1.1 INTRODUCTION

Modern technology depends on materials with precisely controlled properties. In current research, ion beam irradiation is a favoured method to achieve controlled modification of surface and near-surface regions of materials. Ion beams are used to modify the electrical, optical, mechanical, magnetic and superconducting properties of the materials. The ultimate goal of the subject is to understand the basic principles of ion-solid interactions and to apply these principles for the development of modern technology. To understand the modifications in materials properties it is necessary to understand the possible implications of passage of various energetic ions through the materials. When an energetic ion penetrates a solid it undergoes a succession of binary collisions with target atoms and surrounding electrons, losing energy at each encounter. The transfer of energy from projectile ion to the solid can be conveniently divided into two independent processes, namely electronic energy
loss $S_e$ and nuclear energy loss $S_n$ [1]. The former process depicts the interaction of fast ions (MeV) with lattice electrons. An appreciable amount of energy is usually transferred during each electronic collision (so-called inelastic collisions) but the large density of electrons and the high frequency of such collisions cause large amount of energy loss during the slowing down of the incident ion. The later nuclear energy loss process, is constituted by collisions between the incident ion and the lattice atoms where conservation of energy and momentum apply (so-called elastic collisions). The rate at which the projectile ion loses energy with penetration depth, ($x$), $S(E)=\left(\frac{dE}{dx}\right)$ is the sum of electronic and nuclear energy-loss terms, i.e.

$$S(E) = S_e + S_n \tag{1.1}$$

and is known as 'specific energy loss' or 'stopping power'.

1.1.1 Electronic energy loss

An energetic ion passing through a solid interacts simultaneously with many electrons through the attractive Coulomb force. The energy is transferred to the electron by the energetic ion and depending on the proximity of encounter; this energy may be sufficient either for ionization (remove the electron from the atom) or for excitation (raise the electron to a higher-lying shell within the target atom). Electronic energy loss through the inelastic collision is the dominant process at high energy (1MeV/nucleon) and ion paths tend to be quite linear from microns to tens of microns because the ions are not greatly deflected by any single encounter with electron.

The theory of electronic energy loss of highly energetic ions in solids was first given by Bohr [2] in 1913. He derived the expression for $S_e$ on the basis of a model which
considered the target as a collection of harmonic oscillators whose frequency was determined by optical absorption data. The work was extended to relativistic ions by Bethe [3] and Bloch [4]. They solved the energetic ion energy loss problem quantum mechanically in the first Born approximation. The expression that describes the electronic energy loss of a highly energetic ion in a solid is known as Bohr-Bethe formula and is written as

\[
S_e = - \left( \frac{dE}{dx} \right) = \frac{4\pi e^4 Z_p^2 Z_t N_t}{m_e v^2} \left[ \ln \left( \frac{2m_e v^2}{l} \right) - \ln \left( 1 - \frac{v^2}{c^2} \right) - \frac{v^2}{c^2} \right]
\] (1.2)

where \( v \) and \( Z_p e \) are the velocity and charge of the projectile ion, \( Z_t \) and \( N_t \) are the atomic numbers and number density of the target atoms, \( m_e \) is the electron rest mass and \( e \) is the electronic charge. The parameter \( l \) represents the average excitation and ionization potential of the target material, and is usually an experimentally determined parameter for each element.

For non-relativistic projectile ions only the first term in square brackets of Eq. (1.2) is significant. The Eq. (1.2) is generally valid for different types of ions provided their velocity remains large compared with the velocities of the orbital electrons in the target atoms. It can be seen from this equation that for a given non-relativistic ion, \( S_e \) varies as \( 1/v^2 \), or inversely with ion energy. This is due to the fact if the velocity of the ion is low, then it spends a greater time in the vicinity of the electron, and thus transfers greater impulse, and hence larger velocity, to the electron. Fig. (1.1) shows the typical example of variation of \( S_e \) and \( S_n \) with ion energy for the case of \(^{107}\text{Ag}\) ions impinging on Si. This type of curve is usually called as Bragg curve. It is observed from the figure that for low energy \(^{107}\text{Ag}\) ions (energy up to a few MeV), \( S_n \) is the dominant energy loss process. But after that \( S_e \) starts rising sharply with increase in energy of the \(^{107}\text{Ag}\) ion. At an energy of 366 MeV, \( S_e \) attains a maximum value of 13.7 keV/nm. This is called as Bragg peak.
Figure 1.1: Variation of electronic and nuclear energy losses ($S_e$ and $S_n$) of $^{107}$Ag ion in Si as a function of ion energy

After the Bragg peak $S_e$ again starts decreasing with increase in ion energy. It is to be noticed that Bethe-Bohr formula, given by Eq.(1.2), is followed in the region after the Bragg peak. Before this peak region, $S_e$ increases with increase in energy. This is the region where the velocity of the ions is less than the Fermi velocity, $v_F$ of the target electrons. Hence here majority of the target electrons moves much faster than the ion and collisions with the ion are mostly adiabatic with direct energy loss to collisions. Lindhard and Scharff [1] considered the problem of this low velocity energy loss using a model of a slow heavy ion in a uniform electron gas. Relative to ion electrons have a slight drift velocity. During a collision with the ion a net energy is transferred which is proportional to this velocity. One outcome of this model is that the electronic energy loss is found to be proportional to the ion velocity.
To understand how this electronic energy loss is transferred to the crystal lattice, there are two prominent models of microscopic energy transfer from electrons to the lattice atoms: *thermal spike* model and *coulomb explosion* model.

### 1.1.1.1 Thermal Spike Model

In the thermal spike model, the transfer of energy from the bombarding ion to the lattice is a two step thermodynamic process: the first step is the evolution of the energy within the target electron gas via electron-electron interaction and second step is the energy transfer between electron and lattice atom via electron-phonon coupling. The two steps are described by two coupled differential equations that give the time and space dependence of electronic temperature $T_e$ and lattice temperature $T_l$. This energy transfer leads to a local temperature increase that can reach the melting temperature of the material thus creating the so-called latent track after ultrafast quenching of the molten matter. It is to be mentioned here that the energy transfer through electron-electron interaction takes about $10^{-14}-10^{-13}$ seconds, while hot electrons transfer their energy to the lattice through electron-phonon coupling in about $10^{-12}$ seconds. If $\lambda$ is the mean free path of electron scattering, then the mean energy density, $Q$ deposited in the lattice in a cylinder of radius $\lambda$ is given by [6]

$$Q = \frac{0.63S_e}{\pi\lambda^2}$$  \hspace{1cm} (1.3)

where $\lambda$ is related to the thermal electronic diffusivity, $D_e(T_e)$, and to the electron-phonon interaction time, $\tau_a$, by

$$\lambda = (D_e\tau_a)^{1/2}$$  \hspace{1cm} (1.4)

The amorphised track is created if $Q$ exceeds the energy, $\Delta H_f$, required to melt the solid.
1.1.1.2 Coulomb explosion Model

In coulomb explosion model [7] it is assumed that the incoming ion scatters the target electrons, and creates a column of ionized atoms surrounding its path from surface upto the end of range of ion. In ionization spike the charge relaxation is so slow that the ionized region explodes due to coulomb repulsion. The electron excitation energy is rapidly shared with other electrons via electron-electron interaction. The mutual coulomb repulsion of ions produces atomic displacements leading to a dense cloud of interstitial atoms and vacancies along the original ion trajectory. In metals which have large electron mean free paths, the free electrons carry away the excitation energy so efficiently that the sample warm up as a whole without considerable atomic motion. The coulomb spike model is more applicable for insulators while thermal spike model is more valid for metals.

1.1.2 Nuclear energy loss

At the end of ion range in materials where ions have low energy (~1keV/nucleon), nuclear energy loss dominates due to the elastic binary collisions between projectile ion and individual target atoms. The derivation of $S_n$ uses two main assumptions:

(i) A screened Coulomb potential, and

(ii) The impulse approximation.

The interaction potential between two atoms, $Z_1$ and $Z_2$, can be written in the form of a screened Coulomb potential using $\chi$ as screening function,
\[ V(r) = \frac{Z_1 Z_2 e^2}{r} \chi \left( \frac{r}{a} \right) \]  

(1.5)

where 'a' is the Thomas-Fermi screening radius for collision and defined as

\[ a = \frac{0.885 a_0}{(Z_1^{1/2} + Z_2^{1/2})^{2/3}} \]  

(1.6)

where \( a_0 = \frac{\hbar^2}{m_e e^2} \) is the Bohr radius. The values of \( a \) lie between 0.1 and 0.2 Å for most interactions. Apart from Thomas-Fermi potential, there are some other screening potentials that are used to calculate \( S_n \), these are Lenz-Jensen, Moliere and Bohr potentials [8]. Each of these potentials may be considered as a Coulombic term \( (l/r) \) multiplied by a screening function. The expression for the \( S_n \) is given as

\[ S_n = - \left( \frac{dE}{dx} \right)_n = N_t \int_0^{T_{\text{max}}} T d\sigma_n (E, T) \]  

(1.7)

where \( N_t \) is the atomic density of the target, \( T \) is the energy transferred from an incident ion of energy \( E \) to a target atom. \( T_{\text{max}} \) is the maximum value of \( T \), and \( d\sigma_n \) is the differential cross-section. Using the appropriate screening potential and using the impulse approximation, the final expression for \( S_n \) can be derived. For example, if the screening function is taken of the form

\[ \chi = \frac{a}{2r} \]  

(1.8)

The following expression for the nuclear energy loss is obtained

\[ S_n = N \frac{\pi^2}{2} Z_1 Z_2 e^2 a \frac{M_1}{M_1 + M_2} \]  

(1.9)

It gives the correct order of magnitude for \( S_n \) but deviates considerably in energy dependence. Most significantly, it does not display \( l/E \) dependence at high energy, which corresponds to
the Rutherford's scattering process. The appropriate improvements in the expression for $S_n$ are made by using other more realistic potentials like Thomas-Fermi potential [8].

In case of elastic collisions, if the energy given by nuclear encounters to the target atoms is higher than a certain value, $E_d$, the displacement threshold energy ($\sim 15\text{eV for Si}$), the knock-on atom leaves the lattice site and is displaced. If $E'$ is the energy lost by the projectile, the knock-on atom has energy $E'-E_d$ and can displace other target atoms in its turn. The damage distribution is in part related to the distribution of the energy deposited in nuclear collisions. The deposited energy depends only on the mass and the energy of the projectile and on the mass of the target. The final structure of the damage depends on the type of material, e.g., semiconductor, metal, insulator, etc., and on the temperature. For a similar distribution of energy deposited in nuclear encounters the damage structure may be quite different in different materials. The distribution of the deposited energy density can be converted into a damage distribution, assuming that only those recoils receiving an energy greater than $E_d$ are displaced. The number of displacements versus depth can be obtained with the modified Kinchin-Pease [9] relation

$$n_d(x) = \frac{0.8v(E,x)}{2E_d}.$$  

(1.10)

Here $v(E, x)$ is the energy transferred to the recoil atoms at depth $x$ from the surface of the target. The total number of displacements in the implanted volume is

$$N_d = \frac{0.8\int_0^x v(E,x)dx}{2E_d}.$$  

(1.11)

A commonly used unit of damage is the number of displacements per atom (DPA). A unit of 1 DPA means that, on the average, every atom in the affected volume has been
displaced from its equilibrium lattice site once. The dependence of $DPA$ versus depth is given by

$$DPA(x) = \frac{0.8 \nu(E_x) \Phi}{2E_d N}$$

(1.12)

where $N$ is the atomic density (atoms cm$^{-2}$) and $\Phi$ is the ion fluence (ions cm$^{-2}$).

The electronic energy loss is believed to cause modifications in the materials while the nuclear energy loss is responsible for atomic displacements in the materials. Depending on these energy losses ion beams are used to characterize material as well as to modify them. Present thesis concentrate basically on materials science where the major interest in current state of art lies in the studies of effects of high-energy heavy ions called swift heavy ion (SHI) on properties of semiconductor materials.

1.2 ION IRRADIATION STUDIES ON SILICON DEVICES

Silicon is today’s most widely used semiconductor material and lots of Si based devices are used in radiation environment like space, nuclear reactor, nuclear and particle detectors, etc. Metal-semiconductor (MS) structure is one of the important research tools in the characterization of semiconductors. Moreover, MS structure based devices have been of considerable interest due to their widespread application in terahertz meta material devices, microwave FET’s, RF detectors and solar cells [10]. In some fields like development of particle detectors, it is really important to correlate the influence of ion irradiation on the material properties with the electrical characteristics getting modified. Though the studies on low energy ion irradiation induced damage are well documented [11-17], very little has been reported for swift heavy ion irradiation. The aim of present work is to contribute to this new emerging area of the effect of high energy heavy ion irradiation on Si, mainly through
electrical measurements using metal/n-Si Schottky diodes. Studies concerning the effect of swift heavy ion irradiation on various properties of Si have been carried out by various groups. Singh et al [18] studied the effect of 100 MeV $^{16}$O$^{7+}$ ions on Au/n-Si Schottky barrier diode in the fluence range $1 \times 10^{12}$ to $1 \times 10^{13}$ ions-cm$^{-2}$ and found that Schottky barrier height (SBH) remains constant irrespective of irradiation fluence. The possible role of huge electronic energy loss in annealing of defects at the metal-semiconductor interface was invoked to explain the constancy of Schottky barrier parameters. Varichenko et al [19] irradiated silicon by 5.68 GeV Xe ions at various fluences ranging from $5 \times 10^{11}$ to $5 \times 10^{13}$ ions-cm$^{-2}$, and investigated the damage produced by irradiation using spreading resistance, electron paramagnetic resonance, optical absorption and X-ray diffraction techniques. Based on these studies it was concluded that irradiation induced point defects are created predominantly by nuclear energy loss whereas the formation of amorphous areas is strongly suppressed by electronic energy loss. Bogdanski et al [20] irradiated the n-Si by 3.5 GeV Xe ions at a temperature of 77K and measured in situ resistivity of the sample with respect to fluence. These in situ measurements showed that the resistivity of the sample increases with fluence during the whole irradiation. The introduction of irradiation induced defects like divacancy and vacancy-oxygen complex, which trap the free carriers, were held responsible for increase in resistivity of n-Si. The same group performed the 3.6 GeV $^{238}$U ion irradiation study on n-Si at room temperature. In this case the value of $S_e$ is 28 keV/nm. They experimentally determined the introduction rate of above mentioned defects in n-Si crystal using deep level transient spectroscopy (DLTS). Their results indicated that the $S_e$ is insufficient for defect creation in n-Si at room temperature [21]. In experimental studies by Toulemonde et al involving irradiation of crystalline Si with 3.7 GeV Kr and 3.7 GeV Xe ions, it was concluded that the energy deposited by the collective electron excitation of the lattice had no contribution in producing defects in Si.
1.3 MOTIVATION AND ORGANIZATION OF THE THESIS

Semiconductor devices have become very important components in most electronic equipments used in daily human activities. The basis for the development of semiconductor devices lies within the properties of a semiconductor itself. Despite the fact that silicon has been extensively studied for such a long time, there are still many questions to be answered. There have been studies on low energy ion implantation in silicon but systematic studies on modification induced by swift heavy ion are not studied extensively. In the low energy regime nuclear energy loss is dominant phenomena and modifies the properties of material by producing point defects while swift heavy ion irradiation of solids brings in irreversible changes in material such as structural changes, interface modification or alterations of the phase composition. There are only very few reports on modifications of electrical characteristics of Si under the action of high-energy heavy ion irradiation. The implications of large electronic energy loss, which is much larger than the nuclear energy loss for swift heavy ions (MeV), in influencing the electronic properties of Si are not fully understood. Whether this high electronic energy loss leads to creation of defects, or results in annihilation of the defects introduced by nuclear energy loss, has not been understood properly. It is not clear how simultaneous electronic and nuclear energy loss modify the interface states in metal/Si Schottky barrier structures or how the position of Fermi level pinning, which decides the properties of potential barrier at interface, is changed in semiconductor band gap. One more aspect is whether simultaneous electronic and nuclear energy loss create new defect complex or they change the charge state of existing defects, which will strongly affect the defect migration.

Present work is an attempt to address these questions in a proper prospective, using detailed electrical characterization of Si Schottky diodes under the influence of swift heavy ion irradiation. The irradiation induced defects and their influences on electrical
characteristics as a function of ion fluence have been monitored using in situ deep level transient spectroscopy (DLTS), current-voltage (I-V), and capacitance-voltage (C-V) measurements. The prime motivation behind performing in situ measurements is that the evolution in electronic properties of Si as a function of fluence is studied while keeping all other external parameters, e.g., sample to sample variation, vacuum environment and contact geometry, as unaltered.

In chapter 2 the details of experimental setup and measurement procedures have been given. Development of in situ electrical characterization techniques like DLTS, I-V and C-V in materials science beam line is discussed in detail.

In chapter 3 the influence of 180 MeV $^{108}$Ag ions on electrical characteristics of Au/n-Si Schottky barrier structure has been discussed using in situ I-V and C-V measurements. Using temperature dependent I-V and C-V characteristics of irradiated Au/n-Si, it has been shown that ion irradiation results in Fermi level pinning at defect level. The results of the measurements have been discussed considering the basic energy loss mechanism of swift heavy ions in semiconductors.

In chapter 4, the effect of 100 MeV Si swift heavy ion irradiation on defects in Au/n-Si structure has been studied using in situ DLTS characterization. The evolution of defects during irradiation and their correlation with electrical characteristics have been studied using combined in situ DLTS and current-voltage characterization.

In chapter 5, the role of high electronic energy loss in modification of electrical characteristics of Ni/n-Si Schottky barrier diode has been studied. 100MeV O ion beam and 900keV O ion beam have been used for irradiation of Ni/n-Si diodes. These ion beams have same electronic energy loss but different nuclear energy loss at the interface.
In chapter 6, summary and conclusions of this work are presented highlighting their implications for the study of swift heavy ion induced modifications in electrical properties of Si. Towards the end of this chapter, the directions along which future studies can be planned have been suggested.
References


