy amplifier (Ortec 572). This signal is given to a 13-bit ADC which is directly coupled to a multi channel analyzer (Canberra-88 MCA). The pulse height analysis is done in the MCA and finally the data is transferred to a computer connected to the MCA. For RBS analysis the total number of incident ions on the sample is determined by integrating the current on the sample around which there is an electron suppressor.

**Ion implantation/ irradiation:**

For preparation of the samples, implantation of Sb ions (beam energy of 1.5 MeV, beam current $\sim 10 - 15 nA$) and irradiation with C ions (beam energy of 8.0 MeV, current $\sim 30 - 35 nA$) has been done. The implantation beam line is equipped with a raster scanner, operating at 517 Hz. and 64 Hz. in the horizontal and vertical directions, respectively. In order to get rid of neutrals it also has a neutral beam trap (deflector) with a 3° bend in the horizontal plane. The applied voltage to the raster scanner can be large enough to obtain a uniform implanted region. Different masks
can be incorporated to get a chosen implanted area. The implantation chamber is equipped with a turbomolecular pump. The ultimate pressure achieved in the chamber is $\sim 1 \times 10^{-7}$ mbar. The implantation chamber has two view port and one for providing electrical connections to the suppressor assembly and for the measurement of beam current on the target. The target holder has two degrees of freedom (z-position and tilt angle) and multiple samples can be loaded at a time.

3.2 Raman spectroscopy

3.2.1 Introduction

Raman spectroscopy is a versatile, convenient, non-destructive characterization tool widely used in the field of semiconductors. Since it probes lattice vibrations, which are sensitive to internal and external perturbations, it can be used to study the composition, phase, crystallinity, crystal orientation, and in some cases doping, in semiconductors. An important aspect of Raman spectroscopy is its ability to determine the changes in the vibrational frequencies induced by the microstructures and/or by the strain in the lattice. Thus it is a very useful tool for studying structural modifications in semiconductors due to ion implantation. Micro-Raman spectroscopy, where the light of the exciting laser is focused on the sample through a microscope, is especially very useful for microelectronics devices with small dimensions as it allows investigation with micron spatial resolution.

3.2.2 Principle

Raman effect arises from an inelastic scattering of a photon in a material with the creation or annihilation of a phonon.

Here we shall briefly discuss the theory [4, 5, 6, 7] involved in explaining Raman spectra from lower dimensional systems.

Let us consider the wave function of a phonon of wave vector $q_0$ in an infinite crystal:

$$\Phi(q_0, r) = u(q_0, r)e^{i q_0 \cdot r}$$  \hfill (3.19)
where \( u(q_0, r) \) has the periodicity of the lattice. Now, we confine this phonon to a sphere of diameter \( L \). The phonon confinement changes the phonon wave function to

\[
\Psi(q_0, r) = W(r, L)\Phi(q_0, r) = \Psi'(q_0, r)u(q_0, r)
\]  \hspace{1cm} (3.20)

where \( W(r, L) \) is the phonon weighting function such that

\[
|\Psi(q_0, r)|^2 = |W(r, L)|^2
\]  \hspace{1cm} (3.21)

It is clear that \( W(r, L) \) describes the phonon confinement, although many functions can accomplish it. To calculate the Raman spectra, we first expand \( \Psi'(q_0, r) \) in a Fourier series:

\[
\Psi'(q_0, r) = \int C(q_0, q)e^{iqr}d^3q
\]  \hspace{1cm} (3.22)

with Fourier coefficients \( C(q_0, q) \) obtained from

\[
C(q_0, q) = \frac{1}{(2\pi)^3} \int \Psi'(q_0, r)e^{-iqr}d^3r
\]  \hspace{1cm} (3.23)

The nanocrystal phonon wave function is a superposition of eigenfunctions with \( q \) vectors centered at \( q_0 \). Thus, the first-order Raman spectrum \( I(\omega) \) is given by

\[
I(\omega) = \int \frac{|C(0, q)|^2d^3q}{[\omega - \omega(q)]^2 + (\Gamma_0/2)^2}
\]  \hspace{1cm} (3.24)

where \( \omega(q) \) is the phonon dispersion curve, \( \Gamma_0 \) is the natural line width of the curve, \( q_0 = 0 \), which is appropriate for first-order Raman scattering, and the integration must be performed over the entire Brillouin zone.

In order to carry out numerical calculations one has to write suitable functions of phonon confinement \( W(r, L) \) and phonon dispersion \( \omega(q) \).

For the case of semiconductors such as Si, Ge, and for spherical nanocrystallites, Campbell and Fauchet [8] have investigated the influence of the choice of \( W(r, L) \) on the quality of the fit between theory and experiments. They considered three types of functions, given below together with their Fourier coefficients:

\[
W(r, L) = \frac{\sin(2\pi r/L)}{2\pi r/L}, \quad |C(0, q)|^2 \approx \frac{\sin^2(qL/2)}{(4\pi^2 - q^2L^2)^2}
\]  \hspace{1cm} (3.25)
Fig. 3.7. (a) Dispersion curves of silicon in the direction of (100) axis. (b) Confinement of phonon due to finite size $L$ of the crystallite of Si.

$$W(r,L) = \exp(-4\pi^2 r^2/L^2), \quad |C(0,\mathbf{q})|^2 \approx \frac{1}{(16\pi^4 - q^2 L^2)^4} \quad (3.26)$$

$$W(r,L) = \exp(-8\pi^2 r^2/L^2), \quad |C(0,\mathbf{q})|^2 \approx \exp(-q^2 L^2/16\pi^2) \quad (3.27)$$

The first confinement function, Eqn. 3.26, was chosen by analogy with the ground state of an electron confined to a hard sphere. The amplitude of the phonon is zero at the boundary. The second confinement function, Eqn. 3.27, which can be written as $\exp(-\alpha r)$, was chosen by analogy with a wave in a lossy medium. The third confinement function, Eqn. 3.28, which can be written as $\exp(-\alpha r^2/L^2)$, was chosen in anticipation of the size distribution and in agreement with Nemanich et al. [6] and Richter et al. [7]. With this equation, the phonon is confined very strongly to the nanocrystal, since $W(r = L/2, L)$ is very small.

The phonon dispersion relation $\omega(\mathbf{q})$ is taken as:

$$\omega(\mathbf{q}) = \omega_p - A\left(\frac{\mathbf{q}}{q_0}\right)^2 \quad (3.28)$$

where $q_0 = \frac{2\pi}{a_0}$, $a_0$ is the lattice constant, $\omega_p$ corresponds to the phonon energy at $q = 0$ and $A$ is a constant. According to Richter [4], the final result is not critically
dependent on the form of the dispersion relation, as long as \( \omega(q) \) is parabolic near the center of the Brillouin zone. The value of the constant \( A \) can be determined by fitting the available neutron data of phonon dispersion for different crystals to Eqn. 3.29.

Let us discuss the results for nanocrystalline-Si (nc-Si) and bulk crystalline-Si (c-Si). Since the agreement with experimental results is good only for Gaussian confinement [7], we use Eqn. 3.28 as the confinement function. Eqn. 3.25 can now be rewritten as

\[
I(\omega) = \int_0^{2\pi/a_0} \frac{\exp\left(-q^2L^2/16\pi^2\right)4\pi q^2 dq}{(\omega - \omega(q))^2 + (\Gamma_0/2)^2}
\]  (3.29)

For bulk silicon single crystal, the lattice constant \( a_0 = 0.54 \) nm. To calculate the line shape, we have taken the natural line width \( \Gamma_0 = 3.0 \) cm\(^{-1} \), and the phonon energy (at \( q = 0 \)) \( \omega_p = 521.0 \) cm\(^{-1} \) [9] (discussed later in Chapter 6). The value of the constant \( A \) has been chosen as 120 [10]. These parameters reproduce the dispersion relation for the longitudinal optical (LO) phonons along (100) direction in Si well. Dispersion curves for Si along the (100) direction have been shown in Fig. 3.7(a).

Three convenient parameters are used to describe the Raman line shape quantitatively: \( \Delta \omega \), the shift in central Si-peak frequency w.r.t. the peak of bulk crystalline Si; \( \Gamma \), the full width at half maximum of c-Si (FWHM); and \( \Gamma_a/\Gamma_b \), the ratio of the half width at half maximum (HWHM) on the low energy side to the HWHM on the high energy side. These quantities are illustrated in Fig. 3.8.

The evolution of the Raman line using Eqn. 3.30, as a function of decreasing size (L) for spherical Si nanocrystallites is shown in Fig. 3.8. From this figure, it is clear that the size affects the Raman spectra corresponding to bulk crystalline Si and makes the curve asymmetric (\( \Gamma_a/\Gamma_b \neq 1 \)) and shifts (\( \Delta \omega \)) the peak towards lower or higher energy side depending on the nature of the dispersion curve. Hence from a set of experimental Raman data, the \( \Gamma_a/\Gamma_b \) value provides the degree of crystallinity of the sample. If there is a stress in the sample, it may alter \( \Delta \omega \) [11, 12]. From the sign (±) and the value of \( \Delta \omega \), it is possible to measure the type and magnitude of the stress. In case of shift to lower energy (red shift), the stress is tensile and for shift to higher energy (blue shift), the strain is compressive. So the shift (\( \Delta \omega \)) may be because of two effects: grain size and stress. The only difference between these two
Theoretical Raman spectra for bulk crystalline Si (c-Si) and nanocrystalline Si (nc-Si) where $\Delta \omega$, $\Gamma$, $\Gamma_a$ and $\Gamma_b$ are shown. The evolution of Raman line-shape, as a function of decreasing coherence length, $L$ is shown. Note the apparent downward shift in peak position which accompanies the skewing of the Raman peak as $L$ decreases. Line shapes have been obtained using equation 3.30.

Effects is — grain size effect make the Raman spectra asymmetric but the stress effect leaves the curve symmetric. In addition, Campbell and Fauchet have suggested that the two phonon Raman spectrum could be used in conjunction with the one phonon Raman spectrum to distinguish the effect of stress from that of crystal size because stress and crystal size affect these two types of processes differently. Among the other factors, a wide size and strain distribution and surface effects play an important role to alter the $\Gamma$, $\Gamma_a/\Gamma_b$ and $\Delta \omega$.

### 3.2.3 Experimental set-up

In the present study, Raman spectroscopy has been performed both in the 180° backscattering and 90° right-angle scattering geometries. Raman measurements in the right-angled geometry allowed us to skim the probing laser beam incidence at varying angles to the sample surface, in order to study the structural profiles in the near-surface layer of ion-implanted Si. The schematic diagram in Fig. 3.9 shows...
Experimental techniques

Fig. 3.9. Schematic block diagram of the Raman setup with 180° scattering configuration

the Raman set-up with 180° scattering configuration used for the observation of the Raman spectra presented in this thesis.

The experimental set-up for Raman measurements mainly consists of:

- **Excitation source**: Spectra Physics 5 Watt (all line) Ar⁺ laser.

- **Spectrometer**: Spex 1877 E Triplemate with two scattering configurations (90° and 180° geometries).

- **Detection system**: Charged coupled device (CCD) and photo-multiplier detector.

3.3 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is an extensively used technique in the fields of fundamental research, technology and bio-medicine. It does not require the sample to be electrically conductive unlike scanning tunneling microscopy (STM). So the
AFM is applicable to any type of material - insulators and semiconductors as well as electrical conductors. Because its probe is very small and sharp, an AFM can be used to acquire high-resolution real-space topographic images of various sample surfaces. Hence it is a very effective technique to monitor/characterize the morphology and topological changes of ion implanted surfaces.

The atomic force microscope (AFM) probes the surface of a sample with a sharp tip, a couple of microns long and often less than 100Å in diameter. The tip is located at the free end of a cantilever that is 100 to 200 μm long. Forces between the tip and the sample surface cause the cantilever to bend, or deflect. A detector measures the cantilever deflection as the tip is scanned over the sample, or the sample is scanned under the tip. The measured cantilever deflections allow a computer to generate a map of surface topography. A schematic diagram of atomic force microscopy (AFM) has been shown in Fig. 3.10.

AFMs can be used to study insulators and semiconductors as well as electrical conductors. Several forces typically contribute to the deflection of an AFM cantilever. The force most commonly associated with atomic force microscopy is an interatomic force called the van der Waals force. The dependence of the van der Waals force upon the distance between the tip and the sample is shown in Fig. 3.11. Two distance
Fig. 3.11. Interatomic force vs. distance

regimes are labeled on Fig. 3.11: a) the contact regime; and b) the non-contact regime. In the contact regime, the cantilever is held less than a few Å from the sample surface, and the interatomic force between the cantilever and the sample is repulsive. In the non-contact regime, the cantilever is held on the order of tens to hundreds of angstroms from the sample surface, and the interatomic force between the cantilever and sample is attractive (largely a result of the long-range van der Waals interactions).

There are mainly three scanning modes used in AFM. These are the following:

(i) **Contact or repulsive mode**:

In contact-AFM mode, also known as repulsive mode, an AFM tip makes soft 'physical contact' with the sample. The tip is attached to the end of a cantilever with a low spring constant, lower than the effective spring constant holding the atoms of the sample together. As the scanner gently traces the tip across the sample (or the sample under the tip), the contact force causes the cantilever to bend to accommodate changes in topography. This mode is applied on hard crystalline surface 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**:

Non-contact AFM is one of several vibrating cantilever techniques in which an
AFM cantilever is vibrated near the surface of a sample. The spacing between the tip and the sample is on the order of tens to hundreds of angstroms. 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 or Intermittent-contact atomic force microscopy:

In intermittent-contact atomic force microscopy, the vibrating cantilever tip is brought closer to the sample so that at the bottom of its travel it just barely hits, or ‘taps,’ the sample. 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 modes 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.

In this thesis, modification of MeV implanted surfaces have been investigated using contact-mode of AFM and the results are presented in Chapter 7.
Bibliography


