Chapter 6

Characterization of structural modifications in MeV Sb implanted Si(100) by Raman spectroscopy and channeling

6.1 Introduction

MeV ion implantation can produce severe damage in the lattice depending on the nature of the impinging ion, its energy and the implantation dose [1]. During implantation, a projectile while moving forward produces vacancies and interstitials, loses energy primarily due to electronic encounters and is finally deposited at its range governed by its mass and implant energy [2]. Both the quantity and the quality of irradiation induced disorder are largely affected by the ion mass and energy. Hence, for ion implantation to be a viable candidate for the development in semiconductor technology, it is important to estimate and characterize this disorder. This can further lead to an understanding of the amorphization process caused by ion-solid interactions and physical analysis of structural disorder introduced by ion irradiation. As a first approximation, the radiation damage produced in a semiconductor can be computed by applying the Kinchin and Pease model [3] to the distribution of
energy transferred to the crystal via nuclear collisions. In this framework, damage is a linear function of fluence. Processes like dynamic recombination and clustering of simple defects can however produce a damage distribution quite different than that suggested by linear cascade theory.

Rutherford backscattering spectroscopy/ channeling (RBS/C) has proved to be an useful technique for the investigation of radiation damage created due to ion bombardment of single crystals. The damage profile can be extracted from the ion channeled spectrum by applying the multiple scattering formalism [4]. Raman spectroscopy is another powerful tool for investigation and monitoring of radiation induced damage, since the intensity, half width and peak shift of the zone center phonon peak are very sensitive to the structural disorder, damage and strain in the lattice. Formation of defects as well as the presence of impurity atoms in the lattice due to implantation can lead to stress in the planes of the single crystal or changes in the force constants. Corresponding shifts in the phonon frequencies are reflected in the Raman spectra. Moreover, the damage produced due to defects can cause phonon confinement leading to a reduced phonon coherence length as \( k=0 \) selection rule is relaxed, giving rise to an asymmetric broadening in Raman peak. The Raman spectrum thus contains signature of both: the stress and the reduced phonon coherence length due to disorder in the lattice.

In the present study, we have utilized the techniques of Raman scattering and RBS/C to study the structural modifications and radiation damage that occur in Si implanted with various fluences of 1.5 MeV Sb and after annealing at 400\(^\circ\)C and 600\(^\circ\)C. There are still very few studies that utilize the technique of Raman spectroscopy for evaluation of crystallinity and damage produced by MeV ion even though it is a very sensitive probe for small volume defects created during ion implantation. Huang et.al. have investigated the MeV implantation of Si\(^+\) in Si using Raman spectroscopy [5, 6]. However, to our knowledge the present study is the first Raman study of MeV implantation in Si with an ion heavier than Si. An estimation of the phonon coherence length has been done by applying the Phonon Confinement Model (PCM) [7] to the first order Raman peak. Moreover, by using Raman spectroscopy, we have also investigated the development of stress in the Si lattice as the damage
The results from Raman spectroscopy have been compared with those from RBS/C technique which is extensively used for estimating disorder and damage after ion implantation. The damage profiles in the lattice have been extracted from the RBS/C data using the multiple scattering formalism formulated by Feldman and Rodgers [4]. The damage distributions in Si(100), obtained using RBS/C, have been compared with Monte Carlo (MC) simulations performed using SRIM'97 [8]. The total damage accumulated as a function of implantation dose demonstrates two types of behavior. For low doses, a small damage accompanied by a slow damage accumulation rate is observed. This region is characterized by small defects consisting of simple point defects. However, this trend changes and a faster rate of accumulation of damage is observed for fluences higher than $1 \times 10^{13}\text{ions/cm}^2$. During this later stage, defect-zones formed previously enlarge in size by accumulation of defects. It is observed that the total disorder detected by Raman is higher than that from RBS/C technique for the implant doses where the crystalline to amorphous (c/a) transition takes place and when both the crystalline and amorphous phases coexist. The coexistence of nanocrystalline regions and amorphous zones can lead to the confinement of phonons. Existence of a completely amorphous lattice is noticed for Sb doses of $5 \times 10^{14}\text{ions/cm}^2$ and higher by both the techniques.

Using Raman, the depth dependent shifts in Raman peaks have also been measured by varying the angle $\phi$, between the sample normal and the laser. This technique has been used by Park et.al.[9] for depth dependent crystallinity measurements after keV implantation of F$^+$ in silicon. Though the depth profiling using Raman scattering can also be performed by employing a variable wavelength laser source, this however requires conforming changes in the optical components of the spectrometer. We demonstrate that the depth dependent studies are more informative and exhibit a transition in stress from being tensile towards the implanted region to being compressive near the surface. The maximum stress occurs at a dose of $1 \times 10^{12}\text{ions/cm}^2$ and is relieved for higher doses. This is due to the formation of amorphous zones at higher doses which relax the lattice stress.
In section 6.3.1, we discuss the dependence of the observed crystallinity and disorder on dose for the as-implanted as well as annealed samples. In section 6.3.2, the depth dependent Raman scattering results are presented.

6.2 Experimental

A mirror polished (100)-oriented Si single crystal wafer (p-type, \( p=0.008-0.02 \ \Omega\text{-cm} \)) was used in the present study. The samples were implanted at room temperature with a scanned beam of 1.50 MeV Sb ions at various fluences ranging from \( 1 \times 10^{11} \) to \( 5 \times 10^{15} \text{ions/cm}^2 \). The implantation were performed with the samples oriented \( 7^\circ \) off-normal to the incident beam to avoid channeling effects. After implantation, RBS/C measurements were carried out using 2.5 MeV He\(^{+2} \) ions at a scattering angle of 150\(^\circ\).

Raman scattering measurements were performed using a SPEX 1877E Triplemate Spectrometer with a liquid nitrogen cooled, charged coupled device array. The laser power was controlled to avoid laser annealing effect on the sample. Raman experiments were carried out at room temperature using the 514 nm line of an Argon ion laser in the backscattering geometry. Annealing of the implanted samples was performed in pure Ar atmosphere at temperatures of 400\(^\circ\)C and 600\(^\circ\)C for 30 min.

In addition, depth dependent studies of the shifts in Raman peaks were also done with Raman spectroscopy. For this study laser incident angles, \( \phi \), were carefully changed so that the vertical depth of penetration inside the implanted sample varied with the angle of incidence as \( \cos \phi \).

6.3 Results and Discussion

6.3.1 Dose Dependence of Disorder

Figure 6.1 shows the as-implanted Raman spectra from the Si samples implanted with various Sb doses. All these spectra were acquired in the backscattering geometry. The spectrum from a virgin (unimplanted) Si is also shown for comparison. The crystalline Si (c-Si) Raman peak at 521 cm\(^{-1} \) corresponds to the LO phonon mode.
Fig. 6.1. Raman spectra from various fluences of 1.5 MeV Sb implanted Si(100). The spectrum of virgin (unimplanted) sample is also included for reference. The curves are vertically displaced for clarity.

The spectrum for the $1 \times 10^{11}$ ions/cm² sample does not show much change from virgin Si, except that the c-Si peak intensity has markedly decreased. The decrease in intensity indicates the appearance of defects after implantation. With increasing fluence, the intensity of the sharp c-Si peak decreases further and a broad peak centered at $\sim 480$ cm⁻¹ becomes apparent for doses of $1 \times 10^{13}$ ions/cm² and higher. The latter peak (a-Si) is due to the appearance of amorphous silicon in the lattice. The crystallinity and amorphicity of the Si sample, defined as the ratio of area under c-Si peak and a-Si peak to virgin-Si peak respectively, are plotted in Fig. 6.2. A decrease in the ratio of c-Si area and an enhancement in ratio for a-Si area is observed with increasing Sb dose. The Si lattice becomes completely amorphous for doses of $5 \times 10^{14}$ ions/cm² and higher as is observed by the absence of any c-Si peak for these doses. This is in contrast to self ion implantation in Si where Raman scattering detected the co-existence of crystalline as well as amorphous material even for doses as high as $1 \times 10^{15}$ ions/cm² [5]. The higher mass of Sb may result in generation of more
Fig. 6.2. The ratio of area under (a) c-Si peak and (b) a-Si peak to the virgin Si peak area as a function of ion dose and annealing temperature. Symbol size denotes the error in the measurement. Data for virgin sample is also shown. \( \chi_{\text{min}} \) calculated using RBS/C data are shown for the as-implanted samples.

defects and create complete amorphous zones even at a dose of \( 5 \times 10^{14} \text{ions/cm}^2 \). The decrease in intensity of the c-Si peak with increasing fluence is almost linear for the as-implanted samples suggesting a scenario where the defects are randomly distributed in the lattice. On annealing the samples at 400°C, the intensity of the c-Si peak however decreases more rapidly beyond a fluence of \( 1 \times 10^{13} \text{ions/cm}^2 \) and after a 600°C anneal the decrease exhibits a quadratic dependence on dose. Presence of clusters of defects or divacancies can be expected to cause this [10]. For the as-implanted, completely amorphized samples, the c-Si peak is not visible even after an anneal at 400°C, possibly because large amorphous regions still exist. However, a significant improvement in the intensity of c-Si for these doses is observed after a 600°C anneal. The amorphicity (Fig. 6.2b) in the as-implanted samples increases until it saturates at 0.12 for completely amorphized lattices having doses of \( 5 \times 10^{14} \text{ions/cm}^2 \) and higher. For these doses an a-Si peak is observed even after an anneal to 400°C. For lower doses, at this temperature, a large improvement in lattice order takes place as suggested by the disappearance of a-Si peak. Annealing at 400°C is thus sufficient for a/c
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phase transition at these doses. However, once a completely amorphized Si lattice is formed, higher annealing temperatures are required for this transition. After a 600°C anneal, substantial decrease in amorphicity along with the absence of a-Si feature for $5 \times 10^{14}$ ions/cm$^2$ is observed. However an amorphicity of $\sim 7.5\%$ is still present for the highest dose studied. In our earlier investigation by RBS/C (Chapter 4), we had observed that an anneal at 600°C is not sufficient to completely remove damages from a Sb implanted $(5 \times 10^{15}$ ions/cm$^2$) silicon [11]. These results are consistent with the measurements of the present study.

The dose dependent structural modifications in the Sb implanted Si have also been studied using RBS/C. Inset of Fig. 6.3 shows a representative as-implanted RBS spectrum of the 1.5 MeV Sb implanted Si(100) sample, along with the simulated spectrum obtained using GISA-3.95 ion scattering code [12]. For the implantation conditions used in this study, a Gaussian Sb profile peaking at $\sim 690$ nm below the surface with a width of $\sim 130$ nm is obtained. With the penetration depth of the Ar$^+$ 514 nm laser line in Si-crystal being 770nm, it was possible to probe the structural modifications upto the implanted region. In the earlier Raman studies for MeV Si$^+$ implantation in Si, only surface modifications have been studied since the penetration depth (500 nm) of the laser used was much smaller than the implantation range of 1.5$\mu$m [5, 6]. Fig. 6.3 shows the random and the [100] aligned RBS/C spectra of as-implanted Si(100) samples for fluences varying from $1 \times 10^{12}$ to $5 \times 10^{14}$ ions/cm$^2$. An aligned spectrum of the virgin sample is also included for comparison. The RBS/C signal from a $1 \times 10^{12}$ ions/cm$^2$ exhibits very little dechanneling. The Raman spectra from the samples with the fluences of $1 \times 10^{11}$ ions/cm$^2$ and $1 \times 10^{12}$ ions/cm$^2$ appear quite similar to virgin Si, though the c-Si peak intensity has decreased (30% and 50% respectively) sharply (Fig. 6.2a). For detecting very small concentrations of disorder, Raman technique thus seems more sensitive. In Raman, the a-Si feature is first observed at $1 \times 10^{13}$ ions/cm$^2$ denoting the development of some small amorphous regions (Fig. 6.2b) whereas by RBS/C only presence of some disorder is detected at this dose (Fig. 6.3). The two characterizing techniques used here thus provide slightly different doses for c/a phase transition in the Si lattice. This discrepancy over the dose of c/a transition may be due to the fact that disorder at this stage consists of mainly
Fig. 6.3. Random and [100] channeling spectra of 2.5 MeV He$^{+2}$ ions on 1.5 MeV Sb-implanted Si(100) crystal in the as-implanted state for various doses of Sb. The inset shows the random RBS spectrum with Si and Sb regions for an as-implanted sample with a dose of $1 \times 10^{15}$ ions/cm$^2$. The solid line represents the simulated result obtained using GISA-3.95 ion scattering code.
small volume defects (interstitials etc.), and to be detected by RBS, the concentration of these defects has to be quite large. Using RBS/C, the first signatures of the initiation of an amorphized Si lattice appear at a dose of $1 \times 10^{14} \text{ions/cm}^2$ (Fig. 6.3). It is observed that the amorphization initiates at the most heavily damaged region centered at a depth of $\sim$690 nm. The amorphization proceeds towards the surface region as the ion dose is increased and a completely amorphous region, extending from the surface to $\sim$1000 nm below, is obtained for the dose of $5 \times 10^{14} \text{ions/cm}^2$. Both the characterizing techniques are in agreement at this stage and indicate a completely amorphized Si region for this dose.

The damage profiles from various RBS/C spectra have been obtained using the multiple scattering method described by Feldman and Rodgers [4]. Details of this method have been explained in Chapter 2. Fig. 6.4 shows the damage profiles for the Si samples implanted with various fluences of Sb ions. The ordinate is the ratio of the density of the displaced atoms, $N_d$, and the atomic density of host silicon atoms, $N$. A very small disorder is noticed after an implantation with $1 \times 10^{12} \text{ions/cm}^2$. Even after a dose of $1 \times 10^{13} \text{ions/cm}^2$, the increase in damage is small although a broad damage profile is obtained. The damage in the top 100 nm of the surface region (SR) is also small. Maximum damage occurs at about 460 nm below the surface. At a fluence of $5 \times 10^{13} \text{ions/cm}^2$, a distinct damage peak emerges. Though the damage profile is still quite broad, it is asymmetric. A considerable increase of damage in the peak region as well as in the near surface region is observed, though there is not much change in the end of range (EOR) damage. An almost symmetric damage profile develops after a dose of $1 \times 10^{14} \text{ions/cm}^2$. The position of maximum damage is similar to that observed at lower fluences, i.e. about 460 nm below the surface. The Si lattice can be characterized as having a buried amorphous layer at this depth. The damage beyond EOR is still negligible. However in the SR, the damage is similar to that observed for a dose of $5 \times 10^{13} \text{ions/cm}^2$ demonstrating that the damage saturates at a relatively low level near the surface. This region is expected to contain mostly isolated point defects. This is corroborated by Raman studies as discussed earlier. The total number of displacements at any fluence can be calculated by integrating the density of defects over the total damaged region and is found to be
Fig. 6.4. Damage profiles for Si(100) implanted with various fluences of Sb. The profiles are extracted from RBS/C data by using the multiple scattering model. The dotted line at 596 nm indicates the \( R_p \) of Sb in Si.

\[ \sim 2.18 \times 10^{18} \text{cm}^{-2} \] for a Sb fluence of \( 1 \times 10^{14} \text{ions/cm}^2 \). An As ion implantation at the same energy and fluence produces only \( 3.7 \times 10^{17} \text{cm}^{-2} \) displacements [15]. Higher mass of Sb ion can cause an overall increase in damage in the lattice. At a Sb fluence of \( 5 \times 10^{14} \text{ions/cm}^2 \), the damage profile shows the presence of an amorphous layer extending from the surface to \( \sim 900 \) nm below. The total damage produced in Si due to various fluences of Sb has been calculated and will be discussed below. We also notice that the maximum disorder at the fluence of \( 5 \times 10^{15} \text{ions/cm}^2 \) here (for \( 7^\circ \) tilt angle implantation) is \( 3.85 \times 10^{18} \text{cm}^{-2} \) compared to \( 2.96 \times 10^{18} \text{cm}^{-2} \) observed for \( 60^\circ \) tilt angle implantation (Chapter 4) indicating that the angle of implantation crucially effects the damage accumulation.

MC simulations were performed for 1.5 MeV Sb ion implantation in Si using SRIM'97 code. The threshold displacement energy for Si was chosen to be 15 eV [16]. The simulated Sb ion distribution was found to have a mean projected range \( (R_p) \) of 596 nm. The ion profile (in arbitrary units) along with the theoretical damage profile for Si implanted with \( 1 \times 10^{14} \text{ions/cm}^2 \) are presented in Fig. 6.4. It is observed that
though the position of the experimental damage peak is in good agreement with the results from MC, this depth is \( \sim 23\% \) smaller than \( R_p \). RBS/C data provides an even larger \( R_p \) of 690 nm for Sb ions in Si (data not shown) suggesting that the position of peak damage is shallower than the primary position of ion deposition. The spread in the ion distribution however is smaller than the damage distribution. Furthermore, the theory overestimates the damage in the surface region. The dynamic beam self-annealing resulting from the recombination of point defects (e.g. interstitials and vacancies), but not considered by MC, can cause this difference. The sample surface can also act as a sink for vacancies. The recombination processes or the role of surface can also be responsible for the saturation of damage in the SR where no increase in damage is observed beyond a fluence of \( 5 \times 10^{13} \text{ions/cm}^2 \), until a thick amorphized layer forms at a fluence of \( 5 \times 10^{14} \text{ions/cm}^2 \). The distribution of the damage profile is governed by the balance between the production of damage and the annealing of defects. During implantation, knock-ons produce point defects resulting in the accumulation of damage depending on the nuclear energy deposited in the region or form extended defects which affect dechanneling but not the direct backscattering component of the RBS/C spectra. On the other hand, collision cascades can lead to some annealing of defects. The balance between these processes decides the final damage profile.

The dose dependence of the total amount of disorder as obtained by RBS/C and estimated using the damage profiles of Fig. 6.4 has been shown in Fig. 6.2b. The accumulated damage demonstrates two different trends. Initially at low fluences (up to \( 1 \times 10^{13} \text{ions/cm}^2 \)) the total amount of damage increases very slowly with increasing dose. For higher fluences, a reasonable disorder develops which leads to the formation of a buried amorphous layer for a dose of \( 1 \times 10^{14} \text{ions/cm}^2 \) and a thick amorphous layer after a dose of \( 5 \times 10^{14} \text{ions/cm}^2 \). In this region an approximately linear but faster accumulation of damage occurs. In these two regions different defect morphologies may be dominant [17]. For simple point defects the damage accumulates slowly and when the defects become complex, as will happen once the amorphous zones develop, the accumulation of damage becomes faster. For a fluence of \( 1 \times 10^{13} \text{ions/cm}^2 \), the knock-ons are able to produce enough damage that some amorphization is detected.
by Raman. This is accompanied by large structural changes in the Si lattice as observed by the developments in the c-Si and a-Si peaks. In view of this, the transition to a faster disorder rate may be due to the fact that once the critical size of an amorphized-defected zone is formed at a dose of $1 \times 10^{13} \text{ions/cm}^2$, it can easily expand by further accumulation of point defects at higher fluences. Furthermore, the total disorder estimated using channeling is lower compared to Raman scattering for the fluences between $1 \times 10^{13} \text{ions/cm}^2$ and $5 \times 10^{14} \text{ions/cm}^2$. This suggests that during the stages when Si lattice undergoes c/a transition and where the crystalline and amorphous zones coexist, Raman scattering can detect small concentrations of defects more effectively. Once the transition is complete, Raman and RBS/C techniques are in agreement. For self ion implantation in Si, Raman scattering detected the co-existence of crystalline as well as amorphous material even for doses as high as $1 \times 10^{15} \text{ions/cm}^2$ [5]. This is in contrast to our findings here as the Si lattice becomes completely amorphous even for the dose of $5 \times 10^{14} \text{ions/cm}^2$ as is observed by the absence of any c-Si peak for these doses. The higher mass of Sb may result in generation of more defects and create complete amorphous zones at lower doses.

Using Raman spectroscopy, shifts in the position of the c-Si peak for the implanted samples compared to the virgin Si are also observed. The shifts in the peak positions can be affected by the residual stress in the lattice due to ion implantation as well as by phonon confinement. The contributions due to the two effects can however be deconvoluted since the stress does not affect the shape of the spectrum whereas the confinement of phonon does [5]. The stress induced variations in the peak position of the c-Si are shown as a function of dose in Fig. 6.5a. The center and the width of the Raman peaks were determined based on curve fitting using a Voigt function for the c-Si peak and a Gaussian function for the a-Si peak. For the as-implanted samples with doses of $1 \times 10^{13} \text{ions/cm}^2$ and $1 \times 10^{14} \text{ions/cm}^2$ the c-Si peaks show a red shift i.e. appear at wave numbers lower than 521 cm$^{-1}$. This implies that some tensile stress has appeared in the Si lattice [18]. It has also been proposed that during a precursor stage to amorphization the crystal Si force constants are reduced and the Si lattice is softened causing shifts to the Raman peak [19]. In Fig. 6.5a the magnitude of stress calculated assuming the in-plane stress model proposed by Anastassakis [20]
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Fig. 6.5. Center positions for the (a) c-Si and (b) a-Si Raman peaks as a function of ion dose and annealing temperature. Stress in (a) has been calculated using eqn. (6.1). Error bars in (a) are denoted by the symbol size and a typical error bar in (b) has been shown. Data for a virgin sample is also shown.

is also shown. Using this model, stress (σ) is estimated from the wave number shift of the c-Si peak in the stressed sample compared to the Raman line of the virgin silicon according to the following equation:

\[ \sigma (\text{MPa}) = -250 \Delta \omega (\text{cm}^{-1}) \]  

(6.1)

where \( \Delta \omega = \omega_s - \omega_0 \). In this expression, \( \omega_0 \) and \( \omega_s \) denote the wave numbers of the c-Si peak in the stress-free and implanted samples respectively. After a 400°C anneal, no shifts in the center of the Raman peak are observed for the low fluences, however for the \( 5 \times 10^{14} \text{ions/cm}^2 \) and higher doses, the lattice remains primarily amorphous. The absence of shift for fluences that exhibited red shift prior to annealing may be due to the relaxation of stress in the damaged layers. After an anneal at 600°C, peak centers appear at the position of the virgin sample, for all the fluences studied. It is important to note that these shifts and stress correspond to an effective average value from the whole scattering volume i.e. from the surface up to the penetration depth of the laser (770nm). The shifts in the a-Si peak were also calculated and are shown in...
Fig. 6.5b. For the as-implanted samples, the a-Si peak center appears at 480 cm\(^{-1}\) for doses of 1\(\times 10^{13}\)\(\text{ions/cm}^2\) and 1\(\times 10^{14}\)\(\text{ions/cm}^2\) but shows a red shift for higher fluences. Enormous shifts for doses of Sb between 1\(\times 10^{14}\)\(\text{ions/cm}^2\) and 5\(\times 10^{15}\)\(\text{ions/cm}^2\) suggest growth and modification of the amorphous regions. As discussed earlier, both Raman and RBS/C detected completely amorphized lattices for 5\(\times 10^{14}\)\(\text{ions/cm}^2\) and higher doses. For these doses after a 400\(^{0}\)C anneal, the a-Si peak center shift to about 472 cm\(^{-1}\). Lower doses however show no a-Si peak any more. After a 600\(^{0}\)C anneal, though the 5\(\times 10^{14}\)\(\text{ions/cm}^2\) sample also becomes crystalline, the a-Si position still remains at \(\sim 472\) cm\(^{-1}\) for higher doses. The width of the amorphous peak in the Raman spectrum also demonstrates dose dependence. Beeman et.al. have proposed the following linear relationship between the full width at half maximum, \(\Gamma\) (cm\(^{-1}\)), of the a-Si peak and the bond angle deviation, \(\Delta\theta\) (degrees), in Si [21]:

\[
\frac{\Gamma}{2} = 7.5 + 3\Delta\theta
\]  

(6.2)

From the computer simulation results based on the Continuous Random Network model, values of \(\Delta\theta\) ranging between 7\(^{0}\) and 13\(^{0}\) are expected for amorphous silicon [21]. Based on equation (6.2), \(\Delta\theta\) was calculated and is shown in Fig. 6.6 along with the half width at half maximum (HWHM) of the a-Si peak at various doses. For the as-implanted samples, \(\Delta\theta\) varies from 6.7\(^{0}\) to 10.5\(^{0}\) as the dose is increased from 1\(\times 10^{13}\)\(\text{ions/cm}^2\) to 5\(\times 10^{15}\)\(\text{ions/cm}^2\). The value of \(\Delta\theta\) greater than 6\(^{0}\) demonstrates the presence of large densities of amorphous complexes [22]. Existence of 5 or 7 membered rings are expected in the amorphous regions. These rings are not present in c-Si and in order to form crystalline regions it is necessary to transform the wrong rings to the correct 6 or 8 membered rings with annealing. Annealing the samples at 400\(^{0}\)C causes a slight decrease in \(\Delta\theta\) values to \(\sim 9.3^{0}\) for doses 5\(\times 10^{14}\)\(\text{ions/cm}^2\) and higher. For lower doses the a-Si peak is no more present implying the development of crystalline regions. Subsequently annealing to 600\(^{0}\)C reduces the \(\Delta\theta\) further to 3.5\(^{0}\) for doses of 1\(\times 10^{15}\)\(\text{ions/cm}^2\) and higher. The free energy diagram by Motoooka et.al. indicates that a \(\Delta\theta \sim 3.5^{0}\) is in the transition region of amorphous to crystalline phase. Thus we expect a crystal with some combination of defected-amorphous phases. It has been mentioned earlier that some small amorphicity is still present for these
doses, even though it is only 7.5% for $5 \times 10^{15}$ ions/cm$^2$ (Fig. 6.2b), supporting that the transition is incomplete. For lower doses no amorphicity is present and a/c phase transition is expected to have taken place. Earlier, after annealing a Si sample with $5 \times 10^{15}$ ions/cm$^2$ dose to 600°C, using RBS/C we had found a $\chi_{\text{min}}$ of 12.5% for the Si lattice though no amorphicity was detected [11]. Once again it is noticed that while Raman spectroscopy supports presence of some small amorphous zones after annealing at this dose, RBS/C does not detect them.

During implantation, the lattice ions are displaced, creating defects and disordered regions in the process. With increasing lattice disorder, the phonon coherence length is reduced and the $k=0$ selection rule is relaxed, giving rise to measurable shifts and asymmetric broadenings of the Raman peaks [23]. Due to translational symmetry breakdown, PCM developed by Richter et.al. [7] can be used to evaluate the phonon confinement length or the average size of the undamaged crystalline regions. Details of this model have been described in Chapter 3. By fitting the experimental Raman spectra with PCM we have obtained the phonon coherence length $L_c$ in the as-implanted samples. Results of fitting are shown in Fig. 6.7 along with the phonon
Fig. 6.7. Raman spectra of Sb implanted Si(100) at various doses fitted with PCM as described by eqn. (3). •: experimental data, -: phonon confinement model fit to data. L(nm) is the phonon coherence length as determined by the fit to the data. Fitting for a virgin sample is also shown. Inset shows the asymmetric broadening, $\Gamma_a/\Gamma_b$, of the Raman peak as a function of ion dose and annealing temperature.
coherence length for several fluences. The line shapes of Raman spectra from the
as-implanted samples with fluences of \(1 \times 10^{12} \text{ions/cm}^2\) and lower are very symmetric
suggesting the presence of very large crystalline regions. Point defects though present
at these doses, will be isolated and hence cannot cause phonon confinement. A fluence
of \(1 \times 10^{13} \text{ions/cm}^2\) causes an asymmetricity in the Raman peak which can be due to
the presence of some disordered or amorphous regions in the sample that are large
enough for phonon confinement. Using the PCM, a phonon coherence length of 330 Å
is obtained, indicating the presence of undamaged Si regions with an average crys­
tallite size of 33 nm. The Raman c-Si peak after a Sb fluence of \(1 \times 10^{14} \text{ions/cm}^2\) is
highly asymmetric and possesses a phonon coherence length of only 15.5 nm. Results
from the PCM fitting therefore suggest the presence of nanometer sized undamaged
crystalline regions in the as-implanted Si matrix for the fluences of \(1 \times 10^{13} \text{ions/cm}^2\)
and \(1 \times 10^{14} \text{ions/cm}^2\). In addition, the measured \(\Delta \theta\) values (Fig. 6.5) indicate exist­
tence of amorphous regions. Thus a coexistence of nanocrystalline structures as well
as amorphous silicon matrix takes place at these fluences. For higher doses the Si
lattice becomes completely amorphous. It is likely that the small amorphous zones
inflate in size or some new amorphous zones get created with increasing fluence that
finally overlap leading to total amorphization of the lattice. The asymmetric broad­
ening of the c-Si peak for various doses is also displayed using the ratio \(\Gamma_a/\Gamma_b\) in the
inset of Fig. 6.7, where \(\Gamma_a\) and \(\Gamma_b\) indicate the left and right HWHM respectively.
Non-equivalent \(\Gamma_a\) and \(\Gamma_b\) after a 600°C anneal for the highest dose studied, sup­
ports the fact that small amorphicity is still present. Also, big crystalline regions are
expected as the ratio \(\Gamma_a/\Gamma_b\) is quite small.

6.3.2 Depth Dependence of Shifts in Raman Peak

Some depth dependent measurements using Raman scattering have also been per­
formed in the present study by varying the laser angle, \(\phi\), from 65° to 75°. By this
method, the scattering depths probed are defined by \(d_p \cos \phi\) (\(d_p\) being the penetration
depth of the laser) and ranged from 325 nm to 199 nm below the silicon surface. Due
to limitations of the goniometer and the scattering from small excitation volumes,
Fig. 6.8. Raman c-Si peak at various laser angles for an implantation dose of $1 \times 10^{12}$ ions/cm$^2$. A virgin c-Si peak is also shown for reference.

studies at lower and higher angles were at present not possible. In this section, only the results of the shifts in the center position of c-Si peak are discussed in order to show the existence of a gradient in stress in the Si lattice.

The Raman spectra acquired at various angles are shown in Fig. 6.8 for a dose of $1 \times 10^{12}$ ions/cm$^2$. The spectra are not normalized in intensity and the virgin sample showed similar intensity variations with angle. The center of the Raman c-Si peak of the virgin sample did not show any shifts with angle and a reference spectrum is shown. The c-Si peaks from the implanted samples however show distinct shifts from the center of virgin c-Si peak, with varying angles. We further observe that the spectrum at 65° is shifted towards lower wave numbers whereas the one at 75° towards higher. Moreover, for 70° two distinct features are visible one at lower and the other at higher wavenumber compared to virgin peak center. These results strongly suggest that compressive stress or harder force constants are contributing at higher angles and tensile stress or softened force constants dominate towards the lower angles. The transition appears to occur at an angle between 72° and 71° since there is no sign
of tensile component at 72° and it first appears at 71°. In the later spectrum the presence of compressive feature is also observed. The compressive component at this stage can be due to the contribution from the top sample layers which will always contribute with varying intensity, as is distinctly seen at 71°, 70° and 69°. With decreasing angles the tensile peak becomes more dominant whereas the compressive peak reduces in intensity. For a dose of $1 \times 10^{11}$ ions/cm² only one feature is observed at all the angles which though shifts with respect to the center of the virgin peak, always appears at lower wave numbers. However two components, as observed for $1 \times 10^{12}$ ions/cm² in Fig. 6.8, are also observed at higher doses (data not shown here). For qualitatively measuring the associated shifts in a spectrum containing two peaks, a weighted average of the centers was taken. Although this average does not take into account the fact that the scattering intensity from the top layers is higher (and scattering volume is lower) than that from bottom regions, it reflects the presence of the gradient in stress clearly. The shifts are plotted in Fig. 6.9 as a function of laser angle for various doses. The corresponding depth scale as well as the associated stress calculated using equation (6.1) are also indicated. The angular region probed here corresponds to a depth of 199nm to 325nm below the Si surface. Fig. 6.3 indicates that this depth range lies in front of the implanted-layer/Si interface and is crystalline even for the dose of $1 \times 10^{14}$ ions/cm². At a depth of about 325 nm (65°), a red shift in peak center, indicating the presence of tensile stress is observed for all doses (Fig. 6.9). For the Sb dose of $1 \times 10^{11}$ ions/cm² the shift reduces at shallower depths showing a smaller magnitude of stress. However, the behavior is very different at the dose of $1 \times 10^{12}$ ions/cm². Though a red shift in c-Si peak center is observed at 325 nm, at shallower depths (~200 nm) a blue shift of ~ 6.5 cm⁻¹ is observed. It is very clear that the tensile stress at deeper regions has gradually transformed into compressive stress towards the surface. A similar behavior is observed for higher fluences too. Since the implanted Sb atoms as well as the interstitials are present mostly in the vicinity of the implantation depth [25], these may be the cause of the tensile stress in Si lattice. Presence of other kinds of defects can also be responsible for this. Nuclear energy deposited as well as the presence of vacancies in the surface region can result in compressive stress near the silicon surface. Presence of compressive stress
in the surface region has been observed for MeV implanted Si$^+$ in Si [5] whereas for keV implantation of N$^+$ in Si a tensile stress is measured from the whole scattering volume[26]. In the later study, due to the limitation of laser penetration depth, scattering volume extended from the surface upto the depth of implantation. Though the presence of compressive stress in the surface layers [5] and of tensile stress while probing large scattering volumes [26] have been observed earlier in separate studies, the transition in the nature of stress that we observe here is significant. For keV implantations of Si$^+$, P$^+$, Ge$^+$ and As$^+$ in Si, large shifts up to $\sim +6 cm^{-1}$ of the c-Si Raman peak were observed from surface crystalline layers prior to amorphization [19]. Surprisingly, maximum shifts observed in the compressive regime in the present study are similar.

The overall magnitude of stress for the $1 \times 10^{12} ions/cm^2$ implanted sample is larger than that for $1 \times 10^{13} ions/cm^2$ fluence. As observed in Fig. 6.2b, the amorphicity or the a-Si feature in the Raman spectrum first appears at a fluence of $1 \times 10^{13} ions/cm^2$. 

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**Fig. 6.9.** Shifts in c-Si peak as a function of angle, $\phi$, for various fluences. The corresponding depth(nm) below the Si surface is indicated. The magnitude of stress calculated using eqn.(6.1) is also shown.
These findings suggest that at this dose the stress relaxation may be due to the production of amorphous regions. At a Sb dose of $1 \times 10^{12} \text{ions/cm}^2$, the Si lattice will be highly strained having not yet attained the critical dose to overcome the crystalline to amorphous barrier. Although, the stress observed after a fluence of $1 \times 10^{14} \text{ions/cm}^2$ is more than $1 \times 10^{13} \text{ions/cm}^2$ as expected due to increased damage, it is still lower than that observed in $1 \times 10^{12} \text{ions/cm}^2$. Stress relaxation has also been observed for Si\textsuperscript{+} implantation in Si [5] and by bending measurements for Xe implantation in Si [27]. The depth profiling of shifts in peak center demonstrate that a transition from tensile stress in the implanted regions to compressive stress in the shallower regions takes place which can be quantitatively probed using Raman spectroscopy. This is a very useful non-destructive technique for monitoring stress in materials that are used in device related technologies. Moreover the results obtained in Fig. 6.4a provide only an average value of the shift or stress for the total scattering volume (770 nm) unlike the depth dependent results presented in this section. This to our knowledge is the first study that has used Raman scattering to quantify and probe the region of transition. Moreover, the maximum stress in silicon is observed at a Sb dose as low as $1 \times 10^{12} \text{ions/cm}^2$. In the Sb implanted structures the stress is relieved by the development of amorphous zones. Depth dependent studies at wider depth scales and with subsequent annealing will be undertaken in future.

### 6.4 Summary and conclusions

RBS/C and Raman scattering techniques have been used to characterize the radiation damage and the structural modifications in Si lattice which are produced due to 1.5 MeV Sb implantation. From the RBS/C data, multiple scattering formalism has been utilized to extract the damage profile in Si as a function of depth for several fluences. The results have been compared with the MC simulations using SRIM'97 code calculation. Though the damage peak position compares well with the simulation results, it is shallow compared to the peak of Sb ion distribution. Recombination of point defects as well as the role of surface may be significant in surface-region (SR) since they lead to a saturation of damage at low levels in this region for all fluences.
The total accumulated damage demonstrates two distinct trends: a slow accumulation rate switches over to a faster rate at a dose of $1 \times 10^{13}$ ions/cm$^2$. This cross-over may be a result of the formation of a critical size of defected zones where further defect accumulation facilitates their expansion. However, the total damage observed by channeling is far lower than the amorphicity detected by Raman scattering suggesting sensitivity of the Raman technique to the small concentrations of defects formed during the early stages of c/a transition. Raman technique reveals higher disorder than RBS/C at fluences where crystalline regions and amorphous zones exist together in the silicon matrix. In the regime of doses where undamaged and amorphous regions are both present, PCM estimates the crystalline regions to be limited to nanometer sizes. For completely amorphous lattices and for Si crystals with little disorder the extent of damage observed by these two techniques is consistent. Using Raman technique the depth dependent measurements of shifts of c-Si peak show a transition in the nature of stress. The crossover from tensile stress in near implantation depth to compressive stress in surface layers is significant at a fluence of $1 \times 10^{12}$ ions/cm$^2$ which is characterized by a maximum strained lattice. At increased fluences the stress is relieved probably due to the development of the amorphous areas.
Bibliography

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