Chapter 1

Introduction

1.1 General Background

A solid bombarded with energetic ions is driven out of its state of thermal equilibrium. Energy is continuously transferred into the solid through two basic interactions - elastic (nuclear) collisions of the ions with its atoms, and their inelastic collisions with its electrons. The system, thus forced into a state of non-equilibrium, relaxes through a hierarchy of processes involving different time scales. The excited electrons equilibrate around the path of the ion through electron-electron (e-e) interactions within $\sim 10^{-14}$ sec. Electron-phonon (e-p) interactions transfer this energy to the target atoms in $10^{-12}$ sec (inverse of Debye frequency). The elastic collisions enforce atomic transport and structural disorder in the target lattice [1-3].

The displaced target atoms (and vacancies) move through the solid, and rearrange in time scales proportional to their diffusion coefficient under prevailing conditions. If we are primarily concerned with the structure of the crystal lattice, two main processes need to be considered - the atomic transport and resulting structural damage, and the dynamic annealing (relaxation).

The response of solids to low energy ions can be described completely in terms of atomic displacements through elastic collisions. Such collisions produce a continuous network of displaced atoms (Displacement Cascade) [1, 4]. In some cases, overlap of single ion cascades drive the system into an amorphous phase and in others it leads to the formation of defect complexes [1, 5-12]. Under specific irradiation conditions, the reorganization of defects in the form of periodic defect patterns (defect walls and void lattices) has also been observed [12-14]. In this energy range, the role of electronic interactions in defect production, if any, is secondary. At higher energies on the other hand, nuclear collisions are rare and a large amount of energy dissipates into the solid through electronic excitations. In view of a host of relaxation processes competing within a time scale of $10^{-12}$ sec, the emergence of structural disorder in a solid subjected to such large excitations is extremely difficult to analyse theoretically. This
energy is initially stored in the electric field caused by the ionisation of target atoms and also as the kinetic energy of the scattered electrons, and eventually gets transferred to the lattice through ionisation and thermal spikes respectively. The deposited energy density depends in a complex way on the relative time scales of these processes. Once the energy is transferred to the lattice, the resulting structural disorder depends upon its thermodynamic and elastic behaviour. In some cases it has been observed that electronic interactions play a central role in atomic transport if the deposited energy density exceeds a certain threshold [15-24]. Below the threshold, it may cause significant radiation annealing [25-29].

The atomic transport in crystalline solids may eventually lead to structural damage which would depend on the properties of the given solid, and also on the prevalent irradiation environment. Of particular significance, however, is its critical dependence on the single ion disorder. By single ion disorder we mean the nature of lattice damage surrounding the trajectory of a single ion.

In order to clarify the above ideas, the process of energy transfer through ion-solid interactions is reviewed in the following sections. Although the discussion of the resulting damage and its thermal kinetics has deliberately been focused on semiconductors, it is fairly general and applicable to most solids.

### 1.2 Ion Irradiation and Defects in Solids

#### 1.2.1 Ion-Solid Interactions

There are two distinct ways an ion interacts with a solid—(a) elastic scattering with target atoms and (b) inelastic scattering with the electrons (electronic excitations). Of primary interest is the quantity Energy Loss, $S$, defined as the amount of energy deposited per unit depth into the target, i.e., $S = dE/dz$. The total energy loss can be divided into two parts, the nuclear (elastic) energy loss $S_n$ and the electronic energy loss $S_e$, i.e.

$$S = S_n + S_e$$  \hspace{1cm} (1.1)

### Elastic Scattering

Elastic scattering refers to the binary collisions between a projectile ion and individual target atoms. To estimate the loss of projectile energy in such collisions, consider a collision $(E, T)$ between a projectile $(M_1, Z_1)$ of energy $E$ and a stationary target atom $(M_2, Z_2)$, $M$ and $Z$ represent respectively the mass and the atomic number of an atom. The amount of energy $T$,
transferred in the process is given by

\[ T = \frac{4M_1 M_2}{(M_1 + M_2)^2} \cos^2 \phi \, E. \quad (1.2) \]

Here \( \phi \) is the angle through which the target atom is deflected. If a 100 KeV Ag atom collides head on with the Si atom, \( T = 80 \) KeV. Even at \( \phi = 60^\circ \), \( T = 20 \) KeV. Though such large energy transfers are relatively rare, it is evident that huge energy can be lost in such binary collisions.

Probability with which collision \((E, T)\) occurs is defined through the scattering cross section of the target atom. This represents the effective area around the atom through which if the atom passes, collision \((E, T)\) occurs. In the classical hard sphere approximation the scattering cross section is represented by a circle of radius \( r_0 \) around the atom in which projectile of energy \( E \) can not penetrate. \( r_0 \) represents the distance of closest approach and thus the scattering cross section equals \( \pi r_0^2 \). The distance of closest approach depends upon the projectile energy and the form of scattering potential. For illustration, consider a pure coulombic potential

\[ V(r) = \frac{Z_1 Z_2 e^2}{r}. \quad (1.3) \]

At the distance of closest approach, \( V(r_0) = E \). Therefore

\[ \pi r_0^2 = KE^{-2}, \quad (1.4) \]

i.e., the collision probability decreases as the square of the projectile energy. Eq.(1.2) and Eq.(1.4) combined together show that the elastic energy loss is inversely proportional to \( E \). For better quantitative estimates, the hard sphere cross-section can be replaced with more realistic forms. For the collision \((E,T)\), Lindahard et.al. [30] derived the following form for the differential scattering cross section

\[ d\sigma_n(t) = \left( \frac{\pi a^2}{2} \right) \left( f(t^{1/2}) \, dt / t^{3/2} \right) \quad (1.5) \]

where

\[ a = 0.8853 \, a_0 \left( Z_1^{2/3} + Z_2^{2/3} \right)^{-1/2}, \]

\[ t = T E \left( \frac{M_2}{4M_1} \right) \left( a/Z_1 Z_2 e^2 \right)^2 \]

and \( a_0 = \) Bohr radius, 0.529 Å. The scattering function \( f(t^{1/2}) \) depends upon the choice of interatomic potential. The potential function

\[ f(t^{1/2}) = \frac{\lambda t^{1/2-m}}{[1 + (2\lambda t^{1-m})]^{1/2}} \quad (1.6) \]
derived by Winterbon et al. [30] generally gives a good fit to the experimental data. The constants $\lambda = 1.309$, $m = 0.333$, and $q = 0.667$ are a fit to an interatomic potential based upon Thomas-Fermi model of an atom. Eq.(1.5) shows, for a given target and projectile, that the scattering cross section decreases as the product $ET$ increases. This may also be interpreted as if the energy transferred in a given cross section decreases as the projectile energy increases. The energy loss of the projectile in the elastic collisions, as it travels a unit distance inside the solid, $\int Td\sigma$, thus becomes insignificant at high projectile energies. At low projectile energy, though the cross section is very large, maximum energy loss cannot exceed $E$. The elastic energy loss, $S_n$, defined as the loss of energy in elastic collisions per unit depth inside the target, thus passes through a maximum as a function of the projectile energy. Close to its maximum, $S_n$ may be treated as energy independent. In this region Feldman and Mayer [31] derived an analytical expression for the energetic particles undergoing screened Coulomb collision with a $1/r^2$ potential, as

$$\frac{dE}{dx}_n = N(\pi^2/2)e^2a_s^2 Z_1Z_2M_1 \approx \frac{5Z_1Z_2M_1}{M_1 + M_2} \text{ eV/nm}$$

with the screening radius $a_s = 1.4 \times 10^{-2}$ nm. $e^2 = 1.44 \text{ eV-nm}$ and the atomic density $N = 5 \times 10^{22}$ atoms/cm$^3$.

Characteristic values of energy, $E_{\text{max}}$, which correspond to maxima in the elastic loss curve (see Eq. 1.7) and the corresponding energy loss. $S_{n(\text{max})}$ for some ions incident on Si and GaAs targets, are listed in Table 1.1. It may be seen that $E_{\text{max}}$ shifts towards higher values for the heavier ions and the targets.

<table>
<thead>
<tr>
<th>Target</th>
<th>Ion</th>
<th>$E_{\text{max}}$ (KeV)</th>
<th>$S_{n(\text{max})}$ (MeV/µm)</th>
<th>$E_{eq}$ (KeV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>B</td>
<td>3</td>
<td>.10</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>17</td>
<td>.55</td>
<td>140</td>
</tr>
<tr>
<td></td>
<td>As</td>
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<td>1.73</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>Sb</td>
<td>180</td>
<td>2.86</td>
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<tr>
<td></td>
<td>Bi</td>
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<td>6000</td>
</tr>
<tr>
<td>GaAs</td>
<td>B</td>
<td>7</td>
<td>.11</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>P</td>
<td>29</td>
<td>.70</td>
<td>140</td>
</tr>
<tr>
<td></td>
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<td>2000</td>
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<td></td>
<td>Bi</td>
<td>600</td>
<td>10.01</td>
<td>6000</td>
</tr>
</tbody>
</table>
Electronic Interactions

Electronic energy loss is a consequence of direct interaction of the incident ions with the target electrons. The incident ion, depending upon its velocity, either ionizes the target atoms or itself gets further ionized. Energy transferred to the electron in a direct collision is approximately $4m_e E/M$, $m_e$ and $M$ refer to the mass of the electron and the incident ion respectively. If energy transferred to the electron is less than the ionization energy of the target atoms then energy loss to the electron is improbable. If $I_t$ is the ionization potential of the target atom, to ionize it the projectile energy must exceed

$$E_{t1} = I_t M/4m_e .$$  \hspace{1cm} (1.8)

If $I_t = 10$ eV then $E_{t1} = 5$ KeV for proton projectiles and $\sim 200$ KeV for Ar ions. Similarly, threshold for the ionization of a projectile is given as

$$E_{t2} = I_p M/4m_e ,$$  \hspace{1cm} (1.9)

$I_p$ is the ionization potential of the projectile. For hydrogen atom, $I_p = 13.6$ eV and so $E_{t2} \approx 7$ KeV i.e. above 7 KeV bare protons will be the projectiles rather than hydrogen atoms. In case of Ar$^+$ ions, $E_{t2} \sim 300$ KeV. If the ion energy falls below this value, it will collect electrons and pass through the target as neutral Argon atom.

Electronic loss would be significant when ion energy exceeds not only $E_{t1}$ but also $E_{t2}$, as a neutral atom will ionize little even if its energy is above $E_{t1}$. The threshold for the onset of electronic energy loss is thus proportional to the mass of the incident ion. Once the ion energy is above the threshold, energy loss would depend largely upon the charge state of the incident ion. The Bohr's concept can be applied to find the effective charge on the moving atom. He proposed that a moving atom will lose all those electrons whose velocity is less than the velocity of the atom itself. Thomas-Fermi model may be used to estimate the number of electrons whose velocity is less than the atom velocity. It is evident that the effective charge and hence the electronic energy loss would increase with the ion velocity. To a first order approximation

$$S_\varepsilon (= S_L) = K_\varepsilon E^p .$$  \hspace{1cm} (1.10)

In the L-S formula [32], $p = 1/2$ ($S_\varepsilon$ is proportional to the ion velocity) and $K_\varepsilon$ is the velocity independent stopping parameter given by

$$K_\varepsilon (= K_L) = \frac{1.212 Z_1^{7/6} Z_2}{(Z_1^{2/3} + Z_2^{2/3}) M_1^{1/2}} \text{ eV}^{1/2}/\text{Å} .$$  \hspace{1cm} (1.11)

L-S approximation is fairly good at low ion energies (velocities). But for high ion velocity $v$ such that $v > v_0 Z_1^{2/3}$ or $v > v_0 Z_2^{1/2}$, $v_0 = e^2/h = c/137$, one has to use the Bethe-Bloch
approximation [33]. For non-relativistic energies it is expressed as

\[ S_B = \frac{8\pi Z^2 e^4}{I_0 e_B} \ln e_B, \]

with \( e_B = \frac{2m_e v^2}{Z^2 I_0} \).

\( Z^2 I_0 \) is the mean excitation energy. The Bloch constant \( I_0 \) is given by [34]

\[ I_0 = \begin{cases} 
12 + 7Z^{-1} & \text{for } Z_2 < 13 \\
9.76 + 58.5Z^{-1.19} & \text{for } Z_2 \geq 13
\end{cases} \]

(1.13)

It is evident that at low energies, the electronic energy loss increases linearly with the ion velocity and so at a particular ion energy it exceeds the nuclear energy loss. At an energy \( E_{eq} \), both the processes contribute equally to the energy loss. The values of \( E_{eq} \) are also indicated in Table 1.1.

### Projected Range and Straggles

An incident ion loses energy through these two processes as it penetrates and finally comes to rest inside the solid. The range \( R \) is determined by the rate of energy loss along the path of the ion,

\[ R = \int \frac{1}{dE/dz} dE. \]

(1.14)

Here \( E_0 \) is the incident energy of the ion. But all the ions do not have the same range, as their collision with the target atoms and the energy transferred per collision are random processes. The distribution in their ranges is referred to as the range distribution or range straggles. The projection of \( R \) along the surface normal is called penetration depth or the projected range \( R_p \).

Experimentally, ion range distributions are obtained using secondary ion mass spectrometer (SIMS). It is possible to calculate this for semi-infinite targets using an LSS type moments method [35] or a direct construction technique [36]. In another approach, Boltzmann transport equations are integrated numerically [30, 37] and the quantities of interest are determined by calculating, in a stepwise fashion, the momentum distribution of the incident ions as a function of distance \( z \) from the target surface. Lately, however, a more sophisticated method called Transport of Ions in Matter (TRIM) has been developed using Monte Carlo computer simulation techniques [33]. This is almost universally used to find out, among other parameters, the energy loss and the ion range distributions inside the target. We will employ this technique in later chapters.

To a first approximation, projected range distribution \( N_r(z) \) can be described by a Gaussian characterized by a mean value, the projected range \( R_p \) and a standard deviation from the mean.
\begin{equation}
N_r(z) = \exp \left[ -\frac{1}{2} \left( \frac{z - R_p}{\Delta R_p} \right)^2 \right].
\end{equation}

Its full width at half maximum (FWHM) is given by

\[
\Delta z_p = 2(2 \ln 2)^{1/2} \Delta R_p = 2.35 \Delta R_p.
\]

If \( D \) represents the total dose of implanted ions/cm\(^2\) then the concentration distribution \( N(z) \), in the units of atoms/cm\(^2\), is given by

\[
N(z) = \frac{D N_r(z)}{(2\pi)^{1/2} \Delta R_p},
\]

where we have used

\[
\int_0^\infty N_r(z)dz = (2\pi)^{1/2} \Delta R_p.
\]

A rough estimate of the average concentration, \( \bar{N} \), of the implanted ions can be obtained from

\[
\bar{N} \approx \frac{D}{\Delta z_p}.
\]

The projected range of 200 Kev As ions in Si is \( 10^{-5} \) cm (1000 Å) and the range straggle \( \Delta R_p \approx 0.4 \times 10^{-5} \) cm. So \( \Delta z_p \approx 10^{-5} \) cm. If the implanted dose is \( 10^{15} \) ions/cm\(^2\), then the average concentration is \( 10^{20} \) atoms/cm\(^2\).

In addition to the straggle in the penetration depth along the surface normal, there is a transverse straggle \( \Delta R_t \) in a direction \( \perp \) the incident ion beam. This is important in defining the penetration at the edge of a mask. To a first order approximation \( \Delta R_t \approx \Delta R_p \).

It must be emphasized here that the electronic interactions continuously damp the incident particle inside the solid and do not cause any angular deflection. The range straggle and the transverse straggle are only due to nuclear collisions. So, for the incident ion energies below \( E_{eq} \), the straggle is of the order of the projected range \( R_p \), while above \( E_{eq} \) it remains almost constant.

### 1.2.2 Response of the Solid

In the previous section we have discussed the two mechanisms by which energy is deposited into the solid. To understand the response of the solid, let us first consider the spatial extent and the involved time scales of a single ion impact. The incoming ion travels for a maximum of \( 10^{-13} \) sec before settling about its projected range. Consider a very high energy ion, say 100 MeV Ti bombarding a silicon crystal. Its range is \( \sim 25 \) \( \mu m \). At the start of its trajectory, elastic collisions are rare but a large amount of energy is lost in electronic excitations. As it progresses it slows down and by a depth of \( \sim 20 \) \( \mu m \) its energy reduces to a few MeV. At
this stage the elastic collisions become significant and scatter the lattice atoms through direct impact. We first consider the damage induced by nuclear collisions and then the possibilities of damage due to electronic excitations.

**Damage due to Elastic collisions**

Defects introduced due to elastic collisions with low energy ions is a widely studied field. An atom is displaced from its site if the energy received during collision exceeds its displacement energy $E_d$. Target atom displaced directly by the incident ion is called primary knock-on (PKO). A chain of displacements can follow if the transferred energy is in excess of $2E_d$, as the PKO can displace other atoms. But below $2E_d$, only one atom is displaced. To a linear approximation, an incident ion displaces one atom per $2E_d$ of the energy lost in elastic collisions. Total number of atoms displaced per ion, $n_d$, is given by

$$n_d \approx \frac{E_n}{2E_d},$$

where $E_n$ is the nuclear component of the ion energy loss. For the light projectiles($Z_1$) and the target atoms($Z_2$) Eq.(1.17) gives a good estimate of the number of Frenkel pairs generated during implantation. But it largely underestimates the damage level for large $Z_1$ and $Z_2$ and at low incident ion energies. For 10 KeV Bi$^+$ implanted into silicon ($E_d \sim 13$ eV) at 40K, Eq.(1.17) predicts $\sim 400$ displaced atoms per incident ion. But the experimental evidences suggest in excess of 6000 atoms per Bi$^+$ collision cascade. The discrepancy in the linear cascade theory has been attributed to the effects of energy spikes [4]. When $Z_1, Z_2$ are small and $E$ is large, the nuclear cross section which is proportional to $Z_1Z_2/E$ is small. In this limit each successive event can be thought of as a simple binary collision and the spatial distribution of the deposited energy can be described by the linear Boltzmann transport equation [4]. But in the case of low energy heavy ions the nuclear cross section becomes too large for the assumptions of linear cascade theory to be satisfied. In this high-density cascade regime some sort of collective effect or energy spike provides a more realistic model. Basically, when the nuclear loss per atomic plane is high (several eV), the deposited energy in a volume surrounding the ion track can be conceived as either a thermal spike [1] or a displacement spike [4]. In thermal spikes, the average energy supplied to the target atoms exceeds the heat of melting. The local hot-spot extends considerably beyond the original cascade dimensions and the super-heated region (SHR) may ultimately quench into an amorphous state in times of the order of $10^{-11}$ sec to give substantially more damage than expected from the collision theory. The total cascade volume of 10 KeV Bi$^+$ ion ($R_p \sim 20$ Å), for example, contains less than $10^4$ atoms and so the deposited energy density exceeds 1 eV/atom which is comparable to the heat of melting of most substrates. In the displacement spikes, on the other hand, a continuous network of displaced
atoms is created. When the displacement density in a region exceeds a critical level (~ 10\% for semiconductors) [38], it collapses spontaneously to an amorphous state. The details of different spike models can be found in the review article by Thompson [39].

It may be noted here that the energy density deposited in the thermal spikes caused by *pulsed lasers and electron beams* are of the same order as that in the ion irradiation. But the quenching times are $10^2$ to $10^5$ times higher due to larger (~ 1\( \mu \)m) SHR dimensions. So the molten surface layers have sufficient time to recrystallize, unlike in ion irradiation.

**Damage due to Electronic Energy Loss**

In the low energy implants, the electronic energy loss hardly plays any role in structural damage. It merely dissipates as heat in the solid and causes insignificant bulk heating. But recent experiments with high energy ions have established its role in the atomic transport and the defect creation, if it exceeds certain threshold. This effect is best described by the energy spike models, either as an *ionization spike* or as a *thermal spike*. The incoming ion scatters the target electrons, and creates a column of ionized atoms surrounding its path from surface up to almost the implantation site. In ionization spike, charge relaxation is so slow that the ionized region explodes due to Coulomb repulsion. This process in metallic glasses, commonly known as *Coulomb explosion*, causes dimensional changes by net transport of atoms perpendicular to the ion beam direction [10-12]. In crystalline solids it may produce a column of defects, known as columnar defect. Center of this column is amorphised by the direct impact of this explosion. But it can extend beyond the radius of direct impact as the outer regions may undergo displacement spikes if the density of the displaced atoms in those exceeds the critical level.

Thermal spike depends largely upon the electron-phonon (e-p) coupling strength. The electrons scattered by the incident ion may receive several hundred eV of energy and move in all directions away from the ion path. These are known as \( \delta \)-electrons. During their passage these interact with other electrons and heat up a column surrounding the ion path. Energy transfer through electron-electron (e-e) interaction takes about $10^{-14} - 10^{-13}$ sec. Hot electrons transfer their energy to the lattice through e-p coupling in $\sim 10^{-12}$ sec. The lattice column may melt due to thermal spike and quench within $\sim 10^{-11}$ sec which is too fast for recrystallization. If \( \lambda \) is the mean free path of the \( \delta \)-electrons the mean energy density \( Q \) deposited in the lattice in a cylinder of radius \( \lambda \) is [19]

$$Q = \frac{0.63 S_e}{\pi \lambda^2},$$

(1.18)

since only 63\% of the electronic loss \( (S_e) \) is deposited in this cylinder. Columnar defect is produced if \( Q \) exceeds the energy \( \Delta H_f \) required to melt the solid. Experimental data on
irradiated metals has been analysed by Wang et al [19]. Dependence of the defect formation on the parameters like e-p coupling strength, melting point and thermal conductivity is indicative of thermal spike effect.

**Radiation Annealing**

The single ion disorder caused by either of the interaction processes builds up and amorphizes the solid over high dose implants. Amorphization is envisaged to occur through the overlap of isolated regions created by the ions [40], or via the build up of simple defects, leading to the sudden collapse of a large region of material into the amorphous phase [41]. In addition to these, energy deposition density has also been used to predict amorphization [42]. However, some recent measurements of defect accumulation and amorphization in Si irradiated with few MeV ions have proven incompatible with these traditional models. Novel effects like inverse dose rate dependence of the accumulated defects have been observed by Williams et. al. [43]. Evidence has also been found of the extended defects which act as nucleation cites for the amorphous phase [44]. Creation of extended defects during irradiation can be attributed to the effects of radiation annealing. Annealing of defects in crystalline solids during ion irradiation can alter the expected damage level and may induce formation of the defect complexes. Two types of annealing may occur – Dynamic annealing of the damage produced by single ions and thermal (bulk) annealing due to rise in the target temperature. The later is observed only at very high dose and dose rate (flux) implants where target temperature rises significantly [45]. Total damage in such cases has inverse dose rate dependence. At low flux, however, only dynamic annealing is possible. Higher dose rates under such conditions have been found to produce more damage for the same implanted dose [46]. This is believed to arise from different annealing rates for the single ion disorder and the overlapped damaged structures. At higher dose rates, cascades can overlap before each of these has completely relaxed.

Dynamic annealing of defects during ion irradiation is greatly enhanced due to ionization of vacancies and interstitials and prevailing higher local temperatures. Ionized point defects have smaller activation barrier and larger diffusion coefficients. It has been found to recrystallize the amorphous layers grown over the crystalline silicon substrates bombarded with few MeV ions [47]. The effect is much more pronounced with high energy ions and causes anomalous annealing of defects in metals [25-29].

**1.2.3 Irradiation Environment**

To a large extent the response of a solid also depends on irradiation conditions, particularly on the ambient temperature. In semiconductors, for example, there exists a critical temperature
above which these do not amorphize by the irradiation [47, 48]. That is, if the substrate temperature is below the critical temperature, the locally disordered regions overlap to produce continuous amorphous layers. But at higher temperatures, dynamic annealing becomes significant and the local amorphous regions relax before the overlap, thus inhibiting amorphization. Ambient temperature affects the ultimate defect structure in two ways. As annealing proceeds through diffusive processes the temperature provides the required activation. And the rate of diffusion, which is proportional to $\exp(-E_{\text{act}}/K_BT)$, increases with temperature. But this alone cannot account for the critical dependence of the defect structure on the substrate temperature. This is because the temperature in the thermal spike driven superheated regions (SHR) is much higher than the external temperature. So the thermal activation in SHR would hardly be affected by the surroundings. However, there is another way by which the ambient influences SHR. The disordered state within SHR is largely affected by its rate of quenching which in turn depends upon the thermal conductivity $\kappa$ of the surrounding medium. To a rough approximation the temperature profile around SHR is governed by the equation [48]

$$T(r, t) \propto \left(\frac{1}{\kappa t}\right)^{3/2} \exp\left(-\frac{r^2}{4\kappa t}\right),$$

(1.19)

i.e. the smaller the conductivity the larger the time available for defect generation/recombination and their migration. This favours the conditions for dynamic annealing. At higher temperatures $\kappa(T) \sim \kappa_0 T^{-n}$ and for semiconductors $n \sim 1.5$. Thus the rise in temperature reduces the thermal conductivity and slows down the quench-rate. At slow quench-rate, the dynamic annealing sets in and the disordered region can recrystallize.

### 1.2.4 Thermal Annealing

In the previous sections we have discussed how a crystalline material is dragged into a disordered state upon ion irradiation. The disordered state in semiconductors shows a non-trivial evolution upon thermal annealing depending upon the damage level. A completely amorphous (saturated disorder) region smoothly recrystallizes at $\sim 750^\circ\text{C}$. A highly disordered crystalline state (subsaturated disorder) in contrast develops complex defects upon thermal heating which do not anneal even at $\sim 1000^\circ\text{C}$. These defects are in the form of dislocations, dislocation loops and the extended rod shaped \{311\} defects. Some recent literature on this subject can be found in references [8-11].
1.3 Experimental Techniques

1.3.1 Ion Irradiation

The most important step in the process of ion irradiation is the production and the acceleration of ions in the form of a fine beam. This is realised through ion accelerators. There are basically two types of ion accelerators - Electrostatic accelerators and radio frequency (rf) accelerators. Here we will consider only the electrostatic accelerators. In these, the ions are accelerated by a fixed potential difference between a high voltage terminal and the ground. If \( q \) is the charge state of the ion and \( V \) the terminal potential, the energy of the ions leaving the accelerator is given by

\[
E_0 = qV \ \text{eV}
\]  
(1.20)

The terminal is raised to the high potential by the process of charge transfer. This is achieved with the help of a metallic belt which rotates between two pulleys. At one end charge is transferred on the belt while at the other it is taken from the belt and transferred to the terminal. In the conventional Van de Graff generator, the terminal potential cannot exceed a few hundred kilo-Volts. Thus it can produce only low energy ions which are employed in the surface implants. To produce ions of several MeV, potential difference of several million-Volt (MV) is required. A beam of 100 MeV Ag\(^+\) ions, for example, needs a potential difference of 100 MV. But the requirement is greatly reduced by enhancing the charge state of the ion. A beam of 100 MeV Ag\(^{10+}\) ions can be produced only with a potential difference of 10 MV. But the conventional Van de Graff accelerators cannot sustain the potential difference of several MV. The linear accelerator designed specifically for this purpose is known as Pelletron. To raise the terminal potential to such a high value the process of charge transfer has to be very fast. The conveyer belt in it, which is made up of hollow cylindrical steel pellets separated from one another by non-conducting flexible ceramic joints, can carry a large amount of charge instantaneously. Experimental procedure of ion irradiation using a pelletron beam is discussed in section 3.2.2 (page 46).

1.3.2 Defect Investigation

An overview of the different experimental techniques widely employed in the study of radiation damage is given, in a comparative format, in Table 1.2. Transmission Electron Microscopy (TEM) and X-ray Diffraction Topography (XRT) are the diffraction imaging techniques which produce a direct image of the extended defects (dislocations, stacking faults etc.) in perfect crystals. Techniques like Electron Paramagnetic Resonance (EPR), Infrared Absorption (IR) and Deep Level Transient Spectroscopy (DLTS) give information about the nature of point
defects and their clusters. RBS Channeling gives an estimate of the overall damage distribution along the depth of the specimen with a resolution of about 100 Å, while resistivity measurements account only for the total damage in the bulk of the sample.

Table 1.2

<table>
<thead>
<tr>
<th>Techniques</th>
<th>Category</th>
<th>Principle</th>
<th>Resolution</th>
<th>Information</th>
<th>Limitations</th>
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</thead>
<tbody>
<tr>
<td>TEM</td>
<td>Imaging</td>
<td>Electron Diffraction</td>
<td>upto a few Å</td>
<td>Dislocations, Stacking faults etc., Structural changes and amorphous clusters</td>
<td>Only &lt; 1 μm thick samples</td>
</tr>
<tr>
<td>X-Ray Topography</td>
<td>Imaging</td>
<td>X-ray Diffraction</td>
<td>~ 1 μm</td>
<td>-</td>
<td>Only very perfect crystals</td>
</tr>
<tr>
<td>EPR</td>
<td>Resonance</td>
<td>Transition between paramagnetic states</td>
<td>-</td>
<td>Point defects and Defect clusters</td>
<td>Only some specific defects</td>
</tr>
<tr>
<td>IR</td>
<td>Resonance</td>
<td>Transition between vibrational states</td>
<td>-</td>
<td>-</td>
<td>-do-</td>
</tr>
<tr>
<td>DLTS</td>
<td>Electrical</td>
<td>Charge decay in junction capacitance</td>
<td>-</td>
<td>-do-</td>
<td>-do-</td>
</tr>
<tr>
<td>RBS Channeling</td>
<td>scattering of ions with matter</td>
<td>Channeling of ions in perfect crystals</td>
<td>~ 200 Å (depth-wise only)</td>
<td>Depthwise evaluation of the degree of lattice damage</td>
<td>Only overall damage of crystalline layers</td>
</tr>
<tr>
<td>Resistivity</td>
<td>Electrical</td>
<td>Scattering of electrons with defects</td>
<td>-</td>
<td>Overall lattice damage</td>
<td>Total damage only</td>
</tr>
</tbody>
</table>

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Information provided by different techniques is often complimentary and so the application of a particular technique depends upon the kind of study one is interested in. In this thesis our primary interest is in the study of structural defects in high energy ion irradiated semiconductors. We have employed X-ray diffraction topography (XRT) for this purpose. Although its resolution is much inferior to TEM but its flexibility offers some additional advantages. Low scattering of X-rays allows these to penetrate hundreds of micrometer thick samples without significant absorption. So the individual defects in the bulk of thick samples can be imaged non-destructively. Secondly, a large area of the sample (few cm²) can be scanned and a two-dimensional projection of the defect network can be obtained in a single topograph. As supporting evidences we have employed Anisotropic etching and Scanning Electron Microscopy (SEM).

1.4 X-ray Topography of Radiation Defects

X-ray topography identifies the defects by imaging the topography of lattice planes surrounding the defect. It is a powerful non-destructive technique to find out the network of extended defects, their depth distribution and the presence of amorphous regions.

Damage of surface layers following low energy ion implantation has been studied by Gerard [51] using known techniques (details to be found in chapter II) of XRT. At low fluence (fluence is defined as the total dose of ions/cm²) the implanted region undergoes gradual lattice expansion and suffers plastic flow at higher doses. Isolated extended defects are not observed at any stage of ion irradiation. Similar studies with few MeV implants reveal the formation of a damaged layer buried a few microns deep whereas the near surface region retains its crystallinity to a high degree of lattice perfection. At high fluence, when the buried layer transforms to an amorphous phase, a bicrystal (two perfect crystals separated by the buried layer) is formed. Bonse and Hart [52] analysed theoretically the diffraction contrast from such a translational fault and have shown that the interference of rays diffracted from two perfect regions would produce equal thickness fringes in asymmetric reflections if the thickness of the amorphous layer is varied. Experimentally, the intensity of the ion beam falls off at the edges and the amorphous layer has a lens shaped structure. This variation in the amorphous layer thickness gives rise to fringes in X-ray topographs [53]. From the theory of Bonse and Hart [52], it is possible to find out the depth of the buried layer from the visibility of the fringe pattern.
1.5 Scope of the Thesis

In this thesis, we have studied the structural damage in crystalline solids following high energy ion irradiation. Investigations have been carried out on the perfect lattices of Si and GaAs. The structural damage in perfect crystals can be investigated by analysing the deformation of the underlying lattice. In this work we have employed the techniques of X-ray diffraction topography to understand the nature and depthwise distribution of such lattice disortions in the irradiated crystals. Optical microscopy and scanning electron microscopy have been used to assist these investigations.

The two primary interactions in a solid bombarded with high energy ions - electronic excitations and elastic nuclear collisions - occur in spatially separated regions. The former is significant close to surface while the latter near the implanted sheet. Thus, the role of each interaction in the transport of atoms can be distinguished easily from a depthwise analysis of the corresponding lattice disorder. A major part of the work presented in this thesis investigates such a distribution enforced by different types of ions. These investigations not only reveal the sensitivity of a lattice to different interactions but also the dependence of structural damage on single ion disorders as well as on the properties of the irradiated crystal.

Irradiation has been carried out in a stripe geometry. This was achieved by introducing an impenetrable metal grid in the path of irradiating ions. This configuration allowed even small structural changes in the irradiated lattice to be detected in XRT by mapping the strain gradient at the stripe boundary. Such a gradient at the boundary germinates from variation of the lattice parameter in the irradiated region. From this, the effect of electronic excitations on the lattice structure of the irradiated crystal could easily be recognised.

The role of electronic excitations in the transport of atoms, established experimentally in various systems, has two independent interpretations. In glassy systems where dimensional changes have been observed on a macroscopic scale, Coulomb explosion has been proposed as the operating mechanism [16, 17]. Some other studies, particularly relating to crystalline solids, attribute this effect to thermal spikes [19]. Experiments have shown that a solid becomes sensitive to electronic energy loss only above a certain threshold. Crystalline solids transform to an amorphous phase above such a threshold. However, when deposited energy density is below the threshold the effect of electronic excitations on the target lattice is not well understood. In solids with a high degree of lattice defects, such irradiation anneals the preexisting disorder [25–29]. However, the question remains open in perfect lattices which have no defects to start with. Our investigations involving highly perfect lattices of semiconductors shed some light on this subject.

Chapter-2 is a formal introduction to the experimental and analytical techniques of X-ray
diffraction topography (XRT). The theory of X-ray diffraction, which has been discussed in some detail, is extremely germane to the understanding and interpretation of contrast features in X-ray topographs.

In Chapter-3, we present the details of stripe geometry irradiation using a pelletron ion beam. Experimental details of X-ray topography, employed for the subsequent analysis, are also discussed. In topographic analysis, the visibility of a defect depends on the direction of the diffraction vector. So the choice of diffraction vectors is very crucial in the analysis of lattice defects. In the present investigations, diffraction vectors have been chosen broadly according to the visibility of the in-plane and out-of-plane strain-field components.

The irradiated crystals of Si and GaAs have been analysed using the techniques of X-ray Diffraction Topography, Scanning Electron Microscopy and Optical Microscopy. The results of these analyses constitute Chapters-4 and 5.

Chapter-6 deals with a novel experiment of water condensation on the irradiated surfaces of Si, GaAs and CdTe semiconductors. The study reveals drastic changes in the adsorption and wetting properties after irradiation. Our understanding in this regard is as yet limited.

We conclude in Chapter-7 by giving a brief summary of the results obtained in this thesis and discuss some of the issues relating to their possible applications in the defect-engineered semiconductor devices.