# SIMULATION OF FLUORINE DIFFUSION BEHAVIOR AND BORON-FLUORINE CO-INTERACTION IN SILICON

By

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This document is dedicated to all of the past, present, and future SWAMP group members.

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As CMOS (Complimentary Metal Oxide Semiconductor) device dimensions continue to shrink, industry has begun to rely on more novel impurity implant procedures to continually meet junction depth requirements. One such novel procedure is the coimplantation of both boron and fluorine impurities into the silicon system. The addition of fluorine to implant has been shown to reduce the junction depth of boron implants, but the mechanics behind the effect are not well described.

The first goal of this study was to examine the diffusion behavior of fluorine by itself and develop a functioning diffusion model. The apparent surface oriented diffusion of fluorine was previously known, but this work added to the understanding of fluorine diffusion by demonstrating the apparent uphill diffusion of fluorine during the anneal as well as the transient nature of the diffusion process. A functioning fluorine model was developed in the FLOOPS simulator which fit the experimental data well. Through this modeling effort, it was proposed that the primary diffusion instigator for fluorine was the capture of interstitials by fluorine-vacancy products, which in turn releases mobile fluorine.

The next goal of this study was to model the behavior of the total boron-fluorine system by combining the newly developed fluorine model with a previously developed boron model. To produce experimental data, new experiments were conducted which examined boron and fluorine profiles with varying doses to examine the behavior in different impurity diffusion regimes. When the model was developed it was found that the fluorine model could produce the proper effects on boron diffusion itself without any serious modification of boron model parameters. The model results are shown to match experimental data extremely well. Through the modeling efforts, it appears fluorine reduces boron diffusion primarily through capture of silicon self-interstitials. Additionally, there appears to be no direct fluorine-boron reaction involved.

# CHAPTER 1 INTRODUCTION AND BACKGROUND

#### **1.1 Short Background and Motivation**

The relentless scaling of silicon chips has become the most common theme of the body of semiconductor process research over the last 20 years. CMOS (complimentary metal oxide semiconductor) technology still dominates as the most prominent technology [Plummer00]. The pressure to scale comes from two sources: one economic and the other engineering. Economically, if the size of a single chip can be shrunk, then more chips can fit on a wafer, and the economics of semiconductor production will improve. From an engineering standpoint, semiconductor chips are becoming ever more complex and the number of transistors in the average chip is increasing as new functions are integrated and developed. In order to accommodate as many additional transistors as possible, it is ideal to shrink the size of the transistors in the chip to keep the die size as small as possible, which improves yield. Additionally, the power use on modern chips can be improved when the device switches to smaller nominal transistor size [Pierret96].

As the CMOS transistor size continues to scale below the 0.1um mark, the physics of the device operation become much more complex due to the appearance of short channel effects [Pierret96]. Short channel effects can severely degrade the performance of a device and contribute to the standby power consumption of a device. Therefore many developments in silicon front-end processing technology seek to develop answers and workarounds for the problems. Once such method to limit effects is to scale the depth of

the source and drain junctions and extensions with the gate length of the technology. In this way, some of the short channel effects can be mitigated [Plummer00].

As device feature size continued to shrink below 0.5 micron feature size, the traditional gas diffusion and solid source diffusion methods for source and drain creation no longer provided the level of process control required to produce high process yields. Therefore the dominant technology to introduce the impurities into the source and drain became ion implantation, a method which provided both greater process control and the ability to produce shallower junctions than the previous methods. As ion implantation technology matured, the preferred impurity implant to produce p-type device junctions and extensions became BF<sub>2</sub>, which was adopted for a few simple reasons. The first of which was a simple result of physics: if a heavier impurity species such as BF2 is implanted with the same acceleration energy as a lighter species such as elemental boron, then the heavier species will travel less deep in the substrate, and subsequently produce a shallower profile Plummer00]. In this way, shallower profiles could be produced without the need for more expensive equipment at the time. As well as production shallower profiles, the use of  $BF_2$  also allowed for greater control of implantation energy and depth and thus improved reliability and yield across wafers.  $BF_2$  implants are also produced from the gaseous source BF<sub>3</sub>, and in general gaseous sources are simpler to use in the implantation process [Plummer00]. Fluorine is not an active species [Goltzenne85], so its addition at the time was deemed unimportant and harmless. However, soon after its introduction, fluorine diffusion behavior was shown to be anomalous when compared to the behavior of other impurities [Tsai79]. The fluorine appeared to show surface oriented, non-fickian type diffusion behavior, and also, contrary to expectation, appeared

to be present in the sample through most of the front end processing[Tsai79]. Additionally, the introduction of fluorine into CMOS oxides was shown to have beneficial effects [Ma92, Wang92, Nishioka89].

Later in the process technology development, fluorine was shown to in fact have beneficial effects on the boron profile during annealing. Most specifically is the ability of fluorine to reduce the magnitude of boron transient enhanced diffusion [Downey98, Robertson01, Gable05], the specifics of which will be discussed later in this chapter. The appearance of this beneficial effect led to much investigation into the use of fluorine in process development, both when implanted as BF<sub>2</sub> as well as when B and F species are implanted separately.

The importance of fluorine in emerging process technology leads to the thrust of this dissertation: no functional diffusion model of fluorine exists that can fully describe the behavior of fluorine diffusion, and more specifically the effect of fluorine on boron diffusion. Previous published works have only been able to describe fluorine diffusion within a narrow range of implant and anneal conditions, and, as is shown later, do not properly describe the time dependent nature of fluorine diffusion [Diebel03]. The best case for such a model would be to develop one such that both diffusion and effects could be described. This would further the use of the TCAD in development of future process technologies.

#### **1.2 Ion Implantation**

Ion implantation is by far the most prominent method to introduce impurity atoms into silicon crystal. Ion implantation allows the precise positioning of impurities and significant control over implantation dose. For modern processes, ion implantation allows the extremely shallow positioning of impurities, and the control allows for the position of

deep and retrograde impurity profiles which are not possible with the older gaseous or solid source diffusion. Ion implantation has a number of control factors: wafer tilt, wafer rotation, implant temperature, implantation current density, implantation energy, implanted dose, and finally implanted species. An ion implanter is a device which uses electric potential energy to accelerate ions into a beam and direct them into a target source. The impurity ions themselves first come from an impurity source, which can be gaseous or solid, and then are ionized with strong electric charge. At this point, the ions are passed through a separator screen which consists primarily of a curved magnet. This separator magnet works on the simple physics principle that a charged particle placed in a constant magnetic field will follow a curved path, with the radius of curvature being determined by the mass and charge of the particle as well as the strength of the magnetic field. The simple equation of the radius of motion of a charged particle in a magnetic field is given by [Halliday04]:

$$R = \frac{\text{Mass*Velocity}}{\text{Electric charge*Magnetic Field}}$$
(1.1)

Input velocity and magnetic field strength are known and are constant throughout a single implantation; therefore, the primary screening factor is mass to charge ratio. The magnetic field and input velocity are matched such that impurities with the proper mass to charge ratio pass through the center of curvature, which other species will impact on the inside or outside of the magnetic screen. Most species implanted are singly ionized from the source; therefore generally mass is the single separating factor. Ideally, this process selects only one single impurity species, but in some cases contaminant species such as doubly ionized transition metals may be unintentionally implanted. The screen

also must be made selective enough such that species of similar mass (i.e.,, germanium and arsenic) are not co-implanted.

The filtered ions are then directed into an acceleration tube, which accelerates the ions through simple coulombic attraction. The ions acquire acceleration energy given by the following formula as [Plummer00]:

Energy = 
$$q * AcceleratingVoltage$$
 (eV) (1.2)

The resulting beam is then directed across a series of dual-axis deflection plates which direct the beam across the wafer in an ideally uniform manner to provide even exposure across the entire wafer. In more modern production implantation situations, special rotating wafer chucks are sometimes used to improve consistency and yield across wafer lots. The beam current is measured by a simple integrator circuit connected to the wafer and a ground potential. From this beam current, it is possible to determine the total implanted dose of impurities as follows:

Dose = 
$$\int_{t=0}^{t} \text{BeamCurrent} \quad * \frac{\text{Ionization}}{q * \text{Area}} dt$$
 (1.3)

where the ionization is one for a singly ionized impurity, two for a doubly ionized impurity, etc.

#### **1.2.1 Spatial Impurity Distribution from Ion Implantation**

Knowledge of the spatial distribution of implanted ions is extremely important in determining device behavior, reliability and yield. Analytical models have been developed that can approximate the distribution of implanted ions, and the models have been shown to be extremely accurate [Plummer00]. As implanted ions reach the surface of the target, they lose energy from collisions with substrate atoms and electrons within the crystal. The two components of energy loss are called nuclear and electronic stopping. Following the discussion in Plummer et al.[Plummer00], therefore the total energy loss rate can be written as

$$\frac{dE}{dx} = S_n(E) + S_e(E)$$
(1.4)

where  $S_n(E)$  is the nuclear stopping component and  $S_e(E)$  is the electronic stopping component. Values of  $S_n(E)$  and  $S_e(E)$  have been computed for various impurities/energies, or it is possible to compute them for low doses from the following formula:

$$S_{n} \approx 2.8 * 10^{-5} * \frac{Z_{1} * Z_{2} * N * M_{1}}{(Z_{1}^{\frac{2}{3}} + Z_{2}^{\frac{2}{3}}) * (M_{1} + M_{2})}$$
(eV/Angstrom) (1.5)  
$$S_{e} = 1.22 * 10^{-16} * N * \sqrt{\frac{\text{Energy}}{M_{1}}} (eV/\text{Angstrom})$$
(1.6)

where z1 and m1 refer to the implanted ion and  $Z_2$ ,  $M_2$  refer to the crystal ion and N is the atomic density of the crystal, which is  $5 \times 10^{22}$  cm<sup>-3</sup> for silicon. Generally it is not necessary to calculate these values in each case, as the numbers are commonly available in pre-computed tables.

A figure of merit is called the critical energy, which is the point at which the values of  $S_n(E)$  and  $S_e(E)$  are equal. This critical energy may be expressed as

$$E_{\text{crit}} = (S_n * K)^2 \tag{1.7}$$

It is desirable to write a complete expression for the depth range of an implant, or the distance a given implanted ion will travel in the material before losing all of its energy and thus coming to rest. This value itself is not an expression of direct distance from the

surface, as a given ion can change direction several times inside the target, and thus this figure includes such possibilities as lateral travel and reflection back to the surface.

Range = 
$$\int_{0}^{\text{Energy}} \frac{dE}{-\frac{dE}{dR}}$$
(1.8)

This may be approximated as

Range = 
$$\frac{\text{Energy}_{\text{ion}}}{S_n}$$
 (if  $E_{\text{ion}} < E_{\text{crit}}$ ) (1.9)

or

Range = 
$$\frac{\text{Energy}_{\text{ion}}}{S_{e}}$$
 (if  $E_{\text{ion}} > E_{\text{crit}}$ ) (1.10)

It is possible to then determine the average depth from the surface at which an ion will come to rest. This quantity is referred to as the "projected range" and may be expressed as

$$Range_{projected} = Rp = \frac{Range}{1 + \frac{M_2}{3*M_1}}$$
(1.11)

The distribution of the doping profile about the projected range is given by the "straggle" of the implant which may be expressed as

$$straggle = \Delta Rp = \frac{2}{3} * Rp * \frac{\sqrt{M_1 M_2}}{(M_1 + M_2)}$$
 (1.12)

It is now possible to write an expression for a Gaussian distribution to describe the implanted profile:

$$n(x) = \frac{\text{Dose}}{\sqrt{2\pi} * \Delta Rp} \exp(\frac{-(x - R_p)^2}{2 * \Delta Rp^2})$$
(1.13)

The lateral straggle of the implant may be accounted for by the following equation:

$$n(x, y) = n(x) * \exp(-\frac{y^2}{2 * \Delta R_p})$$
(1.14)

Lateral straggle is an increasingly important parameter of note with modern processes. In many cases, a large amount of lateral straggle can reduce the channel length of a device even before any further processing, thus greatly affecting device performance.

## **1.2.2 Damage Produced from Implantation**

As the implanted ions come to rest in the silicon crystal and they disperse their kinetic energy to the lattice, they may locally disrupt the symmetry of the lattice by displacing lattice atoms through direct nuclear collision. The energy required to displace a silicon atom from its lattice site is 15eV [Fahey89]. The typical implantation energy range for modern processes varies from .25 keV to 100 keV; thus basic math indicates it is highly favorable that ion collisions will results in such displacements. The process of removing a silicon atom from a lattice site is referred to as the Frenkel process [Fahey89]. The silicon atom removed from the lattice site is referred to as an interstitial, and the lattice site left unoccupied is referred to as a vacancy. Interstitials and vacancies are commonly referred to as simple point-defects.

For low energies ion implantation, below the critical energy, it is possible to determine the energy dispersed per length within the crystal as

$$\frac{\mathrm{dE}}{\mathrm{dx}} = \mathrm{S}_{\mathrm{n}} \tag{1.15}$$

It is then possible to evaluate the energy displaced per atomic plane as

$$\frac{dE}{lattice\ plane} = S_n * spacing \tag{1.16}$$

The 15eV displacement energy given is simply for the Frenkel process itself. An incoming ion may displace a silicon atom and impart a significant amount of energy onto that silicon atom, which can then displace other silicon atoms to form what is sometimes called a damage cascade [Plummer00]. Silicon atoms displaced directly by impurity atoms are called primary damage, while atoms displaced by other silicon atoms are called secondary damage. The tendency to produce secondary damage is most prominent for heavier impurities such as antimony and arsenic, and much less prevalent for lighter impurities such as boron. Thus it can be inferred that heavier impurities have a greater potential to damage the silicon lattice than lighter impurities.

#### **1.2.3 Ion Channeling**

The silicon crystal itself is a very ordered substrate. Imagine for a moment holding a model of the silicon diamond lattice structure (as many advisors keep in their office), and rotating it freely. From some directions, the representation of the structure in one dimension will appear very dense with atoms, while in a few select orientations, the representation will appear very sparse and long "channels" will appear. As ions are implanted, they have a slight variation in their directions, and certain atoms will either directly find these channels or enter them through collisions. Ions in the channels will experience only electronic stopping and thusly travel a longer distance into the structure before they come to rest. Channeling can be a great problem for silicon manufacturing, as it results in a deeper profile than is predicted by the formulas earlier in the chapter. Channeling is generally a greater problem for lower dose implants and lighter implanted species, as those conditions result in a lower amount of lattice displacement. When examining profiles where channeling is present, the resulting deeper profile is generally said to show a "channeling tail." Larger dose implants and heavier ions produce more

damage, which can block channeling. The primary method of controlling channeling is to tilt and rotate the wafer in the chuck to expose one of the very dense 2-d projections of the lattice mentioned above. For {100} silicon wafers, this generally amounts to a tilt of 7 degrees and a 22 degree rotation.

#### **1.2.4 Amorphization**

At high levels of implantation damage, the long-range order of the crystal begins to be eroded by the high concentration of interstitials and vacancies. It is generally assumed that once 10% of the lattice atoms are displaced, the material is no longer crystalline and is referred to as amorphous [Pelaz01]. The implanted dose necessary to achieve this is referred to as the amorphization dose, which is a strong function of ion mass and weaker function of implantation energy. Heavy ions which are capable of creating a large number of secondary collisions tend to be able to easily amorphize silicon, and lighter ions, such as boron, may not be able to amorphize silicon at all. Ions which are implanted into an amorphous region are almost completely insulated from any channeling issue, because the channels present in ordered silicon are completely removed, and the ions are exposed to a much greater nuclear stopping component. Additionally, when an implant produces an amorphous region, an additional complication is produced, in the form of the end-ofrange region or "EOR." This consists of the still ordered point defect rich region which exists just deeper than amorphous region in a sample. This EOR region becomes a source of additional defects called extended defects that are mentioned later in the chapter.

# **1.2.5 Damage Profiles**

Ion implantation and lattice damage is a much more complex process than can be mentioned in this section, but the synopsis presented in prior sections provides a good grasp of the topic. Modern software programs such as UT-MARLOWE [Tasch98] utilize much more complex calculation and simulation to model the atomic damage cascades and to help estimate the populations of interstitials and vacancies which will be produced in the silicon wafer. The reader is referred to the reference listed if more knowledge of these processes is desired. Implantation tools such as UT-MARLOWE are critical for modeling purposes because such damage and impurity profiles are used as inputs to diffusion models for impurities. If the implantation simulator is not accurate, "garbage in, garbage out" applies.

#### **1.3 Diffusion Theory**

#### 1.3.1 Fick's Laws

The next background subject worthy of note is that of the basic theory of diffusion of impurities of solids. Though it seems that silicon itself is a special topic all by itself, the study of the diffusion of various species in silicon is a subset of the study of diffusion in solids. The basic equations governing diffusion in solids are called Fick's first and second laws of diffusion [Fahey89]. The one dimensional case is examined first as it is the simplest to present. Fick's first law is presented as

$$J = -D \partial C / \partial X, \qquad (1.17)$$

where J refers to the impurity flux, D the constant of proportionality called the diffusion coefficient and C refers to the impurity concentration.

The diffusivity of an individual impurity varies in order with temperature, as with most thermodynamical constants, so in order to obtain the temperature dependence of the diffusivity D, empirical measurements of the diffusivity have been performed and these have shown that the diffusivity can be expressed in terms of an Arrhenius relationship:

$$D = D_0 \exp(-E_a/kT) \tag{1.18}$$

In the above equation  $D_0$  refers to the pre-exponential which is a function of the entropy of the system,  $E_a$  is the activation energy of the diffusing species, k is the Boltzmann constant and T is the absolute temperature in Kelvin. Further discussion of the activation energy is deferred until later in the chapter.

Fick's second law is then presented as

$$\partial C/\partial t = \partial (D\partial C)/\partial X^2$$
 (1.19)

Fick's laws present a very simple case for diffusion if implemented by themselves. If every impurity in silicon followed such a simple set of equations, it would be expected that impurities introduced would follow a simple erfc (error function) profile for surface source introduction, and impurities would diffuse along a simple Gaussian distribution for ion implantation introduced impurities. For a further discussion of the simple diffusion model, the reader is referred to the excellent book by Plummer [Plummer00] At first glance, low concentration boron, can at first glance be roughly modeled by such a simple equation. The cases are generally called "Fickian diffusion", and imply that the diffusion in that case appears to conform to Fick's laws. However, there are many cases where the diffusion behavior of impurities does not obey a simple Fick's law equation. An excellent example of this is fluorine diffusion, mentioned in chapter 2, which does not even follow remotely a Gaussian distribution during diffusion. Most other impurities, especially those introduced by ion implantation, also show non-Fickian behavior. This indicates that Fick's laws by themselves will not be sufficient to describe impurity diffusion, and the diffusion mechanisms must be more complicated.

Fortunately a large amount of research has been conducted on the topic, and the basic mechanisms for impurity diffusion in silicon are much better described. The

diffusion of impurities silicon proceeds mainly by two different mechanisms as explained below. Following that, the thermodynamic theory will be developed.

#### **1.3.2 Interstitial Diffusion Mechanism**

A silicon interstitial, also called a "self-interstitial" to distinguish it from impurity atoms is a silicon atom that resides in one of the open spaces or "interstices" of the silicon lattice. However, more accurately, it has been found that the split interstitial or the "dumbbell" configuration is the most stable equilibrium configuration for the interstitials [Rubia95]. This means that two interstitials along the {110} plane share the same lattice point. Self-interstitial mediated diffusion can occur in one of two ways, called the "kickout" and "coordinated push" mechanisms.

There is a slight distinction between the so-called interstitialcy and interstitial proper mechanisms. Properly, a impurity interstitial is fully in an interstice between atoms in the silicon crystal. An impurity interstitialcy comprises a silicon atom and a impurity atom essentially sharing a lattice site. From a physical perspective, the two are distinct behaviors, but as will be discussed later, are energetically indistinguishable. Therefore in many cases processes may be applied somewhat interchangeably.

To begin the discussion of these mechanisms, let us assume that an impurity resides in a substitutional lattice position, which implies is occupies a lattice position in place of a silicon atom. In this "kickout" mechanism, the substitutional impurity atom is "kicked" out of its substitutional position, by a silicon self interstitial generated by implantation damage or thermal generation, and into the interstice of the silicon lattice. Thus, the interstitial impurity atom can migrate with a small barrier through the open areas of the silicon lattice. The precise nature of this migration is somewhat complex and will be mentioned later in the chapter. After migrating some distance in the lattice, the impurity interstitial can "kickback" into a substitutional silicon site and eject a silicon interstitial and the whole process repeats itself. This process is called the interstitial mechanism since is depends most prominently on the impurity interstitial.

The "coordinated push" mechanism is another form of interstitial mediated diffusion, which is the interstitialcy counterpart to the kickout method. In this case, a silicon self-interstitial could "push" the impurity atom away from its substitutional site. Energetics of the process may indicate that rather than being fully ejected, the lowest energy point by result in the silicon atom and impurity atom somewhat sharing a lattice site, while both atoms are push off of the bond center site. Depending on the binding energy of the individual impurity, the impurity atom may be free to migrate away and repeat this process again with a neighboring silicon atom, and in this way, migrate through the lattice. In each case, the new site would be occupied by shared impurity and silicon atoms, and the diffusion is then governed by the impurity-interstitial pair. However, in the strong binding limit, the new self-interstitial would be bound to the impurity. It is important to note that in this case, the two atoms do not dissociate to diffuse.

#### **1.3.3 Vacancy Mechanism**

An empty lattice site without a silicon atom present is called a vacancy. Vacancy mediated diffusion is often the easiest type of diffusion to visualize. If an impurity diffuses in this fashion, than an impurity in a substitional site exchanges places with an adjacent vacancy, and thus the impurity and vacancy switch places. The impurity atom in this case is said to have diffused one step. However, if the impurity is to diffuse for longer distances, than the impurity and the vacancy must completely dissociate, otherwise, the two defects would just change places.

The case above can be thought of as the analogue of the simple interstitial kickout case. However, certain impurities can have a very strong attraction for vacancies and thus become partially bound, in which case the two produces can become bound to each other. In this case, the vacancy must diffuse away from the impurity atom (i.e., to second nearest neighbor), and then return along a different path. In this way, the vacancy accompanies the impurity species along a series of hops and the diffusing species becomes a impurity-vacancy pair. Examples of some simple models for defect mediated diffusion are included in figure 1-1.

#### **1.3.4 More Realistic Diffusion Models**

In general, the diffusivity D can be expressed as a sum of the contributions of diffusion through the individual impurity-defect species. Mathematically, this can be expressed as

$$D = \Sigma d_i C_i / C_x \tag{1.20}$$

In the above equation  $d_i$  and  $C_i$  refer to the diffusivity and concentrations of the impuritydefect considered that affects the long range migration of the impurity and  $C_x$  refers to the total concentration of the impurity.

Under equilibrium conditions, the evolution of the profile with respect to time is given by a simple Fick's law process as in equations (1.17-1.19). However, most modern silicon processing technologies involve non-equilibrium conditions. Ion implantation damages the crystal, inducing non-equilibrium defect profiles mentioned previously. It has been shown by many [Fahey89, Antoniadias82], that the oxidation process injects interstitials into the silicon substrate while nitridation injects vacancies. Therefore in most cases, the population of both interstitials and vacancies is well above equilibrium

values. During annealing at high temperatures, these defects are annealed and the defect concentrations eventually reach their equilibrium values and the impurities would exhibit equilibrium diffusion. However, until the defect concentrations reach their equilibrium values, the diffusion of the impurity that would be mediated by the defects would be a non-equilibrium problem.

Before some of the more advanced discussion can begin, the term "equilibrium defect concentration" must be elucidated. Thermodynamically, there are always interstitials and vacancies present in any silicon sample, generated though the interstitial and vacancy mechanisms mentioned above. The term equilibrium refers to the case in which there is no remaining additional damage present from ion implantation or other processes. The equilibrium values for interstitials and vacancies will vary with temperature, and the values of both increase as temperature rises. Therefore, the equilibrium interstitial and vacancy concentrations are determined thermodynamically, and called "CIstar" ( $C_1$ \*) and "CVstar" ( $C_V$ \*) respectively. For more discussion on this, the reader is referred to [Fahey89].

In the case of non-equilibrium defect concentrations, the defect concentration at any one moment of all of the impurity and defect species is affected by all of the interaction between the species as well as the diffusion of the individual species themselves. This implies that if an equation to solve for the time evolution of the impurity and/or defect concentrations, we would have to modify equation (1.20) with the addition of the terms to describe creation and annihilation of all of the different products.

Let us assume that we only have interstitial and vacancy mediated diffusion, then, we can rewrite equation (1.20) following the discussion in Plummer et al. [Plummer00] as

$$D_{A} = D_{AI} + D_{AV} = d_{AI} C_{AI} / C_{A} + d_{AV} C_{AV} / C_{A}$$
(1.21)

 $D_A$ ,  $D_{AI}$  and  $D_{AV}$  refer to the instantaneous effective diffusivities of the impurity, impurity-interstitial and impurity-vacancy respectively, in accordance with the diffusion mechanisms of the prior section.  $d_{AI}$  and  $d_{AV}$  refer to the actual diffusivities of the impurity-interstitial and impurity-vacancy pairs respectively.  $C_A$ ,  $C_{AI}$ , and  $C_{AV}$  refer to the instantaneous concentrations of the substitutional impurity, impurity-interstitial and impurity-vacancy complex respectively.

If equilibrium conditions are applied to the equation, equation 1.21 becomes

$$D_{A}^{*} = D_{AI}^{*} + D_{AV}^{*} = d_{AI} [C_{AI}/C_{A}]^{*} + d_{AV} [C_{AV}/C_{A}]^{*}$$
(1.22)

The \* refers to equilibrium values at this point and in all later equations. Therefore,

$$\frac{D_{A}}{D_{A}^{*}} = \frac{d_{AI} C_{AI}/C_{A} + d_{AV} C_{AV}/C_{A}}{d_{AI} [C_{AI}/C_{A}]^{*} + d_{AV} [C_{AV}/C_{A}]^{*}} (1.23)$$
$$= \frac{d_{AI} C_{AI}/C_{A}}{d_{AI} [C_{AI}/C_{A}]^{*} + d_{AV} [C_{AV}/C_{A}]^{*}} + \frac{d_{AV} C_{AV}/C_{A}}{d_{AI} [C_{AI}/C_{A}]^{*} + d_{AV} [C_{AV}/C_{A}]^{*}} (1.24)$$

In order to relate the diffusivity under non-equilibrium conditions to the diffusivity under equilibrium conditions, it would be helpful to define a parameter called the fractional component of interstitial diffusion  $f_{AI}$ . At the same time, the quantity of fractional vacancy diffusion is called  $f_{AV}$ . These parameters are defined as follows:

$$f_{AI} = D_{AI}^{*} / (D_{AI}^{*} + D_{AV}^{*})$$
(1.25)

$$=\frac{d_{AI} \left[C_{AI}/C_{A}\right]^{*}}{d_{AI} \left[C_{AI}/C_{A}\right]^{*} + d_{AV} \left[C_{AV}/C_{A}\right]^{*}}$$
(1.26)

In equation (1.25),  $D_{AI}^*$  and  $D_{AV}^*$  refer to the effective diffusivities at equilibrium of the impurity-interstitial and the impurity-vacancy pairs respectively. A similar equation can be written for  $f_{AV}$  with the numerator in equation (1.25) replaced by  $D_{AV}^*$ . Since only interstitial and vacancy mediated diffusion is considered, a impurity must diffuse by one or the other, and it becomes simple to see that

$$f_{AI} + f_{AV} = 1$$
(1.27)  
or 
$$f_{AV} = 1 - f_{AI}$$

This also implies that if one quantity is known, the other is also known.

Multiplying the numerator and denominator of the first term in Equation (1.8) by  $D_{AI}^{*}$ and the second term in Equation (1.8) with  $D_{AV}^{*}$  we obtain,

$$\frac{D_{A}}{D_{A}*} = \frac{f_{AI}*C_{AI}/C_{A}}{[C_{AI}/C_{A}]*} + \frac{f_{AV}*C_{AV}/C_{A}}{[C_{AV}/C_{A}]*}$$
(1.28)

If we assume that the impurity is dilute,

$$C_A \gg C_{AI}, C_{AV} \tag{1.29}$$

Which implies,

$$C_A^{\text{total}} = C_A + C_{AI} + C_{AV} \approx C_A \tag{1.30}$$

then,

$$C_A = C_A^{*} \tag{1.31}$$

This condition is generally true in most cases under equilibrium, or in cases where the concentrations of I and V are not that much higher than equilibrium.

Under the conditions of equations (1.29) and (1.30), equation (1.28) may be written as

$$D_{A}/D_{A}^{*} = f_{AI} \left[ C_{AI}/C_{AI}^{*} \right] + (1 - f_{AI}) \left[ C_{AV}/C_{AV}^{*} \right]$$
(1.32)

If in addition to the conditions imposed above, we further make the assumption that  $C_X \ll C_A$  and  $d_{AX} \ll d_X$ , then we may write  $C_{AX}/C_{AX}^* = C_X/C_X^*$ . This case assumes that all reactions are of the form A+X=AX. However, if the AX there are other reactions which affect AX, then the equation cannot be simplified as easily.

#### 1.4 Energetics of Point Defects and Their Interactions With Impurities

The formation and migration of defects require energy from some source, and these energy requirements can be quantified as the energy of formation ( $E_f$ ) and energy of migration ( $E_m$ ) of the defect. The activation energy of an impurity atom is defined as the sum of the formation and migration energy of the impurity-defect pairs that mediate the diffusion. It is sometimes possible to measure from experiment the activation energy of a more complex process [Schultz01, Nash99], but is not practical in all cases of simple impurity defect interaction. Therefore the technique used to determine these quantities is entirely based upon computer simulation. A general name for the technique is called "abilitio", and involves computer simulation of a number of impurity and silicon atoms in respect to a number of atoms called a "supercell" [Monkhorst76]. Atoms are introduced in various positions of the lattice until their energies are minimized and then the quantities can be determined. For more information on this technique, see [Schaefer04].

#### **1.4.1 Energy of Formation (E<sub>f</sub>)**

The energy of formation is the energy quantity required to form one unit of the defect. If we assume the defect in question is a silicon self-interstitial then it could be represented as

$$E_{f}(I) = E(I) - [(N+1)/N] E_{bulk}$$
 (1.33)

 $E_{f}(I)$  refers to the formation energy of a silicon interstitial, E(I) refers to the total energy per supercell that contains the silicon interstitial and  $E_{bulk}$  is the total energy of the supercell containing N atoms. Therefore, equation (1.33) gives the energy gained by the system (supercell) due to the introduction of one silicon atom in one of the interstices of the lattice. This energy is highly dependent on the defect configuration in the lattice and also its charge state, and could vary for each case.

However, there are two cases of interstitial type diffusion, the pure interstitial impurity or as a impurity-interstitial pair. To account for this, the previous equation can be extended for an interstitial impurity  $(X_i)$ , the formation energy  $E_f(X_i)$  can be written as

$$E_{f}(X_{i}) = E_{f}(I) + [E(X_{i}) - E(X_{S}-I)]$$
(1.34)

Where  $E_f(I)$  is the formation energy of the self-interstitial from the previous equation and  $E(X_i)$  is the total energy of the supercell containing one interstitial impurity  $X_i$ , and  $E(X_s-I)$  is the total energy of the supercell containing one substitutional impurity – interstitial pair. The second term of the equation is the negative of the binding energy of the equation

In the case of the vacancy mechanism, the formation energy of the impurity vacancy pair  $E_{f}(XV)$  can be written as

$$E_{f}(XV) = E(XV) - E(X_{S}) + [1/N] E_{bulk}$$
 (1.35)

E(XV) is the total energy per supercell that contains one XV pair,  $E(X_S)$  is the total energy of the supercell containing a substitutional impurity and  $E_{bulk}$  is the total energy of a supercell containing pure Si atoms. The third term of the equation refers to the formation energy of a vacancy, which can also be written as

$$E_{f}(V) = E_{bulk} - [(N-1)/N] E_{bulk} = [1/N] E_{bulk}$$
(1.36)

It is important to note that the formation energy is again dependent on the charge state of the pair.

## **1.4.2 Energy of Migration (E**<sub>m</sub>)

Migration energies generally refer to the energy required for any number of impurity atoms, defects, or defect impurity pairs to diffuse through the lattice. Figure 1-2 shows the amount of energy that a defect X at a saddle point lattice site s or s' has to overcome in order to move from one point to the other. This barrier to motion is called the migration energy,  $E_m$ . The magnitude of  $E_m$  depends on the specifically on the type of defect, available migration paths, and charge state of the defect.

For a vacancy mechanism, the migration energy is slightly more complicated to calculate. Let us first consider the case where the impurity and defect pair have a low binding energy, and thus diffuse apart, also called "uncorrelated diffusion." In this case, the activation energy ( $E_a$ ) of the impurity-vacancy pair is given by the sum of the formation energy of the vacancy  $E_f^v$  and its migration energy  $E_m^0$ , i.e.,

$$E_{a} = E_{f}^{v} + E_{m}^{0}$$
(1.37)

If we now consider the case of the impurity vacancy pair, the vacancy has to partially dissociate from the impurity and return along a different path in order to effect the long range migration of the impurity. In this case, the activation energy  $(E_a)$  is given by the sum of the formation energy of the impurity vacancy pair and the vacancy migration energy  $E_m^{v}$  along the partially dissociated path of the vacancy. Generally, in *ab initio* calculations, the partially dissociated path of the vacancy is referred to as the ring path as the vacancy moves to a third nearest neighbor along the ring to return next to the impurity along a different path. The simplest of ring for consideration is the six membered ring, of which a schematic is illustrated in figure 1-3. The large filled circle represents the

impurity and the smaller filled circles represent the lattice atoms. The open circle represents the vacancy. This figure shows the ring process occuring "downwards." Part (a) shows the starting configuration of the impurity-vacancy pair. Part (b) shows the vacancy on the third nearest neighbor site to the impurity atom while moving along the ring path. Part (c) shows the vacancy approaching the impurity atom from the new direction which enables the jump as depicted in Part (d). Although the generic expression for the calculation of the formation energy of a impurity-vacancy pair is given by equation (1.37), it would be useful to revisit the expression for the formation energy of the impurity-vacancy pair in terms of the dissociation energetics of the vacancy. Figure 1-4 shows the vacancy potential as a function of the impurity-vacancy separations. It can be seen from Figure 1-4 that the pair formation energy is  $E_f^v - E_b^{-1}$  where  $E_b^{-1}$  is the binding energy of the pair with the vacancy on the first nearest neighbor site which is commonly referred to as the binding energy of the impurity-vacancy pair. All the terms are depicted pictorially in Figure 1-5. The negative sign is because the energy of the system reduces as the vacancy comes nearer the impurity atom. In Figure 1-5, a linear attractive potential between the impurity and the vacancy is assumed. Therefore, in the case of the impurity-vacancy pair, the activation energy  $(E_a)$  of the impurity-vacancy pair can be written as

$$E_{a} = E_{f}^{v} - E_{b}^{l} + E_{m}^{v}$$
(1.38)

The method for estimating the energy of migration of the vacancy is not yet explained, and the interested reader is referred to [Pankratov97].

There is one last complicating factor in this discussion before this section can conclude. Let us assume that all of the processes discussed take the equation form of
$$X + Y = Z$$

In the above equation, X and Y are generic reactants and Z is their product. However, these reactants may not readily react to form the product Z. If they do not, then the forward reaction is described as having an "energy barrier." This energy barrier is the energy the system must impart upon the two reactants in order to form the Z product. Without external energy applied to the system, the products will not react.

# **1.5 Estimation of the Reaction Rates of Equations**

All of the preceding discussion can be applied to the impurity and defect equations for the silicon lattice, and the equations can be developed for input into any sort of simulator. Each equation that is included will have both a forward and reverse reaction rate that are tied together. To develop this, first consider an equation of the form

$$\mathbf{A} + \mathbf{X} = \mathbf{A}\mathbf{X} \tag{1.39}$$

Where A refers to a substitutional impurity atom, X refers to a point defect and AX refers to a impurity defect pair. Let us assume local equilibrium conditions for the moment, then we may write,

$$C_{AX} = \theta_{AX} (C_A C_X / C_S) \exp(-S_{AX} / k) \exp[(E_b^{AX}) / kT]$$
(1.40)

Where C refers to the concentration of the individual species, and  $E_b^{AX}$  refers to the binding energy of the impurity defect pair. C<sub>S</sub> refers to the concentration of silicon atoms (5 e22 Si atoms/cm3).  $\theta_{AX}$  refers to the degree of freedom for the impurity-defect pair., and S<sub>AX</sub> refers to the entropy of the system[Fahey89]. From this equation, a simple effect is realized, that as the binding energy of a product is increased, it concentration will increase, and vice-versa.

It is also important to mention that there is no energetic difference between the a impurity interstitial and a impurity-interstitial pair, as mentioned in the previous section. In fact, the equation (1.39) would be the same in either case, if X were a self-interstitial, then, AX refers to a impurity -interstitial pair and not an impurity interstitial. Sometimes the subscript notation of  $A_1$  is used to denote that a impurity interstitial is implied specifically. Otherwise there is no conceptual difference. This is because in the case of a impurity-interstitial pair, one may use the concepts explained in Chapter 1, Sections (1.3) and (1.4), and write the formation energy of the pair as

$$E_{f}^{AI} = E_{f}^{I} - E_{b}^{AI}$$
(1.41)

Therefore, in equation (1.41), the formation energy of the pair is dependent on its binding energy.

All product equations can proceed in both forward and reverse directions. The forward reaction rate is termed  $k_f$  and the reverse is termed  $k_r$  If equilibrium conditions are assumed, then the reaction rates are determined by the law of mass action. In short, the law of mass action states that forward and reverse reaction rates are proportional to each other. If this is equilibrium case is assumed, then the mass action equation can be written as,

$$k_f C_A C_X = k_r C_{AX} \tag{1.42}$$

Rearranging terms,

$$C_{AX} = (k_f/k_r) C_A C_X$$
(1.43)

Combining equations (1.41) with (1.40),

$$(k_f/k_r) C_A C_X = (C_A C_X/C_S) \exp[(E_b^{AX}/kT)$$
 (1.44)

Which can also be written as,

$$(k_f/k_r) = (1/C_S) \exp[(E_b^{AX}/kT)$$
 (1.45)

If the binding for a given product is a determined quantity, then, the ratio of the forward and the reverse reaction rates can be determined. However, this arrangement alone could produce many possible combinations, and thus further observation must be used to determine the specific reaction rates for each case.

The answer arrives in the application of the energy barrier concept discussed earlier in the previous section. Apply this concept, the forward reaction rate may be estimated uniquely assuming a diffusion limited process as assuming a diffusion limited process as

$$k_{f} = 4\pi a \left( d_{X} \right) \exp[\left( -\Delta E/kT \right)]$$
(1.46)

Where,  $\Delta E$  refers to the reaction barrier, T refers to the absolute temperature in Kelvin, k is the Boltzmann's constant and d<sub>x</sub> refers to the diffusivity of the defect at the temperature under consideration. One important consideration is that equation (1.46) considers that only one species is mobile in the equation. If more than one reactant species is mobile in the forward direction, than equation (1.46) becomes:

$$k_f = 4\pi a \left(\sum d_X\right) \exp\left[\left(-\Delta E/kT\right)\right]$$
(1.46.1)

Where dxi is the diffusivity of each individual mobile product, and thus the forward reaction rate is now determined by the sum of all of the diffusivities.

Generally also, the binding energy of a impurity product is generally quantified in literature, and is not among the free parameters of adjustment in a simulation. This causes the ratio of the forward and reverse reactions to be fixed, and the only parameter of adjustment is the energy barrier applied in the forward direction.

## **1.6 Extended Defects in Silicon**

Extended defects form upon annealing at high implant doses. The threshold for the formation of the extended defect varies with the implant species. The main factor that determines the thresholds for the formation of extended defects is the mass of the implanted species. To some extent the extended defect formation also depends on the implant energy. These defects can be observed through TEM. The main types of extended defects that form upon implantation can be broadly classified into five types. The nomenclature is extensively described in the seminal paper by Jones [Jones 88, Prussin90]. In this section a very brief summary of the nomenclature of these extended defects will be presented.

#### 1.6.1 Type I Defects

These defects form when the implant damage is insufficient to produce an amorphous layer. Extended defects or dislocation loops will result if the implanted dose or peak concentration is beyond a critical value, which varies based on the implant species. These defects generally form at the projected range of the implant, and usually occur with medium or lighter ions. Most heavy ions will amorphize the material before type I defects are formed.

# 1.6.2 Type II Defects

If the threshold for amorphization is reached as described in section 1.2, then the potential for type II defects exists. Upon annealing, the amorphous region regrows very quickly through solid phase epitaxy into a nearly perfect silicon crystal. However, the region beyond the amorphous-crystalline interface does have residual damage present and so extended defects form at the end of range of the implant at around the original

amorphous-crystalline interface. Hence these End of Range (EOR) or Type II defects refer to those extended defects that form upon amorphization and subsequent annealing.

## 1.6.3 Type III Defects

These defects form due to imperfect epitaxial regrowth. Imperfect epitaxial regrowth leads to the formation of hairpins and microtwin shaped extended defects. The defects can be avoided and generally occur when melting annealing processes such as laser are used.

#### 1.6.4 Type IV Defects

Type IV defects form upon annealing buried amorphous layers. If the dose level of an implant is high enough to meet the amorphization threshold, but the implant energy is high, the amorphous layer formed may be buried in the bulk, rather than being continuous. Upon annealing, the amorphous region regrows very quickly from two fronts, one near the surface, and one from the bulk. Type IV defects will also form where the advancing amorphous-crystalline interfaces meet. These defects are usually "clamshell" like in shape.

# 1.6.5 Type V Defects

These types of defects form when the local concentration of a implanted impurity species exceeds the solid solubility for that impurity at a given temperature. Generally these defects take the form of precipitates, usually interstitial in nature. It is also possible to form vacancy type defects such as vacancy clusters or voids, as can occur with high energy hydrogen implantation.

# 1.7 Transient Enhanced Diffusion, Impurity Clustering, and Other Advanced Effects on Impurities

#### 1.7.1 Transient Enhanced Diffusion

The equations and methods presented in the previous sections provide a good basis for the theory and practice of developing diffusion models. However, many of them still rely on assumptions of equilibrium cases which only occur in low dose cases and at very long time anneals, neither of which are present in modern silicon processes. The damage profiles resulting from ion implantation are most decidedly non-equilibrium, most often resulting in a very interstitial rich situation. Recall that the first estimation of diffusivity was simple "fickian", and from experimental evidence the diffusivity D could be empirically determined in most cases. However, the advanced diffusion mechanism discussed earlier that point defects drive and affect diffusion rates. As such, it is expected that any impurity that is primarily an interstitial would diffuse faster when presented in an excess interstitial environment. This is precisely the environment induced by ion implantation. The enhancement in diffusion of said impurity only persists until defect populations in the sample return to equilibrium conditions, and thus this phenomena is called "transient enhanced diffusion." Generally the enhanced diffusivity is called D, and the equilibrium diffusivity D\*, and the parameter called diffusivity enhancement is  $D/D^*$ .

The precise cause of TED is already apparent, but empirical modeling of the behavior is slightly more complex. For the first part of the discussion, let us assume that we are referring to a sample which has not been amorphized, but is just heavily damaged. In this case, the time period of TED will be primarily governed by the time required for the excess interstitial population to return to equilibrium values. In most cases, this occurs by recombination at the silicon surface [Cowern90]. Therefore this time period is governed by the recombination reaction rate of interstitials at the surface, and of the diffusivity of silicon self-interstitials to reach the surface. Both of these processes increase with temperature, and thus the time period required to reach equilibrium decreases with temperature, which thus reduces the enhanced diffusivity D. Additionally, as temperature increases, the D\* intrinsic diffusivity increases, and thus the total D/D\* parameter is generally greater at lower temperatures. This is precisely what experimental evidence indicates [Cowern90].

Transient enhanced diffusion is most severe at lower temperatures . The primary reasons this is true are because the recombination reactions which annihilate point-defects are stronger at high temperatures which will minimize the period of time during which transient diffusion may occur and the fact that at higher temperatures the value D\* is higher which will lower the D/D\* ratio. Generally as well, it follows that TED will be greater for more heavily damaging implants, such as higher dose, and that deeper damaging implants will produce greater diffusivity enhancements than shallower implants [Griffin94].

# 1.7.2 Extended Defects and Their Role in TED in Crystalline and Amorphous Material

The situation presented for TED in amorphous material is somewhat different than the crystalline situation. The situation of non-equilibrium defect concentrations of silicon self-interstitials is still present, however, since it is generally assumed that upon regrowth, the defect populations in regrown regions are at equilibrium [Pelaz01], the excess defect population lies entirely in the EOR region mentioned in previous sections.

However, if this situation by itself is simulation, the result will indicate a diffusion enhancement which generally be much larger than experimental results indicated.

The solution to this incongruence is the fact that at high concentrations of pointdefects it is energetically favorable for the point-defects to form extended defects [Benton97]. These extended defects may be either rod-like {311} defects, loops, or so called dot defects, all of which are mentioned in section 1.6. Therefore, the recombination process of the silicon interstitial excess is affected because some portion of these silicon self-interstitials end up bound temporarily in the EOR extended defects.

Recent work has shown that rod-type defects which form in the {311} planes dissolve with a time constant approximately equivalent to the time constant of TED. These {311} defects may be imaged using plan view TEM [Jones01]. This indicates that in amorphous silicon the aggregation and dissolution rates of these extended defects play the largest role in determining TED behavior for a given sample. However, more recent work has also suggested that other defects may play a role in storing the interstitials for TED. Work by Saleh et. al. Has shown that the time constant to {311} dissolution is not necessarily consistent with TED at all implant energies. Rather, it is likely that other submicroscopic defects also contribute to the TED. The submicroscopic defects are generally referred to as "sub-micron interstitial clusters" or SMICs and are generally small clusters of silicon self-interstitials which form during the implantation and anneal process. [Saleh00]

The conclusion of this behavior is that in order to properly model and predict diffusivity enhancements in amorphous material, a model of defect formation and dissolution in the end of range must be developed. Work by Law and Avci [Law97,

Avci04] has produced effective models to predict some of this behavior in amorphous and crystalline samples. The discussion of model mechanics is somewhat long and drawn out, so for more information, the reader is referred to the references.

# 1.7.3 Fermi-Level, Electric Field, and High Concentration Effects

Most of the methods and formulas presented in the prior sections have focused primarily on lower dose impurities, for the sake of simplicity. However, the vast majority of modern processing introduces impurities that can reach peak concentrations of ~e21, particularly shallow boron implantation [Fahey89, Plummer00]. At these high doping levels, it is no longer correct to approximate all interstitials and vacancies with a single charge state. [Plummer00, Lenosky00]. Recall the information in sections 1.3 and 1.4. Ab-intio results indicate that each of the different charge states posses a different migrational energy, and the total point defect concentration is now a combination of all of the different charge states. Therefore, equation (1.20) now applies to the equation for silicon self-interstitial diffusivity as well:

$$D_{\text{NET}} = D^{0} + D^{+} * \left(\frac{p}{ni}\right) + D^{++} * \left(\frac{p}{ni}\right)^{2}$$
(1.47)

This may be alternately expressed as

$$D_{\text{NET}} = \Sigma_{i} (D^{1} * f_{i}) \tag{1.48}$$

Where  $D_{net}$  is the total diffusivity,  $f_i$  is the fractional component of each charge state with diffusivity of  $D_i$ . The net effect of these Fermi-level effects is to generally increase the impurity diffusivity with increasing doping concentration.

The physical explanation for this concentration dependent diffusivity is related to the fact that the relative energies of the different defect configurations is a function of the Fermi-level in the material [Zhu97]. Active impurities such as boron at high concentrations have the ability to influence the Fermi level, and thusly the effects and relative energies of the relative energies of the different interstitial charge configurations and that of the boron interstitialcy charge states as a function of the Fermi-level. This implies concentration dependence to the point-defect and impurity interstitialcy diffusivities and the intrinsic carrier density.

For the case of heavily boron-doped silicon, ab-initio results indicate that there are three interstitial configurations and two interstitialcy configurations present [Zhu97]. The relative populations of each are given by the following expressions [Giles89]:

$$C_{i}^{+} = C_{i}^{0} * (\frac{p}{n_{i}}) * \exp(\frac{E^{+} - E_{i}}{kT})$$
 (1.49)

$$C_i^{++} = C_i^{0} * (\frac{p}{n_i})^2 * \exp(\frac{E^{++} - E_i}{kT})$$
 (1.50)

Detailed calculations can lead to the following expressions for the case of boron if it is assumed that the relative energy levels will track the valence band edge with increasing temperature.

$$E^{+} - E_{i} \approx \frac{E_{f}}{E_{g}} * 1.25 - \frac{E_{g}}{2}$$

$$E^{++} - E_{i} \approx -1 + \frac{E_{f}}{E_{g}} * 2.6 - \frac{E_{g}}{2}$$
(1.51)
(1.52)

Where  $E_F$  is the Fermi energy level as determined by Maxwell-Boltzmann statistics for the heavily doped cases, Eg is the temperature dependent energy gap of the semiconductor and E++ and E+ are the relative energies of the singly and doubly positively charged interstitial configurations.

## **1.7.4 Impurity Clustering Processes**

Many experimental studies have been published in which high concentration boron samples appear to be immobile and the profile does not appear to be electrically active when measured with SRP or Hall [Lilak02, Lilak99]. Conventionally, this behavior is observed for many impurities when the local concentration is above the solid-solubility limit, however, these effects have been observed at concentrations below this level in the case of boron. An example of this is shown in figure 1-6. At the same time, results have indicated that co-implanted low concentration boron spikes and a reduction in diffusion and samples show a reduction in  $\{311\}$  formation. The current answer to this is to postulate the existence of stable boron interstitial clusters, which would explain a reduction in interstitial population, activation, and mobility. Multiple ab-initio studies now support this conclusion and are able to describe this behavior more specifically. One such ab-initio results comes from Lawrence Livermore National Laboratories has calculated the binding energies of different boron cluster complexes [Zhu97]. This group of cluster complexes is based upon the premise that a substitutional boron atom may capture either an interstitial, vacancy or boron interstitialcy. Generally, reactions are assumed to be diffusion limited, in the same manner as mentioned in sections 1.3 and 1.4. Therefore, the formation and dissolution rates for these types of reactions can be calculated when the binding energies of the various clusters are provided. The forward reaction rate with diffusion limitation:

K forward=4\* $\pi$ \*D\*radius<sub>capture</sub> (1.46)

The dissolution rate for the clusters is then determined by the binding energy of the cluster in the same manner as any other equation:

$$Krelease = C_{si} * D * 4 * \pi * a_{si} * exp(\frac{-Eb}{kT})$$
(1.47)

where  $E_b$  is the energy required to break up a or the binding energy of cluster. For more specifics on the boron clustering model, the reader is referred to [Lilak02].

Though the example mentioned in prior paragraphs is boron based, there are other impurity species such as arsenic and fluorine [Kikuchi05] which can exhibit clustering behavior. If sufficient ab-initio results are available, a model for cluster formation can be developed in the same manner.

#### **1.8 Analytical techniques**

## **1.8.1 Secondary Ion Mass Spectrometry (SIMS)**

SIMS is one of the primary analysis techniques used in this work for detection of impurity concentrations and depth profiling. This technique can also be used in general to examine samples for general contamination of the presence of multiple impurity species. In this process, the sample is placed in vacuum target chamber, and target beam made of primary ions is accelerated and aimed at the target. Primary ion beams generally consist of oxygen or cesium. When the primary beam ions impact the target, they transfer the energy in a similar manner to ion implantation, except in the case of SIMS the beam energy is high enough that the substrate atoms sputter off. This sputtered material is then examined using a mass spectrometer to determine the elements in the target and their relative concentrations.

Depth profiling of a target sample is achieved by successive sputtering of the target sample in multiple steps. In each step, the sample is sputtered, results are examined, and recorded in a computer. Each step sputters slightly more of the sample, until a target depth is achieved. After this process is complete, a crater is formed in the sample, and a stylus profilometer is used to determine crater depth, and then the raw data from the mass spectrometer can be used to create a depth profile for an impurity. The detection limit for SIMS varies with a number of factors: primary ion, impurity ion, target material, sputter rate, and SIMS system type. Generally, in most silicon samples, impurity detection limits are on the order of 1e16~1e17.

## **1.8.2** Positron Annihilation Spectroscopy

Positron Annihilation Spectroscopy is a relatively new and evolving technique that has become more developed in the last ten years. The technique works as follows: technique is this: positrons, generated from a number of sources, are accelerated and directed into a material. When sent into to semiconductor or metal type materials, these positrons will react and recombine with most specifically electrons and release photons in the x-ray band which are detected by a spectrometer. These released photons will form a spectrum from which a spectral line width or "S" parameter can be determined, and from this information simulation can be used to calculate of positron lifetimes can be determined. Research has indicated this technique is very sensitive to changes in concentrations of vacancy type point defects [Asoka94]. If an ion implanted and thusly damaged sample is examined by this technique, the S parameter of the sample during time points of an anneal can show differences in the vacancy products. The input positron beam energy can be varied in order to develop a depth profile of the S parameter, which can translate to a depth profile of vacancy concentration. Generally, the divacancy type products will produce and S parameter of above one, and vacancy products will produce and s parameter of less than one. Since vacancies are not stable in a silicon sample by themselves, the presence of stable monovacancy products generally indicates a vacancyimpurity complex. However, in many samples, especially Czochralski grown silicon,

oxygen proves to form a very large concentration of vacancy complexes, so care must be taken to eliminate them from contention. For more information on this technique, the reader is referred to [Asoka94].



Figure 1-1 Point-defect mediated diffusion mechanisms.



Figure 1-2. Schematic representation of energy of migration



Figure 1-3 Schematic of ring diffusion



Figure 1-4 Schematic of vacancy potential as a function distance from



Figure 1-5 Schematic representation of reaction barrier



Figure 1-6. Graph indicating sub-solubility threshold boron clustering. From [Michel86]

# CHAPTER2 LOW CONCENTRATION FLUORINE

#### **2.1 Fluorine Introduction**

In approaching the problem of describing and modeling fluorine motion, it becomes apparent from references such as S.P. Jeng and Robertson that fluorine behaves differently depending on the dose of fluorine implanted [Jeng92,Robertson00]. There are two distinct regimes of fluorine diffusion; low concentration which comprises nonamorphizing dose fluorine, and high concentration which consists of amorphizing dose fluorine. The approximate dose required for fluorine to amorphize material is  $1 \times 10^{15}$ <sup>/</sup>cm<sup>2</sup>. Low concentration fluorine diffusion in crystalline material will be discussed first since the behavior and modeling are simpler.

Initial isochronal investigations by S. P. Jeng et al and also Szeles with  $1 \times 10^{13}$ 30keV dose fluorine showed that fluorine diffusion at different temperatures can be characterized by a number of features [Jeng92, Szeles94]. The impurity appears to show non-Fickian motion in diffusion, and appears surface oriented when measure by SIMS. The profile is characterized by peak motion toward the surface, and increase in slope at the deeper edge of the profile, and significant dose loss. The amount of profile motion, tail slope increase, and dose loss increase with temperature.

# **2.2 Experimental Information**

The Jeng/Szeles data by itself does not give enough data to be able to formulate a well functioning model, so further experiments were conducted in order to examine the time-dependence and dose dependence of low concentration fluorine. The experiments

performed for this work were designed to investigate the time dependent diffusion behavior of fluorine in the temperature region of 550-850°C, since the Jeng data indicated that this temperature range was the most useful for examining the diffusion of the profile. N-type silicon wafers implanted with either  $1 \times 10^{13}$ ,  $8 \times 10^{13}$ , or  $2 \times 10^{14}$ ; 30 keV F+ were diced into samples and furnace annealed in a nitrogen ambient. The exact experimental matrix is given in Table 2-1. The samples were then depth profiled with SIMS.

Transmission electron microscopy (TEM) plan-view images were taken of some of  $2 \times 10^{14}$  dose samples annealed at 750°C for times of 15 and 30 minutes to check for the presence of extended defects. Samples of the  $2 \times 10^{14}$  data only were examined since it was assumed that any fluorine effect on defect evolution would be most apparent in the highest dose sample.

Additionally, both float zone and Czochralski grown silicon wafers implanted with  $2 \times 10^{14}$  30keV F+ were sent to be examined by positron annihilation spectroscopy (PAS). Though the data presented in Szeles [Szeles94] was of some use, the age of the data and the rapid advances of PAS science warranted a repeat of the analysis. PAS has the ability to examine the vacancy concentration of samples and help determine some of the initial conditions of the fluorine profile.

# **2.3 Experimental Results**

# 2.3.1 SIMS Results

SIMS results for the samples listed in table 1 are included in the following pages. Fig. 2-1 shows the motion of the  $1 \times 10^{13}$  samples at 650°C. From the sample, it is seen that the motion follows the same general pattern as that seen in the Jeng data. The tail slope the profile increases and appears to move towards the surface along with the peak as time progresses. However, after 30 minutes the motion slows considerably and the profile does not move appreciably through the 60min conclusion of annealing. This is a behavior that had not been seen before in the isochronal data. Fig. 2-2 shows that at 700°C, the same principles of profile motion apply, although the impurity has a higher diffusivity, and thus profile motion occurs more quickly. The motion in this case slows after a shorter anneal time of 15 minutes, and does not move appreciably after that time. Fig. 2-3 shows the 850°C results. The profile diffuses much more quickly, leaving nothing but a small SIMS tail near the surface at 15 and 30 minutes, which is difficult to distinguish from standard SIMS surface noise. At 550°C, no motion of the profile was observed.

Fig. 2-4 shows the  $8 \times 10^{13}$  dose annealed at 650°C. The profile motion at shows somewhat of a peak pile-up as the profile moves toward the surface. The transient period of motion is shorter as well, appearing to be about ten minutes, and the profile ceases motion at 30 minutes. Fig. 2-5 shows that at 700°C, the profile does not show a 15 minute transient as with  $1 \times 10^{13}$  results, but instead moves uniformly and ceases motion at about 30 minutes. Figs. 2-6 and 2-7 show the  $2 \times 10^{14}$  dose results at 650°C and 700°C respectively. The motion is similar to the  $8 \times 10^{13}$  dose, with the exception of the 700°C anneal, in which a greater amount of motion occurs between 20 and 30 minutes.

It should be noted that the time-dependent fluorine behavior at 650°C and 700°C has not been observed before at these doses. The phenomenon is TED-like, yet occurs on a shorter time scale (~15-30 minutes) and at lower temperatures than TED is normally for other impurities. The possible causes of this phenomenon will be discussed in the modeling section later in this chapter.

Fig. 2-8 shows an interesting comparison of dose retention across dose. The general trend shown is that as the implanted dose increases, the percentage of retained dose also increases, although the, the 650°C and 700°C anneals show a different time-dependent pattern. The 650°C anneals retain most of the dose throughout the course of the anneal, while the 700°C anneals show a large drop in the retained dose in the 10-30 minute time period, at the end of which the dose loss stops.

#### 2.3.2 Extended Defect Study

The  $2 \times 10^{14}$  750°C TEM images showed that some defects were present at the 15 and 30 minute times, but almost an order of magnitude less than that observed for Si implants of similar damage potential. Examination of the TEM images indicate that the defects consist primarily of "dot" type defects, rather than recognizable {311}s and loops. At the 15 minute time point, the average defect density  $4.85 \times 10^{10}$ /cm<sup>2</sup>, and an estimated trapped interstitial count of  $1.5 \times 10^{13}$  interstitials/cm<sup>2</sup>. At 30 minutes, the defect density was  $2.3 \times 10^{10}$ /cm<sup>2</sup>, resulting in an estimated  $5 \times 10^{12}$  interstitials/cm<sup>2</sup>. SIMS results for these samples indicate minimal profile motion between these two time points. Therefore, it is reasonable to assume that the TED-like motion of fluorine cannot be totally accounted for by trapping at extended defects. If it were totally accountable by such an affect, then it would be expected to see extremely similar defect densities and trapped interstitial counts for the two time points. It also indicates that at these doses, aside for the lack of {311} defects which would be expected otherwise, the defect dissolution pattern is not greatly affected by fluorine. A "normal" defect dissolution pattern at this temperature would show a peak defect concentration at the 15 minute time point, and dissolution of roughly half or more by the 30 minute time point. Results can be compared to results obtainable with the Avci or Law defect models for similar damage levels mentioned in chapter 1 [Law97, Avci04]. It should also be noted that in this case, the defects present are of type I as mentioned in chapter 1. These results do not necessarily apply to type 2 EOR defects for an amorphizing implant, to be covered later.

## 2.3.3 Positron Annihilation Spectroscopy Results

The PAS results are included in figure 2-9. As per the discussion in chapter 1, the positrons react most specifically with vacancy-type point defects and impurity-vacancy complexes. From the results, the conclusion can be drawn that a vacancy complex is present at conclusion of annealing, in contrast to previous results by Czeles. Comparison to the released spectrum of the sample indicates that a fluorine-vacancy product is present at the conclusion of annealing. Additional analysis points to the fact that this is likely a complex with single vacancy and two to three fluorine atoms surrounding it. This result will figure in to the modeling section later in the chapter. More information surrounding this result is in the paper by Simpson [Simpson04].

## 2.4 Model Development and Basis

Based on the experimental results seen above, it is apparent that there are a number of interesting behaviors that the model must be able to reproduce. The first is the non-Fickian, apparent surface oriented diffusion of the fluorine profile. The second key behavior is the TED-like transient period of impurity motion followed by a period of relative stability in the profile. Lastly, the apparent uphill diffusion at transient times must also be described.

Though fluorine is fairly unique in its exhibition of these features, there is one other impurity which is slightly similar and has an existing model, and that is nitrogen, with the model developed by Adam [Adam02]. Fluorine and nitrogen also share a trait in that they both form complexes with vacancy-type point defects. Therefore, the Adam model was deemed a suitable basis to begin describing the behavior.

One of the more important questions in determining a model is the consideration of the initial state of the profile prior to diffusion. Based on information from the previous references, fluorine has an extremely high diffusivity, and if left in an interstitial state after implantation, would diffuse out quickly even at room temperature. The same paper also indicates that based on ab-initio calculations, the binding energy of a fluorine substitutional complex would also be very low, thusly that product would be unstable, and unlikely to account for the initial condition. SIMS indicates fluorine is stable at room temperature for very long times, so the most likely remaining case is that fluorine is bound at point defects created during implantation. Based on the results from positron annihilation spectroscopy from Szeles *et al* [Szeles94], evidence indicated that fluorine was bound at vacancy type defects after implantation, and this is also supported by abinitio results from Diebel [Diebel04]. Combined with the PAS results from the previous section, we have reasonable initial conditions for the model, an estimate of the final condition.

The basic set of equations for the model was developed in the accordance with the method presented in chapter one. The set of equations, binding energies, and energy barriers used in the model is presented in table 2-2. Reaction rates were based upon formation and binding energy values generally agreed in literature and also on ab-initio calculations obtained from Diebel and Van de Walle et al. [Walle88]. Energy barriers for the reverse rate were treated as fitting parameters during the model development.

The generated equations were input into the FLOOPS [Law02] simulation program and solved to examine the behavior.

## **2.5 Model Results**

The overall action of the model is described in the following manner: after simulated implantation with the UT-MARLOWE implant simulator [MARLOWE98], the majority of fluorine is subsequently bound with vacancy type defects as fluorine-vacancy (FV) during the course of a "room temperature anneal." This room temperature anneal is a simulation of the behavior of fluorine during the time immediately following implantation. The purpose of the room temperature anneal is to set up the initial extended defect damage profile, as presented in chapter 1. (i.e., di-vacancies, di-interstitals). This aligns the initial condition of the fluorine profile with the experimental indications.

During the course of the furnace anneal, the initial FV product reacts in a number of ways. FV dissociates to F and V, FV reacts with the released vacancies to form  $FV_2$ , and interstitials react with both vacancy products to annihilate vacancies. The reaction of the fluorine-vacancy product with the silicon self-interstitials produces the fluorinesubstitutional product, which is very unstable, and subsequently mobile fluorine interstitial is produced. This reaction path is the primary way that mobile fluorine is produced, and thus is the primary limiting factor in the diffusion itself, since the only mobile products in the equations are fluorine interstitial (Fi), Silicon interstitials (I) and vacancies (V)

Based on the modeling efforts, the main reactions that dictate the anomalous diffusion behaviors mentioned in the previous section can be identified. The surface

oriented motion is accounted for simply by the fact that fluorine only appears to be surface oriented, its high diffusivity in an interstitial state indicates that fluorine would diffuse everywhere. However, examination of the simulated defect profiles shows that there is a appreciable concentration of point defects present at the silicon surface both before and during the anneal. Fluorine interstitial has a great tendency to interact with both types of point defects, and therefore simply becomes bound at the surface, simply because the point defects are clustered there.

The peak pile-up is accounted for by a somewhat more complex reaction balance. Released fluorine interstitials also react with the di-vacancy layer near the surface [Fujinami03,Huang00], forming additional immobile FV. Fluorine atoms from the deeper region of the profile can then diffuse and be "captured" nearer to the surface, thus accounting for some of the uphill diffusion.

Additionally, in order to further capture the behavior, reactions with silicon self interstitials were added to the model. Chemical binding data indicates that fluorine has a great tendency to bond with the silicon atom in a gasesous state [Humburd04], and it can be inferred that this same process would take place within a silicon lattice. Additional x-ray photo-electron spectroscopy (XPS) data has also indicated the presence of such bonds [Kinoshita90].

When these reactions are added to the model, fluorine interstitials react with silicon interstitials to form the immobile products  $FI_2$  and  $F_2I_3$ , which preferentially form and restrict the motion at the peak of the profile. This allows the peak pile-up to be well described by the model.

The last behavior to be described is the TED-like motion behavior. Based on the discussion above, it can be derived that fluorine motion will essentially cease when either the free silicon interstitial dose is fairly low, thus little mobile fluorine is produced, or when a significant portion of the fluorine profile is bound in complexes which do not easily react with interstitials, such as the fluorine-interstitial type. Fluorine vacancy type complexes are not sufficient for this task, since ab-initio indicates they would readily interact even with the thermally produced interstitial dose to show significant motion at longer anneal times.

It is in this manner that the fluorine interstitial complex equations work to describe the TED like motion. It is apparent that both dose loss and transient time are reduced as fluorine implantation dose increases. In the same manner, fluorine interstitial complex reaction rates increase as the dose increases. The fluorine interstitial type complexes have relatively high binding energies, which make them relatively stable in the temperature range of the data. Therefore, the primary determinate of transient time is the resolution of the interstitial profile, but as fluorine dose increases, the fluorine interstitial reactions play a larger role. Examination of the simulations show that this fits the behavior, in the  $1 \times 10^{13}$  case, the interstitials are roughly resolved at the 45min time point at 650°C, and at the 20 minute time point at 700°C, which correlate to the transient times for the  $1 \times 10^{13}$  profile. However, in both bases the higher dose samples indicate shorter transient times, which support this theory.

At the anneal time in each simulation at which profile motion has ceased, the primary component of the profile is still FV. Residual amounts of the  $FI_2$  and  $F_2I_3$  products are also present, though at concentrations several orders of magnitude below

fluorine vacancy. This concurs with experiment with the exception of the fact that the end product is not a multi-fluorine product. These reactions were not included because they did not help describe the behavior and did not add anything to the simulation at this point.

As shown in Figs. 2-10 to 2-15, the model obtains good qualitative agreement with the experiment across the time and dose ranges. Overall profile motion and peak movement are modeled well, and at 650°C and 700°C the time dependency and reduction in motion are also in good agreement.

#### **2.6 Comparison to Other Published Work**

Previous results published by Dunham [Dunham02] and Diebel [Diebel03] have presented a fluorine model which matches well with the isochronal data from Jeng earlier in the chapter. The Dunham/Diebel presented model uses a different set of FV-based equations which use FV as a ground state which makes the basis for the equations slightly different than the model presented in this work. The equation list and all binding energies for the Dunham/Diebel model are given in table 2-3. For the purposes of comparison, the Dunham/Diebel model was implemented in the FLOOPS simulator using the same input framework as the current work. Though the Dunham/Diebel reference does not provide the reaction energy barriers for each equation, energy barriers are treated as a fitting parameter as in the case of the presently developed model. The models are compared using data for a  $2 \times 10^{14}$  30keV fluorine implant, annealed at temperatures of 650°C and 700°C. The results are shown in figures 2-16 and 2-17. The figures show that while the Diebel model is capable of qualitatitively describing the motion of fluorine for these cases, it does not effectively capture the time dependence of the fluorine profile motion. In particular, the Diebel model does not capture the TED like motion of the profile and the subsequent stability. As it is not shown in the comparison plots, the Diebel model continues to predict fluorine diffusion until it all diffuses out of the sample. Also significantly, the Diebel model is not able to describe the fluorine peak pile-up present in the samples. Both of these behaviors are critical features of the present work.

	Dose/Anneal times		
Temperature	$1 \times 10^{13}$ 30keV	8×10 <sup>13</sup> 30keV	$2 \times 10^{14} 30 \text{keV}$
650°C	15,30,45min.	10,20,30,45min	10,20,30,45min
700°C	15,30,45min.	10,20,30,45min.	10,20,30,45min
750°C	15/30min.	15/30min.	15/30min.
850°C	15/30 min.	15/30min.	15/30min.

Table 2-1. List of experimental conditions and anneal temperature/times



Figure 2-1. SIMS results for the  $1 \times 10^{13}$  650°C anneals



Figure 2-2. SIMS results for the  $1 \times 10^{13}$  700°C Anneal



Figure 2-3. SIMS results for the  $1 \times 10^{13}$  850°C anneal



Figure 2-4 SIMS results for the  $8 \times 10^{13}$  650°C anneal.


Figure 2-5. SIMS results for the  $8 \times 10^{13}$  700°C anneal



Figure 2-6. SIMS results for the  $2 \times 10^{14}$  650°C anneal



Figure 2-7. SIMS results for the  $2x10^{14}$  700°C anneal



Figure 2-8 Retained Dose Graph



Figure 2-9. Raw S parameter results for the  $2 \times 10^{14}$  30keV samples. From [Simpson04], see this reference for analysis.

Reaction	Binding Energy(eV)	Energy Barrier (eV)
$Fs + I \Leftrightarrow Fi$	1.5	0.1
$Fs + V \Leftrightarrow FV$	3.57	0.08
$Fi + V \Leftrightarrow Fs$	6.1	0.005
$FV + I \Leftrightarrow Fs$	3.17	0.03
$Fi + V_2 \Leftrightarrow FV$	9.0	.09
$Fi + I \Leftrightarrow FI_2$	1.0	.0135
$FI_2 + Fi \Leftrightarrow F_2I_3$	1.0	0.0

Table 2-2 List of reactions with binding energies and energy barriers



Figure 2-10 Simulation results in for the  $1 \times 10^{13}$  650°C case



Figure 2-11. Simulation results for the  $1 \times 10^{13}$  700°C case



Figure 2-12 Simulation results for the  $8 \times 10^{13}$  650°C case



Figure 2-13 Simulation results for the  $8 \times 10^{13}$  700°C Simulation case



Figure 2-14 Simulation results for the  $2 \times 10^{14}$  650°C case



Figure 2-15 Simulation results for the  $2 \times 10^{14}$  700°C case

Reaction	Binding Energy(eV)	Energy Barrier (eV)
Fi+I↔FI	1.5	0.24
F3V+I↔3Fi	.58	0.45
FI+V↔Fi	6.1	0.013
F3V+Fi↔F4V	0.54	0.02
F2V+Fi↔F3V	1.95	.06
FV+Fi↔F2V	2.25	.0.345
FV+I↔Fi	4.78	.1

Table 2-3 Equations and binding energies from the Dunham/Diebel Model



Figure 2-16 Comparison to the Diebel model for the  $2 \times 10^{14}$  650°C case



Figure 2-17 Comparison to the Diebel model for the  $2 \times 10^{14}$  650°C case

# CHAPTER 3 HIGH CONCENTRATION FLUORINE

## **3.1 Overview and Introduction**

In the prior chapter of this work, low concentration fluorine diffusion behavior was examined and a model to describe that behavior was developed. The next step in the evolution of an effective fluorine model is to examine the high concentration behavior fluorine and attempt to adapt the model. A sample fluorine implant condition is called "high concentration" when either the fluorine implant itself is above the amorphization threshold of  $1 \times 10^{15}$  dose, or if the fluorine of amorphization dose is implanted into preamorphized material. As Robertson showed [Robertson01], the behavior of fluorine in this dose range is significantly different than the previous high concentration dose range. Robertson showed that fluorine diffusion behavior in this dose regime is marked by a number of features: The first being the same TED-like motion as mentioned in the previous chapter, though the time constant in this case is different. Also apparent in the behavior is the production of a "flat top" on the profile produced in the range of  $1 \times 10^{20}$  in the sample. This same flat top has been noted and reproduced by others [Uedono97, Pi03, Robertson01]. The gettering behavior of fluorine to EOR damage is also able to clearly manifest itself in many samples. A sample plot from the thesis of Robertson is shown in figure 1 and shows all of these behaviors clearly.

## **3.2 Experimental Information**

Though the Robertson data is an adequate basis for examining the diffusion behavior of fluorine, the data contained in the dissertation is not enough to fully qualify a high concentration fluorine model. The Robertson data has many conditions, but does not provide a range of multiple temperatures in each case or enough data points within the transient period. Therefore, two experiments were devised to extend the data shown in the Robertson dissertation to provide additional data points and conditions to use in model development.

### **3.2.1 Regrowth Experiment**

Fluorine behavior during regrowth poses a good deal of concern to the development of the model. Two key properties lead this: the fact that it is known to interfere and slow down regrowth [Olson88], and also the fact that it has a very high diffusivity in crystalline and amorphous material [Nash99] at the anneal temperatures in this experiment. As seen in the Robertson data and others [Uedono97, Pi03, Robertson01], the "flat top" threshold which forms during the anneal appears in most cases to be formed early in the anneal, begging the question if it is actually formed during regrowth, rather than by diffusion behavior.

In order to examine these behaviors, data points need to be examined at the precise time point at which the silicon is fully regrown, so that the profile without any additional diffusion may be examined. Olson examined many different samples and calculated an activation energy for fluorine-implanted silicon which allows calculation of the regrowth rates. Olson also indicated that the regrowth rate can vary within a sample as the fluorine depth profile changes, however, Olson presents a good average regrowth rate based on fluorine dose. In the Olson case, fluorine was used to amorphize, thus the entire amorphous region is fluorine rich. In this case however, all samples are pre-amorphized to 1500Å with dual silicon implants as in the prior cases, and implanted with  $2 \times 10^{15}$  16keV fluorine. Therefore, the regrowth process for the samples is a certain portion of

intrinsic silicon and a certain portion of fluorine-rich silicon. Based upon Olson's tables, a fluorine concentration of less than  $1 \times 10^{17}$  does not affect regrowth appreciably, which in the  $2 \times 10^{15}$  16keV case amounts to 800Å. Therefore in this case the regrowth can be assumed to be 800Å fluorine rich and 700Å intrinsic. Based upon Olson's tables, this implies a regrowth time for a 750°C anneal to be about 7 seconds, and for a 550 anneal, to be about 2.75 hours. An anneal at 650°C would require 85 seconds to regrow, and an anneal of 900°C would require about 1 second to regrow. Anneal times for the two higher temperatures require the use of the RTA, but the 550°C sample can be annealed in the furnace. Therefore, an experiment was conducted as described above, with the exception that because of some uncertainty in the experimental equipment, the 550°C sample was annealed at 3hrs, the 750°C sample at 10sec, and the 650°C sample at 95 seconds to attempt to make sure the sample was fully regrown. A soak temperature of 400°C was used in the RTA to attempt to minimize any additional uncertainty. Samples were then sent for SIMS analysis to check the fluorine profile, and also checked with XTEM to verify amorphous layer depths.

In addition to the simple regrowth experiment, another small addition to the experiment was devised in order to check for any additional differences in the behavior of fluorine after regrowth at different temperatures. The same samples as above subjected to slightly longer anneals of the 550°C for 3.5 hrs and and 750°C for 30 minutes to reach a stable condition in the fluorine profile. After this process were subjected to post-anneals of 750°C at 15 minutes, or, 900°C for 15 minutes. Samples were then sent for SIMS to check the fluorine depth profile.

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The first result warranting comparison is the chart of the regrowth of the 550°C sample shown in figure 3-1. The profile appears to show a concentration drop at a certain depth which moves toward the surface as time progresses. XTEM analysis indicates that the steep drop-off in the profile coincides with the edge of the amorphous crystalline interface. Later in the time progression of the anneals, you can see the profile continues to lose significant dose as the sample regrows. The time progression of the data also indicates that none of the impurity in the amorphous region appears to move appreciably. Contrast this result with the regrown profiles of the 750°C and 650°C anneals in figure 3-2. The increase in post-regrowth dose retention is apparent as regrowth temperature increases, and the increase is most significant between 550°C and 650C. The 750°C and 650°C profiles also show clear evidence of the "flat top" behavior seen many times before in previous works, which indicates that this behavior does indeed originate from regrowth. The 650°C and 750°C samples also show a very interesting behavior when compared with the as-implanted profile, as shown in figure 3-2. The leading edge of the profile "flat top" actually extends about 70Å deeper than the as-implanted profile, behavior which has not been seen in any of the other profiles, and as later data in the chapter indicates, is gone by the minute time point in the case of the 750°C anneal. The 650°C profile does have one artifact which shows up as a small bump or concentration peak at about 100Å deep. XTEM confirms this is the location of the amorphous crystalline interface in the sample. The RTA system was not able to hold the anneal temperature for the full amount of time in this sample, leaving it with 100A of amorphous layer.

An additional sample was run which was only implanted with the  $2 \times 10^{15}$  16keV F+, producing an amorphous layer depth of 500Å. This sample was annealed at 550C for 2.5 hours and compared to the 1500Å pre-amorphized sample. The profile shape of the 500Å deep sample is slightly different and the sample retains approximately three times the dose. The result for this sample compared the pre-amorphized sample is shown in figure 3-3.

A plausible explanation for the behavior of fluorine regrowth exists based on the insights of Olson, Impellizeri and others. Fluorine is already known to getter toward the amorphous crystalline interface and is theorized to interfere with regrowth by attaching to dangling bonds at the interface. Behavior of fluorine during regrowth can then be described in the terms of three important factors: the diffusivity of the fluorine at the temperature in the material, the gettering of fluorine to the interface, and incorporation of fluorine in to the crystalline material across the interface. Fluorine diffusivity in amorphous material has been examined by [Nash99], and is known to be orders of magnitude less in amorphous material than in crystalline. According to [Nash99], if a rough " $\sqrt{Dt}$ " approximation of diffusion distance is used for a half hour anneal, fluorine at 550°C in amorphous material would diffuse 26Å, at 650°C would diffuse 1470Å, and at 750°C would diffuse 5360Å. This indicates that fluorine does not move appreciably in the 550°C case, while in the 650°C and 750°C case fluorine is mobile enough to perhaps diffuse to the amorphous crystalline interface. The amount of fluorine gettering to the interface is easily correlated to the diffusivity of fluorine by examining the 650 and 550°C samples. There is no apparent pile-up in the 550°C sample, while the 650°C sample shows the pile-up mentioned previously.

A potential explanation for the fluorine "flat top" formation behavior is presented in the following paragraph. Since fluorine is theorized to interact with dangling bonds at the interface, it is possible that the available dangling bonds at the interface could become saturated with a sufficient amount of fluorine. Assume that for fluorine to incorporate it must attach to one of these dangling bonds, and any fluorine not attached to an interface bond remains in another state near the a/c interface and is "shoveled" along. At the lower regrowth temperature, sufficient fluorine does not diffuse to the interface to saturate the dangling interface bonds, and this saturation effect is not achieved. The slight concentration difference between the 650°C and 750°C sample and the similarity of the 750°C and 950°C profiles can be accounted for if this fluorine process is thought of as changing from diffusion to reaction limited somewhere just below 750°C. Between 550°C and 950°C the diffusivity of fluorine and thus the amount of fluorine at the a/c interface increases significantly, but the dangling bond concentration at the a/c interface does not depend significantly with temperature. Between 550°C and 650°C the fluorine diffusivity increases to the point that fluorine begins to pile up significantly at the interface, and thusly between these temperatures the incorporation is limited by the fluorine diffusivity. Between 650°C and 750°C, the fluorine diffusivity again increases and also the size of the interface pile-up, but the concentration of dangling bonds at the interface is constant. The limiting factor now becomes the reaction with the interface dangling bonds. Between 750°C and 950°C the fluorine diffusivity again increases, but the incorporation is strictly limited by the reaction with dangling bonds, and therefore the profile difference is minimal

The dual-anneal experiment produced an unexpected result, as shown in figure 3-4. in all cases, the 550°C regrown sample is much less stable than the 750°C regrown samples, in both the 750°C and 900°C post-anneals. A 900°C 15 min. sample is shown by itself to illustrate the behavior of that annealing condition by itself. The results may indicate that the regrowth temperature influences the specific composition of the fluorine profile post-regrowth. The most likely explanation for this is that the fluorine concentration at the a/c is influential in determining the final composition of the profile. The increased fluorine a/c concentration may favor the formation of one of the more stable fluorine-vacancy products during the regrowth process, while the lower regrowth temperature favors the formation of a less stable product.

### **3.2.2 Furnace Anneal Experiment**

P-type doped FZ silicon wafers of 80-200 $\Omega$ -cm were first pre-amorphized with Si implants to create a uniform amorphous region that is 1800Å deep. Samples were then implanted with the fluorine, and annealed by either traditional furnace or RTA with an N<sub>2</sub> ambient. SIMS was used for depth profiling. Three implant conditions were chosen:  $2 \times 10^{14}$  at 30keV,  $2 \times 10^{15}$  at 16keV, and  $8 \times 10^{15}$  at 16keV, as well as a silicon-only control. Samples were annealed at temperatures of 750°C and 900°C in order to generate data for the model. The precise implant and anneal conditions are shown in Table 3-1. Both PTEM and XTEM images were taken to check for defects.

SIMS results of the annealed samples are shown in figures 3-5, 3-6, and 3-7. The first result worth mentioning is the behavior of the  $8 \times 10^{15}$  sample. It shows a small amount of initial dose loss in the near surface region, but maintains what appears to be a large amount of the peak dose, and is largely immobile for all anneal times. PTEM

performed with a lapping method indicates that the regrown region has a large layer of what appear to be poorly organized loops. It is therefore assumed that this sample poorly or not completely regrown, and that  $8 \times 10^{15}$  dose can be assumed to be an upper limit for a fluorine implant dose before the sample does not regrow properly. Though this sample does not necessarily provide useful data for the model, the result is useful for designing future experiments.

The  $2 \times 10^{15}$  750C samples provide the most useful data for model development. At first glance, the samples show much of the same diffusion behavior as the Robertson data; development of the "flat top" threshold and stability at the 15 minute time point. However, the most interesting and useful behavior for model development occurs prior to the 15 minute time point. As the plot show, the flat top develops in the regrowth process, but the 10 second sample is much deeper than the 15 minute sample. In between 10 seconds and 15 minutes, the sample experiences what amounts to a peak shift toward the surface, a reduction in profile "width", and a dose loss of about 50%. The intermediate samples show that the reduction in profile width occurs first, and after that the profile appears to simply reduce in peak concentration. The intermediate time points also indicate that the transient period of motion ends in somewhere in between the 10 and 15 minute time point of the anneal. Also note that the tail slope of the profile did not change appreciably between the post-regrowth and final time points. The same sample at 900°C exhibits the same sort of diffusion behavior as described above, except the profile reaches the stable time point at approximately 3minutes during the anneal, and is stable afterwards. It is also notable that the profiles of the stable 750°C and 900°C samples from figure 3-4 are extremely similar.

Gettering to EOR damage is also visible in the samples. Though XTEM verifies that the samples are all nominally amorphous to 1400-1500Å, if the deep fluorine peak is assumed to be a marker of the EOR damage, it appears to be much shallower, in some cases as shallow as 1200Å. The only plausible explanation for this is the presence of very large loops during the annealing process. Some confirmation of this is available from the 550°C samples, which were from the exact same wafer as the other samples. At this temperature, fluorine has some appreciable diffusivity, but the EOR defects do not nucleate and grow significantly. In the 550°C sample, the deep fluorine peak appears at around 1400-1500Å at the conclusion of a 3 hour anneal.

The final data sample of note is the  $2 \times 10^{14}$  30keV 700°C sample. The purpose of this sample was to examine the differences in behavior between amorphous and crystalline behavior of fluorine with identical doses and implant energies. Examination of the results in figure 3-7 shows some similarities and differences in the profile between the two cases. The first difference becomes apparent in the 10 minute time point of the anneal, as several intermediate peaks appear in the data at about 300Å, 700Å, and 1800Å. The peak at 1800Å is easily explainable as end of range gettering, and the peaks at 300Å and 700Å are due to the regrowth process, which has earlier in the chapter been shown to produce unconventional profiles. As the anneal progresses, the majority of the fluorine dose appears to move toward the surface, producing some uphill diffusion and steeping of the tail of the profile, much like the low concentration case. The anneal also appears for the most part to be stable at the 20 minute time point. The exact examination of these profile features is deferred to the modeling section of this chapter.

### **3.2.3 Extended Defect Examination**

During the course of all of the experiments mentioned above, PTEM images were taken to examine the fluorine effect on the extended defect population in the EOR. Silicon control samples were also imaged in all cases. Studies of the control sample indicate that the control sample produces a significant population of  $\{311\}$  type defects. Samples with even a lower dose of  $2 \times 10^{14}$  present show a very large reduction in  $\{311\}$  population, though the total defect density does not appear to reduce significantly. The  $\{311\}$  defects are replaced with what appear to be poorly-formed loops and "dot" type extended defects. Further examination of defects is planned.

## 3.3 Model Development and Basis

The high-concentration model was based on the low concentration model of the previous chapter, using the same base equations and binding energies. Also carried over is the assumption that fluorine is initially bound as a fluorine vacancy product at the start of an anneal. In the case of pre-amorphized samples, this fluorine vacancy formation is assumed to occur during the regrowth process. RTA experiments conducted by Uedono [Uedono97] illustrate this and indicate again that it is a fluorine-single vacancy product. The amorphous layer is assumed to regrow instantly without any additional defect or impurity diffusion. Since experiments earlier in the chapter have indicated this is not the case, the initial profile assumed is not the as-implanted, but the post-regrowth profile obtained with SIMS. Previous sections have also indicated that this post regrowth profile must be obtained at the same temperature as the rest of the SIMS data for the simulated anneal. This is an important distinction and essentially requires that a post-regrowth profile be provided as a starting point to help develop an accurate model. The FLOOPS

simulator at this present time has no provision to simulate impurity redistribution during regrowth.

However, the damage profiles for the high concentration case are quite different than a crystalline case. UT-MARLOWE is still used to generate the interstitial and vacancy profiles. However, in accordance with published research [Pelaz01], the best method to simulate amorphous regions is to "zero out" the I and V profiles down to the known amorphous layer depth and replace those concentrations with the intrinsic concentration of point defects at room temperature. This method works upon the assumption that the amorphous layer regrows perfectly, which is the best model available at the time of this writing. The same room temperature anneal as in chapter 2 is used to generate the higher order point defects.

The effect of this modeling assumption is to concentrate almost all of the point defect population in the end of range region of the sample prior to an anneal. If this situation is left alone and simulated, the result from experience will be that diffusion of most impurities will be grossly overestimated. The PTEM images in the prior section indicate clearly that extended defects of {311} and loop-type form in the end of range region of all of the samples. As mentioned in chapter 1, these defects serve to trap interstitials and moderate their release from the EOR.

Avci [Avci04] previously developed a {311}/loop model which can effectively emulate the formation, interstitial trapping, and dissolution of the EOR defects. This model was incorporated into the fluorine model for simulations of fluorine in amorphous samples. In addition the EOR defect model, the model was also extended with two additional Si- $F_x$  complex equations,  $F_2I_3$ , and  $F_3I_4$  with binding energies based upon published chemical data. The presence of the higher order Si- $F_x$  bonds in amorphized samples has been confirmed by XPS [Kinoshita90]. While other reactions present in the model are assumed to be diffusion limited by the conventions of chapter 1, the Si- $F_x$  reactions are assumed to be reaction-rate limited. This property ties the formation rates of the Si-Fx complex to the concentration levels of the two products.

When all of the above elements are combined, the model action can be described as follows: during the course of the anneal, the remaining EOR damage diffuses toward the surface, and the FVs are dissociated through interaction with the interstitials, becoming substitutional fluorine. The substitutional fluorine both dissociates through the Turnbull mechanism and kickout, due to the high concentration of silicon self-interstitials, releasing fast moving fluorine interstitials. With the addition of the newer Si- $F_x$  equations, fluorine interstitials react with silicon interstitials to form the immobile Si- $F_x$  products at the peak concentration, which serve to moderate and control the time dependence of diffusion. The main product at the conclusion of the anneal is still FV.

#### 3.4 Model Results and Discussion

As shown in figures 3-8, 3-9, and 3-10, the model obtains good qualitative agreement with the experimental results. Tail motion, peak concentration, and time dependency are modeled well in the  $2 \times 10^{15}$  750°C and 900°C. The "flat top threshold" is reasonable in both cases. In both cases, the sample starts from a profile the same as that of the 750°C 10 second anneal from the regrowth study. The movement of the profile center toward the surface and the decrease in flat top concentration are replicated by the fact that the

free silicon interstitials tend to preferentially combine with the FV in the deeper portion of the fluorine profile, since all interstitials come originate from the end of range. In this way, the deeper portion of the same is reduced to free fluorine first, and the center of the profile appears to move toward the surface. The precise listing of equations and binding energies for this set of fluorine equations is included in table 3-2.

Annealed samples of the  $2 \times 10^{15}$  16keV 500A fluorine-only sample with model fits are shown in figure 3-9. This sample shows similar behavior as the 1500Å, except for slight differences in the profile width and location. The fits indicate that the model is capable of describing this difference. Though a number of different factors exist between the two samples, such as fluorine presence in the end of range and amorphous depth, the model indicates that the primary factor that affects the diffusion is EOR interstitial concentration and damage, rather than simply amorphous depth. If the damage profile for the EOR damage is kept constant, the length of the amorphous region can adjusted in simulation and the results for each case will come out identical.

The distinct behavior of the pre-amorphized  $2 \times 10^{14}$  700°C sample is also well modeled and shown in figure 3-10. This sample appears to diffuse largely in the same manner as the  $2 \times 10^{14}$  30kev 700°C samples in crystalline material, and the same action of the model applies. The fluorine profile shows tail motion toward the surface, as well as peak pile-up and profile tail steepening. With the new equations, some of sample behavior can be explained. As stated previously, some of the elements of the profile arise due to end of range gettering, such as the 1800-2200Å peaks in the sample. The EOR peak appears to move primarily due to the fact that fluorine is present in appreciable concentration in the end of range, and thus the fluorine reacts with the interstitial population present there, rather than just gettering to EOR extended defects. The initial peak at 1800Å dissolves as the defects in that region dissolve as well. The model does not contain any EOR extended defect-fluorine reactions at this time, so the behavior of the sample EOR is only partially modeled by the fluorine-interstitial reactions.

Of central importance to the model's function is the ability of the model to model both low and high concentration data with minimal modification. This ability is accomplished by examining the relative dose of fluorine to the dose of free silicon interstitials in each case. In the case of a crystalline  $2 \times 10^{14}$  sample, simulated ion implantation with the UT-MARLOWE simulator produces an initial interstitial excess which is roughly a "plus one" condition, in which case the total dose of interstitials is on the order of  $1 \times 10^{14}$ . In the case of the  $2 \times 10^{15}$  sample, after the simulated silicon interstitial profile has been modified to remove and excess in the EOR region in accordance with [Pelaz01], the EOR interstitial dose is still on the order of  $1 \times 10^{14}$ .

As mentioned previously, the entire initial fluorine profile is assumed bound in an FV state. For fluorine to participate in any diffusion, or interact with any other point defects, the FV complex must first absorb an interstitial, which will form the unstable Fs product, and thus form a free fluorine interstitial. In absence of interstitial excess, fluorine will remain bound in the FV complex and remain mostly stable. In the case of the low concentration fluorine, the ratio of FV to initial interstitial excess is nearly one to one. In this case, there is more than enough interstitial excess to react with FV and free the majority of the fluorine profile.

In the high concentration case, the ratio of FV to silicon interstitial excess is much greater, at roughly ten to one. In this case, the amount of interstitial excess is not enough

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to react with all of the FV and produce mobile fluorine. Therefore the profile shows comparably reduced motion and retains most of the features of the as-implanted profile. An accurate test of this theory is examination of the  $2 \times 10^{14}$  30keV samples which are implanted in the pre-amorphized silicon. These samples have FV and silicon interstitial excess concentrations of the same order as crystalline material, and do indeed behave in the same way.

Additionally, a re-simulation of the previous  $2 \times 10^{14}$  30keV 700°C crystalline material is shown in figure 3-11. The model fit remains very good, which indicates that the addition of the newer equations has not changed the ability of the model to describe crystalline behavior.



Figure 3-1 SIMS results for the 550°C regrowth experiment



Figure 3-2 SIMS results showing the comparison between regrowth at the three temperatures.



Figure 3-3 SIMS results comparing the two amorphous layer depths. Both fluorine implants are  $2 \times 10^{15}$  16keV



Figure 3-4 SIMS results for the two-stage anneal experiment

	Dose		
Anneal	$2 \times 10^{15} \text{ cm}^{-2} 16 \text{keV}$	$8 \times 10^{15} \text{ cm}^{-2} 16$	$2 \times 10^{14} \text{ cm}^{-2} 30 \text{keV}$
Temp		keV	
550	15, 30, 60, 120, 180 min		
650	95 sec.		
700			10, 20, 30, 45,60
			min.
750	10 sec, 1,5,10,15, 30,	1,5,10,15, 30 min.	
	120min.		
900	1,5,15 min.		

Table 3-1 Table of experimental conditions



Figure 3-5 SIMS results for the 8x10<sup>15</sup> 16keV 750°C anneals


Figure 3-6 SIMS results for the  $2 \times 10^{15}$  16keV 750°C anneal



Figure 3-7 SIMS results for the  $2 \times 10^{14}$  30keV implant into amorphous material annealed at 700°C



Figure 3-8 Simulation results for the  $2 \times 10^{15}$  16keV pre-amorphized 750°C case



Figure 3-9 Simulation results for the  $2 \times 10^{15}$  16keV non-pre-amorphized case at 750°C



Figure 3-10 Simulation results for the  $2 \times 10^{14}$  30keV 700°C case in amorphous material

Reaction	Binding Energy(eV)	Energy Barrier (eV)
$Fs + I \Leftrightarrow Fi$	1.5	0.1
$Fs + V \Leftrightarrow FV$	3.57	0.08
$Fi + V \Leftrightarrow Fs$	6.1	0.02
$FV + I \Leftrightarrow Fs$	3.17	0.13
$Fi + V_2 \Leftrightarrow FV$	9.0	.075
$Fi + I \Leftrightarrow FI_2$	1.0	.034
$FI_2 + Fi \Leftrightarrow F_2I_3$	1.5	0.1
$F_2I_3 + Fi \Leftrightarrow F_3I_4$	2.0	0

Table 3-2 Listing of newer reactions and energy barrier values for the model



Figure 3-11 Re-simulation of crystalline results with new model parameters.

# CHAPTER 4 INITIAL BORON/FLUORINE MODEL INTEGRATION

#### **4.1 Introduction**

The emphasis of the dissertation up to this point has been to present data on the behavior of fluorine and to develop a predictive model for this behavior. A model for low concentration behavior was presented in chapter 2, and this same model was extended and used to describe high concentration behavior in chapter 3. Several key features of fluorine diffusion behavior were also illustrated.

However, the end of goal of this dissertation is to present and develop a model for an overall behavior of the fluorine-boron system. Boron has not been discussed or investigated yet either in experimental or model form earlier in this work for good reason. The largest reason for this is mentioned in chapter 1; while fluorine is known to influence the diffusion of boron, there is considerable debate about how this happens, and one possible answer is a direct boron-fluorine chemical reaction. This would imply that the fluorine behavior could be influenced in turn from the presence of boron, which could conceivably damage the credibility of a fluorine model developed with both impurities at the same time.

Though a number of interesting additional fluorine-only studies could be proposed, the focus of this project must shift to the fluorine effects on boron due to both time constraints and the main project charter. Also, the primary use of a fluorine model in

industry is to describe the effect of fluorine on the boron diffusion. The addition of boron into the study has benefits; much of the behavior of fluorine can be illuminated when boron is added into the system. For example, it is difficult to determine the exact level of interstitial trapping that fluorine exhibits when present by itself. With boron present in the system, the boron profile can act as a good marker for examining the behavior and concentration of interstitials in the system. [Cowern90]. Therefore it is in some ways essential to the development of a fluorine model to include boron to test additional conditions and parameters.

#### **4.2 Initial Model Integration**

As mentioned in chapter 1, boron is already a well described impurity in research relating to process modeling, and several different distinct models exist to describe its behavior. These models are, with the exception of a full boron clustering model, already present in the FLOOPS simulator [Law02]. The framework for model development provided by the FLOOPS simulator makes integrating the two impurities into a single simulation very simple.

For the purposes of initial modeling, fluorine and boron are assumed to have no direct interaction, the only interaction between the two impurities is assumed to be through the changes in interstitial and vacancy concentrations. More recent research is supportive of this theory [Impellizeri05].

As stated before, there are a number of possible boron diffusion models to implement. Of these, a fully implemented boron clustering model is most desirable. The problem occurs because the experiments consist mostly of amorphous samples, and the BIC model has been presented in the literature to work properly with mostly crystalline samples [Windl]. The information in chapter 1 indicates that the point defect population and time evolution of defects is very different in crystalline and amorphous material. If the published BIC model is used to model amorphous boron samples, the result is that the simulation produces an excess of the boron-interstitial cluster product B3I. As the explanation in chapter 1 indicates, B3I is a very stable boron product, and as a result, boron is immobile in the simulation (Ljubo Radic, private communication). Some research has been presented that indicates corrections to the BIC model to handle amorphous samples [Pelaz04], but such corrections are beyond the scope of initial test integration. Therefore, the simpler pair model was used as the second choice for boron simulation. It is sufficiently complex to be sensitive to interstitial and vacancy concentrations, and as thus is useful for examining fluorine effects, but does not have any of the boron clustering properties.

As an initial data choice to test the integration of the model, some of the Robertson data was chosen to use a test for model integration [Robertson01]. Three conditions from the Robertson data are chosen for the initial test: all samples were pre-amorphized with silicon to a depth of 2800A, the first two data samples are1.1 keV  $1 \times 10^{15}$  boron implanted with  $12 \text{keV} 2 \times 10^{15}$  fluorine, and the second with 500eV boron with 9keV fluorine. There are two anneal cases, each sample is either annealed up to 2hrs in a furnace,or with a 1050°C spike anneal. This data represents a good basis for initial comparison, as it is relevant both to industrial results presented on subject of boron-fluorine co-implantation, and the data provides enough time evolution of the profiles to be useful.

# **4.3 Model Integration Results**

The initial results of the simulations are shown in figures 4-1, 4-2, and 4-3. The first profile of note is the simulation of the boron control profile. The results at 750°C for

2hr in figure 4-1 indicate that the FLOOPS boron pair model is capable of qualitatively modeling boron by itself. The 750°C simulation results at 15 and 2hr require a slightly more complex examination. Between the two data points, the model is capable of predicting the depth of the profile tail diffusion, but is very poor at describing features in the higher concentration portions of the profile. Discussion of this deficiency is delayed until later in this chapter. The 1050C spike anneal in figure 4-2 looks to be a better model fit, with the tail diffusion depth again well modeled. In this case, the issues with the peak region diffusion are less apparent.

The results in figure 4-3 present a interesting picture for model analysis. In this case, the simulated boron control profile appears to capture the behavior of the boron control data very poorly. When the model results are compared to the samples containing fluorine for the later time points, the model shows the consistent behavior of showing consistent qualitative fits for the tail of the boron profile, while modeling the peak regions of the boron profile very poorly.

## **4.4 Model Integration Discussion**

The initial integration of the boron pair model and fluorine models has produced a number of interesting results. The first noticeable result is the failure of the modeling results to reasonably approximate the diffusion of the peak region of the boron profile. This difference can be largely attributed to the failure of the boron pair model itself to accurately capture the boron clustering behavior in the near surface region. Most notably this failure could be partially remedied by use of the full BIC model, but due to previously mentioned constraints this is not possible. It has also been mentioned in the literature that most boron diffusion models work poorly for samples with very shallow energies like the Robertson data for a number of reasons, among them surface

recombination related effects which can drastically affect the diffusion and clustering of the boron profile itself [Radic05]. Therefore, even if the full BIC model were functioning properly, calibration for the 500eV Boron implant would still prove difficult.

The second notable result from the initial simulations is that the fluorine model appears to have the proper effect on the boron diffusion in the sample, that is, significant reduction in the transient diffusion of boron and thus total boron diffusion depth. The model is also able to reach reasonable quantitative agreement with the data as well in terms of the boron diffusion depth. Based on the model results, the primary action which enables the reduction of diffusion is the capture of silicon self-interstitals by the fluorine-vacancy product FV. By reducing the total concentration of silicon self-interstitals, the diffusion of boron is subsequently reduced.

The initial simulation results are supportive that the assumption that boron and fluorine interact most predominantly through fluorine-vacancy capture of interstitials. However, the surety of these results is significantly clouded by the problems associated with the boron model mentioned above in the chapter. Further investigation is required o develop a more consistent determination. The failure of the boron model in this case is also valuable for the experimental design of the set of experiments presented in the next chapter. Since the focus of this dissertation is primarily on the development of the fluorine effect on boron diffusion and not boron diffusion modeling itself, it is desirable to choose experimental data which will not require excessive tuning of the boron model to produce good agreement. The experiment undertaken and results for further development of the model are presented in the next chapter.



Figure 4-1 Simulation results for the 1.1keV  $1 \times 10^{15}$  boron and 12keV  $2 \times 10^{15}$  fluorine at 750°C



Figure 4-2 Simulation results for the 1.1keV 1×10<sup>15</sup> boron and 12keV 2×10<sup>15</sup> fluorine for a 1050°C spike anneal



Figure 4-3 Simulation results for the 500eV 1×10<sup>15</sup> boron and 9keV 2×10<sup>15</sup> fluorine for a 1050°C spike anneal

# CHAPTER 5 NEW FLUORINE/BORON EXPERIMENTS

# **5.1 Introduction**

In chapter 4 the fluorine model was combined for the with the boron model in the same simulation for initial testing of the effects of the two models. The obtained results indicated that while the fluorine model appeared to affect the boron diffusion in the simulation in the proper way, serious limitations with the boron model performance hindered the quality of results. The initial test data provided in chapter 4 also doesn't provide enough data to gauge affects such as time and impurity dose dependency that are critical in developing a model. Therefore further experimentation is necessary to examine the experimental behavior of the impurities and demonstrate the behavior of the model. This chapter presents the major experimental design that was chosen to accomplish the goals of further examination of the boron-fluorine behavior experimental behavior, and later on develop and test the validity of the fluorine-boron model system. Because of the sheer volume of data and discussion presented here, the model results and discussion are presented in chapter 6. This chapter contains only the experimental outline, discussion and results.

## 5.2 Experimental Design and Basis

Before any experimental design and analysis plan can be described, it is beneficial to explicitly state the specific experimental questions that the experiments will hopefully answer. In this case, there are two main experimental goals: to examine the time and dose dependency of the dopant co-diffusion for the purposes of model development, and to examine the nature of any direct boron-fluorine interaction.

As has been mentioned in previous chapters, the question of the precise nature of the boron-fluorine co-interaction has been debated for a long time in literature [refs]. There are three main candidates to account for the co-interaction: direct boron-fluorine interaction, fluorine-vacancy interaction with boron, and simple fluorine/fluorine vacancy interaction with interstitials. The latter reaction is already present in the model and is essential, but the remaining two are undecided.

The primary method to examine these reaction possibilities in the modeling efforts is to "keep it simple." Reactions are added to the model only when they are required to accurately describe the behavior of the experimental behavior. In this way, model development provides physical insight into the diffusion behavior of the samples. If a reaction is not required to explain the diffusion behavior present and the experimental evidence is thorough, the model suggests at minimum that the reaction in question is not prominent in producing the experimental results. If the experimental results can not be modeled without the presence of a reaction in the model, then it is suggested that the reaction is critical in the dopant diffusion process. It appears initially based on the results in chapter 4 that additional reactions may be unnecessary, but according to some researchers [Cowern05], such other boron-fluorine reactions may be important at higher impurity concentrations.

The precise level of interstitial trapping is still a considerable variable in the fluorine model was well. As chapter 3 illustrates, the fluorine profile itself is somewhat insensitive to the interstitial population in amorphous material if the fluorine

concentration is in the  $1 \times 10^{15}$  dose regime, and extremely sensitive at concentrations below the fluorine amorphization threshold. Boron however, is sensitive in all cases due to its interstitial mediated diffusion process. In the initial modeling, fluorine is assumed to be bound as a single fluorine to a single vacancy, giving an initial "interstitial trap" level equal to the fluorine concentration. Fitting is done through adjustment of the energy barrier to the FV-I recombination model reaction, which can allow for a great degree of freedom with high concentration cases. Because of the small experimental sample size of the initial boron integration test, this parameter is easy to adjust and multiple model fits are possible with the same data set. However, with additional experimental data, the true nature of the reactions may be revealed, and the trap level or initial conditions of the experiment may need to be adjusted to provide good fits across all of the experiments, rather than simply adjusting an energy barrier.

### **5.1.Experimental Matrix**

The experimental matrix designed to answer some of the remaining questions is presented as table 5-1, and an overall process flow diagram is shown as figure 5-1. The precise experimental procedure is the following: wafers are first implanted with  $1 \times 10^{15}$  /cm2 dose silicon with implants at both 20keV and 70keV energy. This produces a uniform amorphous layer of approximately 1200A which contains the boron and fluorine implants completely. Samples are then implanted with the boron and fluorine cases listed in table 5.1, and then annealed in either a traditional furnace with nitrogen ambient or a rapid thermal annealing system, also with nitrogen ambient.

The sample matrix breaks down to the following groups: two boron doses, two fluorine doses, and three anneal temperatures. Controls samples which consist of each dopant dose case implanted by itself in the pre-amorphized material are also included for

each boron and fluorine dose. As is noted in the chart itself, there is a nomenclature assigned to each specific case of a boron dose and a fluorine dose which is useful for the purposes of denoting data groups. In case of the higher dose boron and lower dose fluorine, the sample case is a called the "high/low" case. For the higher dose boron and higher dose fluorine, the sample case is called "High/High." The same nomenclature applies to the other two cases as well.

Some explanation is necessary to elaborate on why such specific experimental conditions were chosen. Two different boron doses are implanted,  $1 \times 10^{15}$  /cm<sup>2</sup> and  $3 \times 10^{13}$  /cm<sup>2</sup> dose, both implanted at 5keV energy. The 5keV implant energy is chosen primarily to resolve some of the issues that arose with the data in the previous chapter. Simulation of shallower boron profiles presents a large number of problems which make the results poor and difficult to interpret and model (Ljubo Radic, private communcation). The simplest way to eliminate most of the problems presented by the shallow data is simply to use a higher boron implant energy to produce a deeper boron profile.

Samples of the 5keV implant energy do not exhibit the surface related effects present in the shallow samples which make it difficult to analyze experimental data and later model the sample data. The surface related effects can affect both sides of model development: experiment related effects that make it difficult to reproduce and interpret results, and modeling issues which make it arduous to fit simulations to the data. Experimental effects include boron clustering at the surface, boron enhanced diffusion, and extreme experimental sensitivity to sample surface conditions, all of which can significantly alter the way shallow boron profiles behave. The most prominent modeling

related problem with shallow boron profiles is the requirement to use the full boron clustering model, which requires adjustment of a much larger number of parameters than the boron pair model. Results by Radic have also indicated that shallow boron profiles require significant adjustment of point defect surface recombination parameters, which in general are left as FLOOPS defaults because of uncertainty of their precise values (Ljubo Radic, private communcation). For boron implants of energies of 5keV and above, the experimental issues are minimized, and the boron pair model with a solubility approximation can replicate reasonably the behavior of the boron profile without significant adjustment. This reduced adjustment will increase the usefulness of the results as well as the time required to replicate the experimental results in model form.

The primary purpose of the boron dose variance is to compare samples with and without BIC formation during the annealing process. Since it is known that the boron clustering process itself can consume significant interstitials [Jones84], samples with boron clustering present can significantly affect results. Most specifically affected are any dopants in the sample which are interstitial diffusers or interstitial mediated diffusers, such as fluorine. Since the possibility of BIC formation depends mostly on the peak concentration of the implanted boron profile and the threshold has been determined in the literature to be roughly  $1 \times 10^{19}$  cm<sup>3</sup> peak concentration. The  $3 \times 10^{13}$  dose case produces little boron clustering or BICs because the peak concentration of the implant is below the threshold, and thus allows further exploration of the behavior in the simulation without the possibility of more advanced boron clustering processes affecting the results. The  $1 \times 10^{15}$  dose is expected to produce the clustering behavior that has already been

mentioned. The comparison between the two cases with identical fluorine doses will be valuable to examine any reciprocal boron effects on fluorine diffusion.

Two fluorine doses are proposed for the experiment; 2×10<sup>14</sup>, and 2×10<sup>15</sup>,/cm2 dose at 16keV implant energy. The purpose of this dose variance is to examine whether the variance of the dose has a quantifiable effect on the boron diffusion in terms of total amount of boron diffusion. Most specifically the two fluorine doses were chosen because previous experimental results indicate that the two doses present marked different control diffusion profiles, which are likely to result in a visible change in boron diffusion. Any variance in results will allow calibration of the FV interstitial capture portions of the model as well as examine some of the assumptions about the fluorine initial state as a singly bound fluorine-vacancy complex. The specific 16keV fluorine implant energy is most specifically chosen because this energy has been extensively studied in prior chapters and produces an excellent basis for comparison. Results from Robertson indicate that the relative position of the fluorine and boron profiles has an effect on the behavior of the co-implanted system. This energy variance was investigated, but since it is not directly related to the discussion here, is presented in Appendix A.

The three anneal conditions presented in the matrix serve an important purpose in model development. Since TED in the sample is a reverse activated process, it becomes increasingly difficult to separate out the individual effects of all of the impurity diffusion processes as temperature increases. The 750°C anneal temperature has shown to be very robust for use in model development for previous experiments. The time period for the fluorine transient is relatively long, the boron diffusivity is appreciable and easily measured in 15 minute increments, and the EOR defect evolution is also slow enough to

examine between samples. At the 900°C anneal temperature, the time period of the fluorine transient diffusion is much quicker, and the boron diffusivity is very appreciable, which allows the examination of significant diffusion between data points. These samples are more useful to examine the behavior at an additional temperature range in which the mechanics of TED and the EOR damage evolution will be different, which aids significantly for model calibration. The final temperature, the 1050°C 30s, will be used as a final model calibration step, and also because this type of anneal has the most industrial relevance.

Additional experiments examined to examine other, second order fluorine and boron effects, are presented in appendix A. These results, though relevant for overall understanding, are not as relevant to the core thrust of this dissertation, so they are moved to an appendix.

SIMS analysis is used to produce the depth profiles of both fluorine and boron in all of the samples. XTEM images are taken of the samples in order to quantify and examine the sample amorphous depth after implant, as well as verifying that all samples are fully regrown. PTEM images are taken of most of the samples for the 900°C 15 minute time point to examine any variance in the EOR defect evolution as well as quantify trapped interstitial counts. All XTEM and PTEM images are presented in appendix A.

#### **5.2 Experimental Results and Discussion**

SIMS results for both boron and fluorine are presented at the end of this chapter as figures 5-2-5-15. In general, all of the data containing boron fluorine shows the expected results of fluorine reduction in boron diffusion .However, results for the magnitude of this diffusion reduction vary in each specific case. For clarity and

coherence of the discussion, further discussion of the experimental results is grouped into four categories: high dose boron results, low dose boron results, fluorine results, and regrowth related results.

# 5.2.1 High Dose Boron versus Fluorine Dose

The high dose boron plots are shown in figures 5-2.-5-6. Figure 5-2 shows the comparison between the high and low fluorine doses for two 900C anneal conditions. In both cases, the depth of the boron profile diffusion is reduced when compared to the boron control. However, the figure illustrates a very clear positive relationship between the implanted fluorine dose and the total amount of boron diffusion reduction. In the low dose fluorine case, the depth of boron diffusion is very small, on the order of 100 or 200 angstroms, but persists through both time points of the 900C. anneal. In the high dose fluorine case, the diffusion reduction is much greater, on the order of five times as much in depth terms.

This effect is consistent with the observations gathered in the chapter 2 and 3 model development. The fluorine profile in the low dose case is much less capable of capturing interstitials and thusly becomes more mobile and diffuses from the sample. The fluorine in the high dose case is much more capable of capturing interstitials and as a consequence is more stable, is able to capture more interstitials, thusly reducing the diffusion of boron.

The diffusion depth of the boron profile of the low dose fluorine implanted sample is almost identical to the boron control, indicating that the fluorine profile does not absorb significant interstitials. As the fluorine results in figures 5-7 and 5-8 indicate, the fluorine profile for the low dose is almost completely gone while the high dose case has some remnant remaining at the conclusion of the anneal. This concurs with the earlier

evidence and the model development which indicate that high dose fluorine is much more stable at higher temperatures than low dose fluorine.

Examination of the 750C anneals also produces some interesting results. In this case the high dose fluorine produces an apparent complete suppression of the boron motion when compared to the control while the low dose fluorine implanted samples appear to reduce the depth of diffusion by a factor of two. In general, these results are also consistent with observation of higher dose fluorine stability at temperature. Fluorine SIMS results in figures 5-7 and 5-8 corroborate this assumption by illustrating this difference in stability between the two fluorine doses. However, the control sample for this anneal case doesn't diffuse to a large degree, so direct quantitative conclusions cannot be drawn from this case, since SIMS error could cloud the certainty of results.

## 5.2.2 Low Dose Boron versus Fluorine Dose

SIMS results for the low dose boron cases are presented in figures 5-9-5-12. In general the results for the low dose boron show the same qualitative difference in boron diffusion depth as the high/low and high/high cases. However, the magnitude of the difference in each case is different. For example, in all of the low/high anneal cases, the diffusion depth of boron appears to be insignificant over the as-implanted sample, and at most the diffusion appears within the SIMS noise. The 1050C anneal profile for the low/high case shows a significant loss of dose at the peak, without any noticeable diffusion into the bulk. Specifically this dose loss is attributable somewhat to boron diffusion to the surface, at which point the boron becomes trapped in the oxide, which is hidden in the SIMS noise area of these profiles, therefore it appears that the boron dose has simply disappeared in this sample.

The behavior of the low/low sample does not show this complete shut down of diffusion at any temperature, but the results are more consistent with the high/high results mentioned previously. The boron profile diffusion depth in all cases is reduced, in a qualitative manner similar to the high/high samples. However, in quantitative terms, the reduction in diffusion depth is not a great as the high/high case.

## 5.2.3 Comparison Between Boron Doses

Comparison of the low dose boron results versus the high dose boron results shows that the results between doses are qualitatively similar. That is, in all cases the high dose fluorine implant reduces the boron diffusion to a greater degree than the low dose fluorine.

However, the quantitative effects in terms of absolute depth reduction appear to vary for each dose .For example, the 900C 15 minute low concentration sample appears to diffuse 200A for the  $2 \times 10^{14}$  dose fluorine case, while the high concentration boron sample with the same fluorine dose diffuses about 1100A Comparison of two different dose boron profiles in this manner is somewhat deceptive as will be illustrated below.

Some of this behavior can be explained by examining a simple case of diffusion which consists of a Gaussian approximated impurity implant profile and simple Fick's Law diffusion equations. Consider two dopant profiles of the same implant energy, A and B, where the total dose of implant A is called DoseA, and the total dose of implant B is called DoseB. Also, assume that DoseA is greater than DoseB and the diffusivities of the two profiles are equal. Now simulate anneals of both samples of the same given temperature and a given anneal temperature. Now choose a certain comparison concentration at which the total diffusion of each profile in depth terms will be measured by taking the difference between the final depth and the initial depth. Undoubtedly, the sample of higher concentration will appear to diffuse farther into the bulk than the sample of lower concentration. However, the dopant profiles of both implants A and B can be thought of as being composed of DoseA and DoseB multiplied by a normal Gaussian distribution function respectively. Subsequently, implant profile B can be obtained from the implant profile A by multiplying by DoseB/DoseA, and vice versa. Since both implant profiles have the same diffusivity and were subjected to the same anneal, the results of the simulation profiles are also obtainable by multiplying by the correct ratio of DoseA to DoseB. Therefore, even though the depth diffusion amount for each profile appears different between cases, the two profiles actually experience the same amount of diffusion. The diffusivity of the profiles is what controls this effect.

Since this depth comparison between doses is not directly valid, it is better to examined in terms of diffusivity enhancement comparison. As is mentioned in chapter one, boron profiles which experience TED are often compared in terms of diffusivity enhancement, or the diffusivity which the boron profile in the sample appears to experience versus the boron diffusivity expected if the point defects were in equilibrium. This is most simply obtained by placing the as-implanted profile into a simulation with equilibrium defects, and adjusting the diffusivity in the boron equations until the results with the adjusted boron diffusivity match the experimental results at a given point in time.

The table with these diffusivity comparisons is included as table 5.14. From this table, the diffusivity enhancement of the low/low case is 16, while the high/low diffusivity enhancement is 26. While there is a difference in the absolute diffusivity enhancement between the two cases, it is not the extreme that the depth comparison

would seem to imply. In another sense, define the term "diffusivity enhancement factor" for a specific sample is defined to mean the diffusivity enhancement of the co-implanted sample divided by the boron control for the same anneal condition. For the low/low case, this number is 0.8, and for the high/low case this number is 0.86. This method of comparison makes the fluorine effect on the sample more clearly in quantitative terms for each sample, as well as highlights the fact that the same fluorine dose has similar effects on both boron doses.

## **5.2.4 Fluorine Diffusion Results**

Figures of the fluorine diffusion results are shown in figures 5-7,5-8,5-13, and 5-15. The results indicate that in general, the fluorine diffusion process is similar to that presented in the data in chapters 2 and 3. Experimental results indicate one important distinction from the fluorine control cases. In all samples with boron present, a greater amount of fluorine is retained in the sample at the end of the anneal than in the fluorine control itself. The comparisons of figures identical fluorine controls versus boron dose between figures 5-8 and 5-13 also demonstrate that this affect scales with boron dose. Samples with greater boron doses retain greater fluorine at the end of the anneal, in some cases the retained dose of fluorine is an order of magnitude over the fluorine control itself.

However, this result has an easily accessible explanation. The diffusion of boron itself affects fluorine diffusion in two ways: the interstitial mediated diffusion of boron itself capturing interstitials, and boron clustering processes capturing interstitials. In the case of simple interstitial mediated diffusion, an interstitial that "kicks out" a boron atom from a substitutional atom is not able to also react with a fluorine vacancy and eventually create mobile fluorine. Thusly, fluorine diffusion is reduced simply because of the competition with boron for the available interstitial population. The second effect, boron clustering, is additive above the simple boron diffusion processes, and captures additional silicon self interstitials which then do not react with fluorine vacancies to produce mobile fluorine. Since the clustering process happens only in the higher concentration boron, this effect is more important in the higher dose boron cases. The experimental results in all sample cases and temperatures reflect this phenomenon exactly.

Since further discussion of this phenomenon is benefited by comparison with modeling results, further discussion of this phenomenon is deferred to the modeling information in chapter 6.

# **5.2.5 Fluorine Energy Effects**

Discussion in the previous cases has focused on dose related effects for a specific fluorine and boron implant energy. Another aspect worthy of examination is the effect of a varying fluorine implant energy on the diffusion of boron in the samples, especially given the results of Robertson. To test this, another experimental condition was chosen:  $2 \times 10^{15}$ /cm2 dose fluorine implanted at 24keV energy, and  $1 \times 10^{15}$ ,/cm2 dose boron implanted at 5keV energy. To accommodate this, the pre-amorphization was changed to a  $1 \times 10^{15}$ /cm2 100keV energy Si+  $1 \times 10^{15}$ /cm2 dose 40keV energy Si dual implant. The annealing scheme was exactly the same as the 16keV fluorine cases. The results are presented in figures 5-16 and 5-17. Figure 5-16 shows the comparisons between the control cases for current sample versus the previous  $2 \times 10^{15}$ /cm2 16keV fluorine and 1  $\times 10^{15}$ /cm 5keV boron case, which indicate that the change in pre-amorphization has not significantly altered the boron behavior itself. Figure 5-17 shows the boron SIMS results indicate that the boron TED is reduced by a visible margin in the case of the 24keV

energy fluorine dose. To provide a better comparison, the overall diffusivity enhancement for the 24keV fluorine case is 16 versus 18 for the 16keV fluorine case.

A simple explanation for this can be built upon the discussion in the preceding two pages. By placing fluorine slightly deeper in the sample, the interstitial flux from the EOR must travel farther through the fluorine profile to reach the boron profile than in the 16keV case. Because fluorine acts as an effective interstitial sink, this increases the chance that a given interstitial will be captured by a fluorine-vacancy complex before it reaches the boron profile.

## 5.2.6 Regrowth Related Behavior

Due to the regrowth related results shown in chapter 3, all samples presented in this section were annealed for minimum times of 10 seconds at 750C to examine the fluorine and boron profiles immediately after regrowth for dual purposes of model initial condition and also to examine if the regrowth behavior was significantly different between the two cases. The SIMS results are presented in figure 5-15.

Based on the Olson results mentioned in previous chapters, it is known that while the presence of fluorine in a sample slows down the velocity of the regrowth front below intrinsic rates, the presence of boron alone can accelerate the regrowth of a sample above the intrinsic regrowth rate for a given temperature If the two impurities are present in the same sample, then they can compensate for each other and in some cases cause the regrowth velocity to be near intrinsic regrowth rates. Therefore it is reasoned that the regrowth rates in the boron-implanted samples will be faster and this may have some effect on the fluorine incorporation into the sample.

Comparison of the post-regrowth SIMS profiles indicates that boron does have an effect on fluorine retention of the profile. More specifically, the presence of boron

appears to initially increase the amount of fluorine retained in the sample post regrowth. The effects also tend to be related to the boron dose in the sample. More specifically, in the case of the low/high sample, the post-regrowth fluorine profile appears the same as the fluorine control. In the high/low, low/low, and high/high samples however, the fluorine dose retained after regrowth is higher than the fluorine control itself.

A reasonable explanation for this can be developed based on the discussion in chapter 3. If the boron is assumed to act during regrowth as a simple regrowth "accelerator", then the only factor different between the fluorine control and the boron implanted sample is the velocity of the regrowth front. The two factors governing fluorine incorporation in this case are the diffusion constant of fluorine and the regrowth velocity. To quickly paraphrase the chapter 3 discussion, fluorine is able to diffuse both to the amorphous crystalline interface and the surface in the amorphous region during regrowth, and during this process, a significant amount of fluorine can be lost at the surface as well as significant amount of pileup at the regrowth front. Both of these processes interfere with fluorine incorporation as mentioned in chapter 3 and therefore lower the amount of fluorine present post regrowth.

However, if the velocity of the regrowth front is now accelerated, the fluorine profile itself has a much lower chance of diffusing to the surface or piling up at the interface since the time in the amorphous region is much lower. Therefore, the fluorine profile is "frozen in" during the regrowth process. According to this theory, the effect of boron should increase as the ratio of boron dose to fluorine dose increases, and this is what is presented in the data results. Though a more extensive study of this phenomenon is possible, it is not the focus of this dissertation and is therefore deferred to future work.

	Pre- amorphization	1×10 <sup>15</sup> 70keV Si+1×10 <sup>15</sup> 20keV Si	$1 \times 10^{15}$ 100keV Si+1×10 <sup>15</sup> 40keV Si	1×10 <sup>15</sup> 40keV Si
	Fluorine doses	$2 \times 10^{14}$ , $2 \times 10^{15}$ , at 16keV, None (control)	2×10 <sup>15</sup> , at 24keV energy	2×10 <sup>15</sup> , at 24keV energy
	Boron doses	3×10 <sup>13</sup> , 1×10 <sup>15</sup> at 5keV	1×10 <sup>15</sup> at 5keV	1×10 <sup>15</sup> at 5keV
Anneal Temp(s)/times		750: 10sec. 15 min, 30min, 1hr. 900:10 sec, 15min, 30min. 1050C: RTA /(30s)	750C 30min, 900:15min, 30min. 1050C: RTA /(30s)	750C 30min, 900:15min, 30min. 1050C: RTA /(30s)

Table 5-1 Experimental matrix



Figure 5-1 Experimental flow



Figure 5-2 Comparison of the  $2 \times 10^{15}$  dose boron implant versus two fluorine doses for the 900C 15minute anneal case.



Figure 5-3  $1 \times 10^{15}$  dose boron implant with  $2 \times 10^{15}$  dose fluorine implant diffusion results for 750C



Figure  $5-4 \times 10^{15}$  dose boron implant with  $2 \times 10^{15}$  dose fluorine implant diffusion results for 900C and 1050C



Figure 5-5  $1 \times 10^{15}$  dose boron implant with  $2 \times 10^{14}$  dose fluorine implant diffusion results for 750C


Figure 5-6  $1 \times 10^{15}$  dose boron implant with  $2 \times 10^{14}$  dose fluorine implant diffusion results for 900 and 1050C



Figure 5-7 Fluorine results for the  $1 \times 10^{15}$  dose boron implant with  $2 \times 10^{15}$  dose fluorine



Figure 5-8 Fluorine results for the  $1 \times 10^{15}$  dose boron implant with  $2 \times 10^{14}$  dose fluorine.



Figure 5-9 Boron SIMS results for the  $3 \times 10^{13}$  dose boron implant with  $2 \times 10^{15}$  dose fluorine for the 750C anneal.



Figure 5-10 Boron SIMS results for the  $3 \times 10^{13}$  dose boron implant with  $2 \times 10^{15}$  dose fluorine for the 900C and 1050C anneals



Figure 5-11 Boron SIMS results for the  $3 \times 10^{13}$  dose boron implant with  $2 \times 10^{14}$  dose fluorine for the 750C anneal



Figure 5-12 Boron SIMS results for the  $3 \times 10^{13}$  dose boron implant with  $2 \times 10^{15}$  dose fluorine.

	$3 \times 10^{13}$ dose boron	$1 \times 10^{15}$ dose boron			
Control (no	20	30			
fluorine)					
$2 \times 10^{14}$ dose fluorine	16	26			
$2 \times 10^{15}$ dose fluorine	(Not measurable)	18			

Table 5-2 Extracted diffusivity enhancements for the 900C 15minute anneal case



Figure 5-13 Fluorine SIMS results for the  $3 \times 10^{13}$  dose boron implant with  $2 \times 10^{15}$  dose fluorine for the 900C and 1050C anneals



Figure 5-14 Fluorine SIMS results for the  $3 \times 10^{13}$  dose boron implant with  $2 \times 10^{14}$  dose fluorine for the 900C and 1050C anneals



Figure 5-15 Fluorine SIMS results for the 750C 10second regrowth anneals.



Figure 5-16 Boron SIMS control results for the  $1 \times 10^{15}$  dose boron implant with 70keV versus 100keV energy silicon pre-amorphization.



Figure 5-17 Fluorine SIMS results for the 1×1015 dose boron implant with 2×1015 dose 24keV energy fluorine implant. Results are presented in comparison to the 16keV fluorine implant case

## CHAPTER 6 FLUORINE/BORON SIMULATION RESULTS

### **6.1 Introduction**

In the previous chapter the experiment developed to try and gather further model data was presented. In this chapter, the model results for that data will be presented and analyzed. The implications and additional insight that the modeling effort provided will also be discussed.

#### 6.2 Model Development and Basis

The simulation procedure for the model efforts in this chapter is generally as chapters three and four. The first step is to simulate the silicon pre-amorphization implants using the UT-MARLOWE simulator. The resulting defect profiles were modified by zeroing the portions of the defect profiles for which the depth is shallower than the amorphous crystalline interface depth, which was measured by TEM in the previous chapter. In this case, all samples have an amorphous depth of 1200A. The modified defect profiles from the implant simulation were then input into the FLOOPS simulate and the "room temperature anneal" was performed to resolve damage and form the extended defect populations necessary for the later anneal stages. Next, the post regrowth SIMS profiles for fluorine and boron were used for initial starting profiles for the simulation. For all of the simulations the profiles used for initial input to the simulation were the 10sec. 750C SIMS profile for both fluorine and boron.

The reasons for which the post-regrowth profile is used for fluorine were clearly identified in chapter 3. However, recent research by Gable et. Al has clearly indicated

that boron itself can also diffuse significantly during regrowth the sample regrowth process [Gable05]. The FLOOPS simulator does not currently have the ability to simulate either the regrowth related distribution of fluorine or the amorphous diffusion of boron. Such capabilities could be implemented in the future, however, are not implemented for any simulation in this dissertation. Therefore, the post-regrowth boron profiles are used for the simulation to alleviate any concerns.

Fluorine is also again assumed to be bound entirely as the fluorine-vacancy product FV for the initial condition for the simulation. The boron model used for all of the simulations in this chapter is again the pair model with the solubility adjustment mentioned in chapter 4 [Law02]. In accordance with the conventions of this model, the entirety of the boron profile is initially set to boron substitutional. The fluorine model used for the results in this section is the same low and high concentration fluorine that was presented in chapters three and four, using the same base equations and binding energies. The Avci extended defect model is also incorporated into the simulation for {311} and loop simulations.

The next step in the simulation procedure is the tuning of the EOR extended defect model to match the boron control simulations. Specifically, the parameter of adjustment most extensively used in the binding energy of the {311} interstitial release in the Avci model. The purpose of this is to try and match the behavior of the interstitial excess release from the EOR defects in both general quantity and time dependent behavior. This is the parameter which, as mentioned in chapter one, directly governs TED and the diffusion of boron for these cases. Since boron is an interstitial mediated diffuser and is therefore very sensitive to the interstitial population in the simulation and provides

a good marker for the tuning procedure. Since the only source of interstitials in the simulation is the EOR defects, this is naturally the place to adjust the simulation parameters. The boron model used for these simulations is very well established and no parameters of the boron model are ever adjusted.

The simulations in this chapter also make use of a simple coding trick to simulate a reflecting boundary which approximates the effect of the amorphous crystalline interface on defects in the EOR. The extra code works by setting the diffusivity of all simulation species to zero for depths above a given depth for each time step. The initial setting of this depth is the starting amorphous depth, and the rate in depth change for each time step is the same as the regrowth rates given in Olson. For samples implanted with boron, intrinsic regrowth rates are assumed, even though in theory the boron implant can accelerate the regrowth process. For any samples with fluorine only, the box-like approximation for regrowth rates mentioned in chapter 3 is used. This coding change has the net effect of confining the simulated silicon self-interstitial population beneath simulated amorphous/crystalline interface during the simulation, which in turn fosters further formation of extended defects in the simulation. The effect of this modeling assumption is to concentrate almost all of the point defect population in the end of range region of the sample prior during the room temperature anneal If this situation is left alone and simulated, the result from experience will be that diffusion of most impurities will be grossly overestimated because of the excess of interstitials released during the simulation. The is change also causes a simulation to require much less tuning in order to match control simulations, and no significant tuning is needed if the boron profile changes between simulations as long as the pre-amorphization conditions stay the same.

Once the EOR model is tuned such that the boron diffusion controls match well to experiment, the parameters for both the EOR model as well as the boron model are not adjusted further in any simulation case. The only adjusted parameters are the reaction energy barriers of the fluorine model, in the same procedure as mentioned in chapter three.

### 6.3 Model Results and Discussion

### **6.3.1 Model Results**

Model results pertaining to the boron simulation are shown in figures 6-1-6-5. As the model results indicate, the combination of the fluorine and boron models is able to qualitatively and quantitatively match the behavior of the boron profiles used for the simulation. More specifically, the boron results in all cases are well matched in terms of dose loss, depth of diffusion, and time dependency. Model results pertaining to the fluorine profiles are shown in figures 6-6-6-9. Specific energy barriers and binding energies used in this iteration of the model are presented in figure 6.10. As the figures indicate, the model is still able to qualitatively match the behavior of the samples, even though the results are slightly different than the fluorine sample controls. The fluorine fits in the sample are quantitatively poorer than in the previous cases, though the time dependency and general motion of the profile is correct. The largest deficiency is the amount of fluorine dose predicted to be left in the simulation, which the model continually under predicts. However, further discussion of this is presented later in the chapter.

### 6.3.2 Discussion

Based on the results presented in the figures, the model appears able to replicate the fluorine effect of boron for the all of the samples cases. Additionally, a number of

important features appear to be accounted for with the combination of the two models. The first of which is the reduction of boron diffusion present across all of the samples with fluorine and boron present. The model is able to replicate accurately the quantitative effect of the difference in boron diffusion reduction present between the two fluorine doses. This is accounted for in the model action primarily by the difference in fluorine stability present between the low and high dose samples. As mentioned in chapter 3, the total amount of fluorine-vacancy traps available outnumbers the total interstitial dose by a possible factor of ten in the higher dose case, and the ratio is one for the lower dose case. Therefore, the higher dose is not only able to capture more interstitials but is also more stable. The lower fluorine dose case becomes more mobile during the diffusion and thus by diffusing out cannot capture as much interstitial dose and thusly reduce boron diffusion. For the reasons mention previously, the reduction of boron diffusion is in the cases of the low dose fluorine is substantially less than the high dose fluorine for the for the 750 and 900C anneal cases.

In the case of the 1050C anneals, the low dose fluorine does not appear to produce any measurable reduction in boron diffusion over the control. This is partially due to the factors listed in the previous paragraph. However, as the fluorine SIMS data for the sample indicates, the fluorine is completely gone by the conclusion of the 1050C anneal. As such a high anneal temperature, the fluorine model itself expects the fluorine dose to be unstable even in equilibrium defect populations. This indicates that fluorine is likely diffusing from the sample at a very high rate even before the EOR interstitials reach the projected range of the profile. Therefore the results make sense with the prior model observations for both fluorine itself and when combined with boron.

There is an important distinction between the two boron doses as well, as in the low/high sample, boron diffusion is completely suppressed while in the high/high case, significant diffusion is observed. A portion of this is explainable by the diffusion enhancement discussion presented in the previous chapter, higher dose samples generally appear to diffuse greater when in fact they may not indicate a difference in boron diffusivity. The other portion of this behavior is answered by the discussion in the previous paragraph. Though the fluorine model significantly reduces the total interstitial population by capturing them, it does not totally prevent interstitials from reaching the boron profile.

Additionally, as the discussion in chapter one describes, the equations for both boron substitutional and fluorine vacancy interaction with interstitials have reaction rates which vary with the boron and fluorine dose. For the purposes of this example, consider only the reaction rates of the fluorine and boron equations at the peak of the profile. If the concentration of the fluorine profile is much greater than the boron profile, then the chance of the fluorine capturing an interstitial is much greater than the boron profile capturing one and diffusing. However, if the ratio of the two profiles is closer, then the probability of the boron capturing an interstitial and diffusing is much greater. In this way, the four cases can be examined by comparing total boron and fluorine dose. For the low/high dose, fluorine outweighs boron by a significant margin and thusly boron diffusion is almost completely suppressed. For the low/low and high/high cases, the ratio of boron and fluorine is similar and thusly significant diffusion is observed. In the high/low sample, boron far outweighs fluorine and thusly much greater diffusion is observed, in some cases similar to the control.

The results in chapter 5 also indicate that the relative position of the fluorine profile also has an effect on the resulting boron diffusion when compared to both the control and the previous case. Specifically, the results indicate that the samples implanted with 24keV fluorine show reduced boron diffusion of a magnitude greater than that of the 16keV fluorine implanted samples. The model is also able to replicate this behavior without much additional tuning. The explanation for why the model is able to easily reproduce this behavior is almost the same as the explanation for the experimental result itself: by placing the fluorine profile slightly deeper, the EOR interstitials must travel through a greater concentration of fluorine before they can reach the boron profile. Because of this, the fluorine catches a higher percentage of the interstitials, which reduces the interstitial flux reaching the boron profile, and thusly boron diffusion is reduced.

The simulation results also reveal an interesting result which is related to the above discussion. As fluorine has an effect on boron diffusion, boron has a reciprocal effect of reducing diffusion of fluorine to a slight degree. As the results in chapter 5 mentioned, the fluorine dose retained at the conclusion of the anneals when boron is co-implanted is in some cases higher than the dose of the fluorine control by sometimes and order of magnitude. The model is able to at least qualitatively replicate this effect. The model also provides insight by indicating that this effect is due to the same reasons mentioned above. The boron profile effectively "competes" for interstitials, especially in the higher dose case where boron clustering processes are present. Thus the boron capture of interstitials reduces the amount of interstitials which combine with the fluorine, thus slowing the diffusion of fluorine compared to the control.

## **6.3.3 Other Fluorine Reactions**

As mentioned previous, the only fluorine boron interaction considered in these model results is the FV-I interstitial capture reaction. As the model results indicate, the model appears capable of replicating all major features of both the boron and fluorine diffusion in all of the experimental cases. Based on this, it appears at minimum that no additional reactions are required to describe the model behavior, and thusly, the model indicates that neither B-F or FV-B reactions are important in these cases. Additionally, examination of the experimental features of both profiles indicates nothing different in terms of general diffusion behavior is present that cannot be attributed simply to the reduction of the interstitial population reducing the diffusion of both fluorine and boron.. Results by Cowern have indicated through extensive hall effect measurement that there may bee a further B-F reaction, but it is not important in the time ranges presented for the experiments in this chapter [Cowern05]. However, for the purposes of simulation, the FV-I reaction appears to be most important in the context of modeling the boron and fluorine implant doses and temperatures presented in this chapter.



Figure 6-1 Boron simulation results for the  $1 \times 10^{15}$  dose boron implant with  $2 \times 10^{15}$  dose 16keV energy fluorine implant condition.



Figure 6-2 Boron simulation results for the  $3 \times 10^{13}$  dose boron implant with  $2 \times 10^{15}$  dose 16keV energy fluorine implant condition.



Figure 6-3 Boron simulation results for the  $1 \times 10^{15}$  dose boron implant with  $2 \times 10^{14}$  dose 16keV energy fluorine implant condition.



Figure 6-4 Boron simulation results for the  $3 \times 10^{13}$  dose boron implant with  $2 \times 10^{14}$  dose 16keV energy fluorine implant condition.



Figure 6-5 Boron Simulation results for the  $1 \times 10^{15}$  dose boron implant with  $2 \times 10^{15}$  dose 24keV energy fluorine implant condition.



Figure 6-6 Fluorine simulation results for the  $1 \times 10^{15}$  dose boron implant with  $2 \times 10^{15}$  dose 16keV energy fluorine implant condition.



Figure 6-7 Fluorine simulation results for the  $3 \times 10^{13}$  dose boron implant with  $2 \times 10^{15}$  dose 16keV energy fluorine implant condition.



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Figure 6-8 Fluorine simulation results for the  $1 \times 10^{15}$  dose boron implant with  $2 \times 10^{14}$  dose 16keV energy fluorine implant condition.



Figure 6-9 Fluorine simulation results for the  $3 \times 10^{13}$  dose boron implant with  $2 \times 10^{14}$  dose 16keV energy fluorine implant condition.

Reaction	Binding Energy(eV)	Energy Barrier (eV)				
$Fs + I \Leftrightarrow Fi$	1.5	0.12				
$Fs + V \Leftrightarrow FV$	3.57	0.08				
$Fi + V \Leftrightarrow Fs$	6.1	0.065				
$FV + I \Leftrightarrow Fs$	3.14	0.132				
$Fi + V_2 \Leftrightarrow FV$	9.0	.063				
$Fi + I \Leftrightarrow FI_2$	1.0	.034				
$FI_2 + Fi \Leftrightarrow F_2I_3$	1.5	0.1				
$F_2I_3 + Fi \Leftrightarrow F_3I_4$	2.0	0.2				

Table 6-1 Listing	of newer	reactions	and	energy	barrier	values	for the	model

# CHAPTER 7 SUMMARY AND FUTURE WORK

#### 7.1 Summary

The body of this dissertation has presented many ideas which are useful to furthering the development of silicon processing technology. This dissertation began by investigating the diffusion behavior of the fluorine impurity itself, by examining multiple SIMS profiles. The general diffusion behavior of crystalline fluorine as a non-Fickian, surface oriented diffusing impurity was expanded upon by examining the time dependent behavior. Through this investigation, it was demonstrated that fluorine itself has a number of important diffusion behaviors which isochronal plots do not reveal. The most important of these behaviors is the apparent transient nature of the fluorine diffusion which is present both for crystalline and amorphized samples. Also presented was evidence of pileup or uphill diffusion in the peak region in the sample.

After the time dependent data on the fluorine diffusion was gathered, a model for fluorine diffusion was developed using the work of Adam as a basic initial equation framework since nitrogen diffusion showed similar diffusion behaviors. Binding energies for the equation products were gathered from results presented by Dunham. However, the fluorine transient behavior and peak pile-up behavior are quite different than nitrogen diffusion and required adjustments to the model.

As the investigation continued, positron annihilation spectroscopy results were presented to examine the composition of the fluorine profile as the anneal progressed.

Though the initial condition of fluorine bound as a fluorine-vacancy type defect was agreed upon in literature prior to the investigation, the positron annihilation spectroscopy indicated that the fluorine vacancy product was also dominant at the conclusion of the anneal.

Based upon this data, a working model was developed for fluorine diffusion in crystalline material was developed and presented. It was suggested that the anomalous diffusion behavior of crystalline material comes from two main behaviors which the model developed highlighted. The first behavior was the capture of silicon selfinterstitials by the initial fluorine vacancy product which in two steps produces the mobile fluorine product. The second behavior was the reaction of fluorine with both vacancy and interstitial type defects which congregate at the surface of the sample during annealing, among them most specifically divacancy products. Mobile fluorine reacting with divacancies at the surface produced immobile fluorine vacancy product at the surface, which in turn accounts for both the surface oriented diffusion behavior as well as the peak pile-up present in the profile. The model also suggested that the stability of the fluorine product in the anneal generally was related to concentration of interstitial-type point defects. When the fluorine-vacancy concentration in the sample exceeded the interstitial population, fluorine became stable.

In the next step, investigation of the high concentration or amorphizing dose fluorine samples highlighted the difference in diffusion behavior between the crystalline and amorphizing dose. Rather than surface oriented diffusion with the features presented in the previous paragraphs, amorphizing dose fluorine appeared to coalesce simply into a "flat top" shaped profile, with the only diffusion behavior an apparent overall dose loss

between the initial data point during an anneal to the final data point. Amorphizing dose fluorine samples also showed considerable temperature stability above that of crystalline fluorine.

Behavior of non-amorphizing dose fluorine samples in amorphized material was also investigated and found to be similar to the behavior in the crystalline case. Features such as surface oriented diffusion, peak pile-up, and the transient nature were all examined in the same way as the crystalline case.

Additionally, because the fluorine samples in amorphized material showed such a large difference between the as-implanted profile and the first anneal data point, it was deemed prudent to examine the behavior of fluorine immediately following regrowth using the RTA system. When the fluorine profile was examined for samples annealed just long enough for regrowth, it was found that a significant amount of the fluorine profile shape for the amorphized samples is created entirely by the regrowth process. The mechanics of the regrowth were examined and results were found to vary based on fluorine dose, but most specifically the dominant "flat-top" profile feature was found to be created by regrowth related processes.

With the additional experimental information gathered from the high concentration data, the fluorine model was extended to replicate the behavior of the samples in amorphized material. The model was found to replicate well the experimental behavior of the samples for the data provided. Since the regrowth process was responsible for the major features of the final profile, the data from the samples annealed just long enough for regrowth to complete were used as initial conditions. From the model development, the model also suggested the dominant mechanism which differentiates the high and low concentration behavior. The mechanism is simply the fact that for low concentration or crystalline samples, the total silicon self interstitial dose in the bulk for crystalline samples or in the EOR for amorphized samples is either higher or on the same order as the fluorine dose in the sample. In the high concentration case, the fluorine dose is higher than the interstitial dose by an order of magnitude. Thusly, the low concentration dose is less able to capture a significant dose of interstitials before it becomes almost completely mobile, while the high concentration is able to absorb more interstitials and experience minimal dose loss.

Based on the fluorine model work, the fluorine model was combined with the boron pair model and the combined model was compared against previous data by Robertson. The combination assumed that there was no direct interaction between boron and fluorine atoms in the simulation. The results from the simulation indicated that the combined model appeared to be able to replicate the fluorine reduction on boron diffusion, but the boron model results were very poor because of the shallow boron implant in the data samples. The simulation did imply however that the fluorine vacancy capture of interstitials may be primarily responsible for the reduction.

To further clarify and examine the nature of the co-implanted system, further experiments were conducted to examine the behavior. The experiment examined fluorine doses both low and high, and boron doses at both clustering and below clustering dose. A number of notable behaviors were gathered from these experiments. The reduction of boron TED is greater for the higher dose fluorine case than for the lower, and the reduction for the higher dose fluorine case persists at higher temperatures than for the lower dose case. These behaviors are directly consistent with fluorine behavior itself, and

imply that behavior may be as simple as the capture of interstitials by fluorine vacancy products. Additionally, it was also found that the presence of boron appears to alter regrowth such that the amount of fluorine retained after regrowth increases.

The newer boron/fluorine experiments were used to evaluate and further tune the model. After the modeling effort was completed, it was found that little effort was need to modify the existing fluorine model to fit the boron data well. Model parameters required minimal adjustment and no new equations were added. From the modeling efforts, a reasonable conclusion was drawn from the fact that no new model reactions were required to describe the behavior. This conclusion is that the model suggests any direct boron-fluorine atomic reaction is unnecessary.

#### 7.2 Future Work

As the dissertation progressed, a number of opportunities for further study of work related to the topic of this dissertation presented, but were not pursued because of the scope of the work and time constraints, those specific ideas are listed here.

## 7.2.1 Empirical Regrowth Impurity Modeling

The examination of the high concentration fluorine regrowth introduced the issue of fluorine redistribution during regrowth. Results from Gable et. Al have noted that the fluorine regrowth related effects can have significant effect on boron profiles by slowing the regrowth rate sufficiently to increase the diffusion of boron in the amorphous phase. Most specifically, this issue is important for spike or flash type annealing in which the bulk of the diffusion is in the hold or pre-warm phase of the anneal.

The method which this work uses to sidestep this issue is to examine the boron and fluorine profiles immediately post regrowth. The FLOOPS simulator does not currently simulate regrowth or regrowth related processes, but could conceivably be extended to
model some of the regrowth related processes. Most specifically, the regrowth rate for varying concentrations of boron and fluorine is present in data by Olson et. Al, and the segregation constant for fluorine is known. It is possible then to implement additional functionality which could produce a simulated post regrowth profile for fluorine. From this simulated post regrowth profile, the amorphous diffusion of boron could then be approximated based on the concentration-dependent regrowth rates produced from the regrowth simulation.

In this way, the usefulness of the boron/fluorine model system would be increased because the amount of required calibration data would be reduced significantly, as well as general accuracy of the simulated system would increase. The functionality required to add this feature would also be useful to apply to other co-implanted dopant systems.

#### 7.2.2 Shallow Boron Profiles

Chapter four of this work briefly mentioned some of the inherent problems associated with modeling boron profiles with implant energies less than 2keV. The primary reason such profiles were not investigated in this work is for experimental cost reasons. However, the primary importance of the boron/fluorine co-dopant system is for shallow source/drain extensions in submicron transistors. As such, current industry implant energies are well below the 2keV effective boron energy implant threshold. Therefore for maximum industrial relevance the model must be extended to model the lower energy boron.

The primary barrier to modeling such lower energy boron implants is the ineffectiveness of the existing boron models present in FLOOPS and other process simulators. As mentioned previously, the full boron clustering model is required to fully model the behavior of boron implants with high peak concentrations produced by sub-

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2keV implants in amorphized material. However, no published works present a complete model with which the proper results can be replicated in simulation. A working amorphous phase boron clustering model is the first step to extending the results to shallow profiles.

The second problem which inhibits proper modeling of shallow boron profiles is the sensitivity of shallow boron profiles to surface condition factors which vary from sample to sample. Results from Radic have indicated that boron diffusion results for shallow profiles are extremely sensitive to simulation factors such as the point defect recombination rate at the silicon surface. For most simulation this factor is left unchanged from simulator default values because of the uncertainty of its value, as changing this factor can change a large number of unexpected other parameters in a simulation such as TED time dependency and the excess interstitial magnitude.

# APPENDIX A FLOOPS CODE

BEGIN FILE rrflmodel.tcl

#High Concentration Fluorine Model #Robert R Robison # # set mesg "Started on [exec date].\n" set sec0 [clock seconds] # #Directly below is some floops comparison to Ibo's model.Little relation to current situation # \*\*\*\*\*\* #Input file for 50 keV 1e15 cm^-2 Si implant. Anneal temp 700C # LjR model description # file containing the equation proc pdbSetString Si B ClusterModel full source ~ljradic/floops/B cluster/B3.params source ~ljradic/floops/B cluster/B3b.d.tcl # reaction description  $\{\{x \ y\} \ \{z\}\}\$  (means x+y->z) in a list set F reactions { {{FV Vac} {FV2}} {{FV Int} {Fs}} \  $\{\{Fs V2\} \{FV2\}\} \{\{Fs Vac\} \{FV\}\} \{\{Fs Int\} \{Fi\}\} \land$ {{Fi V2} {FV}} {{Fi Vac} {Fs}} {{Fi Int} {FI2}} \ {{FI2 Fi} {F2I3}} \ {{F2I3 Fi} {F3I4}} pdbSetString Si Fi Reactions \$F reactions # name all species to be solved for set species { FV2 FV Fs Fi FI2 F2I3 F3I4 } pdbSetString Si Fi Species \$species pdbSetString Si Fi InitProc InitReactEqns pdbSetString Si Fi EquationProc BICEquations pdbSetString Si Fi ExtraEquationProc Fi xtra proc Fi xtra { } { # where is sigma1,2 defined in your equationProc? set sigmal 5e-2 set sigma2 3e-3 pdbSetString Oxide Silicon Fi Equation m2 {-\$sigma1 \* (Fi m2 - 1.0e8)} pdbSetString Oxide Silicon Int Equation m2 {-\$sigma2 \* (Int m2 - [pdbGetDouble Si I

Cstar])}

pdbSetString Oxide\_Silicon Vac Equation\_m2 {-\$sigma2 \* (Vac\_m2 - [pdbGetDouble

Si V Cstar])}

}

# in order for each reaction to be taken into account, one has to define Ea pdbSetDouble Si Fi FVVac Ea 0.491 pdbSetDouble Si Fi FVVac Eb 7.9 pdbSetDouble Si Fi FVInt Ea 0.41 pdbSetDouble Si Fi FVInt Eb 3.17 pdbSetDouble Si Fi FsV2 Ea 0.151 pdbSetDouble Si Fi FsV2 Eb 2.9 pdbSetDouble Si Fi FsVac Ea 0.1 pdbSetDouble Si Fi FsVac Eb 3.57 pdbSetDouble Si Fi FsInt Ea 0.101 pdbSetDouble Si Fi FsInt Eb 1.5 pdbSetDouble Si Fi Dstar {[Arrhenius 8e-13 0.0]} array set Params&Silicon&Fi {ActiveModel {Switch 0 { None Solid Precipitation }}} pdbSetDouble Si Fi FiV2 Ea 0.2 pdbSetDouble Si Fi FiV2 Eb 9.0 pdbSetDouble Si Fi FiVac Ea 0.151 pdbSetDouble Si Fi FiVac Eb 6.1 pdbSetDouble Si Fi FiInt Ea 0.0122 pdbSetDouble Si Fi FiInt Eb 0.977 pdbSetDouble Si Fi FI2Fi Ea 0.0135 pdbSetDouble Si Fi FI2Fi Eb 1.2 pdbSetDouble Si Fi F2I3Fi Ea 0.0101 pdbSetDouble Si Fi F2I3Fi Eb 1.0 #proc Data { } { global WinDataNall set WinDataNall [CreateGraphWindow] AddtoLine \$WinDataNall Nall800 15 4.3e14 AddtoLine \$WinDataNall Nall800 30 4.3e14 AddtoLine \$WinDataNall Nall800 60 4.5e14 AddtoLine \$WinDataNall Nall800 120 4.4e14 AddtoLine \$WinDataNall Nall800 240 4.3e14 AddtoLine \$WinDataNall Nall800 960 4.4e14 global WinDataDall set WinDataDall [CreateGraphWindow] AddtoLine \$WinDataDall Dall800 15 1.9e11

AddtoLine \$WinDataDall Dall800 15 1.9e11 AddtoLine \$WinDataDall Dall800 30 1.8e11 AddtoLine \$WinDataDall Dall800 60 1.7e11 AddtoLine \$WinDataDall Dall800 120 1.5e11 AddtoLine \$WinDataDall Dall800 240 1.1e11 AddtoLine \$WinDataDall Dall800 960 8e10

global WinDataRp set WinDataRp [CreateGraphWindow]

AddtoLine \$WinDataRp Rp800 15 60 AddtoLine \$WinDataRp Rp800 30 65 AddtoLine \$WinDataRp Rp800 60 70 AddtoLine \$WinDataRp Rp800 120 75 AddtoLine \$WinDataRp Rp800 240 80 AddtoLine \$WinDataRp Rp800 960 110

```
#}
#Data
```

#Instantiate the grid line x loc=-0.005 tag=top1 spac=0.0005 line x loc=0.0 tag=bot1 spac=0.0005 #line x loc=0.4 tag=bot2 spac=0.001 line x loc=1 tag=bot3 spac=0.001 line x loc=100 tag=bot4 spac=10 region oxide xlo=top1 xhi=bot1 region silicon xlo=bot1 xhi=bot4 init

#set up the equations

solution add name=Fi solve damp !negative

```
if {0.0} {
```

```
solution add name=FV
                       solve damp !negative
                       solve damp !negative
solution add name=FS
solution add name=Int solve damp !negative
solution add name=Vac solve damp !negative
solution add name=I2 solve damp !negative
solution add name=V2 solve damp !negative
                        solve damp !negative
solution add name=FI2
solution add name=F2I3 solve damp !negative
solution add name=FV2 solve damp !negative
solution add name=F3I4 solve damp !negative
#Source Ibo's loop model files
source Loop Params.modified.tcl
source Loop modified.tcl
source Defect.tcl
#proc EORLNuc { InitTempC FinalTempC file} {
```

#proc EORLNuc { InfrempC FinalTempC file} {
set InitTempC 25
set FinalTempC 650
set file Outlancedata

SetTemp \$InitTempC

init inf = "\${file}.str"

pdbSetSwitch Si I DiffModel Numeric pdbSetSwitch Si V DiffModel Numeric

sel z=1.0 name = Nall store sel z=1.0 name = Dall store sel z = 0.33 name=SoR store sel z=Int name=Smic store sel z=Fi name=FV store sel z=1.0 name=Fi store sel z=1.0 name=Int store sel z=1.0 name=Boron store

#loop model stress parameters

sel z=20e-20 name=RpStrain store stressSolve pdbSetDouble Silicon Int K {[Arrhenius 4.97907134361e+14 2.8]} pdbSetDouble Silicon Dall KRp {[Arrhenius 2.9973065794e-07 1.93116264949]}

#pdbSetDouble Silicon Int K {[Arrhenius 4.97907134361e+14 2.7]}
#pdbSetDouble Silicon Dall KRp {[Arr 2.20328492116e-11 1.078589369]}
#pdbSetDouble Silicon Dall KRp 0.1e-15
#pdbSetDouble Silicon Nall K311 {[Arrhenius 38376653.297 2.1804736674]}
pdbSetDouble Silicon Nall K311 {[Arrhenius 360.59 1.2]}

temp\_ramp clear #plot.xy min = {0 1.0e-3} max = {245 14.0}

global ct set ct [open time2e15\_700\_40keV w]

global WinDataDall WinDataNall WinDataRp

if {0.0} { #create equation terms

term name=kickout add eqn= { kf2 \* FS \* Int - kr2 \* Fi} term name=dissociation add eqn= { kf3 \* Int \* FV - kr3 \* FS} term name=I2pair add eqn= { kf4 \* I2 - kr4 \* Int \* Int} term name=Turnbull add eqn= { kf5 \* Fi \* Vac - kr5 \* FS} term name=V2pair add eqn= { kf6 \* Vac\*Vac - kr6 \* V2} term name=IVRecomb add eqn= {  $8.2e-13 * (Int*Vac \ - [pdbGetDouble Si I Cstar]*[pdbGetDouble Si V Cstar])$ } term name=FVreaction add eqn= { kf7 \* FS \* Vac - kr7 \* FV} term name=FVreaction add eqn= { kf7 \* FS \* Vac - kr7 \* FV} term name=Flcomp add eqn= { kf9 \* Fi \* Int - kr9 \* FI2} term name=F2Icomp add eqn= { kf10 \* F12 \* Fi - kr10 \* F2I3} term name=F3Icomp add eqn= { kf14 \* F2I3 \* Fi - kr14 \* F3I4} term name=FsV2 add eqn= { kf12 \* FS \* V2 - kr12 \* FV2}

#Use this to enter equations
proc Myfluoreq { Mat Sol } {

pdbSetString Si FV2 Equation {ddt(FV2) - FsV2 - FVV} pdbSetString Si F2I3 Equation {ddt(F2I3) - F2Icomp + F3Icomp} pdbSetString Si F3I4 Equation {ddt(F3I4) - F3Icomp} pdbSetString Si FI2 Equation { ddt(F12) - FIcomp + F2Icomp} pdbSetString Si FV Equation { ddt(FV) + dissociation - FVreaction - careful + FVV} #pdbSetString Si Fi Equation { ddt(Fi) - \$D1 \* grad(Fi)} pdbSetString Si Fi Equation { ddt(Fi) - \$D1 \* grad(Fi) - kickout + Turnbull + careful + FIcomp + F2Icomp + F3Icomp} pdbSetString Si FS Equation { ddt(FS) + kickout - dissociation - Turnbull + FVreaction - 2 \* FsV2}

#pdbSetString Si I2 Equation { ddt(I2) + I2pair} pdbSetString Si V2 Equation "[pdbGetString Silicon V2 Equation] +careful +FsV2" #pdbSetString Si V2 Equation { ddt(V2) - V2pair + careful- \$D4 \* grad(V2)+ FsV2} #pdbSetString Si Int Equation { ddt(Int) - \$D2 \* grad(Int) + kickout +dissociation - 2 \* I2pair + IVRecomb + FIcomp} pdbSetString Si Int Equation "[pdbGetString Si Int Equation] + kickout + dissociation +FIcomp" pdbSetString Si Vac Equation "[pdbGetString Si Vac Equation] + Turnbull + FVReaction + FVV" #pdbSetString Si Vac Equation { ddt(Vac) - \$D3 \* grad(Vac) + IVRecomb + Turnbull + FVreaction - 2 \* V2pair +FVV}

pdbSetString Oxide\_Silicon Fi Equation\_m2 {-\$sigma1 \* (Fi\_m2 - 1.0e8)} pdbSetString Oxide\_Silicon Int Equation\_m2 {-\$sigma2 \* (Int\_m2 - [pdbGetDouble Si I Cstar])} pdbSetString Oxide\_Silicon Vac Equation\_m2 {-\$sigma2 \* (Vac\_m2 - [pdbGetDouble Si V Cstar])} }

pdbSetString Silicon Fi EquationProc Myfluoreq

SetTemp 650 pdbSetDouble Silicon Fi D0 8e-13

```
set kf2 [DiffLimit Si I .1010]
set kr2 [expr $kf2* [ConcBind Si 0.0 1.5]]
#set kf3 3.5e-16
set kf3 [DiffLimit Si I .41]
set kr3 [expr $kf3 * [ConcBind Si 0.0 3.17]]
set kf4 [DiffLimit Si I .11]
set kr4 [expr $kf4 * [ConcBind Si 0.0 3.5]]
set kf5 [DiffLimit Si {Fi V} .1515210]
set kr5 [expr $kf5 * [ConcBind Si 0.0 6.1]]
set kf6 [DiffLimit Si {V} .167810]
set kr6 [expr $kf6* [ConcBind Si 0.0 2.1]]
set kf7 [expr 1 * [DiffLimit Si V .10]]
#set kr7 1e-3
set kr7 [expr $kf7 * [ConcBind Si 0.0 3.57]]
set kf8 [DiffLimit Si {Fi V2} .20]
set kr8 [expr $kf8 * [ConcBind Si 0.0 9.0]]
```

```
set kf9 [DiffLimit Si {Fi I} 0.0122]
set kr9 [expr $kf9 * [ConcBind Si 0.0 .9764]]
set kf10 [DiffLimit Si {Fi} .0135]
set kr10 [expr $kf10 * [ConcBind Si 0.0 1.2]]
```

```
set kf12 [DiffLimit Si {V2} 0.151]
```

```
set kr12 [expr $kf12 * [ConcBind Si 0.0 2.90]]
set kf13 [DiffLimit Si {V} 0.49101]
set kr13 [expr $kf13 * [ConcBind Si 0.0 7.90]]
set kf14 [expr [DiffLimit Si {Fi} 0.0101]]
set kr14 [expr $kf14 * [ConcBind Si 0.0 1.0]]
set D1 [pdbGetDouble Silicon Fi D0]
set D2 [pdbGetDouble Silicon I D0]
set D3 [pdbGetDouble Silicon V D0]
set D4 1e-20
set sigma1 5e-2
set sigma2 3e-3
; # if {0.0}
set WinDose [CreateGraphWindow]
diffuse init=4e-10 temp=650 time=30 lstress movie = {
  set mt [expr ($time)/( 60.0 )]
  sel z = Nall
  set n [FindDose]
  AddtoLine $WinDataNall SimNall${FinalTempC} $mt $n
  sel z = Dall
  set dl [FindDose]
  AddtoLine $WinDataDall SimDall${FinalTempC} $mt $dl
  set R [expr sqrt($n/($d1*3.14*1.5e15))*1e8]
  AddtoLine $WinDataRp SimRp${FinalTempC} $mt $R
  sel z = Nall
  set n [FindDose]
  sel z = D311
  set d [FindDose]
  sel z = C311
  set c [FindDose]
  sel z = Dall
  set dl [FindDose]
  set mt [expr ($time)/( 60.0)]
# point.xy x = $mt y = log10($n) name = Nall
#
   point.xy x = $mt y = log10($d) name = D311
#
   point.xy x = ty = log10(sc) name = C311
#
   point.xy x = $mt y = log10($dl) name = Dall
  set R [expr sqrt($n/($dl*3.14*1.5e15))*1e8]
# point.xy x = $mt y = $R name = Rp
   sel z = "1.0e-3*D311"
#
#
    set nr [FindDose]
        sel z=log10(Int)
    plot.1d label=Idef-diffused max=0.4
         set list {Vac asimp Fi FI2 F2I3 F3I4 FV FV2 FS Int Vac I2 V2}
           foreach specie $list {
                 sel z=$specie
                 set d [FindDose]
                 if {$d > 1e7 } { AddtoLine $WinDose $specie $time $d}
                 sel z=log10(\{secie\}+1.0\}
                 plot.1d !cle label=${specie} max=0.4
```

```
}
sel z=log10(FV+FS+Fi+FI2+F2I3+FV2+F3I4+1.89e20*exp(-x/0.0028))
plot.1d !cle label=F-sum,present max=0.4
puts -nonewline $ct $mt
puts -nonewline $ct "
puts -nonewline $ct "
puts -nonewline $ct $d
puts -nonewline $ct $d
puts -nonewline $ct $c
```

```
puts -nonewline $ct " "
puts -nonewline $ct $dl
puts -nonewline $ct " "
#puts $ct $nr
```

```
puts $ct " "
```

flush \$ct

}

struct outf = "OutStr/Out\${file}\_\${FinalTempC}.str"

close \$ct

append mesg "Finished on [exec date].\n" append mesg "Simulation took [expr [clock seconds] - \${sec0}] seconds.\n" set outf [open timing.txt a+] puts \$outf \$mesg close \$outf

# APPENDIX B ADDITIONAL SIMS PROFILES

Contained in this appendix section are additional data profiles which were either not included in the major chapters because they were not directly relevant, or are included for the purposes of data archiving. The processing conditions of each sample are included in the figure caption below each figure.



Figure B-1. Boron SIMS results for a 24keV energy fluorine implant with shallow amorphization. The sample is pre-amorphized with 40keV energy  $1 \times 10^{15}$  dose Si, then implanted with  $1 \times 10^{15}$  dose 5keV energy boron and  $2 \times 10^{15}$  dose 24keV energy fluorine.



Figure B-2. Fluorine SIMS results for a 24keV energy fluorine implant with shallow amorphization. The sample is pre-amorphized with 40keV energy  $1 \times 10^{15}$  dose Si, then implanted with  $1 \times 10^{15}$  dose 5keV energy boron and  $2 \times 10^{15}$  dose 24keV energy fluorine.



Figure B-3. Fluorine SIMS results for a 24keV energy fluorine implant with a deep preamorphization. The sample is pre-amorphized with 100keV and 40keV energy  $1 \times 10^{15}$ dose Si, then implanted with  $1 \times 10^{15}$  dose 5keV energy boron and  $2 \times 10^{15}$  dose 24keV energy fluorine.



Figure B-4. Boron SIMS results for a 5keV boron implant into crystalline material. The sample is implanted with  $1 \times 10^{15}$  dose 5keV energy boron and then annealed.



Figure B-5. Boron SIMS results for a 5keV boron implant plus 16keV fluorine implant into crystalline material. The sample is implanted with  $1 \times 10^{15}$  dose 5keV energy boron and  $1 \times 10^{15}$  dose 24keV fluorine and then annealed.



Figure B-6. Fluorine SIMS results for a 5keV boron implant plus 16keV fluorine implant into crystalline material. The sample is implanted with  $1 \times 10^{15}$  dose 5keV energy boron and  $1 \times 10^{15}$  dose 24keV fluorine and then annealed.

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### **BIOGRAPHICAL SKETCH**

Robert Russell Robison was boron in Raleigh, North Carolina, on January 4<sup>th</sup>, 1979. His family moved to Valrico, Florida, when he was two years old and have resided there since that time. In June 1997 he graduated with honors from Bloomingdale High School in Valrico, FL. He went on to pursue undergraduate studies at the University of Florida for a degree in engineering. He was conferred the Bachelor of Science degree with honors in August of 2001. His interest in semiconductor process and devices led him to continue his studies in graduate school at the University of Florida in electrical engineering. There he studied under Mark Law and Kevin Jones in the areas of process simulation, dopant diffusion and activation, and ion implantation. He received the Master of Science degree in May 2003. Upon receipt of the Doctor of Philosphy in 2006, he will join IBM Corporation in Burlington, Vermont.