# DIFFUSION OF ION IMPLANTED BORON IN SILICON: THE EFFECTS OF LATTICE DEFECTS AND CO-IMPLANTED IMPURITIES

By

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## A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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Chairman: Dr. Kevin S. Jones

Major Department: Materials Science and Engineering Ion implantation is used to introduce dopant atoms into the silicon lattice during the processing of integrated circuits. For deep sub-micron transistors the electrical junction formed by the implanted dopant is constrained by maximum levels of sheet resistance, junction depth and junction leakage current. Ion implantation inherently produces large concentrations of excess silicon interstitials. These interstitials mitigate three processes: dopant activation, dopant diffusion, and extended defect formation, which directly affect the aforementioned junction characteristics. This work is the culmination of two consecutive projects centering on ion implantation of dopants in silicon. The first project was to investigate the fundamental processes associated with amorphizing ion implantation, particularly the correlation between extended defect evolution and dopant diffusion. The second project was more applied, seeking to determine if it was possible to introduce an impurity into silicon, co-implanted with boron, that would decrease boron diffusion. The result of this work is a greater understanding of boron diffusion in the presence of fluorine, an element that is pervasive in integrated circuit manufacturing.

## CHAPTER 1 INTRODUCTION

#### **Motivation**

Since its discovery as a uniform and controllable mechanism to introduce dopant into semiconductors, ion implantation has grown to be the principal doping technology used in the manufacturing of integrated circuits (ICs). Because of its wide use in the fabrication of semiconductor devices, extensive research has been devoted to the materials science of ion implantation. One of the most pertinent issues associated with ion implantation in silicon is the inherent introduction of excess point defects, namely silicon interstitials. The evolution of interstitial point defects during subsequent thermal treatment has a significant impact on the final properties of both the device and the silicon from which it is manufactured. These interstitials mitigate three processes pertinent to IC manufacturing: dopant activation, dopant diffusion, and extended defect formation. These three processes directly affect the crucial device parameters of junction sheet resistance, junction depth and junction leakage current, respectively. Understanding these processes is crucial to the development of front-end processes for future generations of ICs, both for process modeling and for process improvement. Without such advancement, the inability of front-end processes to produce ultrashallow, low resistivity junctions will impede the ability of the semiconductor industry to continue scaling devices within the next decade.

Of the two main dopants currently used to produce electrical junctions in silicon (arsenic and boron) boron has greater limitations in creating ultra-shallow, low-resistivity junctions due to its lower solid solubility and high diffusivity after ion implantation. Since both transient enhanced diffusion (TED) and clustering of boron are caused by silicon interstitial supersaturation, silicon interstitials caused by implant damage are an impediment to ultra-shallow junction formation. The foundation of this work is the hypothesis which supposes that by introducing an impurity into the silicon lattice that has an affinity for either boron or silicon self-interstitials, the impurity may prevent the interstitial from interacting with boron in the lattice. The result of the presence of the impurity would then be to reduce the TED of the boron. This work tested the viability of this hypothesis.

#### **Dissertation Statement**

The contributions of this work to the fields of silicon processing and materials science are the following:

1. Correlation between end-of-range defect density and interstitial flux toward the silicon surface.

- 2. Conclusive evidence of the existence of sub-microscopic interstitial clusters.
- 3. Observation of heterogeneous nucleation of end-of-range dislocation loops at {311} defect sites.

 Determination of the effect of co-implanted fluorine on the diffusion of ion implanted boron in silicon as a function of fluorine co-implantation conditions.
 Observation of a fluorine trapping silicon interstitials, thereby reducing

transient-enhanced diffusion of boron in ion-implanted silicon.

## CHAPTER 2 LITERATURE SURVEY

#### Ion Implantation Damage

Ion implantation produces damage to single crystal silicon through lattice displacements by energy transfer to the lattice atoms from the primary ion or from recoiled ions during the implantation. Lattice displacements occur when the energy transferred to a lattice atom through nuclear collisions exceeds 15 eV. This progression of lattice displacements along the path of the ion through the crystal is referred to as the collision cascade. Displacement of a lattice atom produces both an interstitial and a vacancy, called a Frenkel pair. During the relaxation of the collision cascade, many of the Frenkel pairs recombine. The probability of recombination is proportional to the separation distance of the interstitial and vacancy, temperature, and the existence of point defect traps. After recombination of interstitials and vacancies during the relaxation of the collision cascade, a fraction of the Frenkel pairs remain. The number of interstitials and vacancies that remain after ion implantation is a function of the implant conditions including ion mass, ion dose, wafer temperature, and ion dose rate. Upon annealing, an array of different defects can arise depending on the asimplanted state of the silicon. The three possible as-implanted morphologies include 1) a damaged (potentially including isolated amorphous pockets) crystalline silicon lattice; 2) the formation of a continuous buried amorphous layer centered around the peak of the damage profile with crystalline silicon above and below the amorphous layer; or 3) an amorphous layer that is continuous from the surface down to a depth determined by the implant conditions. If no continuous amorphous layer is present, then upon annealing most interstitial/vacancy (I-V) recombination occurs at relatively low temperatures (<500°C). If an amorphous layer is formed, then upon annealing this layer will recrystallize by solid phase epitaxial regrowth, typically between 550°C and 650°C.

#### Crystalline Silicon with Implant Damage

Introduction of ions with energies in the keV range into a single crystal lattice produces extensive lattice perturbations as a result of energy and momentum transfer from the impinging ion to the lattice. Atoms may be displaced from initial lattice positions when the energy transferred from the primary or recoiled ion by nuclear collisions exceeds the binding energy of the lattice. The probability of the created Frenkel pair surviving beyond the collapse of the collision cascade is proportional to the amount of energy transferred to the displaced atom. After non-amorphizing ion implantation, the majority of point defects are located in the projected range of the implant where most nuclear collisions occur. For non-amorphizing ion implantations in the approximate energy range 10 to 100 keV and moderate doses similar to those used in modern industrial processes  $(10^{12} \text{ to } 10^{15}/\text{cm}^2)$ , the number of excess interstitials is

believed to be approximately equal to the implant dose. This was first noted when quantitative analysis of the trapped interstitial concentration in subthreshold dislocation loops paralleled the implant dose.<sup>1</sup> A subsequent model was formally proposed and labeled the "plus 1" model to indicate the interstitial concentration should match the dose.<sup>2</sup> This model holds reasonably well for Si<sup>+</sup> implants. However, for higher mass implants, Herner et al.<sup>3</sup> and Pelaz et al.,<sup>4</sup> showed that the "plus" value increases sublinearly with increasing ion mass. Damage agglomerates at the projected range in crystalline silicon. Agglomerates of interstitials may follow a number of evolutionary pathways toward a lowest energy state.

#### Surface Amorphized Silicon

When the amount of damage in the surface region of the silicon exceeds a critical point, typically near 10% atomic displacements,<sup>5</sup> the material undergoes a first-order phase transformation from crystalline to amorphous. The dose range over which the threshold for amorphization is exceeded depends on the ion mass, ion energy, ion dose rate, and implant temperature.

Upon annealing, solid phase epitaxial (SPE) regrowth of the amorphous region occurs and the recrystalized region is once more defect-free. A highly damaged layer, termed the end-of-range (EOR) damage region, is located below the former amorphous-to-crystalline interface. It is believed there are two principle sources of the interstitials in the EOR damage region. The first are transmitted ions which come to rest below the amorphous/crystalline interface. Transmitted ions are analogous to the "plus 1" number of interstitials in non-amorphizing implants except that a significant number of the implanted ions are contained in the amorphous region and do not contribute to the excess interstitials. Thus, the number of transmitted ions is much less than the dose because of the presence of the amorphous layer. The second major source of interstitials in the EOR is the recoiling of lattice atoms into interstitial positions below the amorphous-to-crystalline interface by the forward momentum of the ion beam. Venables et al.<sup>6</sup> and Laanab et al.<sup>7,8</sup> showed that modeling which takes into account both the transmitted ions and the recoils, most accurately predicts the effect of implant energy, dose and implant temperature on the trapped interstitial concentration in the EOR. Upon annealing, the interstitials in the EOR follow similar evolutionary pathways to those in the projected range of the non-amorphized case.

#### **Evolutionary Pathways of Excess Interstitials**

#### Recombination

Interstitials and vacancies are produced by the primary ion and recoil atoms during ion implantation. After the relaxation of the collision cascade,  $\sim 10^{-13}$  seconds,<sup>9</sup> Frenkel pairs that remain contribute to the supersaturation of interstitials and vacancies. Although studies have

indicated the mobility of vacancies<sup>10</sup> and interstitials in silicon at liquid helium temperatures, it is believed that the effective mobility of point defects at room temperature is relatively low. This is due to the trapping of the point defects at a number of sites with a higher capture cross-section than the complementary component of the Frenkel pair. As a result, it is assumed at room temperature that any Frenkel pairs that survive the implantation remain until annealing. At elevated temperatures ( $T > 600^{\circ}$ C) however, the mobility of the point defects is significant. During annealing, many of the interstitials and vacancies recombine either at the surface or in the bulk. The driving force of this reaction is to move both interstitial concentration ( $C_v$ ) and vacancy concentration ( $C_v$ ) toward equilibrium. If the strain fields of an interstitial and vacancy overlap it is expected that they will recombine and annihilate, assuming no other trapping mechanism interferes. The fraction of point defects which do not recombine, either at the surface or in the bulk, form clusters with other point defects and/or impurity atoms.

#### Self-interstitial Clusters

Point defects in crystalline materials inherently add free energy to the system. Free interstitials in silicon are thermodynamically unstable and in high concentrations cluster to reduce free energy. Many forms of the interstitial cluster have been observed. The interstitial cluster configurations believed to occur in ion-implanted silicon include the di-interstitial, interstitial chain, {311} rod defect, and dislocation loops. The TEM micrograph images of {311} defects and dislocation loops are shown in Figures 2-1 and 2-2, respectively.

The most unstable form of the interstitial in silicon is the free interstitial. The free interstitial has strain energy associated with it because it is larger than any interstitial site. It also has a free energy of 1 eV from each unbonded orbital. A di-interstitial represents a more stable configuration compared to the free interstitial since it reduces the number of unbonded orbitals. Theoretically, by forming an interstitial chain in which interstitials are bonded both to the lattice and to each other in a linear fashion, the number of dangling bonds can be further reduced. This is supported by recent results<sup>11</sup> obtained by modeling interstitial supersaturation measurements which suggest that interstitial clusters have stable configurations (e.g. n=8) below the size of a {311} defect. The interstitial chain configuration has been used in many models for the formation of extended defects in silicon.<sup>12-14</sup> Formation of such an interstitial chain elongated in the <011> direction is the foundation for modeling  $\{311\}$  defects by adding several <011> chains in the <233>direction, forming an extrinsic stacking fault on the {311} habit plane. It has been shown that such an extended defect further reduces the free energy of the excess interstitials since the {311} defect has no dangling bonds along the sides of the defect (strained reconstructed bonds exist at

the ends of the rod).<sup>14</sup> Of the aforementioned defects, only {311} defects and dislocation loops have been directly observed by electron microscopy.

#### {311} Defect Evolution

Interest grew in the {311} defect after studies of Si+ implants into doping superlattices showed that the dissolution kinetics of these defects matched the time scale of the effect known as TED.<sup>15</sup> TED is a well-known phenomena which describes the enhanced diffusion of implanted dopants during annealing of ion implanted layers. The TED process is complex and its consequences are dramatic. While the dopant profile after implantation may be shallow, upon annealing the profile can diffuse as much as several thousand Å into the crystal, resulting in unacceptably deep junctions. The source of the TED process is the release of excess interstitials from the implanted region. It has been proposed that the source of the interstitials for TED is the {311} defect.<sup>15</sup> Strong correlation has been shown between the duration of TED and the dissolution process of the {311} defects.<sup>16,17</sup>

#### **Dislocation Loop Evolution**

The other type of ion implantation-induced defect most commonly observed in silicon is the dislocation loop. The formation threshold for these defects (around  $1 \ge 10^{14}$ /cm<sup>2</sup> for implants below 100keV)<sup>1</sup> is considerably higher than the reported threshold dose for  $\{311\}$  defects of only 7 x  $10^{12}$ /cm<sup>2</sup> for 40 keV Si<sup>+</sup> implants.<sup>16</sup> Thus, it appears that the nucleation barrier for formation of a dislocation loop is higher than that of a {311} defect. For higher energy implants (380 keV to 1 MeV) the threshold dose for loops can drop as low as  $4 \times 10^{13}$ /cm<sup>2</sup>.<sup>18</sup> The decrease in the threshold dose with increasing energy is thought to be due either to the increase in damage deposition<sup>18</sup> in the crystal or to the increased separation of the Frenkel pairs<sup>19-21</sup> which reduces the I-V recombination efficiency. It has been proposed that loops may simply evolve from unfaulting of {311} defects.<sup>16</sup> For nonamorphizing implants, all of the dislocation loops that were observed to form, came from  $\{311\}$  defects at 800° C.<sup>22</sup> It has not been proven that the same process occurs at high temperatures (900-1200° C). Once the nucleation stage for dislocation loops has been completed, loops either remain stable, coarsen, or dissolve. Dislocation loop dissolution can provide interstitials for some diffusion enhancement,<sup>23</sup> but since the temperature is so high, the relative enhancement,  $C_{I}/C_{I}$  \* ( $C_{I}$  \* is the equilibrium concentration of interstitials), is not as large as the effect from {311} dissolution at lower temperatures. Dislocation loops that remain in submicron silicon transistors after processing can be detrimental to the

device. Dislocation loops in silicon tend to getter metal impurities that disrupt the electron transport in the vicinity of the loop.<sup>24</sup> Landi has shown that if dislocation loops exist in the space charge region of a junction they can cause high leakage currents.<sup>25</sup> For these reasons, the electrical junction of a silicon transistor must form deep enough so that dislocation loops are never in the space charge region of the device.

### Diffusion in Silicon

Diffusion is the process by which random atomic motions result in matter transport. In the presence of a chemical potential gradient, there is a driving force for diffusion. In simplest terms, the chemical potential gradient is merely due to the gradient in the concentration of the diffusing species. If enough energy is supplied to the system to overcome the activation barrier, diffusion will occur to reduce the concentration gradient and homogenize the system. The process of diffusion has been described on two different levels: on the macroscopic level through continuum models and on the microscopic level with atomistic models.

#### Continuum Theory

Continuum theory deals with the various atomic processes involved in matter transport in an inhomogeneous system as components in a black box and focuses on the result of the processes on the macroscopic scale. Continuum theory is grounded in continuity equations which mathematically express the physical conservation of matter in a system. The continuity equations may be derived in a mathematically rigorous fashion,<sup>26</sup> or in a physically based manner<sup>27</sup> similar to the following discussion.

The general mathematical descriptions of diffusion on a continuum level are known as Fick's Laws. Fick's first law describes the flux of a component along a concentration gradient

$$J = -D \frac{c}{x}$$
(2.1)

where J is the flux, c is the concentration, x is the gradient direction, t is time, and D is the diffusion coefficient. Fick's first law is most applicable to steady state conditions where the concentration gradient is constant as a function of time. In systems where the concentration gradient is changing with time Fick's second law

$$\frac{c}{t} = D \frac{^2c}{x^2}$$
(2.2)

is applied.

## Atomistic Theory

There are several mechanisms by which atoms may diffuse through a crystal lattice. The mechanisms applicable to diffusion in the covalently bonded silicon lattice are the vacancy, interstitial, and interstitialcy

mechanisms. The ring exchange mechanism is not a likely mechanism in the diamond cubic lattice.

In a lattice there are always a certain number of vacant lattice sites. If an atom on a lattice site jumps to occupy a nearest-neighbor vacancy, it has diffused by a vacancy mechanism. An atom that occupies an interstitial position in the lattice is termed an interstitial. If an interstitial atom jumps to an adjacent interstitial position without completely displacing any lattice atoms from a lattice site, it has diffused by an interstitial mechanism. The interstitial mechanism is equivalent to a vacancy mechanism which operates on the sub-lattice of interstitial sites. If an interstitial atom jumps to a lattice site position and in the process displaces the lattice atom into an adjacent interstitial position, it has diffused by an interstitialcy mechanism.

One of the cornerstones to atomistic-based modeling of diffusion is random walk. Regardless of the physical mechanism, atoms move from one position in the lattice to another by making jumps in random directions. The ensemble of the combined summations of the jumps of all the diffusing species in the lattice give rise to the macroscopically observed matter transport. The rate of movement of an atom is directly proportional to the vibrational frequency of the atom and therefore directly proportional to the lattice temperature. It has been shown<sup>27</sup> that by defining the jump frequency as

<u>n</u>			(2.3)	
t			(-	,

where n is the atomic jump distance and t represents time, the diffusion coefficient is related to the jump frequency by the expression

$$D = \frac{1}{6} n^2$$
(2.4)

This differs from the typical rule of thumb for diffusion  $x = 2\sqrt{Dt}$  by a factor of 3 because it is the diffusion in three dimensions instead of one dimension. From Equation 2.4, it is apparent that the diffusion characteristics of a system are dependent on the jump frequency of the diffusing species. The jump frequency, , is a function of the temperature dependent lattice vibration frequency, (T), the probability of an adjacent site being vacant, and the probability that the atom will jump into a vacant adjacent site. If the diffusion mechanism is interstitial as opposed to vacancy, then the probability of an adjacent site being vacant refers to an adjacent interstitial site. It is possible for both diffusion mechanisms to operate simultaneously in a system. The interstitialcy mechanism is treated as interchangeable with the interstitial mechanism from this point on, since the two are indistinguishable by empirical methods. By correlating the continuum and atomistic diffusion theories, the role of point defect population on the diffusion fluxes and on the resulting concentration profiles may be extracted. If both vacancy and interstitial diffusion mechanisms are allowed to operate independently, i.e. the

diffusing atoms do not interact, then the diffusion coefficient can be defined<sup>28</sup> as

$$D_{A} = D_{AV} \frac{C_{AV}}{C_{A}} + D_{AI} \frac{C_{AI}}{C_{A}}$$
(2.5)

where  $D_A$  is the diffusion coefficient of species A,  $D_{AV}$  is the vacancy diffusion coefficient of species A,  $D_{AI}$  is the interstitial diffusion coefficient of species A,  $C_{AV}$  is the concentration of A occupying host lattice sites with adjacent vacancies,  $C_{AI}$  is the concentration of A occupying interstitial positions in the host lattice, and  $C_A$  is the concentration of species A. The fraction of the diffusion of a species through each mechanism may then be defined for the interstitial mechanism as

$$f_{AI} = \frac{D_{AI}}{D_A} \quad \frac{C_{AI}}{C_A}$$
(2.6)

and for the vacancy mechanism as

$$f_{AV} = \frac{D_{AV}}{D_A} \frac{C_{AV}}{C_A}$$
(2.7)

It has been shown<sup>28</sup> that  $f_{AI}$  1 for boron under intrinsic diffusion conditions. Since by definition,

$$f_{AI} + f_{AV} = 1 \tag{2.8}$$

and the definition of the fraction of interstitial and vacancy diffusion components were defined under intrinsic (quasi-equilibrium) conditions, it follows that

$$\frac{D_{A}}{D_{A}^{*}} = (1 - f_{AI}) \frac{C_{AI}}{C_{AV}^{*}} + f_{AI} \frac{C_{AI}}{C_{AI}^{*}}$$
(2.9)

where those variables with \* superscripts indicate intrinsic values and those without are the observed values. In addition to the assumption of intrinsic conditions, Equation 2.9 requires that the supersaturation of  $C_{AI}$  and  $C_{AV}$  are sufficiently small such that

$$C_{A}^{\text{total}} = C_{A} + C_{AI} + C_{AV} \qquad C_{A}$$
(2.10)

Since for boron  ${\rm f}_{\rm AI}~$  1, Equation 2.9 can be rewritten

$$\frac{\mathbf{D}_{\mathbf{A}}}{\mathbf{D}_{\mathbf{A}}} = \mathbf{f}_{\mathbf{A}\mathbf{I}} \frac{\mathbf{C}_{\mathbf{A}\mathbf{I}}}{\mathbf{C}_{\mathbf{A}\mathbf{I}}}$$
(2.11)

The above equation shows that the relationship between the observed diffusion of species A, which for the present case is boron, divided by its intrinsic diffusion value is directly proportional to the supersaturation of species A in interstitial positions. If Equation 2.10 holds, then  $C_{AI}$  can be related to  $C_{I}$  by the equation

$$\frac{C_{AI}}{C_{AI}}^{*} = \frac{C_{I}}{C_{I}}^{*}$$
(2.12)

Under these conditions

$$\frac{\mathbf{D}_{\mathrm{A}}}{\mathbf{D}_{\mathrm{A}}^{*}} \quad \frac{\mathbf{C}_{\mathrm{I}}}{\mathbf{C}_{\mathrm{I}}^{*}} \tag{2.13}$$

in which case the diffusion enhancement of boron is directly proportional to the supersaturation of interstitial point defects. Under the conditions produced by ion implantation, Equation 2.10 does not hold, since  $C_{A}$   $C_{I}$ . As the interstitial supersaturation increases, eventually each boron atom is associated with an interstitial and Equation 2.13 fails since subsequent increase in the interstitial population produces no net increase in the diffusion of the boron. Although the assumptions in the derivation of  $f_{AI}$ fail at high interstitial supersaturations such as those created by ion implantation, recent *ab initio* calculations<sup>29</sup> have shown that the conclusion of  $f_{AI}$  1, holds even at high supersaturation. It is for this reason that ion implantation-induced interstitial point defects lead to the process known as TED.<sup>23,30,31</sup> In the presence of excess interstitials the diffusivity of the boron may be enhanced by up to 5 orders of magnitude.<sup>32</sup> Boron TED leads to the formation of junctions which are unacceptably deep. For example, a 1 keV 1 x  $10^{14}$ /cm<sup>2</sup> B<sup>+</sup> implant may have a projected range of ~100Å, however after annealing the junction depth exceeds 1000Å. This phenomena is illustrated in Figure 2-3, a secondary ion mass spectrometry (SIMS) plot of a shallow boron implant. It is evident from the profile of the boron that the boron diffusion rate is significantly higher at short times (< 15 minutes) than at longer times (> 15minutes).

#### Boron Clustering

#### Boron-interstitial complexes

When crystalline silicon is implanted with boron, immobile dopantinterstitial complexes are observed after moderate thermal treatments.<sup>33</sup> These boron complexes are commonly referred to as boron-interstitial clusters (BICs). The size and structure of BICs is not known. Several models involving reactions between boron and silicon interstitials to form BICs have been proposed.<sup>34-37</sup> The exact path of the evolution is not known, but generally the final precipitate is believed to be an SiB<sub>3</sub> complex as predicted by the silicon-boron phase diagram.<sup>38</sup> BICs cannot be directly observed by TEM, however, the formation of BICs reduces the formation of {311} defects. Law and Jones observed this by noting the reduction in trapped silicon interstitials in {311} defects in the presence of boron.<sup>39</sup> Zhang noted that lower energy boron implants do not form {311} defects but exhibit BICs.<sup>33</sup> Haynes observed boron clustering by comparing the number of {311} defects in boron doping wells with different concentrations, after identical silicon implants.<sup>40</sup> Haynes' experiment showed that samples with increasing boron concentration and hence increasing concentrations of BICs exhibit decreasing {311} defect density.

Boron Clustering above Solid Solubility

Above certain concentrations, boron exceeds its solid solubility in silicon. When the solubility is exceeded, the excess boron forms second phase precipitates with the host silicon atoms. The stoichiometry of the precipitates is  $B_3Si.^{38}$  This phase formation process results in self-interstitial injection into the silicon lattice. The interstitial injection process leads to enhanced diffusion of the boron and is known as boron enhanced diffusion (BED).<sup>41</sup> Recent studies of high dose boron implantation in silicon have suggested that certain boron clusters may act as dopants. Mizushima et al.<sup>42,43</sup> showed that boron activation continues to increase with increasing boron dose above the solubility limit for doses above  $5x10^{15}$ /cm<sup>2</sup>. The activation of the boron at high concentrations was attributed to  $B_{12}$  clusters. Calculations indicate that the  $B_{12}$  cluster is deficient 2 electrons and contributes 2 holes to the valence band for each cluster.

#### Activation of Boron in Silicon

Boron is introduced into the silicon wafer through ion implantation in modern IC processing. After impacting the surface of the silicon wafer with kinetic energy in the range from one to tens of keV, the boron traverses a path known as the ion track until coming to rest in a disordered region produced by nuclear collisions with lattice atoms. In order to act as a dopant and to contribute a free hole to the valence band, the boron must first occupy a substitutional site in an ordered region of silicon. In the active state, the boron is bonded to four nearest-neighbor silicon atoms and due to its deficient valence the boron contributes a hole. The process of moving the boron atom from its initial position to a substitutional site is known as activation. During annealing required to activate the boron, once the activation energy barrier is exceeded by thermal energy, the main impediment to activation is boron clustering. Typically, if a boron atom clusters with another boron atom, impurity, or silicon interstitial, it will not serve as an active dopant. Once the boron is electrically active, it is possible that the hole created by the bond orbital deficiency of the boron in the silicon lattice will not contribute to the electrical conductivity of the silicon. First the hole must have sufficient thermal energy in order to overcome the ionization potential of the boron atom. At room temperature substitutional boron atoms have enough thermal energy that all holes are assumed to be ionized. Ionized holes still may not contribute to the silicon conductivity if there are compensating species in the silicon lattice which recombine with the holes or trap holes. The possibility of hole compensation is an important consideration when impurities are present in concentrations comparable to the boron concentration.

#### **Impurity Implantation**

#### Carbon

The effect of carbon on TED of boron and extended defect formation has been studied in detail recently. It was initially suggested by Gosele that carbon atoms in the silicon lattice could trap interstitials.<sup>44</sup> Later, after TED had become a significant issue for implanted boron in the formation of shallow junctions, Nishikawa et al.<sup>45</sup> investigated the possibility of using implanted carbon to reduce the diffusion enhancement of boron due to excess silicon interstitials during post-implantation annealing. The results from Nishikawa's work showed that carbon incorporation into the lattice at sufficient concentration was able to reduce the diffusion of boron significantly in the presence of excess interstitials. Later Stolk et al.<sup>46</sup> showed similar effects for both carbon implantation and carbon incorporation during epitaxial growth. Others have shown that carbon incorporation retards the formation of excess interstitial related extended defects in ion implanted silicon.<sup>47-50</sup> A recent study of the effect of carbon implantation on boron diffusion, boron activation, and junction leakage was performed that confirmed the diffusion reduction effect, but indicated a negative effect on boron activation.<sup>51</sup> These results conflict with earlier results by Stolk et al.<sup>46</sup> that showed carbon to have no effect on the activation of boron.

#### Chlorine

Chlorine has been implanted into silicon to study its effect on oxidationinduced stacking fault formation and growth, as well as diffusion enhancement of dopant atoms. Chlorine incorporation controls the growth of oxidation-induced stacking faults when HCl gas is introduced into the annealing ambient during wafer processing. It is presumed that this is due to consumption of excess silicon interstitials. Implantation of chlorine was later shown to have the same effect despite the addition of excess interstitials introduced by the implantation process.<sup>52,53</sup> At high enough chlorine concentration, stacking fault formation is suppressed completely. Due to this observed interaction between chlorine and silicon interstitials, Solmi et al.<sup>54</sup> studied the effect of chlorine implantation on the diffusion of phosphorus tail during deposited phosphorus drive-in. When silicon was implanted with chlorine before phosphorus diffusion, the diffusion of the phosphorus tail was significantly reduced. The effect has been attributed to chlorine reducing the concentration of excess silicon interstitials. In the same study, measurement of the donor concentration in the phosphorus diffused region remained constant as a function of chlorine dose, indicating that the chlorine was electrically inactive.

#### Fluorine

Excluding traditional dopants, of the non-isoelectronic impurities intentionally added to silicon, fluorine has received the greatest attention for several reasons that evolved based on the particular IC processing difficulty at the time of investigation. Fluorine is a highly electronegative element that is a gas at standard temperature and pressure. Fluorine is present in many steps of the IC manufacturing process such as etching during wafer patterning. The unique interactions between fluorine and silicon can be both advantageous and deleterious, therefore understanding the interactions and balancing the trade-off is vital in order to maintain process integrity.

One of the most significant advantages of fluorine in the process of ion implantation for IC manufacturing is its ability to increase the effective beam current of a boron ion implantation process. The common source gas for boron ion implantation is boron tri-fluoride  $(BF_3)$ . In a manufacturing environment, the beam current of the ion implanter is a critical parameter for processing throughput since the implantation time is inversely proportional to the beam current. Therefore, in order to maximize wafer throughput the beam current of the ion implanter must be maximized. The maximum stable beam current achievable by a particular ion implanter is a function of many parameters. Holding all other parameters equal, the beam current of an ion implanter is directly proportional to the product of the probability of ionizing a particular molecule and the partial pressure of the molecule. Starting from a source gas of BF<sub>3</sub>, in a closed system such as the ionization chamber of an ion implanter the partial pressure of BF<sub>2</sub> is much greater than the partial pressure of B. The larger number of BF<sub>2</sub> molecules leads to a higher number of  $BF_2^+$  ions that are accelerated by the voltage plates, resulting in a higher beam current.

In an ion implanter, the kinetic energy imparted to each ionized molecule by the accelerator is the product of the ionic charge and the acceleration voltage

 $\mathbf{E}_{\mathbf{k}_{\text{top}}} = \mathbf{q}\mathbf{V} \tag{2.14}$ 

where q is the charge of the ion and V is the voltage difference between the anode and cathode between which the ion has been accelerated. Comparison of 50 keV B<sup>+</sup> ions and 50 keV BF<sub>2</sub><sup>+</sup> ions shows that the kinetic energy of the 50 keV B<sup>+</sup> ion is much greater than the energy of the boron in the 50 keV BF<sub>2</sub><sup>+</sup> ion. This is a result of the partitioning of the total kinetic energy of the molecular ion to each constituent atom. Given that the kinetic energy of the ion may also be expressed as a function of the ion mass and velocity by the classical relation

$$E_{k_{ion}} = \frac{1}{2} m_{ion} v^2$$
 (2.15)

where  $m_{ion}$  is the mass of the ion and v is the velocity of the ion, the partitioning of the energy of a tri-atomic molecular ion is made evident by expanding equation X as follows

$$E_{k_{ion}} = \frac{1}{2} v^2 (m_1 + m_2 + m_3)$$
(2.16)

where  $m_1$ ,  $m_2$ , and  $m_3$  are the respective masses of the constituent atoms. In the case of  $BF_2^+$  ions the partitioning of energy is such that the energy of a boron atom has an energy of approximately 22% (11:49) of the total ion energy. The reduction in the effective implantation energy of boron when implanted as  $BF_2^+$  has an important consequence on the beam current of the ion implanter. The maximum beam current is related to the acceleration voltage of the implanter in a superlinear fashion, I  $V^{\frac{2}{2}}$ , a relation known as Child's Law.<sup>55</sup> At lower ion implantation energies that are required in order to produce shallow boron depth profiles, the loss of beam current due to the reduced electric field between the anode and cathode is a significant issue. Therefore, the use of  $BF_2^+$  implantation to introduce boron as a dopant to the silicon results in an increase in beam current.

In addition to enabling a higher effective beam current,  $BF_2^+$  ion implantation reduces boron channeling. During ion implantation of boron ions into a crystalline silicon substrate, the boron ions are able to travel large distances without suffering any nuclear collisions by traversing the "open" channels of the silicon lattice. Channeling leads to a trailing tail in boron depth profile which is a large deviation from the depth profile of boron implanted into an amorphous silicon substrate as shown in Figure 2-4 (from Ajmera et al.<sup>56</sup>).

Molecular ion implantation of  $BF_2^+$  ions typically results in amorphization of the silicon substrate at moderate doses (>5x10<sup>14</sup>cm<sup>-2</sup>) whereas implantation of B<sup>+</sup> typically does not. Amorphization of the silicon substrate is advantageous during boron implantation because 100% of the implanted boron below the solubility limit becomes electrically active immediately following SPE. Boron implanted into crystalline silicon typically requires higher annealing temperatures and longer annealing times in order to achieve similar levels of electrical activation. The combination of higher boron activation due to SPE and shallower boron profiles due to the reduction of boron channeling made  $BF_2^+$  ions an attractive alternative to direct implantation of B<sup>+</sup>.

In spite of the aforementioned advantages of using  $BF_2^+$  ions, their use created another processing issue namely residual fluorine impurities remained in the wafer following post-implantation annealing. The most significant problem associated with residual fluorine is the diffusion of boron through the gate oxide which leads to severe shifts of the threshold voltage in metal-oxide-semiconductor field effect transistors (MOSFET). During the fabrication of MOSFETs with a n-type channel using the standard self-aligned process, a polysilicon gate is deposited prior to the formation of the source and drain extension regions by ion implantation of boron. The polysilicon gate is used as a mask to prevent boron from entering the channel region of the transistor during ion implantation. When B+ ions are implanted directly, there is no noticeable effect on the transistor performance resulting from the boron in the gate. However, when  $BF_2^+$  is implanted to introduce boron into the source and drain regions, it has been shown<sup>57,58</sup> that the presence of fluorine in the polysilicon gate enables the diffusion of boron through SiO<sub>2</sub> gate dielectric. The addition of fluorine into the gate presumably enhances boron diffusion through the SiO2 by preferentially forming F-SiO<sub>x</sub> bonds thereby inhibiting the formation of B-O<sub>x</sub> and B-SiO<sub>x</sub> complexes which would otherwise have slowed the diffusion of boron through the gate

dielectric. The penetration of boron through the  $SiO_2$  into the n-type silicon channel region results in significant shifts in the threshold voltage of the transistor. If  $BF_2^+$  is used to create the source and drain regions of the device then the penetration of boron into the channel must be accounted for by other processing steps.



Figure 2-1: Micrograph of  $\{311\}$  defects in silicon. Czochralski silicon implanted with 160 keV  $1x10^{14}$ /cm<sup>2</sup> Si<sup>+</sup>, annealed at 750° C for 105 minutes.



Figure 2-2: Micrograph of dislocation loops in silicon. Czochralski silicon implanted with 112 keV  $1 \times 10^{15}$ /cm<sup>2</sup> Si<sup>+</sup>, annealed at 1000° C for 10 seconds.



Figure 2-3: Plot of boron concentration profile. Silicon implanted with 4 keV  $1x10^{14}$ /cm<sup>2</sup> B<sup>+</sup>, annealed at 700° C.



Figure 2-4: Illustration of channeling tail in ion implanted silicon. SIMS profiles of 8 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> implants into (a) crystalline (100) silicon

and (b) pre-amorphized (100) silicon. Profiles are shown as-implanted and after annealing at 1050° C for 10 s.

## CHAPTER 3 TRANSIENT ENHANCED DIFFUSION IN REGROWN SILICON

#### **Introduction**

In order to investigate the effect of impurities on boron activation, boron diffusion, and extended defect evolution, other intervening variables must accounted for and, if possible, eliminated. Prior to investigating the effect of impurities on boron activation, boron diffusion, and extended defect evolution, it was necessary to perform fundamental studies of boron diffusion and extended defect evolution in regrown silicon. The preliminary studies have shown the impact of implantation process parameters such as beam current<sup>59</sup> and wafer temperature on defect evolution and boron diffusion. Additionally, fundamental information such as the kinetics of defect nucleation<sup>60</sup> and the relationship between extended defect evolution and boron diffusion<sup>61</sup> have been probed. The results from these preliminary studies have created a knowledge base that has allowed proper design of the following experiments on impurity co-implantation. Furthermore, it has enabled the discernment of the impurity effects from other anomalies due to the firm understanding of the behavior of the control specimens.

## Dopant Diffusion in Regrown Silicon

Some previous studies have reported that during annealing, interstitials from the EOR may induce transient enhanced diffusion (TED) of the dopant contained in the regrown silicon layer, 56,62-65 whereas some authors propose that TED does not occur in regrown silicon.<sup>66-68</sup> It has been suggested that there may be a correlation between the EOR defect microstructure and the diffusion enhancement of dopant in the regrown silicon.<sup>64</sup> At low ion implantation temperatures that result in extremely low EOR defect densities, it has been shown that the interstitial flux toward the surface and into the bulk of the wafer are equal.<sup>69</sup> In order to verify the validity of the correlation between EOR defect microstructure. an experiment was designed which could independently vary the density of the EOR defects without significantly changing the net number of interstitials in the EOR damage region. By varying the EOR defect density without changing the number of excess interstitials and monitoring dopant diffusion above and below the /c during post-implantation annealing it was possible to determine the relationship between EOR defect morphology and interstitial flux both into the bulk of the crystal and toward the surface. This experiment was designed to verify and augment previous works on the relationship between ion implantation temperature and dopant diffusion as well as examine the effects of the ion implantation dose rate on dopant diffusion.

#### End-of-Range Damage

The number of interstitials remaining in a silicon wafer following SPE regrowth during post-implantation annealing may be estimated by

integrating the area under the damage density curve (Figure 3-1) beginning at x= /c (the position of the amorphous-crystalline interface) and ending at x= 2 /c (a reasonable approximation for the more precise bound of x= ). This integrated area is approximated by the truncated tail of a Gaussian shaped profile, as shown in Figure 3-1. The value of the damage density at the amorphous/crystalline interface is constant for a given material regardless of the amount of damage introduced into the crystal lattice during ion implantation or depth of the amorphous layer. Therefore, the effect changes in the ion energy and dose of the ion implantation have on the number of excess interstitials trapped below the amorphous/crystalline interface is weaker than the effect of those changes on the amorphous layer depth.<sup>70</sup> Furthermore, process changes which have small effects on the amorphous layer depth are expected to have negligible effects on the number of excess interstitials in the EOR damage region.

## Ion Implantation Dose Rate

The relation between implantation beam current or dose rate and residual damage (which leads to amorphization and extended defects) has been explored for both Si and GaAs. Many groups have found that as the dose rate increases, the amount of residual damage also increases.<sup>71-73</sup> For amorphizing ion implantation in silicon, the result of this increase in the amount of residual damage with increasing dose rate is that higher dose rates create thicker surface amorphous layers. Although the relationship between dose rate and amorphous layer depth is a second order effect compared to other implant parameters such as implant dose and energy, it is possible to change the amorphous layer depth by 10% or more by varying the dose rate. Since varying the dose rate does not drastically change the ion implantation damage profile and the threshold damage density is for amorphization is constant, varying the dose rate should not change number of excess point defects in the EOR damage region following SPE regrowth even though it results in variation of the amorphous layer depth.

It has previously been shown<sup>74</sup> that there is a direct correlation between the roughness of the amorphous-crystalline interface and the density of extended defects following the regrowth of amorphous layers. The supposition of this experiment was that varying the dose rate would result in differences in the EOR defect density due to variation of the amorphous-crystalline interface roughness as a function of dose rate. Since the number of excess interstitials in the EOR damage region will remain constant as a function of the dose rate, correlation between dopant diffusion and EOR defect density will provide direct evidence of the relationship between EOR defect microstructure and dopant diffusion in regrown silicon. The direct correlation between the EOR defect density and diffusion of dopant in the regrown region of the silicon is theorized to be due to the EOR defects serving as interstitial trap sites. Ion Implantation Temperature

In order to cross-correlate the results of the experiment on implant dose rate and the findings of previous works, the effect of varying the implant temperature was also investigated. The temperature of the silicon substrate during ion implantation has a significant effect on the residual damage in the silicon lattice following ion implantation. As the implanted ion travels through the lattice, it transfers its kinetic energy through electronic and nuclear collisions. Many of these collisions result in the formation of a Frenkel pair. At absolute zero temperature, the interstitial and vacancy lack the thermal energy required to activate the point defect recombination process. As the temperature of the lattice is increased the point defects become more mobile and Frenkel pair recombination occurs. Higher substrate temperatures during ion implantation result in greater amounts of Frenkel pair recombination through a process known as dynamic annealing.<sup>75</sup> At sufficient temperatures it is impossible to create an amorphous layer because the driving force for point defect recombination and amorphous layer recrystallization overcome the damage formation process. Conversely, at low implantation temperatures, amorphous layers form more rapidly, resulting in a lower implantation fluence needed in order to create a continuous amorphous layer than would be required at higher temperatures.

Implant temperature has also been observed to significantly alter the EOR defect microstructure. A considerable amount of research has been performed on the effects of varying the implant temperature.<sup>76</sup> Many studies of "hot implants" with silicon wafer temperatures typically between 50° and 150° C, were performed in order to prevent the formation of an amorphous layer by increasing the amount of dynamic annealing. The defect density resulting from "hot implants" is extremely high, yielding a dislocation density that can only be quantified as a dislocation network. Low temperature implants with temperatures as low as 77° K, were performed in order to create deep amorphous layers by utilizing the low thermal energy of the substrate at low temperatures to lower the threshold dose for amorphization.<sup>77</sup> Lowering the implant temperature has been shown to result in a dramatic reduction of the EOR defect density following post-implantation annealing.<sup>69</sup>

#### Experimental Methods

In order to test the validity of the hypothesis that interstitial flux into the regrown region of the silicon is inversely proportional to the density of EOR defects, boron doping superlattices in silicon were used to monitor boron diffusion. The use of doping superlattices enabled monitoring of the boron diffusion as a function of depth independent of the damage normally associated with the introduction of dopant in silicon and allowed monitoring of differences in interstitial flux into the bulk of the crystal and toward the surface. The boron doping superlattices in <100> silicon were grown by low temperature molecular beam epitaxy. The

doping superlattices contained three boron concentration spikes with depths of 105,313, and 521 nm, each with a concentration of  $1 \times 10^{18}$ /cm<sup>3</sup> as shown in Figure 3-2. Following growth of the doping superlattices, they were each implanted using an Eaton NV-GSD 200 high current ion implanter. Due to the size discrepancy between the doping superlattice samples and the end station of the ion implanter, the doping superlattice specimens were mounted onto larger silicon wafers prior to ion implantation. Each specimen of the doping superlattice was mounted on a 150 mm Czochralski (CZ) grown n-type silicon wafer ensuring a planar fit and thermal conductivity. The entire wafer was then implanted with 112 keV Si<sup>+</sup> at a dose of  $1 \times 10^{15}$ /cm<sup>2</sup>, followed by a 30 keV,  $1 \times 10^{15}$ /cm<sup>2</sup> implant. The two overlapping implants were performed to produce a continuous surface amorphous layer.

In the first set of samples the dose rate of the 112 keV implant was varied from 0.13 to 1.13 mA/cm<sup>2</sup>, while the endstation temperature was maintained at 20° C ± 1° C. In the second set of samples, the dose rate of the 112 keV implant was maintained at 0.13 mA/cm<sup>2</sup>, while the endstation temperature was varied from 5° - 20° C ± 1° C. The tilt/twist angles for each implant were 5°/0°. Post-implantation annealing was performed in an A.G. Associates Thermopulse 410T RTA in a N<sub>2</sub> ambient. Each wafer was annealed at 800° C for either 5, 30, or 180 seconds.

Following implantation and annealing, the boron diffusion and the EOR defect evolution were characterized. The diffusion of the boron was measured by performing atomic concentration depth profiles using secondary ion mass spectrometry (SIMS). The SIMS profiles were performed on a Cameca IMS-4f. The counts of  ${}^{11}B^+$  were obtained using an 8 keV  $O_2^+$  beam rastered over 225  $\mu$ m by 225 µm area, with 80 µm diameter detected area. The EOR defect evolution was studied using transmission electron microscopy (TEM). Plan-view TEM of the samples was performed on a JEOL 200CX with images taken in  $g_{220}$  weak beam, dark field. Cross-sectional TEM was used to measure the amorphous layer depth. The majority of the TEM was performed on CZ wafers that were used as backing wafers to mount small,  $4 \text{ cm}^2$ , pieces of the MBE grown doping superlattice material in the ion implanter. Selected MBE grown samples were also prepared into TEM samples to correlate the EOR defect evolution in the MBE samples with the CZ wafers. The two main types of defects observed in the TEM were {311} defects and dislocation loops. The concentration of interstitials bound by the {311} defects was found using an image processor to find the projected line length of the defects from a micrograph. An assumption of constant defect width of 60 Å was used to find the interstitial concentration by multiplying the line length by 26 interstitials/nm and then dividing by the area observed to yield the number of interstitials per cm<sup>2</sup>. A similar process was used in the analysis of the dislocation loops, however in this case the area of the loops was found. The projected area of the loops was multiplied by  $1.6 \times 10^{15}$ /cm<sup>2</sup>, the approximate atomic density on the {111} plane. This result was divided by the area observed to yield the density of interstitials bound by loops.

#### **Results**

Ion Implantation Dose Rate

It has previously been shown that TED of boron can occur in preamorphized silicon.<sup>64</sup> A plot of the boron concentration versus depth for the sample implanted at a dose rate of  $1.13 \text{ mA/cm}^2$  with an implant temperature of 20° C and annealed at 800° C for times ranging from 5 seconds to 3 minutes along with the as-implanted profile is shown in Figure 3-3. The evolution of the boron doping spikes indicates a relatively large amount of diffusion for boron in silicon at 800° C, indicating that TED is occurring. At all three annealing times, the boron diffusion in the bulk regions below the a/c interface is greater than the diffusion in the regrown region of the silicon. As the annealing times lengthen, gettering of the boron to the EOR damage region also becomes apparent. The effect of varying the dose rate is illustrated in Figure 3-4, which shows the boron depth profiles of the samples implanted with  $Si^+$  at dose rates of 0.13, 0.30, and 1.13 mA/cm<sup>2</sup> with a constant implant temperature of 20° C and annealed at 800° C for 3 minutes along with the as-implanted profile. It is apparent from Figure 3-4 that there is an increase in the amount of boron diffusion in the regrown region of the silicon as the dose rate is increased, as evidenced by the profile broadening in the most shallow doping spike. Since boron diffusion enhancement is caused by excess silicon interstitial concentrations, this observation indicates that as the dose rate is increased the amount of interstitial flux into the regrown layer also increases. In order to quantify the observed diffusion differences, simulations of the diffusion behavior were performed with the aid of the process simulation tool FLOOPS. The simulations were performed using the as-implanted boron depth profiles as the initial state and a complementary error function diffusion model with the intrinsic diffusion coefficient given by Fair.<sup>78</sup> The diffusivity enhancements were found by dividing the intrinsic diffusion time necessary to match the experimentally observed boron profile by the actual annealing time as shown in Equation 3.1

 $\frac{\langle \mathbf{D}_{\mathrm{B}} \rangle}{\langle \mathbf{D}_{\mathrm{B}}^{*} \rangle} = \frac{\mathrm{t}}{\mathrm{t}^{*}}$ 

where  $D_B$  is the measured diffusivity,  $D_B^*$  is the intrinsic diffusivity, t is the experimental diffusion time, and t<sup>\*</sup> is the simulated diffusion time. Plots of the diffusivity enhancements of the boron in the first and second doping spikes (from the surface) as a function of dose rate after annealing at 800° C for 3 minutes are shown in Figure 3-5. The nomenclature used in the graph legend is that peak 1 is the doping spike closest to the surface and peak 2 is the middle spike. Peak 1 resides in the region of the silicon that was amorphized during ion implantation and subsequently recrystallized, henceforth referred to as the regrown silicon. Peak 2 resides in the region of the silicon approximately 1000Å below the EOR damage region. In the regrown silicon, the diffusion enhancement increases with increasing dose rate. There is no measurable change in the diffusion enhancement into the material below the /c as a function of

(3.1)

dose rate. The calculated diffusivity enhancements indicate the flux into the crystal is at least an order of magnitude greater than the flux toward the surface for these implant conditions. The ratio of interstitial flux into the crystal to flux toward the surface may be greater than a factor of ten if the interstitial concentration is so high that the ability of the boron doping spike is saturated such that the relationship between interstitial supersaturation and diffusion enhancement (Equation 2.13) enters a nonlinear regime.

Microstructural changes in the samples as a function of dose rate were also characterized by TEM. The threshold dose for amorphization has previously been observed to decrease with increasing dose rate.<sup>71,73</sup> Under the implant conditions of this study, variation of the dose rate by an order of magnitude changes the amorphous layer depth by 10%. The /cdepth was found to increase monotonically with dose rate from 2000 Å at 0.13 mA/cm<sup>2</sup>, to 2200 Å at 1.13 mA/cm<sup>2</sup>. The cross-sectional TEM micrographs in Figure 3-6 show a transition region of dark strain contrast (in bright field) just beyond the a/c interface, between the amorphous layer and perfect crystal. The strain contrast in this region is due to the large amount of crystal damage that exists in the crystalline region immediately below the /c interface. The thickness of the transition region is indicative of the amount of damage beyond the /c interface. It was found that although the amorphous layer depth increased with increasing dose rate, the transition region thickness remained constant at 300 Å. Figure 3-7 shows plan-view TEM micrographs of the EOR defects of the three different dose rates after RTA at 800° C for 3 minutes. It is apparent from the micrographs that the EOR defect density decreases with increasing dose rate. In Figure 3-8, the density of {311} defects in the EOR versus annealing time at 800° C for the different dose rates is presented. The density of {311} defects remains constant over the annealing time interval 5 seconds to 3 minutes. There is no measurable effect of the dose rate on the density of {311} defects in the EOR. Figure 3-9 shows a plot of the number of interstitials bound by the {311} defects versus annealing time for different dose rates. The number of interstitials bound by {311} defects remains constant over the annealing interval and there was no measurable effect of the dose rate variation on the concentration of interstitials bound by {311} defects. The density of EOR dislocation loops is plotted as a function of annealing time at 800° C for the three dose rates in Figure 3-10, which shows that the density of dislocation loops is inversely proportional to the dose rate of the amorphizing implantation. However, the total number of interstitials bound by EOR dislocation loops remained constant as a function of dose rate as shown in Figure 3-11. It is also clear that the interstitial content of the loops increases significantly for these annealing times, although the {311} defects are stable in the same annealing interval.

Ion Implantation Temperature

The profiles of the samples implanted with  $Si^+$  at 5° and 20°C annealed at 800° C for 3 minutes are shown in Figure 3-12, along with the as implanted profile. As the implant temperature is increased the amount of interstitial flux into the regrown layer decreases as indicated by the reduction in diffusive broadening of doping peak 1. There is no measurable effect of the implant temperature on the interstitial flux into the bulk of the silicon as shown by the diffusive broadening of peak 2. As discussed in the previous section this may be either due to constant interstitial fluxes as a function of implant temperature or because both implant temperatures produce such high interstitial concentrations that the ability of the doping spike to detect additional interstitial flux is saturated. The diffusivity enhancements of the boron were quantified using FLOOPS to simulate the boron diffusion. Plots of the diffusivity enhancements in the regrown layer of the two implant temperatures versus annealing time are shown in Figure 3-13. Peak 1 is the doping spike closest to the surface and peak 2 is the middle spike. In the regrown silicon, the diffusion enhancement increases with decreasing implant temperature. It appears that the diffusion enhancement into the bulk of the silicon below the /c also increases with decreasing implant temperature. The diffusivity enhancements indicate that the flux into the crystal is at least an order of magnitude greater than the flux toward the surface for these implant conditions.

Microstructural changes in the samples as a function of implant temperature were also characterized by TEM. The depth of an amorphous layer created by ion implantation varies as a function of implant temperature. Under the implant conditions of this study, a 15° C variation in temperature has a strong effect on amorphous layer depth. As indicated in Figure 3-14, the amorphous layer depth was found to increase with decreasing temperature from 2000 Å at 20° C, to 2350 Å at 5° C. Figure 3-15 shows TEM micrographs of the EOR defects of the two implant temperatures after RTA at 800° C for 3 minutes. It is apparent from the micrographs that the EOR defect density decreases with decreasing temperature. In Figure 3-16, the density of {311} defects density is plotted as a function of annealing time at 800° C for both implant temperatures. The number of interstitials bound by {311} defects is shown in 3-17 as a function of annealing time at 800° C for both implant temperatures. Both the number of {311} defects and the interstitials bound by {311} defects increases with increasing implant temperature. Figure 3-18 shows a plot of the EOR dislocation loop density versus annealing time for both implant temperatures. The number of interstitials bound by EOR is shown in 3-19 as a function of annealing time at 800° C for both implant temperatures. Although the EOR loop density in the EOR damage region did vary with implant temperature, the number of interstitials bound by EOR loops remained constant as a function of implant temperature. It is also clear that the interstitial content of the loops increases significantly for these annealing times.

#### Discussion

Explanation of the variation in diffusion enhancement as a function of dose rate is centered around the /c interface. The observation that the transition region thickness is independent of dose rate is consistent with the observation that the number of interstitial point defects in the EOR extended defects after annealing is relatively independent of dose rate. The excess interstitials in the wafer after implantation are widely believed to be the source of TED of boron in ion implanted silicon. 56,62-65,79 Since the number of interstitials appears to be constant as a function of dose rate, the diffusion differences are presumably not the result of a shift in the concentration of EOR interstitials but, instead, may be a function of the EOR defect nucleation/evolution process. It is interesting to note that, as stated, the EOR loop density varies significantly (3x) with dose rate, whereas the interstitial content in the defects does not vary substantially with dose rate. This implies the loop nucleation process may be heterogeneous. However, the {311} density appears to be independent of dose rate which is consistent with homogeneous nucleation of these defects. It has been proposed<sup>16</sup> that  $\{311\}$ unfaulting may be the source of the loops, however the results from this experiment provide no correlation to suggest that this process accounts for any significant fraction of loops. The EOR loop density and the diffusivity enhancement follow inverse trends. This is consistent with a model that predicts the EOR loops act as interstitial trapping sites and screen the flux of interstitials toward the surface. This argument which correlates EOR loop density with the amount of interstitial flux to the surface was previously proposed by Jones et al.<sup>79</sup> The shift in amorphization depth may be attributed to dynamic annealing differences with dose rate variation. As set forth by Morehead,<sup>9</sup> the lifetime of a collision cascade is on the order of  $10^{-13}$  s. Assuming a collision cascade diameter of approximately 100Å, the minimum time between collisions for this dose rate regime varies between  $1.8 \times 10^{-4}$  and  $1.6 \times 10^{-3}$  seconds, making the probability of cascade overlap negligible. If it is also assumed that the jump frequency of free interstitials and vacancies is 10<sup>-6</sup> seconds and that on average 100 successful random jumps are required for interstitial-vacancy recombination, the lifetimes of displaced Frenkel pairs in the collision cascade are approximately 10<sup>-4</sup> seconds.<sup>80</sup> Since the time constants for interstitial-vacancy recombination and the time between collisions within the damage region of the collision cascade are the same, variation of the time between collisions by an order of magnitude could logically effect the recombination process. The mechanism by which the subsequent collision cascade perturbs the interstitial-vacancy recombination process may be attributed to either of two prevailing theories. The first theory relates perturbation of the recombination process due to the momentum of the collision cascade. Particularly, if a silicon interstitial created by a collision cascade is subsequently displaced by a later collision cascade prior to recombining with a vacancy, net number of silicon interstitials per implanted ion remaining after ion implantation will increase. It is expected that this effect will occur predominantly in the latter part of the track of the implanted ion, near the projected range, in the region of nuclear stopping. This is due to the fact that the density of damage in the

shallower regions of the lattice is significantly higher and the effect overlapping collision cascades would be overshadowed by the overall damage density. Furthermore, the effect of a subsequent cascade further displacing an interstitial atom would be negligible since point defect population is sufficiently high in shallower regions that the probability of the interstitial interacting with a vacancy would remain high after the secondary displacement. Therefore, by decreasing the effective amount of dynamic annealing near the end of the range of the implanted ions through increasing the dose rate, the threshold for amorphization is achieved at deeper regions of the crystal. Alternatively, the effect of the implantation dose rate may be attributed to the interaction between point defects created by initial and subsequent collision cascades. If an interstitial created by a collision cascade interacts with an interstitial created by a subsequent collision cascade prior to recombining with a vacancy, it may complex with the second interstitial to reduce its number of unbonded orbitals and form a di-interstitial complex. The same process may occur for vacancies created by the collision cascade. The migration energy of the higher order point defect complexes is significantly higher than that of isolated point defects, therefore higher order complexes are less mobile. Therefore, the formation of these point defect complexes would reduce the amount of dynamic annealing by inhibiting Frenkel pair recombination which would result in a deeper amorphous layer at higher implantation dose rates. Regardless of which theory most accurately describes the phenomena, the change in the dynamic annealing process near the /c appears to change the morphology of the /c interface. This observation has been confirmed in a recent article by Banisaukas et al.81 which showed a direct correlation between the roughness of the /c interface and the implantation dose rate via high resolution TEM. The /c interface morphology has an effect on the morphology of the EOR defects such that if the loops are nucleating heterogeneously, there are fewer nucleation sites at higher dose rates. The results of this experiment are not sufficient to discern the exact nature of the loop nucleation sites. The variation in diffusion enhancement as a function of implant temperature is also closely related to the morphology of the /c interface. Excess interstitials

also closely related to the morphology of the /c interface. Excess interstitials lead to TED of boron in ion implanted silicon. Since the number of interstitials below the /c interface is expected decrease with decreasing implant temperature, the diffusion differences are presumably not the result of a shift in the concentration of EOR interstitials but, instead, may be a function of the EOR defect nucleation/evolution process. The EOR loop density and the boron diffusivity enhancement follow inverse trends, as seen in the experiment on dose rate variations. This is consistent with the model that predicts the EOR loops are acting as traps and screening the flux of interstitials toward the surface. Similar to the results of the experiment on dose rate variations, the shift in amorphization depth with varying implantation temperature may be attributed to dynamic annealing differences. By decreasing the amount of dynamic annealing through decreasing the implant temperature the threshold for amorphization is achieved at deeper regions of the crystal. This change in the dynamic annealing process also appears to change the morphology of the amorphous/crystalline interface as evidenced by the reduction in the number of EOR extended defects. However, the shift in defect density may alternatively be attributed to a reduction in the number of excess interstitials and the interstitial supersaturation.

#### Summary

In summary, upon annealing, decreasing the implantation temperature and increasing the implantation dose rate both have the effect of increasing interstitial flux from the EOR damage region toward the surface and decreasing the EOR defect density. For these moderate temperature implants the interstitial flux into the crystal is approximately an order of magnitude greater than toward the surface. It was found that decreasing the temperature or increasing the dose rate of the amorphizing implantation increases the amorphous layer thickness. The observation that the EOR dislocation loop density varies with implantation dose rate despite a similar trapped interstitial content implies the loop nucleation process may be heterogeneous. The dependence of the interstitial flux toward the surface on the EOR loop density is consistent with the loop layer acting as a barrier to interstitial backflow. The variation of the interstitial flux toward the surface with changes in the EOR dislocation loop density and the ratio of flux into the bulk of the crystal versus toward the surface are key findings. The results of these experiments combined with the results of previous works<sup>64,68,82</sup> show that the EOR dislocation loops mitigate the diffusion of interstitials toward the surface recombination sites, however they are not sufficient to trap all the excess interstitials and do not significantly effect the flux of interstitials into the bulk of the crystal.


Figure 3-1: Schematic illustration of a damage profile following an amorphizing ion implantation. The depth is measured from the surface of the silicon wafer.



Figure 3-2: Boron concentration versus depth profile of the as-grown boron doping superlattice. The profile was measured using SIMS.





Figure 3-3: Boron concentration versus depth profiles measured by SIMS for the boron doping superlattices following amorphizing ion implantation at a dose rate of  $1.13 \text{ mA/cm}^2$  and annealing at 800° C for times varying from 5 seconds to 3 minutes.



Figure 3-4: Boron concentration versus depth profiles of the boron doping superlattices measured by SIMS following amorphizing ion implantation at different dose rates and annealing at 800° C for 3 minutes.



Figure 3-5: Diffusion enhancement of boron versus annealing time at 800° C for the three different ion implantation dose rates. Peak 1 refers to the boron doping spike in the regrown region of the silicon. Peak 2 refers to the boron doping spike immediately below the EOR damage region.



 $0.2\ \mu m$ 



(b)

Figure 3-6: As-implanted cross-sectional TEM micrographs of samples implanted at dose rates of (a)  $0.13 \text{ mA/cm}^2$  and (b)  $1.13 \text{ mA/cm}^2$ . Micrographs imaged in bright field mode on the [011] zone axis.



Figure 3-7: Plan view TEM micrographs of samples implanted at three different dose rates, (a)  $0.13 \text{ mA/cm}^2$  (b)  $0.30 \text{ mA/cm}^2$  (c)  $1.13 \text{ mA/cm}^2$ , after annealing at 800° C for 3 minutes. Micrographs imaged using weak-beam dark field conditions with  $g_{220}$  as the diffracted beam.



Figure 3-8: Density of {311} defects as a function of annealing time at 800° C for the three different ion implantation dose rates.



Interstitials in {311} Defects (cm

Figure 3-9: Density of interstitials bound by  $\{311\}$  defects as a function of annealing time at 800° C for the three different ion implantation dose rates.



Figure 3-10: Density of dislocation loops as a function of annealing time at  $800^{\circ}$  C for the three different ion implantation dose rates.



Figure 3-11: Density of interstitials bound by dislocation loops as a function of annealing time at 800° C for the three different ion implantation dose rates.

Interstitials in Dislocation Loops (cm



Figure 3-12: Boron concentration versus depth profiles of the boron doping superlattices measured by SIMS following amorphizing ion implantation at different temperatures and annealing at 800° C for 3 minutes.

Boron Diffusivity Enhancement <D



Figure 3-13: Diffusion enhancement of boron versus annealing time at 800° C for the two different ion implantation temperatures. Peak 1 refers to the boron doping spike in the regrown region of the silicon. Peak 2 refers to the boron doping spike immediately below the EOR damage region.



0.2 µm



Figure 3-14: As-implanted cross-sectional TEM micrographs of samples implanted at (a)  $5^{\circ}$  C and (b)  $20^{\circ}$  C. Micrographs imaged in bright field mode on the [011] zone axis.



# 100 nm



(b)

(a)

Figure 3-15: Plan view TEM micrographs of samples implanted at two different temperatures, (a) 5° C and (b) 20° C, after annealing at 800° C for 3 minutes. Micrographs imaged using weak-beam dark field conditions with  $g_{220}$  as the diffracted beam.



Figure 3-16: Density of  $\{311\}$  defects as a function of annealing time at 800° C for the two different ion implantation temperatures.



Interstitials in {311} Defects (cm

Figure 3-17: Density of interstitials bound by  $\{311\}$  defects as a function of annealing time at 800° C for the two different ion implantation temperatures.



Figure 3-18: Density of dislocation loops as a function of annealing time at  $800^{\circ}$  C for the two different ion implantation temperatures.



Interstitials in Dislocation Loops (cm

Figure 3-19: Density of interstitials bound by dislocation loops as a function of annealing time at 800° C for the two different ion implantation temperatures.

# CHAPTER 4 CORRELATION OF DOPANT DIFFUSION AND EXTENDED DEFECT EVOLUTION IN REGROWN SILICON

Introduction

It is commonly accepted that excess interstitials in the silicon wafer lead to enhancement of the diffusion rate of dopants such as B, P, and As which diffuse either principally or in part by an interstitialcy mechanism in silicon.<sup>28</sup> It has been reported that extended defects maintain a supersaturation of interstitials in the EOR.<sup>62</sup> Many studies report that during annealing, interstitials from the EOR may induce transient enhanced diffusion (TED) of the dopant contained in the regrown Si layer<sup>56,59,63,79</sup> while others reported that no diffusion enhancement occurs in the regrown silicon. <sup>66-68</sup> In the preceding chapter, the correlation between the microstructure of the EOR dislocation loops and the flux of interstitials was explored. Experiments on the ion implantation dose rate and temperature provided evidence of interstitial flux both into the bulk of the crystal and toward the surface. It was shown that the flux of interstitials toward the surface is inversely proportional to the density of EOR dislocation loops. In the discussion of these experiments, the source of the interstitials during postimplantation annealing was generally referred to as the EOR damage region. For non-amorphizing implants, it has previously been reported that {311} defects are a source of interstitials that induce TED.<sup>15</sup> For amorphizing implants the same conclusion has been reported in a more qualitative manner.<sup>64</sup> In order to determine if the same process that has been reported for non-amorphizing ion implantation occurs in amorphized silicon, an experiment was designed to quantitatively correlate the evolution of extended defects in the EOR with the diffusion of dopant in the regrown silicon. The purpose of this experiment was to study in greater detail, the source of interstitials that drive TED during postimplantation annealing of amorphized silicon.

**Experimental Methods** 

In order to investigate the correlation between the evolution of extended defects in the EOR damage region and the diffusion of dopant in the regrown silicon, a 150 mm <100> n-type Czochralski silicon wafer was implanted using an Eaton NV-GSD 200 ion implanter. The wafer was first pre-amorphized using two overlapping Si<sup>+</sup> implantations, 120 keV followed by 30 keV each at a dose of  $1 \times 10^{15}$ /cm<sup>2</sup>, in order to create a continuous amorphous layer. The amorphized wafer was then implanted with 4 keV  $1 \times 10^{14}$ /cm<sup>2</sup> B<sup>+</sup> which created a shallow boron profile fully contained within the amorphous layer. The dose rate of the 120 keV implant was maintained at 0.87 mA/cm<sup>2</sup>, while the wafer temperature was maintained at 20° C ± 1° C. The tilt/twist angles for each implant were 5°/0°. Post-implantation annealing was performed in a tube furnace at 750° C in a N<sub>2</sub> ambient. Annealing times ranged from 15 minutes to 6 hours. SIMS profiles were performed on a Cameca IMS-3f. The counts of <sup>11</sup>B<sup>+</sup> were obtained using an O<sub>2</sub><sup>+</sup> beam with a net impact energy of 3 keV and 250 nA nominal beam current,

rastered over a 250  $\mu$ m by 250  $\mu$ m area, with 60  $\mu$ m diameter detected area. Planview TEM of the samples was performed on a JEOL 200CX with images taken in g<sub>220</sub> weak beam, dark field. Cross-sectional TEM was used to measure the amorphous layer depth. The two main types of defects observed in the TEM were {311} defects and dislocation loops. The concentration of interstitials bound by the {311} defects was found using an image processor to find the projected line length of the defects from a micrograph. An assumption of constant defect width of 60 Å was used to find the interstitial concentration by multiplying the line length by 26 interstitials/nm and then dividing by the area observed to yield the number of interstitials per square centimeter. A similar process was used in the analysis of the dislocation loops, however in this case a stereographic grid technique was used to find the area of the loops. The areal fraction of the loops was then multiplied by 1.6x10<sup>15</sup>/cm<sup>2</sup>, the approximate atomic density on the {111} plane, in order to obtain the concentration of interstitials bound by dislocation loops in the EOR damage region.

### Results

A plot of the as-implanted boron concentration profile versus depth for the boron implanted into the pre-amorphized silicon is shown in Figure 4-1. The depth of the amorphous layer created by the Si<sup>+</sup> implants was measured using crosssectional TEM. The amorphous layer depth was approximately 2400Å. The profiles of the implanted boron after annealing at 750° C are shown as a function of annealing time in Figure 4-2. It is evident from the evolution of the profiles that the boron is exhibiting TED for the first 2 hours. The correspondence of the profiles annealed for 4 hours and 6 hours indicate that by 4 hours the enhancement has decayed to near intrinsic value. Although the as-implanted, peak concentration of the boron profile is  $4 \times 10^{19}$ /cm<sup>3</sup> which is greater than the observed clustering limit for non-amorphizing boron implants,<sup>83</sup> the boron exhibits no clustering after post-implantation annealing. The lack of clustering is indicated by the mobility of the boron even at the highest boron concentration regions during the post-implantation anneals. The apparent discrepancy between the current experiment and previously reported results is likely due to differences in the interstitial supersaturations between non-amorphizing and amorphizing implantations. The lack of clustering of boron in amorphous layers has been reported previously.69

The profiles of boron concentration versus depth shown in Figure 4-2 indicate that the diffusion characteristics of the tail are anomalous not only in the exhibition of enhanced diffusion, but also abnormal boron distribution following post-implantation annealing. Implant profiles into amorphous solids follow the Pearson-IV distribution and profiles annealed at moderate temperatures and times generally diffuse in a similar distribution. However, the profiles observed for intermediate time intervals at 750° C in Figure 4-2 show an exponential distribution of boron in the diffused tail. The exponential shape of the tail of the boron profiles made it difficult to accurately determine an overall enhancement of the boron in the regrown silicon since the diffusion enhancement varied as a function of depth into the wafer. Therefore, in order to quantify the enhancement

of the boron diffusion, the shift in the junction depth of the boron implant was measured at a concentration of  $1 \times 10^{17}$ /cm<sup>3</sup> as shown in Figure 4-3. The junction depth increases rapidly as a result of TED through the first 2 hours of annealing, then the motion drops back toward the intrinsic diffusion value. After 2 hours the junction depth has moved approximately 1000 times further than would be expected by intrinsic diffusion values.<sup>78</sup> The expected junction motion of the initial as-implanted profile in Figure 4-1 after a 2 hour anneal, is less than 5 nm under intrinsic diffusion conditions due to the boron concentration gradient. During the first 2 hours of annealing, the diffusion enhancement is nearly constant as shown by the constant rate of increase in the junction depth. After annealing at 750° C for 2 hours, the TED decays to near intrinsic values. The microstructure of the samples was monitored by TEM over the same annealing time interval that the boron diffusion was examined. The evolution of the EOR defects is shown in the series of TEM micrographs in Figure 4-4. In qualitative terms the microstructure initially showed a predominance of {311} defects along with small dislocation loops. As the annealing times progressed, the number of {311} defects decreased rapidly and the number of dislocation loops increased slowly. With increasing time the mean size of the {311} defects increased rapidly, while the mean size of the loops grew more slowly. Since interstitial supersaturation induces TED, the density of EOR defects and the number of interstitials bound by these defects was quantified as a function of annealing time in order to reveal the relationship between the evolution of the extended defects in the EOR and the boron diffusion. The density of {311} defects in the EOR damage region as a function of annealing time at 750° C is shown in Figure 4-5. By the end of the first 15 minutes of annealing, there is a large number of {311} defects in the EOR. During the subsequent annealing intervals the number of {311} defects decreases. This indicates that the nucleation stage of the {311} defects is predominantly occurring in the first 15 minutes and after that the  $\{311\}$  defects are in the dissolution stage. A plot of the number of interstitials bound by the  $\{311\}$  defects as a function of annealing time at 750° C is shown in Figure 4-6. The trend of the number of interstitials bound by the  $\{311\}$  defects closely mimics the behavior of the density of  $\{311\}$  defects. Initially, there is a large concentration of interstitials bound by the {311} defects, with its maximum number most likely occurring before the end of the first annealing interval of 15 minutes. During the subsequent annealing stages the number of interstitials bound by the {311} defects continues to decrease. Both the density of interstitials bound by  $\{311\}$  defects and the density of  $\{311\}$ defects have fallen below the detection limits of the TEM after annealing for 2 hours at 750° C. In the annealing interval between 15 minutes and 2 hours at 750° C, the number of {311} defects that have dissolved is  $3.8 \times 10^{10}$ /cm<sup>2</sup> ±  $6x10^{9}/cm^{2}$ . The dissolution of these defects released  $1.9x10^{13}/cm^{2} \pm 5x10^{12}/cm^{2}$ interstitials into the EOR damage region. The density of dislocation loops in the EOR damage region as a function of annealing time at 750° C is shown in Figure 4-7. By the end of the first 15 minutes of annealing, there is a large number of dislocation loops in the EOR. During the subsequent annealing intervals the number of dislocation loops continues to increase. After the first annealing

interval of 15 minutes at 750° C, the density of dislocation loops in the EOR is  $2.0 \times 10^{10}$ /cm<sup>2</sup> ± 2x10<sup>9</sup>/cm<sup>2</sup>. After 45 minutes of annealing at 750° C, the density of dislocation loops in the EOR has increased to  $3.4 \times 10^{10}$ /cm<sup>2</sup> ± 5x10<sup>9</sup>/cm<sup>2</sup>. After 45 minutes of annealing, the number of dislocation loops remains constant through 6 hours of annealing. This indicates that the nucleation stage of the dislocation loops occurs over the first 45 minutes of annealing at 750° C. A plot of the number of interstitials bound by the dislocation loops as a function of annealing time at 750° C is shown in Figure 4-8. Over the annealing interval from 15 minutes to 6 hours, the number of interstitials bound by the EOR loops is increasing with annealing time. Between 15 minutes and 6 hours, the number of interstitials bound by the loops increased from  $5.5 \times 10^{13}$ /cm<sup>2</sup> ±  $6 \times 10^{12}$ /cm<sup>2</sup> to  $1.3 \times 10^{14}$ /cm<sup>2</sup> ±  $1 \times 10^{13}$ /cm<sup>2</sup>. Simultaneous to loop growth, the number of interstitials released by {311} defects over the annealing interval was  $2 \times 10^{13}$ /cm<sup>2</sup> ±  $5 \times 10^{12}$ /cm<sup>2</sup>.

The initial increase in loop density is consistent with some of the  $\{311\}$  defects unfaulting and forming the loops as has been recently reported for both amorphizing<sup>60</sup> and non-amorphizing implants.<sup>22</sup> Over the annealing times studied, the dislocation loops were not in the "coarsening" regime, but rather in a growth stage since the density of dislocation loops was constant from 45 minutes through 6 hours and the number of interstitials bound by the loops increased over the same interval. The increase in the number of interstitials bound by the loops was fit with an exponential function of the form  $(1-\exp(-t/))$  as shown in Figure 4-9. The time constant for the saturation of loop growth was found to be approximately 70 minutes. The  $\{311\}$  defects were unstable over this annealing interval. The dissolution of interstitials from  $\{311\}$  defects was fit with an exponential for the dissolution of interstitials from  $\{311\}$  defects was fit with an exponential for the dissolution of  $\{311\}$  defects was fit with an exponential for the dissolution of  $\{311\}$  defects was fit with an exponential for the dissolution of  $\{311\}$  defects was fit with an exponential decay function as shown in Figure 4-9. From the decay function, the characteristic time constant for the dissolution of interstitials from  $\{311\}$  defects was found to be approximately 50 minutes.

## **Discussion**

In this experiment, the boron was implanted into an amorphous silicon layer. The interstitials that induce TED originate in the EOR damage region below the initial amorphous-to-crystalline interface. It is apparent that EOR dislocation loops are not contributing to TED over the annealing interval since they are not releasing interstitials, but instead are capturing interstitials. The concentration of interstitials bound by {311} defects decreases by 95% in the first 2 hours of annealing. The diffusion enhancement of the boron decays after 2 hours of annealing. Thus, there is a correspondence of the time to dissolve {311} defects and the time over which TED decays to an intrinsic value. This shows that {311} defects are releasing interstitials during TED and are no longer present after TED has decayed.

Despite this evidence, the theory that {311} defects are the most significant source of interstitials that induce TED in the regrown region of the silicon remains in question. This study can not confirm or disprove this theory due to

several uncertainties. Of these uncertainties, the most significant are whether submicroscopic interstitial clusters (SMICs) exist, the number of interstitials needed to induce TED, and whether interstitials released by {311} defects leave the EOR or are incorporated into dislocation loops in the EOR. Resolution of the latter two uncertainties is beyond the scope of the experiment. Concerning the existence of SMICs, the results of the experiment indicate that they do exist. Evidence for this is the inability to account for the growth of the dislocation loops in the EOR by considering only the interstitials released by {311} defects since the dislocation loops grew by  $8x10^{13}$  interstitials/cm<sup>2</sup>, and the number of interstitials released by dissolving {311} defects was  $3x10^{13}$ /cm<sup>2</sup>. Additionally, the similarity of the time constants for loop growth and {311} dissolution indicates that the same phenomenon controls both processes. In order to justify the two aforementioned observations, it becomes necessary to invoke another interstitial source in the silicon, such as SMICs.

Given that the smallest {311} defect that is routinely observable by TEM contains approximately 100 interstitials, there are two general theories which can explain the discrepancy between the number of interstitials released by  $\{311\}$  and the number of interstitials captured by dislocation loops. The first is that all excess interstitials (not in dislocation loops) exist in visible {311} defects and there are very few interstitial defects in the lower end of the size distribution of interstitial clusters. In this case, in order to rectify the discrepancy between {311} interstitial release and loop growth, it is necessary to deny the accuracy of the established method of counting interstitials that was described in the experimental section of this chapter. The second possibility is that the peak of the distribution of interstitial cluster distribution is below the resolution limit of the microscope (sub 100 atoms) and the {311} defects observed comprise the higher end of the size distribution. This possibility implicitly requires the existence of SMICs. Since the theories of electron microscopy and geometry employed in the quantification of interstitials bound by extended defects are significantly more robust than the theories related to quantifying the number of interstitial point defects created by ion implantation using an approximation known as the "+1" model, the theory which includes SMICs has more credibility. By beginning with a supposition that the accuracy of the interstitial counting method is reasonable, the observation of growth in the interstitial content in the loops in excess of the interstitial content of the {311} defects suggests that the second possibility may be correct.

#### **Summary**

In summary, upon annealing, excess interstitials in the EOR damage region of amorphized silicon precipitate into  $\{311\}$  defects, dislocation loops and possibly SMICs. At 750° C, as the annealing time increases, the  $\{311\}$  defects dissolve releasing interstitials into the EOR damage region. At the same time that  $\{311\}$ defects release interstitials, the boron in the regrown silicon exhibits TED. The correspondence of the time to release interstitials from  $\{311\}$  defects and the decay of TED in the regrown silicon supports the theory that interstitials from  $\{311\}$  defects are contributing to the interstitial supersaturation that causes TED. Dislocation loops are not releasing interstitials over the annealing interval studied but in fact are growing in both density and interstitial content. The increase in interstitial density in the loops cannot be explained quantitatively by interstitial release from the {311}'s and this strongly suggests the existance of submicroscopic interstitial clusters (SMICs) since no other defects are visible by TEM. In addition, these SMICs which may in theory be the principle source of TED must dissolve and release interstitials over approximately the same time interval as the {311} defects.

At present, the EOR damage region is probably best viewed as a "leaky box", containing interstitials in an undetermined number of configurations undergoing conservative and non-conservative point defect reactions. The non-conservative reactions release interstitials which induce TED. For amorphizing implants {311} defects in the EOR serve as a useful indicator of interstitial supersaturation and therefore TED because of the correlation of the timescales of {311} dissolution and TED. This correlation does not denote causation nor does it deny the existence of SMICs.



Boron Concentration (atoms/cm

Figure 4-1: As-implanted boron concentration profile for 4 keV  $1 \times 10^{14}$ /cm<sup>2</sup> B<sup>+</sup> implant into pre-amorphized silicon.



Figure 4-2: Boron concentration profiles for a 4 keV  $1 \times 10^{14}$ /cm<sup>2</sup> B<sup>+</sup> implant after annealing at 750° C for times ranging from 15 minutes to 6 hours.



Figure 4-3: Shift in the metallurgical junction depth relative to the as-implanted junction depth for a 4 keV  $1 \times 10^{14}$ /cm<sup>2</sup> B<sup>+</sup> implant after annealing at 750° C for times ranging from 15 minutes to 6 hours.



Figure 4-4: TEM images of the EOR damage region resulting from the 120 keV 1x1015/cm2 Si+ implant after annealing at 750° C for (a) 15 minutes, (b) 45 minutes, (c) 1 hour, and (d) 6 hours.



Figure 4-5: Density of  $\{311\}$  defects in the EOR damage region as a function of annealing time at 750° C.



Figure 4-6: Number of silicon interstitials bound by  $\{311\}$  defects in the EOR damage region as a function of annealing time at 750° C.



Figure 4-7: Density of dislocation loops in the EOR damage region as a function of annealing time at  $750^{\circ}$  C.



Figure 4-8: Number of silicon interstitials bound by dislocation loops in the EOR damage region as a function of annealing time at 750° C.



Figure 4-9: Number of silicon interstitials bound by dislocation loops and {311} defects in the EOR damage region as a function of annealing time at 750° C. Exponential fits to both curves indicate the time scales of loop growth and {311} dissolution.

# CHAPTER 5 SUB-MICROSCOPIC INTERSTITIAL COMPLEXES

#### **Introduction**

Energetic ions which impinge upon the silicon wafer during ion implantation cause significant damage to the silicon lattice. At sufficient energies and doses of ions, the implantation produces an amorphous layer on the surface of the wafer. During post-implantation annealing, the amorphous layer recrystalizes via solid phase epitaxial regrowth at approximately 550-600° C. Following regrowth, a damaged layer termed the end-of-range (EOR) damage region remains below the former amorphous-to-crystalline (a/c) interface which contains a supersaturation of excess interstitial point defects. During higher temperature annealing the excess interstitials in the EOR both diffuse away to regions of lower interstitial concentration and precipitate into EOR (Type II) extended defects.<sup>1</sup> These extended defects can lead to two main difficulties in creating shallow junctions in amorphized layers: leakage current from defects in the space charge region of the device<sup>25</sup> and junction depth increase by transient enhanced diffusion (TED) of the dopant which is caused by excess interstitials which may be released by extended defects during post-implantation annealing.

In the previous chapter, the source of interstitials that drive TED during postimplantation annealing of amorphized silicon was investigated. A correlation between the dissolution of interstitials from {311} defects and transient enhanced diffusion of boron in the regrown region of the silicon was established. The investigation also uncovered evidence that suggests the existence of submicroscopic interstitial clusters (SMICs). This evidence was based on the inability to account for growth of dislocation loops during an annealing interval based on the release of interstitials from {311} defects.

One aspect of the evolution kinetics of EOR extended defects that has been speculated about for many years, and to date remains in question, is the nature of dislocation loop nucleation in the EOR. Some authors have proposed models for the homogeneous dislocation loop nucleation.<sup>14</sup> Others argue the existence of different heterogeneous nucleation sites. Wu et al.84 suggested that EOR dislocation loops nucleate by the collapse of isolated amorphous pockets below the a/c interface during annealing. Hiraga and Hirabayashi proposed impurities such as oxygen or carbon may serve as nucleation sites.<sup>85</sup> Recently, Li and Jones showed that, for non-amorphizing implantations, {311} defects serve as the nucleation site for subthreshold dislocation loops<sup>22</sup> in silicon and are in fact "the source of the loops". The results presented in the previous chapter show that {311} defects can account for dislocation loop nucleation based on conservation of defect sites. This conclusion is obtained by comparing the number of  $\{311\}$ defects that dissolve to the number of dislocation loops that nucleate over the annealing interval between 15 minutes and 6 hours at 750° C. However, it was also shown that there was an inability to account for growth of dislocation loops during an annealing interval based on the release of interstitials from {311} defects. The purpose of this experiment was to study the extended defect

nucleation process in the EOR damage region of amorphizing ion implantations in silicon in order to determine if {311} defects transform into dislocation loops in the EOR damage region during post-implantation annealing.

**Experimental Methods** 

In order to investigate the kinetics of extended defect evolution in the EOR damage region in ion implanted silicon a <100> n-type Czochralski silicon wafer was implanted using an Eaton NV-GSD 200E ion implanter. The wafer was amorphized using a Si<sup>+</sup> implantation, with an energy of 20 keV at a dose of  $1 \times 10^{15}$ /cm<sup>2</sup>, which created a continuous amorphous layer. The dose rate of the implant was maintained at 0.3 mA/cm<sup>2</sup>, while the endstation temperature was maintained at  $20^{\circ} \text{ C} \pm 1^{\circ} \text{ C}$ . The ion beam was tilted 5 degrees off the wafer normal towards the <110> direction. Post-implantation annealing was performed in a tube furnace at 750° C in a N<sub>2</sub> ambient. Annealing times ranged from 15 minutes to 370 minutes. After an initial anneal of 15 minutes at 750° C, the sample was made into a plan-view transmission electron microscopy (TEM) specimen by first mechanically polishing the sample to a thickness 100 µm and then chemically etching the sample from the backside using a HF:HNO<sub>3</sub> (ratio of 1:3) solution to create a specimen with a thin region suitable for viewing in a TEM. A JEOL 200CX TEM was then used to take micrograph images of the specimen. The micrographs were taken under weak beam dark field imaging conditions with a g=[220] two-beam diffraction condition. The imaging of particular regions in the specimen as a function of *ex situ* annealing time was performed at 750° C. More specifically, a region of a specimen was imaged, the sample was removed from the TEM, annealed in a tube furnace (ex situ) and imaged in the TEM once more after the annealing interval. Care was taken in specimen handling in order to maintain specimen integrity. The specimen was carefully positioned in the specimen cup of the TEM to insure uniform orientation of the specimen with respect to the electron beam. The exact diffracting conditions, nominally g=[220], were maintained throughout the experiment for identical imaging conditions. The two main types of defects observed in the TEM were {311} defects and dislocation loops. The concentration of interstitials bound by the {311} defects was found using an image processor to find the projected line length of the defects from a micrograph. An assumption of constant defect width of 60 Å was used to find the interstitial concentration by multiplying the line length by 26 interstitials/nm and then dividing by the area observed to yield the number of interstitials per cm<sup>2</sup>. A similar process was used in the analysis of the dislocation loops, however in this case a stereographic grid technique was used to find the area of the loops. The areal fraction of the loops was multiplied by  $1.6 \times 10^{15}$ /cm<sup>2</sup>, the approximate atomic density on the {111} plane.

Results

In order to validate the legitimacy of the experimental procedure, the effects of certain aspects of the procedure were investigated prior to performing the *ex situ* experiment. Recognizing that the sample under observation had been thinned

prior to annealing and experienced several temperature ramps, the effect of sample thickness and temperature ramping were investigated by comparing four samples, A, B, C, and D, each annealed at 750° C for 75 minutes. Samples A and B were annealed prior to thinning, samples C and D were annealed after thinning. Samples B and C were annealed in 11 time intervals, samples A and D were annealed in 2 time intervals. As is evident from the TEM micrographs in Figure 5-1(a-d) it is apparent that neither factor had an observable effect on the final density or size distribution of the EOR defects in the samples. The evolution of extended defects in the EOR of the sample examined in the ex situ experiment is shown in the series of micrographs in Figure 5-2. The images show that the number of {311} defects is decreasing with increasing annealing time and the number of loops is increasing with increasing annealing time. The same region of the sample that was analyzed ex-situ after annealing for 45 minutes and 75 minutes is shown in Figure 5-3. The defect labeled "a" is seen to evolve from a  $\{311\}$  defect in Figure 5-3(a) to a dislocation loop in Figure 5-3(b). The density of {311} defects in the EOR damage region as a function of annealing time at 750° C is shown in Figure 5-4. By the end of the first 10 minutes of annealing at 750° C, the density of {311} defects in the EOR is  $3.8 \times 10^{10}$ /cm<sup>2</sup> ± 4x10<sup>9</sup>/cm<sup>2</sup>. After 75 minutes of annealing at 750° C, the density of {311} defects in the EOR has decreased to  $1.3 \times 10^{-10}$  /cm  $\pm 1 \times 10^{-10}$  /cm. During the subsequent annealing intervals the number of {311} defects continues to decrease, until by 370 minutes of annealing the density of {311} defects has dropped below the detection limit of the TEM. This indicates that the nucleation stage of the {311} defects is occurring within the first 10 minutes and after that the {311} defects are in the dissolution stage. A plot of the number of interstitials bound by the {311} defects as a function of annealing time at 750° C is shown in Figure 5-5. The trend of the number of interstitials bound by the {311} defects mirrors the behavior of the density {311} defects. Initially, there is a large concentration of interstitials bound by the {311} defects, with its maximum number most likely occurring prior to the end of the first annealing interval of 10 minutes. During the subsequent annealing stages, the number of interstitials bound by the {311} defects continues to decrease. The density of dislocation loops in the EOR damage region as a function of annealing time at 750° C is shown in Figure 5-6. By the end of the first 10 minutes of annealing, there is a significant number of dislocation loops in the EOR. During the subsequent annealing intervals the number of dislocation loops continues to increase. The number of interstitials bound by dislocation loops as a function of annealing time at 750° C is shown in Figure 5-7. The number of interstitials bound by the dislocation loops increases monotonically with annealing time during the time interval from 10 minutes to 6 hours. The number of {311} defects which disappear,  $3.7 \pm 0.5 \times 10^{10}$ /cm<sup>2</sup>, was over 10 times greater than the number of dislocation loops observed to nucleate,  $2.2 \pm 0.2 \times 10^9$ /cm<sup>2</sup>, during the annealing time interval from 10 minutes to 6 hours. This indicates that {311} unfaulting is a viable mechanism for the nucleation of the dislocation loops in this time interval in terms of conservation of defect sites. The number of interstitials released by
{311} defects over this time interval was  $3.0 \pm 0.5 \times 10^{13}$ /cm<sup>2</sup> and the number of interstitials captured by dislocation loops was  $4.6 \pm 0.5 \times 10^{13}$ /cm<sup>2</sup>.

A plot of the percentage of dislocation loops formed as a function of annealing time is shown in Figure 5-8. The percentage of the loops formed was calculated using the sum of the number of loops observed to form and the initial number of loops as the total. A small number (~15%) of the dislocation loops dissolved in the interval between 75 and 370 minutes. For the plot in Figure 5-8, the dissolution was ignored and only the addition of loops observed to nucleate was considered. From Figure 5-8 it is apparent that 45% of the loops had nucleated by 10 minutes at 750° C. The nucleation site of each dislocation loop observed to nucleate was studied by comparing sequential TEM micrograph images. The loops that nucleated were divided into one of two classifications; dislocation loops that nucleated at a {311} defect site or at a site where no perturbation of the lattice visible by TEM was observable. The percentage of the loops that nucleated at {311} defect sites is plotted in Figure 5-9. The average percentage loops that nucleated at {311} defect sites during the interval from 10-370 minutes was approximately 75%.

## Discussion

Of the aforementioned data the most salient point is that the majority of the dislocation loops observed to nucleate did so at  $\{311\}$  defects, as illustrated in Figure 5-3. This indicates that at 750° C,  $\{311\}$  unfaulting is the preferential path of dislocation loop nucleation. Understanding the mechanism of loop nucleation is an important step in the process of determining the evolution kinetics of point and extended defects in ion implanted silicon. As set forth in a previous paper by Li and Jones,<sup>22</sup> the possible unfaulting reactions of a  $\{311\}$  to a dislocation loop are as follows:

Frank loops	$a/21[1 \ 1 \ 6] + a/21[6 \ 6 \ 1] = a/3[1 \ 1 \ 1]$

Shockley loops

 $a/21[1\ 1\ 6] + a/42[19\ -2\ 9] = a/2[1\ 0\ 1]$ 

Systematic study of the habit plane of EOR dislocation loops has previously shown that loops reside on the {111} planes,<sup>86</sup> whereas {311} defects reside on the {311} plane.<sup>13,87</sup> Therefore nucleation of a dislocation loop by the unfaulting of a {311} defect also involves the climb of the interstials from the {311} plane to the final habit plane either during or immediately after the unfaulting reaction. The direct observation of the unfaulting reaction of the {311} defect transforming into a dislocation loop is a powerful result of this work. The other data observed also support the assertion that this is not merely a statistical anomaly. Other authors have observed that in the EOR, at short times at moderate temperatures there is initially a large number of {311} defects and a smaller number of dislocation loops.<sup>64,79,88</sup> With the progression of annealing to longer times, the number of {311} defects decreases and the number of dislocation loops increases. At longer times and higher temperatures {311} defects disappear and only dislocation loops remain. These data indicate that {311} defects serve as intermediate defects in the silicon lattice.

One question raised by the results of this experiment is the nature of the origin of the ~25% of the loops which do not appear to nucleate from  $\{311\}$  defects. In a previously published paper<sup>22</sup> the authors report that all of the dislocation loops observed to nucleate did so at  $\{311\}$  defect sites. In the current experiment it has been observed that  $\{311\}$  defect sites serve as the preferential site for dislocation loop nucleation, and several possible explanations are able to account for the origin of the remaining 25% of the loops.

Images of extended defects in silicon are obtained because of the lattice strain around the defects. All extended defects have a certain amount of strain associated with them, however not all defects are visible under a single set of imaging conditions based on the principles of electron microscopy. Theoretically, roughly 85% of all possible {311} defect configurations are visible under a single g=[220] imaging condition, using the  $g \bullet b=0$  invisibility criterion (assuming those defects do not have  $g \cdot b \times u > 0.64$ ). However, the ability to image defects in a TEM is dependent both upon the contrast and brightness of the defect image. Both brightness and contrast are functions of the deviation parameter s<sub>g</sub>. Small variations in s<sub>o</sub> have dramatic effects on contrast and brightness. These variations can determine whether a defect will have residual contrast in spite of fulfilling the invisibility criterion. Additionally, the brightness of an image is a function of the strain field of the defect. The strain field of a defect is directly proportional to its Burger's vector. Since the numerical value of the Burger's vector in angstroms is .294 for a {311} defect and .577 for a Frank loop and .707 for a Shockley loop, the brightness of the dislocation loops is much greater than that of the  $\{311\}$ defects. Given these conditions, it is conceivable that a {311} could exist yet be invisible via TEM, then after unfaulting become visible. Another possibility that accounts for the 25% of the loops not observed to nucleate from {311} defects is that those loops nucleated at a sub-microscopic interstitial cluster (SMIC). The existence of SMICs in this sample is suggested by the inability of the release of interstitials from {311} defects to account for the growth in the number of interstitials bound by the dislocation loops. The structure of SMICs is not known. It is possible that a SMIC may merely be a small {311} defect, since the minimum size for a {311} defect that may be imaged in conventional TEM is approximately 100 atoms. It may also be an interstitial cluster with a stable number of intersitials below the resolution of TEM, i.e. n=8.11 In the work by Li and Jones, the nucleation stage had progressed farther initially compared to the present work as evidenced by the fact that the first data point in Li and Jones corresponded to 60% of the dislocation loops already nucleated versus 45% for the present work. If SMICs are small {311} defects, then it would seem plausible that some of the nucleation sites would be smaller defect sites compared to earlier work by Li and Jones.<sup>22</sup>

Summary

In summary, the kinetics of extended defect evolution in the EOR, both {311} defects and dislocation loops, have been investigated quantitatively via *ex situ* 

TEM. It has been shown that {311} defects serve as the preferential site for dislocation loop nucleation, which correlates to previous findings for non-amorphizing implants. These conclusions provide not only a source of EOR dislocation loops but also yield the two possible evolutionary pathways for {311} defects; dissolution and unfaulting. Since {311} defects are presumed to be the source of interstitials for TED, the results of this work imply that process models must account for both the dissolution and unfaulting of {311} defects in order to accurately predict diffusion of dopant atoms in regions where an amorphizing implantation has been performed.



(b)

50 nm





Figure 5-1: Plan view TEM images showing the effect of sample thickness and temperature ramping (a) Sample A with 2 step anneal, thinned after annealing, (b) Sample B with 11 step anneal, thinned after annealing, (c) Sample C with 11 step anneal, thinned prior to annealing, and (d) Sample D with 2 step anneal, thinned prior to annealing.



(b)

50 nm





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Figure 5-2: Plan view TEM images showing time evolution of extended defects in the EOR after annealing at  $750^{\circ}$  C for (a) 16 minutes, (b) 28 minutes, (c) 45 minutes, and (d) 75 minutes.



(b)

**50** nm

Figure 5-3: Plan view TEM images of the extended defects in the EOR showing  $\{311\}$  defects transforming into dislocation loops. Samples annealed at 750° C for (a) 45 minutes and (b) 75 minutes. The  $\{311\}$  defect indicated by the arrows in (a) corresponds to the loop indicated by the arrow in (b).



Figure 5-4: Density of  $\{311\}$  defects in the EOR as function of annealing time at  $750^{\circ}$  C.



Figure 5-5: Number of interstitials bound by  $\{311\}$  defects in the EOR as function of annealing time at 750° C.



Figure 5-6: Density of dislocation loops in the EOR as function of annealing time at  $750^{\circ}$  C.



Figure 5-7: Number of interstitials bound by dislocation loops in the EOR as function of annealing time at  $750^{\circ}$  C.



**Percentage of Loops Nucleated** 

Figure 5-8: Percent of final number of EOR dislocation loops nucleated as a function of annealing time at  $750^{\circ}$  C.



Figure 5-9: Percent of EOR dislocation loops nucleating at  $\{311\}$  defect sites at each time interval monitored at 750° C.

## CHAPTER 6 FLUORINE EFFECTS ON BORON DIFFUSION

**Introduction** 

The experiments described in the preceding chapters provided detailed investigations of the evolution of extended defects in the end-of-range damage region and the correlation of this evolution to the diffusion of boron in regrown silicon. Due to the technological push to achieve ultra-shallow low resistivity electrical junctions in silicon, a process which could mitigate the interaction between ion implanted boron and silicon interstitials is highly desirable. Previous authors have shown that impurities incorporated into the lattice of silicon have the ability to mitigate this process. This effect has been shown for both carbon<sup>46</sup> and fluorine.<sup>89</sup> Reduction of transient enhanced diffusion (TED) via fluorine co-implantation is of greatest interest due to its current pervasiveness in integrated circuit processing and specifically its current incorporation in the ion implantation process through implantation of BF<sub>2</sub><sup>+</sup> molecular ions.

The inherent damage produced by ion implantation results in a large supersaturation of silicon self-interstitials during post-implantation annealing. This interstitial supersaturation leads to an increase in the diffusivity of dopants<sup>28,31,63,90</sup> such as boron, phosphorus, and arsenic during the initial stages of annealing, a phenomenon commonly known as transient enhanced diffusion (TED). In sub-keV boron implants, since the final junction depth is dominated by boron diffusion that occurs during the activation anneal,<sup>91</sup> the formation of ultrashallow, low resistivity junctions in the source and drain extension regions of transistors is hindered by TED. In previous studies,<sup>89,92-96</sup> fluorine has been coimplanted with boron, mainly in the form of a  $BF_2^+$  molecular implant, to determine its effect on the characteristics of implanted boron. Many important observations have been brought forth by these previous investigations. One of the most noteworthy conclusions of these studies was that a  $BF_2^+$  molecular implant produced a shallower junction than a  $B^+$  implant with equivalent energy for the boron ion. These results were promising, however some ambiguity remained. This is due to the fact that crossing the amorphization threshold in silicon leads to significant changes in the point defect population and impurity diffusion characteristics during post-implantation annealing. Since  $BF_2^+$  implantation typically leads to amorphization and  $B^+$  implantation generally does not, in many cases it was difficult to separate certain intervening variables from the chemical species effect of fluorine. A recent study by Downey et al.<sup>89</sup> has conclusively shown that the reduction in boron TED is a chemical species effect. The exact nature of this effect remains unknown. The purpose of the experiments described in this chapter is to elucidate the nature by which fluorine so dramatically effects the diffusion of boron during post-implantation annealing.

**Experimental Methods** 

In order to investigate nature of the effect of fluorine on the diffusion of ion implanted boron in silicon, pre-amorphized n-type Czochralski wafers were

implanted with boron and fluorine at varying energies. In the first set of experiments, wafers were first implanted with a 70keV  $1 \times 10^{15}$  ions/cm<sup>2</sup> Si<sup>+</sup>, which formed a 1500 Å deep continuous surface amorphous layer, as measured by ellipsometry and cross-sectional transmission electron microscopy. The first set of experiments investigated the effect of varying the energy of the fluorine implantation while holding the energy of the boron ion implantation constant. In a second set of experiments, the effect of varying the implantation dose of the fluorine while holding the boron dose constant was investigated. In the experiments on the effect of the varying dose, first the boron was implanted into crystalline silicon, then amorphization of the wafer was accomplished with a fluorine implantation. Admittedly, this scenario was less desirable than the one employed in the experiment on the effect of fluorine energy, however due to the constraints of wafer processing capability, use of this scenario was a necessity. The purpose of using the pre-amorphization step was to maintain a constant amount of damage independent of the energy and dose of the boron and fluorine ion implantations. This was possible as long as the ion profiles and damage profiles of the boron and fluorine implants were contained within the amorphous layer so that they did not contribute to the final damage state of the wafer. This is necessary in order to eliminate the extraneous effect of the damage from the impurity implantation. In spite of the failure to eliminate damage as extraneous variable in the experiment on the effect of fluorine dose the interpretation of the results is consistent with the expected differences between pre-amorphized and crystalline silicon.

In the experiment on the effect of fluorine energy, following the preamorphization, the wafers were implanted with low energy  $B^{\dagger}$  ions at an energy of 500 eV or 1.1 keV at a dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup>. Following boron implantation, the wafers were implanted with  $F^+$  ions with energies ranging from 2keV to 36 keV and at a dose of  $2x10^{15}$  ions/cm<sup>2</sup>. Post-implantation annealing of the wafers was performed in either a tube furnace at 750° C with times ranging from 15 to 120 minutes or in a rapid thermal annealing furnace at 1050° C with a spike annealing profile. Spike annealing is a technique designed to anneal samples at a high temperature while maintaining a low total amount of thermal energy in the process. The purpose of such a technique is to attain high temperature in order to activate certain thermally activated processes such as dopant activation while minimizing the effects of processes which are reverse activated (having a negative activation energy) such as TED. Since spike anneals have no dwell time at the maximum temperature and have large temperature ramp rates (>  $50^{\circ}$  C/s) which minimize the total amount of annealing time at temperatures below the peak temperature, they successfully minimize the effects of processes which are reverse activated. The ramp rates of the spike anneals in this experiment were either 75° C/s or 250° C/s. Following post-implantation annealing, microstructural, chemical, and electrical characterization was performed in order to measure the results of the experiments.

Under the aforementioned processing conditions, the interstitial source during annealing is the EOR damage region (following solid phase epitaxial recrystallization (SPER)). Since the boron and fluorine implants were contained

within the amorphous layer, the interstitials remaining after SPER are determined only by the pre-amorphization implant. Therefore, the addition of boron and fluorine did not affect the concentration of interstitials. Ellipsometry and XTEM measurements confirmed that neither the boron or the fluorine implants resulted in an increase in the amorphous layer thickness. Such an experimental structure eliminated damage as an extraneous variable and enabled the drawing of reasonable deductions concerning the nature of the process by which fluorine reduces TED of boron.

In the experiment on the effect of fluorine dose, the wafers were first implanted with low energy  $B^+$  ions at either 500 eV with a dose of  $4x10^{15}$  ions/cm<sup>2</sup> or 1.1 keV at a dose of  $1x10^{15}$  ions/cm<sup>2</sup>. Following boron implantation, the wafers were implanted with  $F^+$  ions with an energy of either 6 keV or 12keV and with doses ranging from  $1x10^{15}$  ions/cm<sup>2</sup> to  $8x10^{15}$  ions/cm<sup>2</sup>. Post-implantation annealing of the wafers was performed in either a tube furnace at 750° C with times ranging from 15 to 120 minutes or in a rapid thermal annealing furnace at 1050° C with a spike annealing profile. The ramp rate of the spike anneals in this experiment was 250° C/s. Following post-implantation annealing, microstructural, chemical, and electrical characterization was performed in order to measure the results of the experiments. Although the experimental conditions did not eliminate damage as an extraneous variable, it was still possible to draw reasonable deductions about the effect of fluorine on the diffusion of boron during post-implantation annealing and the effect of varying the fluorine dose.

## Results

Recently, Downey et al.<sup>89</sup> showed that the addition of co-implanted fluorine to boron implanted into pre-amorphized silicon reduces the diffusion of boron by a chemical species effect. However, the nature of this effect remained unknown. Simplistically, if fluorine addition reduces the diffusion of boron in ion implanted silicon, there are two general explanations. Transient enhanced diffusion of boron in silicon is caused by a supersaturation of silicon self-interstitials that results in a large increase in the diffusivity of the boron atom (either by an interstitial or interstitialcy diffusion mechanism). Therefore, fluorine must either form a complex with the silicon interstitial or the boron atom thereby inhibiting the interaction between boron and silicon interstitials that causes TED. In an attempt to deduce which of the possibilities appeared most probable, a 1.1 keV  $1 \times 10^{15}$ ions/cm<sup>2</sup> B<sup>+</sup> implant was performed into pre-amorphized silicon wafers. Fluorine co-implantation was then performed into the silicon wafers. The dose of the fluorine implantation was  $2 \times 10^{15}$  ions/cm<sup>2</sup> and the implantation energy was varied from 2 to 36 keV. The boron concentration profiles measured by SIMS after annealing the samples co-implanted with fluorine at selected energies for 15 minutes at 750° C are shown in Figure 6-1. Comparison of the boron control to the samples containing fluorine shows that the addition of fluorine has a significant effect on the diffusion of the boron. The boron concentration profiles after annealing the samples co-implanted with fluorine at various energies for 2 hours at  $750^{\circ}$  C are shown in Figure 6-2. It is evident from comparison of the boron control to the samples containing fluorine that the addition of fluorine

dramatically reduces the boron TED. The fluorine addition not only effects the magnitude of the boron diffusion, but it also effects the shape of the diffusion profile. Both of these effects are dependent on the energy of the fluorine implantation. The reduction of the boron TED by fluorine addition results in the reduction of the junction depth (measured at a boron concentration of  $7 \times 10^{17}$ /cm<sup>3</sup>), as shown in Figure 6-3 as a function of fluorine co-implantation energy. It is evident from Figure 6-3 that the reduction in boron TED shows a strong dependence on energy. Increasing the ratio of the fluorine implantation energy to boron implantation energy above the  $BF_2^+$  equivalent (2 keV F<sup>+</sup> for 1.1 keV B<sup>+</sup>) results in a shallower junction depth initially, however above 12 keV, the trend appears to reverse. The boron concentration profiles after the  $1050^{\circ}$  C spike anneal are shown in Figure 6-4. Even at higher temperatures the addition of fluorine can reduce the boron TED. The 12 keV fluorine co-implantation still produces the shallowest junction, however, for the highest energy (36 keV) fluorine co-implantation boron TED was increased compared to the control sample.

The boron and fluorine concentration profiles for the sample co-implanted with 1.1 keV  $1 \times 10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> and 12 keV  $2 \times 10^{15}$  ions/cm<sup>2</sup> F<sup>+</sup> after a sequence of anneals at 750° C with times ranging from 15 to 120 minutes are shown in Figure 6-5. It is evident from Figure 6-5 that the diffusion of the boron in the region of high fluorine concentration is significantly altered compared to the boron in the control sample and to typical Fickian diffusion. The boron profile appears to shift roughly equivalent distances independent of concentration in the concentration range from  $10^{17}$  to  $10^{20}$ /cm<sup>3</sup> during the annealing interval between 15 and 120 minutes. This diffusion behavior leads to another interesting effect of the fluorine co-implantation; the boron profile takes on a more "box" like shape as the energy of the fluorine implant increases. Another way to describe the shape of the boron profile is in terms of the abruptness of the metallurgical junction which refers to the steepness of the boron concentration gradient near the depth at which the electrical p-n junction will be formed between the p-type implanted layer and the n-type background wafer. This abruptness can be measured quantitatively as the slope of the boron concentration profile near a boron a concentration of  $1 \times 10^{18}$ ions/cm<sup>3</sup>, as shown in Figure 6-6. After annealing at 750° C for 2 hours, the junction is most abrupt for the sample co-implanted with 12 keV fluorine, which is almost as abrupt as the as-implanted boron profile.

The boron and fluorine concentration profiles for the sample co-implanted with  $1.1 \text{ keV } 1 \times 10^{15} \text{ ions/cm}^2 \text{ B}^+$  and  $2 \text{ keV } 2 \times 10^{15} \text{ ions/cm}^2 \text{ F}^+$  (implantation conditions which correspond to a 5 keV  $1 \times 10^{15} \text{ ions/cm}^2 \text{ BF}_2^+$  implant) after annealing at 750° C with times ranging from 15 to 120 minutes are shown in Figure 6-7. Although the implantation conditions of the boron are identical the boron diffusion behavior is significantly effected by the difference in the fluorine profile. Two key differences are apparent from comparison of Figure 6-7 to Figure 6-5. One effect of lowering the implantation energy of the fluorine is that the amount of fluorine retained after annealing is much lower compared to the 12 keV fluorine sample, as indicated from the graph in Figure 6-8. In addition to diffusing out of the surface of the silicon into the surface oxide, the 2 keV fluorine

implantation energy resulted in a low fluorine concentration in the tail region of the boron profile. These effects resulted in deeper boron diffusion and a less steep boron concentration gradient. It is evident from Figures 6-1 through 6-3 that fluorine implantation energies greater than 12 keV result in deeper diffusion of the boron profile. The boron and fluorine concentration profiles for the sample co-implanted with 1.1 keV 1x10<sup>15</sup> ions/cm<sup>2</sup> B<sup>+</sup> and 36 keV 2x10<sup>15</sup> ions/cm<sup>2</sup> F<sup>+</sup> after a sequence of anneals at 750° C with times ranging from 15 to 120 minutes are shown in Figure 6-9. The surface clearly plays a significant role in controlling the amount of fluorine dose retention following annealing as evidenced from Figure 6-8. At an implantation energy of 36 keV, the fluorine is deep enough in the sample to avoid out-diffusing significant percentages of the implanted dose during annealing at 750° C for times of 2 hours or less. The main differences between the sample implanted with 36 keV F<sup>+</sup> compared to the sample implanted with 12 keV F<sup>+</sup>, are the lower concentration of fluorine particularly in the first 100 Å and the deeper depth that the fluorine concentration profile extends to in the silicon.

In addition to investigating the effect of the fluorine co-implantation on the boron diffusion, the microstucture of the EOR damage region was monitored for these samples. Plan view TEM images of the EOR damage region for the control sample and the samples implanted with 12 keV  $2x10^{15}$  ions/cm<sup>2</sup> F<sup>+</sup> and subsequently annealed for 2 hours at 750° C are shown in Figure 6-10. The images show that the effect of the fluorine co-implantation on the evolution of the EOR damage was negligible.

The goal of the experiment just described was to determine the nature of the phenomena by which fluorine reduces boron TED in silicon. The results already described have given some insight into this, however, the results also seemed to pose more questions than they had answered indicating that further experimentation over a larger range of conditions was necessary in order to fully explain the phenomena. The main point brought out by the initial experiment on varying the fluorine implantation energy was the importance of the position and concentration of the fluorine. It still remained unclear whether it was the position and concentration of the fluorine relative to the silicon self-interstitials or the implanted boron.

To further examine the effect of fluorine on boron diffusion in ion implanted silicon, another set of experimental conditions were investigated. In this case, the same parameters were used for the silicon wafers and pre-amorphizing ion implantation. Subsequent to pre-amorphization, boron was implanted at 500 eV with a dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup>. Following the boron implantation the wafers were implanted with a  $2 \times 10^{15}$  ions/cm<sup>2</sup> dose of F<sup>+</sup> with the implant energy varied from 3-9 keV. After implantation the samples were annealed in a tube furnace at 750° C for 15 minutes or 120 minutes, or in a RTA at 1050° C with a spike temperature profile.

The boron concentration versus depth profiles for the samples co-implanted with 500 eV  $1x10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> and  $2x10^{15}$  ions/cm<sup>2</sup> F<sup>+</sup> at various energies are shown in Figure 6-11 after annealing at 750° C for 15 minutes. The fluorine samples have exhibited a larger amount of boron diffusion compared to control sample

containing no fluorine although the junction depths for all the samples a roughly equivalent. This indicates that there is a higher mobile fraction of the boron during the early stages of annealing for the samples containing fluorine. The difference between the boron control sample and the samples co-implanted with fluorine becomes more pronounced after the annealing time is extended to 120 minutes. The boron concentration profiles after annealing for 120 minutes at 750° C are shown in Figure 6-12. After 2 hours of annealing the control sample exhibited a much greater amount of boron diffusion in the tail region of the concentration profile compared to the samples co-implanted with fluorine. This resulted in a greater metallurgical junction shift (measured at a concentration of  $1 \times 10^{18}$  atoms/cm<sup>3</sup>) for the control sample as shown in Figure 6-13. In addition, the boron control sample appeared to have a larger fraction of clustered boron as indicated by the lower break-point in the concentration profile at which the boron began diffusing. As evident from Figure 6-12, the effect of the fluorine on the diffusion of boron was dependent on the implantation energy of the fluorine. The concentration profiles of both the boron and fluorine after annealing at 750° C are shown for the control sample and the samples co-implanted with fluorine at energies of 3, 6, and 9 keV shown in Figure 6-14, Figure 6-15, Figure 6-16, and Figure 6-17, respectively. The main differences between the 3 keV sample and the 6 and 9 keV samples are the lower retention of fluorine following annealing for the 3 keV sample as shown in Figure 6-18, and the shallower depth at which the fluorine concentration falls to low levels ( $<1x10^{18}$  atoms/cm<sup>3</sup>). The effect of fluorine co-implantation was not as drastic after the spike anneal at 1050° C as it was after the furnace anneal for 2 hours at 750° C. The boron concentration profiles after the spike anneal are shown in Figure 6-19. The samples that were co-implanted with fluorine at 6 keV and 9 keV exhibited a greater amount of boron diffusion than the control sample after the spike anneal. The amount of boron diffusion increased with increasing energy of the fluorine co-implantation. The sample co-implanted with 3 keV fluorine and the control sample exhibited a similar amount of boron diffusion after the spike anneal, although the shape of the boron concentration profiles were different. The sample co-implanted with 3 keV fluorine had a similar junction depth to the control sample, however, the fluorine co-implanted sample had diffused further at higher boron concentrations and had a steeper concentration gradient. The microstructure of the EOR damage region was monitored for these samples. Plan view TEM images of the EOR damage region for the control sample and the samples implanted with various doses of fluorine and subsequently annealed for 2 hours at 750° C are shown in Figure 6-20. The images show that the effect of the fluorine co-implantation on the evolution of the EOR damage was negligible.

In order to continue investigation of the effect of the fluorine on the boron diffusion, an experiment was performed in which the dose of the co-implanted fluorine was varied. In this experiment, boron and fluorine were implanted into a crystalline n-type silicon wafer. The boron was implanted at 1.1 keV with a dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup>. The fluorine implant energy was 12 keV and the dose was varied from  $1 \times 10^{15}$  ions/cm<sup>2</sup> to  $8 \times 10^{15}$  ions/cm<sup>2</sup>. Following implantation the samples were annealed in a tube furnace at 750° C for 15 minutes or 120 minutes.

The control wafer from the experiment on the effect of the variation in the energy of the fluorine co-implantation  $(1.1 \text{ keV } 1 \times 10^{15} \text{ ions/cm}^2 \text{ B} + \text{ into the wafer pre-amorphized with 70 keV } 1 \times 10^{15} \text{ ions/cm}^2 \text{ Si}^+)$  was used as standard for comparison in this experiment.

The boron concentration profiles for the samples co-implanted with 1.1 keV  $1 \times 10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> and 12 keV F<sup>+</sup> at various doses are shown in Figure 6-21 after annealing at  $750^{\circ}$  C for 15 minutes. Both the magnitude of the boron diffusion as well as the profile shape were significantly effected by the addition of fluorine. In all cases the addition of fluorine resulted in a shallower metallurgical junction depth and a steeper gradient in the boron concentration profile as compared to boron implanted into pre-amorphized silicon. Increasing the amount of fluorine above a dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup> resulted in a larger amount of boron diffusion during the first 15 minutes of annealing at 750° C. When the annealing time was increased to 2 hours at 750° C, the effect of fluorine addition became more drastic as shown in Figure 6-22. After 2 hours the control sample had diffused much deeper into the sample than the samples with fluorine. The fluorine samples also showed steeper gradients in the boron concentration profile. An increase in the amount of fluorine above a dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup> caused an increase in the boron motion through 2 hours of annealing at 750° C. There was a stark contrast between the diffusion behavior of the control sample and samples that had been co-implanted with fluorine as a function of the annealing time at 750° C. In order to illustrate this point, the concentration profiles of the boron after annealing for 15 minutes and 2 hours are illustrated in Figures 6-23, 6-24, 6-25, 6-26, and 6-27. The annealing time interval in which the majority of the boron motion occurred is shown in these figures. For the samples co-implanted with fluorine the majority of the boron motion takes place in the first 15 minutes of annealing, whereas for the pre-amorphized sample the majority of the diffusion takes place between 15 minutes and 2 hours at 750° C. The evolution of the EOR damage region was also monitored for these samples. Plan view TEM images of the EOR damage region for the samples implanted with various doses of fluorine and subsequently annealed for 2 hours at 750° C are shown in Figure 6-28. Comparison of the EOR damage for the samples amorphized with fluorine to the sample pre-amorphized with silicon (Figure 6-10 (a)) shows the effect of the difference in implant mass and implant energy. The number of excess interstitials residing in the EOR damage region immediately after solid phase epitaxial recrystallization has been shown to inversely proportional to implant mass.<sup>97</sup> The number of interstitials produced by ion implantation has also been shown to be directly proportional to the energy of the ion implantation for non-amorphizing implants,<sup>4</sup> although this effect should show a weaker energy dependence for amorphizing ion implantation. The competition of these two effects is illustrated by the comparison of the defects produced by the 12 keV  $2x10^{15}$ ions/cm<sup>2</sup> F<sup>+</sup> implant to the defects produced by the 70 keV  $1 \times 10^{15}$  ions/cm<sup>2</sup> Si<sup>+</sup> implant with the identical fluorine and boron implants in the amorphous layer. The silicon implant produces a lower EOR defect density with a larger mean defect size as compared to the defects in the sample amorphized using fluorine. The series of images in Figure

6-28 show that increasing the dose of the fluorine increases the size of the EOR defects.

The effect of varying the dose of the fluorine that was co-implanted with boron was also investigated at lower implant energies. Beginning again with a crystalline n-type wafer silicon, boron and fluorine were co-implanted into the wafer. The boron was implanted at 500 eV with a dose of  $4 \times 10^{15}$  ions/cm<sup>2</sup>. Fluorine was then implanted at 6 keV with doses varying from  $2 \times 10^{15}$  ions/cm<sup>2</sup> to  $8 \times 10^{15}$  ions/cm<sup>2</sup>. Following implantation the samples were annealed in a tube furnace at 750° C for 15 minutes or 120 minutes, or in a RTA at 1050° C with a spike temperature profile.

The boron concentration profiles of the 500 eV  $4x10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> after annealing at 750° C for 15 minutes are shown in Figure 6-29. The addition of fluorine enhanced the boron diffusion during the 15 minute annealing interval at  $750^{\circ}$  C. This effect increased with increasing fluorine dose, with the highest dose of fluorine causing the greatest amount of diffusion enhancement compared to the control sample. After annealing the samples for 2 hours at 750° C, the contrast between the control sample and the samples implanted with fluorine was drastically different. After 2 hours of annealing, the boron in the control sample had diffused much deeper into the silicon than the boron in the samples coimplanted with fluorine as shown in Figure 6-30. The addition of fluorine reduced the amount of diffusion of the boron as compared to the control sample after annealing at 750° C even though after 15 minutes the boron had diffused more in the samples with fluorine. The effect of fluorine co-implantation on the reduction of boron TED decreased with increasing fluorine dose. In addition, the presence of the fluorine increased the concentration of the break-point in the boron concentration profile at which the boron began diffusing. Fluorine also resulted in a steeper concentration gradient in the boron profile near the metallurgical junction (~ concentration of  $1 \times 10^{18}$  Boron atoms/cm<sup>3</sup>). The boron diffusion as a function of annealing time interval is shown in Figures 6-31, 6-32, 6-33, and 6-34 for the sample pre-amorphized with silicon and the samples coimplanted with fluorine. For the samples co-implanted with fluorine the majority of the boron motion takes place in the first 15 minutes of annealing, whereas for the control sample the majority of the diffusion takes place between 15 minutes and 2 hours at  $750^{\circ}$  C. The same samples were also annealed in an RTA at  $1050^{\circ}$ C with a spike temperature profile as shown in Figure 6-35. The addition of fluorine increases the diffusion of boron during a spike anneal at 1050° C. The diffusion of boron increases with increasing fluorine dose, similar to the results of the experiment where fluorine dose was varied for boron and fluorine coimplantation at slightly higher implant energies. The evolution of the EOR damage region was monitored for these samples. Plan view TEM images of the EOR damage region for the pre-amorphized sample and the samples implanted with various doses of fluorine and subsequently annealed for 2 hours at 750° C are shown in Figure 6-36. The silicon implant produces a lower EOR defect density with a larger mean defect size as compared to the defects in the sample amorphized using fluorine. The series of images in Figure 6-36 show that increasing the dose of the fluorine increases the size of the EOR defects.

Discussion

The effect of fluorine on the reduction of boron diffusion has been previously observed. Molecular boron implants  $(BF_2^+)$  were shown to produce shallower junctions.<sup>94</sup> Initially it was unclear whether this was a chemical species effect or a result of the pre-amorphization although a recent experiment showed the chemical effect.<sup>89</sup> The dependence of the boron diffusion break-point, diffusion depth and concentration profile abruptness on the fluorine implantation energy and implantation dose are findings that have not been reported previously. In simplistic terms the hypothesis of the experiments described in this chapter was that fluorine must reduce the diffusion of boron by forming a complex with either silicon interstitials or boron, the two components of transient enhanced diffusion. That question has not been answered unequivocally mainly since the phenomena seem to be slightly more complex than two hypothetical possibilities (and also because the most unequivocal aspect about the study of most atomic mechanisms is uncertainty). In spite of this, the results of this experiment help to clarify the issue.

The essence of the results presented in the preceding paragraphs may be boiled down to the following list of observations:

• The amount of boron diffusion is greater in the annealing interval from 15 minutes to 2 hours than in the annealing interval from 0 to 15 minutes for samples implanted with boron only.

• The amount of boron diffusion is greater in the annealing interval from 0 to 15 minutes than in the annealing interval from 15 minutes to 2 hours for samples co-implanted with boron and fluorine. Therefore the boron profiles of the samples co-implanted with fluorine and annealed at 750° C for 2 hours are primarily determined by the diffusion in the first 15 minutes.

• The boron profiles of a given sample or series of samples follow similar trends after annealing at  $750^{\circ}$  C for 15 minutes and after a spike anneal at  $1050^{\circ}$  C.

• After annealing at 750° C for 2 hours, samples co-implanted with fluorine exhibit less boron diffusion than samples without fluorine. The samples co-implanted with fluorine also have steeper gradients in the boron concentration profile and a higher fraction of mobile boron as indicated by the concentration of the break-point in the boron profile.

• Boron diffusion in the samples co-implanted fluorine at different energies was dependent on the energy of the fluorine implantation energy.

• Boron diffusion in samples co-implanted with fluorine at different doses increased with increasing fluorine dose for the dose range studied, though this effect may be a result of the increase in damage to the crystal with increasing fluorine doses.

From these observations, it seems that in general the addition of fluorine reduces transient enhanced diffusion while simultaneously increasing the solubility of the boron in ion implanted silicon. The reduction in boron diffusion seen by the

comparison of the samples implanted with boron versus the samples co-implanted with boron and fluorine after annealing at 750° C for 2 hours. The apparent increase in the solubility of the boron in silicon is indicated by the increase in the break-point of the boron concentration profile at which the boron began to diffuse in the samples co-implanted with fluorine compared to the samples without fluorine. Solubility is a term that inherently refers to an equilibrium state. The situation after ion implantation and annealing at moderate temperatures or short times is far from equilibrium. Liberty has been taken with the use of the term in the context of this experiment. In this context, use of the term solubility refers only to the concentration of the implanted boron which were not in immobile clusters and diffused from the initial position during post-implantation and solubility also led to a steeper gradient in the boron concentration profile following post-implantation annealing.

In order to confirm the observations about the solubility and diffusion of the boron during post-implantation annealing, the process simulation tool FLOOPS was used to perform empirical simulations of the hypothesized processes. In order to extract information about the physical processes, key parameters of the physically based models already in FLOOPS were empirically adjusted. In this case, FLOOPS was being used as a data analysis tool rather than to perform predictive simulations. By adjusting only parameters related to the boron solubility and the diffusion enhancement and maintaining all other parameters constant, a comparison between samples with identical boron implants with and without fluorine co-implantation shows the effect of the fluorine addition on the boron solubility and diffusion enhancement. The diffusion model that was used to perform this analysis in FLOOPS was the Fermi model. The Fermi model uses a classical complimentary error function concentration dependent diffusion model with the addition of a Fermi level dependence for the diffusion of charged species such as  $B^+$ . The Fermi model does not take the effect of interstitial supersaturation on boron diffusion into effect. Instead this effect is accounted for by changing the diffusion time since as follows from the treatment of diffusion in Chapter 2

$$\frac{\langle \mathbf{D}_{\mathrm{B}} \rangle}{\langle \mathbf{D}_{\mathrm{B}}^{*} \rangle} = \frac{\mathbf{t}_{\mathrm{sim}}}{\mathbf{t}_{\mathrm{exp}}}$$
(6.1)

The input script files for the FLOOPS simulations are shown in the appendix. FLOOPS was used to analyze the samples implanted with 500 eV boron with a dose of  $1 \times 10^{15}$  ions/cm<sup>2</sup> both with and without a co-implantation of 6 keV  $2 \times 10^{15}$  ions/cm<sup>2</sup> F<sup>+</sup> after annealing at 750° C for 2 hours. The same procedure was also employed for the samples implanted with 500 eV boron with a dose of  $4 \times 10^{15}$  ions/cm<sup>2</sup> both with and without a co-implantation of 6 keV  $2 \times 10^{15}$  ions/cm<sup>2</sup> F<sup>+</sup> after annealing at 750° C for 2 hours.

A plot showing the experimental profiles and the simulated profiles are shown in Figure 6-37 for the sample implanted with 500 eV  $1x10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> after annealing at 750° C for 2 hours. Initial attempts to simulate the profile of the control sample were less successful than the excellent match between experiment and simulation shown in Figure 6-37, which is why the convolution function was

added to the simulated profile. The difficulty experienced in the initial simulations is likely due to the inability to achieve a high degree of absolute accuracy when measuring ultra-shallow profiles using SIMS, although high precision was achieved. In order to account for SIMS artifacts such as ion beam mixing, a convolution function was used to find the "actual" as-implanted profile. By using the "actual" as-implanted profile as the starting point for the simulation and using the convolution function after the final step of the diffusion simulation, better agreement between the experimental profiles and the simulations was achieved. The convolution function was essentially a function that gave a moving average of the data in which data point n was weighted by the points n-1 and n+1. The script for the convolution function is included in the appendix. The plot in Figure 6-38 shows the as-implanted function as measured by SIMS along with the "actual" as-implanted profile (which was assumed to be a Gaussian function based on theory of ion trajectories and distributions in amorphous solids) and the result of the operation of the convolution function on the "actual" as-implanted profile. It is evident from Figure 6-38 that there is excellent agreement between the experimental profile and simulation of the as-implanted boron profile. A plot showing the experimental profiles and the simulated profiles are shown in Figure 6-39 for the sample co-implanted with 500 eV  $1 \times 10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> and 6 keV  $2x10^{15}$  ions/cm<sup>2</sup> F<sup>+</sup>. The only differences between the simulation for this sample and the sample without fluorine co-implantation are diffusion times, the boron solubility, and the addition of the exponential diffusion tail. The exponential diffusion tails for boron profiles have previously been observed by several authors.<sup>98-100</sup> The observation typically occurs after low thermal budget anneals for low dose (  $< 1 \times 10^{13}$  ions/cm<sup>2</sup>) non-amorphizing ion implantation. Those conditions are different than the conditions of the current experiment, however, the presence of fluorine may change the state of the system sufficiently to make the previous observations applicable to the current experiment. The exponential tail in the boron diffusion profile is a result of trap limited diffusion or the "one-hop" diffusion mechanism. The theory of this phenomenon is that once a boron is knocked from its substitutional site by an interstitial and diffuses by either a interstitial or interstitialcy mechanism, it will diffuse at a high rate until it interacts with a trap such as a vacant lattice site. This mechanism is thought to occur over a wide range of implantation and annealing conditions, however, it only becomes dominant at low interstitial supersaturations. At low interstitial supersaturations, the decay length of the exponential tail in the boron profile is inversely proportional to the density of trap sites. If fluorine reduces the interstitial supersaturation, then it would be possible for the same mechanism to occur in the current experiment as was seen in previous works. The decay length for the exponential tail was comparable to the decay length found by Collart et al.100 at 750° C.

The same methodology just described was employed to extract information about the boron solubility and diffusion enhancement for the sample implanted with 500  $eV 4x10^{15} ions/cm^2 B^+$  and the sample co-implanted with 500  $eV 4x10^{15} ions/cm^2 B^+$  and 6 keV  $2x10^{15} ions/cm^2 F^+$ . A plot of the experimental and simulated profiles for the boron implanted sample is shown in Figure 6-40. The plot of the

experimental and simulated profiles for the sample co-implanted with boron and fluorine is shown in Figure 6-41. In both cases the experimental and simulated profiles showed close agreement. The values for the boron solubility, boron diffusion enhancement, and decay length of the exponential tail are shown in Table 6-1 for the four samples that were simulated. In both cases it was seen that the addition of the fluorine increased the boron solubility and decreased the boron diffusion after 2 hours of annealing at 750° C. The solubility values in the table are artificially high as compared to the values of the break-point in the boron concentration profiles revealed by inspection of the SIMS plot. This is partly due to the smoothing function used in FLOOPS to eliminate a discontinuity in the equations near the solid solubility. Regardless of the exact numerical values, the relative difference between the control samples and the samples co-implanted with fluorine is significant. In order to confirm the apparent change in solubility as a result of fluorine addition, the samples implanted with  $500 \text{ eV} 1 \times 10^{15}$ ions/cm<sup>2</sup> B<sup>+</sup> and 500 eV  $4x10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> both with and without the and 6 keV  $2x10^{15}$  ions/cm<sup>2</sup> F<sup>+</sup> co-implantation were annealed at 1050° C with a spike temperature profile. These four samples were subsequently analyzed using spreading resistance profiling (SRP) to determine the spatial distribution of the carriers. The SRP results are shown in Figures 6-42 and 6-43. The plots in Figures 6-42 and 6-43 show that the addition of fluorine increases the number of boron atoms on substitutional lattice sites as indicated by the increase in the carrier concentration. This result indicates that the addition of fluorine increases the solubility of the boron. The result illustrated in Figure 6-43 has two parameters changing simultaneously, which clouds the interpretation of the result. There may be a different concentration of excess interstitials in the EOR damage region for the sample implanted with fluorine compared to the sample preamorphized with silicon. However, this change in the number of excess interstitials is probably not the dominant effect and the effect of the fluorine appears to increase the boron solubility.

The results from the simulations combined with the experimental evidence have confirmed the validity of the interpretation that the addition of fluorine increases the boron solubility and reduces the boron diffusion. The simulations were unable to independently determine the mechanisms by which the fluorine increases boron solubility and decreases boron diffusion. However, combining the results from the previously described experiments with the established behavior of ion implanted boron in silicon narrows the realm of possibilities. It is well established the diffusion of boron in silicon is greatly enhanced by an interstitial supersaturation. In the presence of excess interstitials, the probability of a boron atom on a substitutional lattice site being involved in a kick-out reaction with a silicon interstitial is directly proportional to the concentration of silicon interstitials. In the kick-out reaction the substitutional boron is displaced to the interstitial position. Once in an interstitial position the probability of boron diffusing through the lattice by either an interstitial or interstitialcy mechanism is much greater. Since the diffusion of boron via interstitial or interstitialcy diffusion is much faster than the substitutional diffusion rate, the interstitial supersaturation leads to a large increase in the boron diffusivity. In order for the

co-implanted fluorine to reduce the enhanced diffusion of ion implanted boron during post-implantation annealing, it must interfere with one or more of the aforementioned processes which control boron TED. Therefore the possibilities for the fluorine effect on the boron-interstitial interaction are as follows:

1. Fluorine forms an immobile complex with boron which prevents the boron from interacting with a silicon interstitial.

2. Fluorine increases the trap density that limits the diffusion distance of a boron atom that is diffusing through the lattice via an interstitial or interstitialcy mechanism.

3. Fluorine reduces transient enhanced diffusion by trapping silicon selfinterstitials thereby reducing the interstitial supersaturation.

Considering first the possibility that fluorine forms an immobile complex with the boron, comparison with the experimental results reveals certain discrepancies. If the fluorine forms a complex with boron atoms which is immobile, the complex must form after the early stages of annealing since all the boron profiles with co-implanted fluorine exhibited much greater diffusion in the first 15 minutes of annealing at 750° C than in the annealing interval from 15 minutes to 2 hours. In this case, the fluorine also has an additional effect on the diffusion of the boron in the early stages of annealing that leads to an initial diffusion enhancement compared to the control sample. This effect of boron diffusion enhancement prior to the formation of a boron-fluorine complex would also have to increase with increasing fluorine dose. While this possibility is not inconceivable, it is unlikely. The likelihood of this occurring is low considering the fact that the formation of the complex that immobilizes the boron occurs after the concentration of fluorine has decreased and the diffusion enhancement occurred when the fluorine concentration was at its highest point.

The possibility of fluorine reducing boron diffusion by increasing the trap density for boron diffusing by an interstitial or interstitialcy mechanism makes the most sense when the boron profiles after annealing at 750° C for 15 minutes are ignored and only the results after annealing for 2 hours are considered. This stems from the fact that after 15 minutes the samples co-implanted with fluorine exhibited a greater amount of boron diffusion than the control samples. If fluorine has a high affinity for the boron atoms, it is unclear why this effect does not manifest itself in the early annealing stages. However, if another process dominates the diffusion behavior of the early annealing stages it is possible that an increase in trap density would reduce the diffusion of boron in later annealing stages.

The final possibility is that fluorine acts as an interstitial trap. Trapping of interstitials that reduces the effective interstitial supersaturation would reduce the effect of the interaction between boron and silicon interstitials. The result of this would be a reduction in the boron TED. Unfortunately, this final possibility still does not account for the fluorine enhancing boron diffusion relative to the control sample during the initial stages of annealing at 750° C. Once more it is necessary to invoke an additional process that leads to the observed results. However, the argument of interstitial trapping is attractive from the aspect of increasing the

boron solubility. The solubility of boron at 750° C observed in the experiments in this chapter as estimated from the SIMS profiles are near 1x10<sup>19</sup> Boron atoms/cm<sup>3</sup> for the samples with no fluorine and approximately 1x10<sup>20</sup> Boron atoms/cm<sup>3</sup> for the samples containing fluorine. The solubility observed for the control sample is below the reported values for boron in silicon from earlier literature references,<sup>38</sup> whereas the observations for fluorine are similar to values reported in literature for the B-Si system. Similar to boron TED, the clustering of boron that limits its solubility is driven by excess silicon self-interstitials. Therefore, trapping of interstitials by fluorine atoms explains both the reduction of boron TED at longer times and the increase in the boron solubility.

In order to corroborate the supposition that fluorine can trap interstitials an experiment was performed using a fluorine well structure in silicon. In this experiment a silicon wafer was first pre-amorphized with two overlapping silicon implants, 150 keV  $1 \times 10^{15}$  ions/cm<sup>2</sup> Si<sup>+</sup> followed by a 40 keV  $1 \times 10^{15}$  ions/cm<sup>2</sup> Si<sup>+</sup>, creating a continuous amorphous layer to a depth of 2800Å. Following preamorphization, the wafer was implanted with 16 keV  $2x10^{15}$ ions/cm<sup>2</sup> F<sup>+</sup>. The sample was annealed in a tube furnace at 750° C for 3 hours to create a fluorine well. The SIMS plot of the fluorine concentration profile after the 3 hour anneal at  $750^{\circ}$  C is shown in Figure 6-44. Following the 3 hour anneal the sample with the fluorine well and a control sample, that had been pre-amorphized and annealed for 3 hours at 750° C but had no fluorine implantation, were both implanted with a non-amorphizing silicon implant. The energy and dose of the silicon implant were 25 keV and 1x10<sup>14</sup>ions/cm<sup>2</sup> Si<sup>+</sup> which placed the projected range at 390 Å, approximately the center of the fluorine well. Following the silicon implant the samples were annealed at 750° C for 30 minutes. The microstructure of the projected range damage was imaged by TEM, using the weak-beam, dark field technique. The micrograph images taken of the initial well structure prior to silicon implantation, the fluorine well after implantation and annealing, and the control sample after silicon implantation and annealing are shown in Figure 6-45. Comparison of Figure 6-45(b) and Figure 6-45(c) shows that the presence of the fluorine retards the formation of  $\{311\}$  defects, which are agglomerates of silicon interstitials. The sample without fluorine has a high concentration of {311} defects after the 30 minute anneal whereas the sample implanted with fluorine shows no {311} defects. There are defects which give contrast in the TEM images for both the initial fluorine well and the fluorine well with the silicon implant. There is no distinguishable difference between the two samples, indicating that whatever type of defect is present is a result of the fluorine implantation not the silicon implant. The defects in the fluorine implanted samples are likely either small fluorine precipitates or regrowth related defects that originate in the near surface region since they did not grow or coarsen with increasing annealing time as extended defects containing silicon interstitials typically do. Regardless of the nature of the defects, the point remains that the fluorine inhibits the formation of {311} defects in the projected range of a silicon implant into silicon. This same phenomenon has been observed in similar experiments where concentration wells of phosphorus,<sup>101</sup> arsenic,<sup>102</sup> or boron<sup>40</sup> were created in silicon and then implanted with non-amorphizing silicon ion

implants. The presence of the dopant at significant concentrations was shown to reduce the concentration of {311} defects. The concentration of {311} defects was shown to be inversely proportional to the dopant concentration in previous well experiments. This effect was shown to be a result of the formation of dopant-interstitial clusters. Presumably the same process is occurring in the case of the fluorine. This gives evidence that fluorine can trap silicon interstitials. The interpretation of the experimental data that fluorine traps silicon interstitials provides a plausible explanation of the effect of fluorine on both the boron diffusion and boron solubility. The dependence of the diffusivity of the charged species such as  $B^+$  on the Fermi level can explain the diffusion enhancement at short times. In this scenario, the high concentration of boron in the near surface region (at depths < 50 Å) could essentially pump boron into the sample. However, as the concentration level of the boron dropped the Fermi level would also move toward the intrinsic level and therefore the diffusivity of the charged species would approach the intrinsic diffusivity values for boron in silicon (which are extremely low at 750° C). In addition, the fluorine in the vicinity of the tail of the boron profile would reduce the diffusion of the boron in that region of the silicon. The effect of this scenario on the diffusion characteristics of the boron profile lead to the "box shaped" profile exhibited by the samples that were coimplanted with fluorine following annealing at 750° C.

Although this scenario is possible and seems to satisfactorily fit the data presented, there is another plausible explanation that may explain the full data set with more accuracy. This alternative explanation incorporates the trapping of interstitials by fluorine atoms. It also ties in previous studies on the effects of fluorine on the regrowth of amorphous silicon layers and the disordered state of amorphous silicon. These effects can all be traced back to the chemistry of fluorine and its large electronegativity.

Data recently presented by Jin et al.<sup>103</sup> has shown enhancement of boron diffusion during short time anneals of amorphized silicon samples when fluorine is used as the pre-amorphizing ion as compared to the diffusion of boron implanted into layers that had been pre-amorphized with either silicon or germanium. The boron diffusion enhancement in the temperature range from  $550^{\circ}$  -  $650^{\circ}$  C was shown to have a time transient that decreased with increasing temperature. The regrowth of the same amorphous layers was monitored over the same time that the diffusion was examined. There was a correlation shown between the diffusion enhancement of the boron and the regrowth of the amorphous layer at the depth where the boron diffusion was occurring. The boron was diffusing rapidly while the silicon layer had reached the annealing temperature but had not yet recrystalized. Once the layer had recrystalized the diffusion rate of the boron decayed to near intrinsic levels. This result was shown at both 550° and 650° C. This behavior differentiates boron diffusion in amorphous layers with significant concentrations of fluorine from the diffusion of boron in amorphous silicon containing no appreciable amount of fluorine. In a pre-amorphized layer implanted with boron, no measurable diffusion of boron occurs during a low temperature anneal (T  $< 650^{\circ}$  C) with a time on the order of the time required for solid phase epitaxy of the amorphous layer. However, in the case of samples

implanted with significant doses of fluorine (~  $1 \times 10^{15}$  ions/cm<sup>2</sup> F<sup>+</sup>) the boron diffuses at rates which are several orders of magnitude above the intrinsic values. The explanation of this phenomenon of enhanced boron diffusion in the presence of fluorine during the solid phase epitaxial regrowth anneal can be traced back to previously published observations concerning the effect of fluorine on amorphous silicon layers. Fluorine has been shown<sup>104</sup> to act as an effective dangling bond terminator in amorphous silicon. This behavior is similar to the behavior of hydrogen passivation of dangling bonds<sup>105-108</sup> in amorphous silicon except that the fluorine effect persists at higher temperatures due to the fact that hydrogen rapidly effuses from the silicon even at modest annealing temperatures (~  $350^{\circ}$ C). Studies of the effect of fluorine on the regrowth of amorphous layers have shown that fluorine retards the regrowth rate of amorphous layers.<sup>109</sup> Although this effect has previously been attributed to accumulation of fluorine at the advancing regrowth front,<sup>109</sup> it may be related to the observations of dangling bond termination in amorphous silicon. There are several models<sup>110-113</sup> that have been proposed to explain the regrowth of amorphous silicon during solid phase epitaxy including the geometric model, the stress relaxation model, and the surface reconstruction model. Regardless of the model, bond reconstruction is required to restore the long range order to the silicon layer during the phase transformation from amorphous silicon to crystalline silicon. If a significant percentage of the silicon bonds that do not form tetrahedral covalent bonds to other silicon atoms are terminated by fluorine atoms, the bond reconstruction during regrowth would be hindered.

The termination of dangling bonds in amorphous silicon is most likely a result of the high electronegativity of fluorine which gives fluorine a large affinity for available electrons such as those in the unbonded orbitals of silicon. Typically, amorphous silicon has a large number of dangling bonds as revealed by electron spin resonance measurements.<sup>114,115</sup> Similar measurements of amorphous silicon layers with significant concentrations of fluorine have shown a reduction in the concentration of dangling bonds as a result of the fluorine addition. The dangling bonds in amorphous silicon should serve as efficient trap sites for boron as it diffuses in the amorphous silicon. In this way the diffusion of boron in amorphous silicon would be restricted even though the amorphous silicon has a larger specific volume, and therefore lower density structure, than single crystal silicon by approximately 10%.<sup>116</sup> In the absence of trap sites, a more open structure such as amorphous silicon (relative to single crystal silicon) would be expected to provide a lower energy diffusion pathway. In non-fluorinated amorphous silicon, the diffusion of boron exhibits no measurable increase over the values observed in crystalline silicon. In the case of amorphous silicon containing significant concentrations of fluorine the diffusion enhancement is observed. This difference may logically be attributed to the termination of silicon dangling bonds which may act as trapping sites for diffusing boron. The reduction in the regrowth rate of amorphous silicon by fluorine exacerbates the effect of fluorine on the diffusion of boron in the amorphous layer. By reducing the regrowth rate, the boron has a longer time to diffuse through the amorphous silicon with the thermal energy available at the regrowth temperature.

The explanation of the diffusion behavior of boron in the presence of fluorine that incorporates the termination of dangling bonds and the diffusion of boron in the amorphous silicon, also explains the diffusion behavior of boron co-implanted with fluorine after the spike anneals. In order to provide accurate temperature control near the peak temperature, spike anneals incorporate a lower temperature stabilization step prior to ramping the temperature to the maximum value. In the case of the 1050° C spike anneals presented in the results section of this chapter the stabilization step was at 750° C for 10 seconds. This step helps to explain the increase in the diffusion of the boron in the samples co-implanted with fluorine relative to the control sample after the high temperature anneal and the similarity between the diffusion profiles after the spike anneal at 1050° C and the anneal at 750° C for 15 minutes.

The dangling bond termination argument also correlates well with the effect of the variation of the fluorine implantation dose. For two separate boron implant conditions, the effect of fluorine dose on the diffusion of boron in the annealing interval between 0 and 15 minutes at 750° C was that increasing fluorine dose increases boron diffusion. It has previously been shown that the effect of fluorine on the reduction of the amorphous layer regrowth rate becomes stronger at higher fluorine implantation doses or equivalently higher fluorine concentrations. This larger reduction in the regrowth rate compounded with the increased amount of dangling bond termination at higher fluorine implantation doses would logically result in a greater amount of boron diffusion during annealing prior to completion of the SPE regrowth. It should be noted that the effect of increasing the fluorine dose may be convoluted since the increase in the dose of the fluorine was not performed into a pre-amorphized layer. Under these conditions the increase in the dose of the fluorine inherently increases the amount of damage in the EOR which is known to induce TED of boron. However, the effect of increasing dose on the number of excess interstitials in the EOR shows a sub-linear dependence after the amorphization threshold is exceeded. In addition, if the increase in the EOR damage overcomes the trapping by the fluorine atoms (the number of which increases directly with increasing dose), then the effect of the increase in boron diffusion has a transient that is less than 15 minutes at 750° C. After 15 minutes of annealing at 750° C the highest dose fluorine implants exhibit diffusion that is near intrinsic values. Regardless of the predominance of the effect of the increasing damage with increasing fluorine dose, or the lack thereof, the argument of fluorine passivating dangling bonds in amorphous silicon retains its merits.

## **Summary**

In summary, the effect of fluorine co-implantation has been investigated over a range of processing conditons. It has been shown that the addition of fluorine reduces boron TED after annealing for 2 hours at  $750^{\circ}$  C. After annealing at  $750^{\circ}$  C for 15 minutes, the effect of the fluorine was different. For the boron implants at 1 keV, the addition of fluorine reduced the diffusion of the boron after 15 minutes. However, for the boron implants at 500 eV, the addition of fluorine enhanced the diffusion of the boron. The reason for this difference is not fully understood although it is expected that if shorter anneal times were examined,

both implant energies would result in an enhancement of the boron diffusion relative to the control samples. The co-implantation of fluorine was also shown to increase the solubility of the boron as revealed by the empirical results from both SIMS and SRP and the simulations. It was shown that the effects of fluorine coimplantation on the diffusion of boron display dependence on both the energy and dose of the fluorine co-implantation. The main mechanism that appears to control these phenomena is the trapping of interstitials by the implanted fluorine. This mechanism was independently confirmed by an experiment on the effect of fluorine on the formation of extended defects. Finally, it was postulated that the same attributes of fluorine that cause fluorine to trap interstitials also lead to the passivation of dangling bonds in amorphous silicon. It was proposed that the passivation of the dangling bonds is the reason for the effect of fluorine on amorphous layer regrowth and the enhancement in the diffusion of boron at short times in post-amorphization annealing.

Implant Conditions	Annealing	Solubility	Diffusivity	Exponential
	Conditions	(atoms/cm <sup>3</sup> )	Enhancement	Tail Decay
			$(< D_B / D_B^* >)$	Length (nm)
500 eV $1x10^{15}$ ions/cm <sup>2</sup> B <sup>+</sup>	750° C 2 h	$7 x 10^{19} / cm^3$	15	
500 eV 1x10 <sup>15</sup> ions/cm <sup>2</sup> B <sup>+</sup> 6 keV 2x10 <sup>15</sup> ions/cm <sup>2</sup> F <sup>+</sup>	750° C 2 h	$1 \times 10^{21} / \text{cm}^3$	0.1	4.3
$500 \text{ eV } 4\text{x}10^{15} \text{ions/cm}^2 \text{ B}^+$	750° C 2 h	$4x10^{19}/cm^3$	25	
$ \begin{array}{c} 500 \text{ eV } 4x10^{15} \text{ions/cm}^2 \text{ B}^+ \\ 6 \text{ keV } 2x10^{15} \text{ions/cm}^2 \text{ F}^+ \end{array} $	750° C 2 h	$4x10^{20}/cm^3$	0.2	4.3

Table 6.1: Summary of results from FLOOPS simulations.



**Boron Concentration (atoms/cm** 

Figure 6-1: Boron concentration profiles after annealing at 750° C for 15 minutes for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> at energies ranging from 2 to 36 keV.



**Boron Concentration (atoms/cm** 

Figure 6-2: Boron concentration profiles after annealing at 750° C for 2 hours for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> at energies ranging from 2 to 36 keV.



Figure 6-3: Metallurgical junction depth measured at a concentration of  $7x10^{17}$ /cm<sup>3</sup> versus fluorine co-implantation energy after annealing at 750° C for 2 hours for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> at energies ranging from 2 to 36 keV.



**Boron Concentration (atoms/cm** 

Figure 6-4: Boron concentration profiles after a  $1050^{\circ}$  C spike anneal for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> at energies ranging from 2 to 36 keV.


Figure 6-5: Boron and fluorine concentration profiles after annealing at 750° C for times ranging from 15 minutes to 2 hours for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 12 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-6: Abruptness (slope) of metallurgical junction measured near a concentration of  $1 \times 10^{18}$ /cm<sup>3</sup> versus fluorine co-implantation energy after annealing at 750° C for 2 hours for 1.1 keV  $1 \times 10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with  $2 \times 10^{15}$ /cm<sup>2</sup> F<sup>+</sup> at energies ranging from 2 to 36 keV.



Figure 6-7: Boron and fluorine concentration profiles after annealing at 750° C for times ranging from 15 minutes to 2 hours for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 2 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-8: Amount of fluorine dose retained after annealing at 750° C for times ranging from 15 minutes to 2 hours for  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> implanted at 2, 12, and 36 keV.



Figure 6-9: Boron and fluorine concentration profiles after annealing at 750° C for times ranging from 15 minutes to 2 hours for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 36 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



## $0.2 \ \mu m$

Figure 6-10: Plan view TEM images after annealing for 2 hours at 750° C for samples pre-amorphized with 70 keV  $1x10^{15}ions/cm^2$  Si<sup>+</sup> and implanted with (a) 1.1 keV  $1x10^{15}ions/cm^2$  B<sup>+</sup> and (b) 1.1 keV  $1x10^{15}ions/cm^2$  B<sup>+</sup> and 12 keV  $2x10^{15}ions/cm^2$  F<sup>+</sup>.



Figure 6-11: Boron concentration profiles after annealing at 750° C for 15 minutes for 500 eV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> at energies ranging from 3 to 9 keV.



Figure 6-12: Boron concentration profiles after annealing at 750° C for 2 hours for 500 eV  $1 \times 10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with  $2 \times 10^{15}$ /cm<sup>2</sup> F<sup>+</sup> at energies ranging from 3 to 9 keV.



Figure 6-13: Metallurgical junction depth measured at a concentration of  $1x10^{18}$ /cm<sup>3</sup> versus fluorine co-implantation energy after annealing at 750° C for 2 hours for 500 eV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> at energies ranging from 3 to 9 keV.



Figure 6-14: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for a 500 eV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> implant.



Figure 6-15: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for 500 eV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 3 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-16: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for 500 eV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-17: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for 500 eV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 9 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-18: Amount of fluorine dose retained after annealing at 750° C for 15 minutes and 2 hours for  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> implanted at energies ranging from 3 to 9 keV.



Figure 6-19: Boron concentration profiles after a  $1050^{\circ}$  C spike anneal for 500 eV  $1 \times 10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with  $2 \times 10^{15}$ /cm<sup>2</sup> F<sup>+</sup> at energies ranging from 3 to 9 keV.



(a)

(b)

0.2 μm



(d)

Figure 6-20: Plan view TEM images after annealing for 2 hours at 750° C for samples pre-amorphized with 70 keV  $1x10^{15}$ ions/cm<sup>2</sup> Si<sup>+</sup>, implanted with 1.1 keV  $1x10^{15}$ ions/cm<sup>2</sup> B<sup>+</sup> and co-implanted with (a) none (control sample), (b) 3 keV  $2x10^{15}$ ions/cm<sup>2</sup> F<sup>+</sup>, (c) 6 keV  $2x10^{15}$ ions/cm<sup>2</sup> F<sup>+</sup>, and (d) 9 keV  $2x10^{15}$ ions/cm<sup>2</sup> F<sup>+</sup>.



Figure 6-21: Boron concentration profiles after annealing at  $750^{\circ}$  C for 15 minutes for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 12 keV F<sup>+</sup> at doses ranging from  $1x10^{15}$ /cm<sup>2</sup> to  $8x10^{15}$ /cm<sup>2</sup>.



Figure 6-22: Boron concentration profiles after annealing at 750° C for 2 hours for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 12 keV F<sup>+</sup> at doses ranging from  $1x10^{15}$ /cm<sup>2</sup> to  $8x10^{15}$ /cm<sup>2</sup>.



Figure 6-23: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for a 1.1keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> implant.



Figure 6-24: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 12 keV  $1x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-25: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 12 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-26: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 12 keV  $4x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-27: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for 1.1 keV  $1x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 12 keV  $8x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



 $0.2 \, \mu m$ 



Figure 6-28: Plan view TEM images after annealing for 2 hours at 750° C for samples implanted with 1.1 keV  $1x10^{15}$ ions/cm<sup>2</sup> B<sup>+</sup> and amorphized with 12 keV F<sup>+</sup> at a dose of (a)  $1x10^{15}$ ions/cm<sup>2</sup>, (b)  $2x10^{15}$ ions/cm<sup>2</sup>, (c)  $4x10^{15}$ ions/cm<sup>2</sup>, and (d)  $8x10^{15}$ ions/cm<sup>2</sup>.



Figure 6-29: Boron concentration profiles after annealing at 750° C for 15 minutes for 500 eV  $4x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV F<sup>+</sup> at doses ranging from  $2x10^{15}$ /cm<sup>2</sup> to  $8x10^{15}$ /cm<sup>2</sup>.



Figure 6-30: Boron concentration profiles after annealing at 750° C for 2 hours for 500 eV  $4x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV F<sup>+</sup> at doses ranging from  $2x10^{15}$ /cm<sup>2</sup> to  $8x10^{15}$ /cm<sup>2</sup>.



Figure 6-31: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for a 500 eV  $4x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> implant.



Figure 6-32: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for 500 eV  $4x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-33: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for 500 eV  $4x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV  $4x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-34: Boron concentration profiles after annealing at 750° C for 15 minutes and 2 hours for 500 eV  $4x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV  $8x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-35: Boron concentration profiles after a  $1050^{\circ}$  C spike anneal for 500 eV  $4x10^{15}$ /cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV F<sup>+</sup> at doses ranging from  $2x10^{15}$ /cm<sup>2</sup> to  $8x10^{15}$ /cm<sup>2</sup>.



0.2 μm



Figure 6-36: Plan view TEM images after annealing for 2 hours at 750° C for samples implanted with 1.1 keV  $1x10^{15}$ ions/cm<sup>2</sup> B<sup>+</sup> and (a) pre-amorphized with 70 keV  $1x10^{15}$ ions/cm<sup>2</sup> Si<sup>+</sup>, (b) amorphized with 6 keV  $2x10^{15}$ ions/cm<sup>2</sup> F<sup>+</sup>, (c) amorphized with 6 keV  $4x10^{15}$ ions/cm<sup>2</sup> F<sup>+</sup>, and (d) amorphized with 6 keV  $8x10^{15}$ ions/cm<sup>2</sup> F<sup>+</sup>.



Figure 6-37: Plot of boron concentration profiles comparing the experimental results with simulations for a 500 eV  $1 \times 10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> implant after annealing at 750° C for 2 hours.



Figure 6-38: Plot of boron concentration profiles comparing the experimental results with simulations for 500 eV  $1 \times 10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> as-implanted.



Figure 6-39: Plot of boron concentration profiles comparing the experimental results with simulations for 500 eV  $1x10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> after annealing at 750° C for 2 hours.


Figure 6-40: Plot of boron concentration profiles comparing the experimental results with simulations for a 500 eV  $4x10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> implant after annealing at 750° C for 2 hours.



**Boron Concentration (atoms/cm** 

Figure 6-41: Plot of boron concentration profiles comparing the experimental results with simulations for 500 eV  $4x10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> after annealing at 750° C for 2 hours.



Figure 6-42: Carrier concentration versus depth profiles obtained by SRP after a  $1050^{\circ}$  C spike anneal for 500 eV  $1x10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> with and without co-implantation with 6 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Figure 6-43: Carrier concentration versus depth profiles obtained by SRP after a  $1050^{\circ}$  C spike anneal for 500 eV  $4x10^{15}$  ions/cm<sup>2</sup> B<sup>+</sup> with and without co-implantation with 6 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup>.



Fluorine Concentration (atoms/cm

Figure 6-44: Fluorine concentration profile after annealing at  $750^{\circ}$  C for 3 hours for 16 keV  $2x10^{15}$ /cm<sup>2</sup> F<sup>+</sup> implanted into pre-amorphized silicon.









Figure 6-45: TEM micrographs of: (a) initial well microstructure after postimplantation anneal at 750° C for 3 hours to form fluorine well, (b) fluorine well after 25 keV  $1 \times 10^{14}$ /cm<sup>2</sup> Si<sup>+</sup> implant and subsequent anneal at 750° C for 30 minutes, (c) sample that has received processing history identical to sample in (b) except fluorine implantation.



(c)

# 0.2 μm

Figure 6-45-- continued

## CHAPTER 7 SUMMARY AND RECOMMENDATIONS FOR FUTURE WORK

#### Summary

To date, ion implantation remains the dominant method to introduce dopants into silicon during IC processing. Inherently, ion implantation produces considerable damage to the silicon crystal in the form of excess point defects. During postimplantation annealing, interstitial point defects have been shown to follow many complex evolutionary pathways as the system moves back toward equilibrium. As the interstitials evolve, they interact with point defects, extended defects, and impurity atoms. Though the path may vary, the evolution of an interstitial leads to phenomena, such as transient enhanced diffusion and dopant clustering, that have detrimental effects upon the transistor doping. In order to continue advanced process development of doping technologies for future transistor generations, it is crucial to understand the behavior of ion implantation induced defects and their interaction with dopant atoms. This work represents a series of efforts toward such an understanding. A summary of this work and recommendations for future exploration of this topic are given below. Until recently the concept of transient enhanced diffusion in the regrown region of the silicon during post-implantation annealing remained equivocal both in literature and in the minds of the scientific community. It was not clear how the excess interstitials from the end-of-range(EOR) damage region evolved during post-implantation annealing or what effect this evolution had on dopants in the regrown region and below the EOR. Furthermore the effect of variations in ion implantation processing parameters on the evolution of excess interstitials remained uncertain. The experiments on the effects of ion implantation dose rate and temperature were designed to help elucidate these issues. Both experiments were built upon the foundation of the previous works in our research group by Jones et al.<sup>64,69,79</sup> The experiment on the effect of ion implantation temperature showed that the amount of interstitial flux into the regrown region was inversely proportional to the density of dislocation loops in the EOR. The same effect was seen in the experiment on the effect of ion implantation dose rate. It was shown that, upon annealing, decreasing the implantation temperature and increasing the implantation dose rate both have the effect of increasing interstitial flux from the EOR damage region toward the surface and decreasing the EOR defect density. The dependence of the interstitial flux toward the surface on the EOR loop density is consistent with the loop layer acting as a barrier to interstitial backflow. For these moderate temperature implants with the EOR dislocation loop densities observed, the interstitial flux into the crystal is approximately an order of magnitude greater than toward the surface. It was found that decreasing the temperature or increasing the dose rate of the amorphizing implantation increases the amorphous layer thickness. The results of these experiments combined with the results of previous works<sup>64,68,82</sup> show that the EOR dislocation loops mitigate the diffusion of interstitials toward the surface recombination sites, however they are not sufficient to trap all the excess interstitials and do not significantly effect

the flux of interstitials into the bulk of the crystal. These results also demonstrated the importance of two ion implantation process parameters, dose rate and temperature, on the doping profile following post-implantation annealing. Given the dependence of interstitial flux on EOR dislocation loops during postimplantation annealing, the relationship between extended defect evolution in the EOR and boron diffusion in regrown silicon was investigated. It was shown that, upon annealing, excess interstitials in the EOR damage region of amorphized silicon precipitate into {311} defects, dislocation loops and possibly submicroscopic interstitial clusters (SMICs). By the end of the first annealing interval of 15 minutes at 750° C, an ensemble of point and extended defects exist in the EOR damage region. As the annealing times increase, the {311} defects dissolve while the loops continue to nucleate and grow. At the same time that {311} defects dissolve and presumably release interstitials, the boron in the regrown silicon exhibits TED. The correspondence of the time to release interstitials from {311} defects and the decay of TED in the regrown silicon supports the theory that interstitials from {311} defects are contributing to the interstitial supersaturation that causes TED since dislocation loops are not releasing interstitials over the same annealing interval studied. The increase in interstitial density in the loops cannot be explained quantitatively by interstitial release from the {311}'s and this strongly suggests the existance of submicroscopic interstitial clusters (SMICs) since no other defects are visible by TEM. In addition, these SMICs which may in theory be the principle source of TED must dissolve and release interstitials over approximately the same time interval as the {311} defects.

The observations in the experiment on the correlation between extended defect evolution and boron diffusion in regrown silicon indicated that {311} defects may serve as nucleation sites for dislocation loops in the EOR damage region. In order to confirm this theory an experiment was designed to follow the evolution of a selected group of extended defects in the EOR damage region during annealing. In this experiment, the kinetics of the evolution of both {311} defects and dislocation loops in the EOR, were investigated quantitatively via *ex situ* TEM. It was shown that {311} defects serve as the preferential site for dislocation loop nucleation, which correlates to previous findings for non-amorphizing implants. These conclusions provide not only a source of EOR dislocation loops but also yield the two possible evolutionary pathways for {311} defects; dissolution and unfaulting. Since {311} defects are presumed to be the source of interstitials for TED, the results of this work are important to the development of physically based process simulation tools. The results indicate that both the dissolution and unfaulting of {311} defects must be considered in order to accurately predict the behavior of diffusing dopant atoms in regrown silicon.

After investigating several aspects of boron diffusion in ion implanted silicon, the possibility of mitigating the diffusion of boron during post-implantation was investigated. Previous authors have shown that impurities incorporated into the lattice of silicon have the ability to mitigate boron diffusion. This effect has been shown for both carbon<sup>46</sup> and fluorine.<sup>89</sup> In the experiments described in Chapter 6, the effect of fluorine co-implantation was investigated over a range of

processing conditions. These experiments investigated the effect of fluorine on boron diffusion over a wider range of implantation than previously explored. After careful analysis, it was possible to deduce the mechanism by which fluorine mitigates boron diffusion. It was shown that the addition of fluorine reduces boron TED after annealing for 2 hours at 750° C, in agreement with previous works.<sup>89</sup> The co-implantation of fluorine was also shown to increase the solubility of the boron as revealed by empirical results from both SIMS and SRP and simulations. It was shown that the effects of fluorine co-implantation on the diffusion of boron display dependence on both the energy and dose of the fluorine co-implantation. The main mechanism that appears to control these phenomena is the trapping of interstitials by the implanted fluorine. It was hypothesized that the same properties of fluorine that lead to interstitial trapping are responsible for the passivation of dangling bonds in amorphous silicon. It was proposed that the passivation of the dangling bonds is the reason for the effect of fluorine on amorphous layer regrowth and the enhancement in the diffusion of boron at short times in post-amorphization annealing.

#### Future Work

Although great strides have been made in the study of the effects of fluorine on the diffusion of boron in ion implanted silicon during post-implantation annealing, many questions remain. The complex behavior of fluorine in ion implanted silicon makes experiments on its effects akin to peeling an onion; each layer removed exposes a subsequent layer. Following the culmination of this work, the most pertinent unresolved issues which stem from the results presented are as follows:

• Determine the effects of fluorine on boron diffusion during solid phase epitaxy- In the experiments on the effects of fluorine on boron diffusion it was postulated that the enhancement of boron diffusion by fluorine co-implantation after short annealing times was due to an enhancement of boron diffusion during post-implantation annealing prior to solid phase epitaxy (SPE). This effect was attributed to a combination of two effects, fluorine passivation of dangling bonds in amorphous silicon and fluorine retarding the rate of SPE recrystalization. In order to confirm this hypothesis empirically, a series of low temperature anneals (T < 700° C) should be performed that span several data points both prior to SPE recrystalization and immediately after it. These anneals should ideally be performed at several temperatures and each isothermal set should include a sample with a subsequent anneal at higher temperature (T > 800° C) in order to confirm the nature of the enhanced diffusion at short times and low temperatures and the reduction of fluorine diffusion at higher temperatures or longer annealing times.

• *Expand the fluorine well experiment to further investigate the interstitial trapping behavior*- The experiment with the fluorine well provided conclusive evidence of fluorine trapping silicon interstitials in ion implanted silicon. Further experiments may provide a more suitable well structure that will provide cleaner results. After determination of the optimal fluorine well structure, the experiment should expanded to a wider range of experimental conditions. In particular, it

would be useful to perform a time and temperature study of ion implantation induced defects into several well structures with various fluorine concentrations. Performing analysis at several times at several different temperatures will allow the determination of the activation energies for the dissolution of defects as a function of fluorine concentration (assuming that a suitable well can be formed that partially inhibits the formation of {311} defects). Investigating the effect at several fluorine concentrations may reveal information about the trapping efficiency of fluorine and possibly the configuration of the fluorine-interstitial complex.

• Perform SPE anneals to investigate the defects in the initial fluorine well-Transmission electron microscopy (TEM) revealed the presence of defects of undetermined nature in the initial fluorine well. It was unclear if these were regrowth related defects or precipitates. Plan view TEM following SPE recrystalization at low temperature (T < 550° C) and then following higher temperature (T > 700°) annealing would provide evidence as to whether the defects were SPE regrowth related defects. Secondary ion mass spectrometry measurements to confirm the motion of the fluorine during these anneals combined with the TEM results would confirm that the defects were regrowth related assuming that the fluorine showed negligible diffusion following the low temperature regrowth and that the defects were present after the low temperature SPE recrystalization. If the defects do not appear after the SPE recrystalization, but do appear after the higher temperature anneal, then they are presumably precipitates of fluorine.

• *Repeat the experiment on the effect of varying the fluorine dose into preamorphized silicon*- The lack of pre-amorphization in this experiment was not the optimal situation. Repeating the experiment with a pre-amorphization to remove damage as an extraneous variable would remove the ambiguity from the results obtained in this experiment.

## APPENDIX INPUT FILES FOR SIMULATIONS USING FLOOPS

<u>Pre-amorphized 500 eV 1x10<sup>15</sup>/cm<sup>2</sup> B<sup>+</sup> annealed at 750° C for 2 hours</u> source Convolute

source Dopant2.tcl solution name=Boron add solve damp !negative

SetTemp 750

set oldDp [expr [pdbGetDouble Si B I Dp] + [pdbGetDouble Si B V Dp] ] set ActModel 1

set t 1800

```
line x loc=0 spacing=0.0001 tag=top
line x loc=.025 spacing=0.005
line x loc=.12 spacing=0.01
line x loc=.3 spacing=0.1
line x loc=5 spacing=1
line x loc=100 spacing=10 tag=bot
region silicon xlo=top xhi=bot
```

init

profile name=Boron inf=42-3-6asimpdecon profile name=match inf=42-3-6-750C2hn

```
sel z=log10(Boron)
plot.1d label=Boron min=0.0 max=0.1
sel z=log10(match)
plot.1d !cle label=match min=0 max=0.1
```

```
sel z=Boron name=Asimp store
sel z= "Boron - 7.0e19*(1.0-exp(-Boron/7.0e19))"
name=BoronClust
```

```
sel z=log10(Asimp)
plot.1d !cle label=Asimp min=0 max=0.1
pdbSetSwitch Si Boron DiffModel Fermi
diffuse time=$t temp=750 !adapt movie= {
    sel z=log10(Asimp)
    plot.1d label=Asimp min=0 max=0.1
    sel z=log10(match)
    plot.1d !cle label=match min=0 max=0.1
    sel z=log10(Boron)
    plot.1d !cle label=Boron min=0 max=0.1
    Convolute Boron Sims 0.0015
    sel z=log10(Sims)
```

plot.1d !cle label=Sims min=0 max=0.1

}

# Pre-amorphized 500 eV 1x10<sup>15</sup>/cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV 2x10<sup>15</sup>/cm<sup>2</sup> F<sup>+</sup> annealed at 750° C for 2 hours

```
source Convolute
```

```
source Dopant2.tcl
solution name=Boron add solve damp !negative
```

```
SetTemp 750
```

```
set oldDp [expr [pdbGetDouble Si B I Dp] + [pdbGetDouble Si B V Dp] ]
set ActModel 1
```

set t 11

```
line x loc=0 spacing=0.0001 tag=top
line x loc=.025 spacing=0.005
line x loc=.12 spacing=0.01
line x loc=.3 spacing=0.1
line x loc=5 spacing=1
line x loc=100 spacing=10 tag=bot
region silicon xlo=top xhi=bot
```

init

```
profile name=Boron inf=42-3-6asimpdecon
profile name=match inf=42-3-8-750C2hn
```

```
sel z=log10(Boron)
plot.1d label=Boron min=0.0 max=0.1
sel z=log10(match)
plot.1d !cle label=match min=0 max=0.1
```

```
sel z=Boron name=Asimp store
sel z= "Boron - 1.0e21*(1.0-exp(-Boron/1.0e21))"
name=BoronClust
```

```
sel z=log10(Asimp)
plot.1d !cle label=Asimp min=0 max=0.1
```

pdbSetSwitch Si Boron DiffModel Fermi

diffuse time=\$t temp=750 !adapt movie= {

sel z=log10(Asimp) plot.1d label=Asimp min=0 max=0.1 sel z=log10(match) plot.1d !cle label=match min=0 max=0.1 sel z=log10(Boron) plot.1d !cle label=Boron min=0 max=0.1 Convolute Boron Sims 0.0015 sel z=log10(Sims) plot.1d !cle label=Sims min=0 max=0.1

}

Pre-amorphized 500 eV 4x10<sup>15</sup>/cm<sup>2</sup> B<sup>+</sup> annealed at 750° C for 2 hours

source Convolute source Dopant2.tcl solution name=Boron add solve damp !negative SetTemp 750

set oldDp [expr [pdbGetDouble Si B I Dp] + [pdbGetDouble Si B V Dp] ] set ActModel 1

set t 3000

```
line x loc=0 spacing=0.0001 tag=top
line x loc=.025 spacing=0.005
line x loc=.12 spacing=0.01
line x loc=.3 spacing=0.1
line x loc=5 spacing=1
line x loc=100 spacing=10 tag=bot
region silicon xlo=top xhi=bot
```

init

profile name=Boron inf=boronin-trunc profile name=match inf=42-3-10-750C2hn

```
sel z=log10(Boron)
plot.1d label=Boron min=0.0 max=0.1
sel z=log10(match)
plot.1d !cle label=match min=0 max=0.1
```

```
sel z=Boron name=Asimp store
sel z= "Boron - 4.0e19*(1.0-exp(-Boron/4.0e19))"
name=BoronClust
```

```
sel z=log10(Asimp)
plot.1d !cle label=Asimp min=0 max=0.1
```

pdbSetSwitch Si Boron DiffModel Fermi

diffuse time=\$t temp=750 !adapt movie= {

sel z=log10(Asimp) plot.1d label=Asimp min=0 max=0.1 sel z=log10(match) plot.1d !cle label=match min=0 max=0.1 sel z=log10(Boron) plot.1d !cle label=Boron min=0 max=0.1 Convolute Boron Sims 0.0015 sel z=log10(Sims) plot.1d !cle label=Sims min=0 max=0.1

}

# Pre-amorphized 500 eV 4x10<sup>15</sup>/cm<sup>2</sup> B<sup>+</sup> co-implanted with 6 keV 2x10<sup>15</sup>/cm<sup>2</sup> F<sup>+</sup> annealed at 750° C for 2 hours

```
source Convolute
```

```
source Dopant2.tcl
solution name=Boron add solve damp !negative
```

```
SetTemp 750
```

```
set oldDp [expr [pdbGetDouble Si B I Dp] + [pdbGetDouble Si B V Dp] ]
set ActModel 1
```

set t 22

```
line x loc=0 spacing=0.0001 tag=top
line x loc=.025 spacing=0.005
line x loc=.12 spacing=0.01
line x loc=.3 spacing=0.1
line x loc=5 spacing=1
line x loc=100 spacing=10 tag=bot
region silicon xlo=top xhi=bot
```

init

```
profile name=Boron inf=boronin-trunc
profile name=match inf=42-3-11-750C2hn
```

```
sel z=log10(Boron)
plot.1d label=Boron min=0.0 max=0.1
sel z=log10(match)
plot.1d !cle label=match min=0 max=0.1
```

```
sel z=Boron name=Asimp store
sel z= "Boron - 4.0e20*(1.0-exp(-Boron/4.0e20))"
name=BoronClust
```

```
sel z=log10(Asimp)
```

plot.1d !cle label=Asimp min=0 max=0.1

pdbSetSwitch Si Boron DiffModel Fermi

diffuse time=\$t temp=750 !adapt movie= {

sel z=log10(Asimp) plot.1d label=Asimp min=0 max=0.1 sel z=log10(match) plot.1d !cle label=match min=0 max=0.1 sel z=log10(Boron) plot.1d !cle label=Boron min=0 max=0.1 Convolute Boron Sims 0.0015 sel z=log10(Sims) plot.1d !cle label=Sims min=0 max=0.1

}

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### **BIOGRAPHICAL SKETCH**

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