BORON DIFFUSION WITHIN AMORPHOUS SILICON MATERIALS

By

JEANNETTE MICHELLE JACQUES

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by

Jeannette Michelle Jacques

For Mom.

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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

BORON DIFFUSION WITHIN AMORPHOUS SILICON MATERIALS

By

Jeannette Michelle Jacques

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Chair: Kevin S. Jones Major Department: Materials Science and Engineering

In complimentary metal-oxide-semiconductor (CMOS) devices it is difficult to decrease the depth of source and drain extensions due to dopant diffusion during postimplant processing at elevated temperatures. Our shallowest junctions will be determined by as-implanted dopant concentration profiles and their diffusion during the solid phase epitaxial (SPE) recrystallization process. Boron diffusion characteristics in amorphous silicon material were characterized in order to cultivate a knowledge base for the formation of ultra-shallow p-type transistors via conventional processing techniques.

Boron dopant diffuses in amorphous silicon under a variety of processing conditions, resulting in undesirably deeper junctions. In the absence of annealing, successive germanium, fluorine, and boron implants can lead to enhanced boron motion in amorphous silicon. The combination of these implanted species in the substrate matrix and the use of individual implantation steps can lead to the annihilation of dopant trapping sites in the amorphous network, thereby facilitating room temperature boron diffusion at concentrations below approximately 1×10^{19} atoms/cm³.

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During the SPE process, boron diffuses in amorphous material. Time-averaged boron diffusivities were found to be five orders of magnitude greater than extrapolated values for crystalline silicon, irrespective of the preamorphization species or the presence of co-dopants. The energy barrier for boron diffusion in amorphous silicon is 2.5 eV; 30% lower than the activation energy for diffusion in crystalline silicon (3.75 eV). Species such as fluorine determine the magnitude of boron diffusion during annealing by controlling the recrystallization rate. They are not believed to directly participate in the diffusion process. The effective boron diffusivity is dependent on the dopant concentration profile, suggesting that boron may follow a concentration dependent or trap-mediated diffusion mechanism in amorphous silicon.

Structural relaxation annealing does not impact boron diffusion when fluorine and boron are co-implanted in either self or germanium-amorphized silicon. Similar results are observed when boron is implanted alone in a self-amorphized substrate. However, the magnitude of boron diffusion is retarded in germanium-amorphized material containing boron alone due to an accelerated recrystallization rate. In all cases the relaxation process does not measurably influence the boron diffusivity or level of activation.

CHAPTER 1 INTRODUCTION

Silicon-based microelectronic devices continue to be aggressively scaled in accordance with Moore's Law [Moo65], leading to novel advancements in materials and processing development. Moore's Law suggests that the average dimensions and manufacturing costs of transistors will continuously decrease by a factor of two every 18 to 24 months [Moo65]. Figure 1-1 illustrates the historical trends and future industry projections for the minimum feature size used in integrated circuits fabrication [SIA97]. The integrated circuit was invented by Jack Kilby in 1958 and has evolved into a platform that can integrate tens of millions of transistor components within a square cm of silicon [Plu00]. Figure 1-2 shows micrographs of integrated circuits manufactured in (a) the 1960's and (b) the early 1990's [Plu00]. Attempts are currently under way to reach gigascale integration (GSI), where each chip will have one billion transistors [Hum93]. Integrated circuit technologies pervade our modern society and serve as a major economic driving force.

Metal oxide semiconductor (MOS) transistors are the fundamental structures comprising integrated circuits [Plu00]. A transistor is defined as a three-terminal or contact switching device [May90, Plu00]. Transistors contain a source of charge carriers, a drain or collector of the charge carriers, and a third terminal or gate that modulates and controls the flow of carriers [May90, Plu00]. Electrons and holes are both referred to as charge carriers, electrons being negatively charged and holes being positively charged. N-type and p-type transistors differ in their majority and minority carrier populations

[Mah99]. In an n-type transistor, electrons comprise the majority of charge carriers. Conversely, p-type transistors utilize holes as their majority carriers. In digital circuits, the most basic representation of the switching element is a simple switch that is opened and closed by an isolated control terminal [Plu00]. The open and closed states represent digital 0 and 1 states in binary code [May90, Plu00]. Analog circuits, on the other hand, amplify input signals through a controlled current source [Plu00]. The controlled current is equivalent to an applied input or control signal [Plu00]. Figure 1-3 shows schematic representations of three-terminal devices used in (a) digital and (b) analog semiconductor devices.

The most basic MOS transistor device contains a source, drain, and gate [May90, Plu00]. Figure 1-4 depicts cross sectional views of simple NMOS or n-type devices in three separate states: off, intermediate, and on [Plu00]. The N⁺ regions in Figure 1-4 represent the source and drain extensions [Plu00]. The source and drain serve as contact points for the region under the gate, known as the active portion of the device. They also provide a source of carriers during normal device operation, electrons in NMOS and holes in PMOS devices [Plu00]. The central area of the device located under the gate, as shown in Figure 1-4, is formed by a thin layer of metal on top of an insulating layer on top of the bulk silicon substrate [Plu00]. The device name MOS is derived based on this structure. The substrate in a NMOS device is p-type, containing few electron carriers. Device junctions are usually at zero bias or reversed biased, such that minimal current flows across the junctions [Plu00]. When a negative or zero voltage is applied to the gate, no connection is made between the source and drain regions and devices operate as open circuits. A negative applied voltage attracts positively charged holes to the active region,

inhibiting the flow of current from electrons. Figure 1-4 (a) depicts an open circuit, a state known as accumulation [Plu00]. When a positive voltage is applied to the gate, a vertical electric field is produced across the gate dielectric, attracting electrons toward the surface and repelling holes. A depletion region is formed in the active region below the gate, representing an area in the substrate where there are no mobile carriers. The depletion or intermediate state for an NMOS device is shown in Figure 1-4 (b) [Plu00]. When the applied positive voltage is high enough, electrons can become the majority carriers in a narrow region at the surface below the gate, referred to as the channel region. Under these conditions, the channel becomes n-type during a process known as inversion [Plu00]. When an inversion layer is present, the source and drain regions become connected, forming a closed switch. In this fashion, the gate controls the device state. When the transistor is in an inversion state or on, as shown in Figure 1-4 (c), the gate voltage is proportional to the number of electrons in the inversion layer [Plu00]. The resistance of the inversion layer is dependent upon the gate voltage, making the device current flow a function of the applied gate voltage. This feature enables MOS devices to be used in both analog and digital applications [Plu00]. For PMOS devices, gate voltages opposite in charge to those previously discussed for NMOS transistors facilitate transistor function.

Transistors are primarily used as switches that turn on and off [May90, Plu00]. The speed at which a transistor moves between these two states is referred to as the device switching speed. The switching speed is determined by how fast charge carriers traverse the distance between source and drain extensions within the channel region [May90]. Semiconductor devices are scaled as small as possible in order to decrease carrier travel

distances and improve switching speeds. Faster switching speeds correlate to improved data processing capabilities and lower power consumption. In addition, scaling maximizes the expensive real estate of semiconductor substrates by increasing the device packing factor.

In today's integrated circuits, MOS transistors dominate [Plu00]. For highperformance silicon technologies, ultra-shallow source and drain junction regions are required. Advanced complementary metal oxide semiconductor (CMOS) devices are defined by junctions with low contact and sheet resistances, ultra-shallow extension regions, high surface dopant concentrations, and low junction leakage currents [Mah99]. CMOS devices incorporate both NMOS and PMOS transistors and are thus termed complementary. The performance of MOS circuits depends directly on the magnitude of transistor drive current, which is in turn determined by the series combination of the parasitic series resistance associated with diffusion and contacts and the intrinsic channel resistance [Osb98]. As devices are scaled in size, the channel resistance remains fairly constant when the device dimensions and voltages are scaled proportionately. When device characteristics are not scaled proportionately, the channel resistance varies linearly with the scaling factor. However, the contact resistance increases as the square of the scaling factor, becoming the dominant parameter regarding device performance [Osb98]. The contact resistance R_{co} is related to the sheet resistance of the source and drain R_{sd} , the contact width W, the contact length L_c , the contact resistivity ρ_c , and the transfer length L_t by the expression [Osb98]

$$R_{co} = \frac{\sqrt{\rho_c R_{sd}}}{W \times \tanh(\frac{L_c}{L_t})}$$
(1-1)

The transfer length is defined as the average distance charge carriers travel before meeting the contact [Osb98]. To meet projected device dimensions, as outlined in Figure 1-1, the contact resistance must be reduced for each new technology generation. By decreasing both the sheet resistance of the source and drain extension regions and the transfer length, the contact resistance can be lowered, improving device performance.

Junction depth is a key parameter influencing device scaling [Mah99, Osb98]. The term junction depth is used synonymously with the terms source and drain extension depth. To date, several approaches have been investigated to meet the depth challenges facing advanced transistor devices [Kwo96, Mah99]. However, low-energy ion implantation remains under widespread commercial use for source and drain extension formation [Mah99]. Ion implantation is used to form transistor junctions by introducing doping species into substrate materials, such as silicon [Mah99, May90, Zie04]. When foreign atoms are intentionally introduced, they are aptly termed dopants. Ion implantation is an inherently uniform and reproducible process, providing precise control over doping levels [Mah99, May90, Zie04]. During implantation, a beam of dopant ions is rastered across the sample surface at a fixed energy. Ions subsequently penetrate the sample surface and come to rest at depths determined by their energy and weight [May90, Zie04]. One of the key advantages of the ion implantation technique is that adjustment of the ion beam current and implantation time enables the achievement of a specific dopant concentration [May90, Zie04]. When energetic ions penetrate a sample surface, they experience a trail of collisions with target atoms and electrons, often displacing lattice atoms [Cha96b, Mah99, May90, Zie04]. The high-purity silicon substrates used in conventional semiconductor manufacturing are highly resistive

materials [Bra00]. The introduction of dopants can enable bulk silicon to become highly conductive and suitable for electronic applications. However, in order for dopant species to become electrically active, they must occupy substitutional lattice sites [Bra00, Fey88, May90]. Post ion-implantation, activation annealing techniques are commonly employed to facilitate the placement of dopant atoms onto lattice sites via diffusion and to remove lattice damage caused by the implantation process [Fey88]. During heat treatment, dopant species can diffuse within bulk substrate materials and increase the transistor junction depth. Within crystalline silicon material, dopants have been shown to exhibit anomalous enhanced diffusion during post-implant annealing. Diffusion enhancements exceeding conventional thermal diffusion by more than 100X have been observed. The duration of this phenomenon is highly temperature dependent, decreasing rapidly with increasing temperature [Eag94]. This diffusion enhancement is commonly referred to as transient enhanced diffusion (TED) and impacts all semiconductor dopants to a certain degree.

Novel activation processes have demonstrated that our shallowest junctions will be determined by as-implanted dopant concentration profiles and dopant diffusion during the solid phase epitaxial regrowth (SPER) process [Gab05]. To date, dopant diffusion in amorphous silicon has not been extensively studied. Figure 1-5 portrays boron concentration profiles for samples receiving flash activation annealing [Gab05]. The majority of boron diffusion occurs during SPER, as samples are ramped up to the intermediate temperature (*Ti*). Minimal diffusion, on the order of only 10 Å, occurs during the flash portion of the process. Clearly, dopant diffusion, whether in amorphous or crystalline material, has a direct impact on junction depth.

The various studies presented in this work focus on the technological need for ultra-shallow, low resistivity junctions. They are beneficial not only to the field of materials science and engineering, but also to the semiconductor industry at large. These works offer the following key contributions:

- 1. Observation of room temperature boron diffusion in amorphous silicon resulting from the passivation of trapping sites in the amorphous network by preceding germanium and fluorine implants.
- 2. Evidence of boron diffusion in amorphous silicon during SPER in the absence of additional species, enhanced over phenomena recorded in crystalline silicon under otherwise identical conditions.
- 3. Determination of the roles of germanium, hydrogen, and fluorine in regards to boron diffusion in amorphous silicon.
- 4. Characterization of the effects of structural relaxation on the recrystallization rate of amorphous silicon, boron diffusivity in non-crystalline material, and boron activation in both the presence and absence of fluorine co-doping.
- 5. Characterization of the effects of preamorphization implant species, silicon versus germanium, on boron diffusion characteristics.
- 6. Identification of potential diffusion mechanisms for boron diffusion in amorphous silicon during low temperature annealing.



Figure 1-1: Illustration of the historical trends and future industry projections for the minimum feature size used in integrated circuits fabrication. [SIA97]



Figure 1-2: Micrographs of integrated circuits manufactured in (a) the 1960's and (b) the early 1990's. [Plu00]



Figure 1-3: Schematic representations of three-terminal devices used within (a) digital and (b) analog semiconductor devices.



Figure 1-4: Cross sectional depictions of a simple NMOS or n-type device in three separate states: (a) off (accumulation), (b) intermediate (depletion), and (c) on (inversion). [Plu00]


Figure 1-5: Boron concentration profiles for samples receiving Flash activation annealing. The majority of boron diffusion occurs during SPER, as samples are ramped up to the intermediate temperature (*Ti*). Minimal diffusion occurs during the flash portion of the process. [Gab05]

CHAPTER 2 LITERATURE REVIEW – BULK SILICON AND BULK GERMANIUM

Ion Implantation

Conventional semiconductor processing requires the seamless integration of literally thousands of individual processing steps. These steps can be organized into specific categories, including deposition, photolithography, chemical mechanical polishing, etch, diffusion, ion implantation, test, and packaging [Adv02, Hum93, Mah99, May90]. Each process step must have an average success rate of at least 99% in order to successfully manufacture a silicon-based CMOS product line.

Ion implantation is used to form transistor junctions by introducing doping species into substrate materials, such as silicon [Mah99, May90, Zie04]. When foreign atoms are intentionally introduced into a substrate material, they are referred to as dopants. Ion implantation is an invariant and repeatable process, providing precise control over resultant doping levels [Mah99, May90, Zie04]. During implantation, a beam of doping ions is rastered across the sample surface at a fixed energy. Ions then penetrate the sample surface and come to rest at depths determined by their energy and weight [May90, Zie04]. The implant dose Q_I is measured in ions/cm². The dose is defined as follows, where F_I is the flux of incident ions given in ions/cm² s and t_I is the time given in seconds that the ion beam was incident on the sample surface [May90]:

$$Q_I(\underset{cm^2}{\text{ions}}) = F_I(\underset{cm^2s}{\text{ions}}) t_I(s)$$
(2-1)

A flux of ions, with a charge q_I per ion, represents a current that can be directly measured with a current meter. The ion current q_IF_I often fluctuates with time, such that the total integrated charge C_I is provided in Coulombs for a given implant time t_I [May90].

$$C_I = \int_0^u q_I F_I dt \tag{2-2}$$

For singly and doubly ionized species, q_I is a constant of 1.6×10^{-19} C or 3.2×10^{-19} C, respectively [May90]. The total number of implanted dopants/cm² is calculated according to the following relation where *A* is the area of the implanted surface given in cm²:

$$Q_I = \frac{C_I}{q_I A},\tag{2-3}$$

One of the key advantages of the ion implantation technique is that adjustment of the ion beam current and implantation time enables the achievement of a specific dopant concentration [May90, Zie04]. These concentrations can range over six orders of magnitude from 10^{15} to 10^{21} dopants/cm³ [May90]. Another primary advantage of implantation is that only selected areas can be implanted, through the use of masking materials [Mah99, May90, Zie04]. Masking layers must be greater in thickness than the penetration depth of the energetic ions and can be comprised of a variety of materials, including photo-resist and silicon dioxide or silicon nitride. These materials can be thermally grown on the sample surface or deposited. Masking layers are only present over areas where implantation is not desired and are removed for subsequent processing steps [May90]. Figure 2-1 illustrates ion implantation into a silicon wafer, where portions of the sample are masked by a SiO₂ layer whose thickness is greater than the ion penetration range.

Ion implantation tools are systems comprised of an ion source, acceleration tube, and target chamber [May90, Zie04]. Figure 2-2 shows a diagram of a commercial ion implantation system, detailing the tool layout [May90]. Dopant atoms are initially introduced into the ion source in the form of a gas or vapor. Vapors are commonly generated from a liquid or solid that is heated in an oven connected to the ion source. The materials used are highly dependent upon the species implanted and whether they are more stable in a gaseous, liquid, or solid form during transport and storage [May90, Zie04]. Once in the source, dopant atoms are ionized by energetic electrons emitted from a nearby hot filament. These electrons collide with the clouds of atomic electrons surrounding the dopant atoms, knocking electrons out of their orbits and ionizing the dopant atoms. If only one electron is lost, a positive charge of e results and the ion is termed singly ionized. If two electrons are lost, an ion is doubly ionized with a positive charge of 2e [May90]. These positively charged dopant ions are then extracted through an aperture in the ion source and moved into the acceleration tube. The tube is an insulating column that contains a vacuum whose effective pressure draws and accelerates ions from the ion source to the target chamber, without colliding with residual gas atoms in the tube. The ion source is maintained at a positive voltage V_I , referred to as the acceleration voltage potential. Ions exit the acceleration tube with an energy $q_I V_I$ and velocity v_I . M_I denotes the mass of the dopant atom and is related to the ion energy and velocity according to the following expression [May90]:

$$\frac{1}{2}M_{I}v_{I}^{2} = q_{I}V_{I} \tag{2-4}$$

An analyzing magnet is also contained within the acceleration tube [May90, Zie04]. The ion source produces a multitude of ion species, but only specific species, such as ¹¹B⁺, are desired for implantation. Ions are deflected by a magnetic field applied directly normal to their path. The force *F* on the ions is defined as $F = q_I(v_I \times B)$, where *B* is the magnetic

flux density [May90]. In a homogeneous magnetic field, charged particles move in a circular path. The velocity and charge of a particle are unaffected by deflection in the magnetic field; however, they experience a centripetal force *F* calculated as $F = \frac{Mrvr^2}{r}$, where *r* is the radius of their path. With the appropriate substitutions, *r* can also be represented as [May90]

$$r = \frac{1}{B} \left(\frac{2M_I V_I}{q_I} \right)^{\frac{1}{2}}$$
(2-5)

In addition to deflection by an analyzing magnet, ions are directed toward the sample surface with the assistance of electrostatic lenses and deflection plates. A mono-energetic beam of ions is supplied to the target chamber and rastered over the sample [May90].

When energetic ions penetrate a sample surface, they experience a trail of collisions with target atoms and electrons [Cha96b, Mah99, May90, Zie04]. The ion range *R* is dependent upon the rate of energy loss along the ion path dE/dx according to the mathematical expression [May90]

$$R = \int_{E_0}^{0} \frac{1}{dE/dx} dE$$
(2-6)

where E_o is the incident energy of the ion. The term dE/dx is negative in sign, as it represents an incremental energy loss. Similarly, *R* can also be defined in terms of the ion energy *E*, the number density of target atoms *N*, and the effective stopping power of the solid *S*(*E*) [Mah99].

$$R = \frac{1}{N} \int_{E}^{0} \frac{dE}{S(E)}$$
(2-7)

The primary factors influencing R are the ion energy, the atomic number of the incident ion, and the atomic number of the target material [May90, Zie04]. All ions do not have

the same range, even when they are of similar type, because the distance traveled between collisions and the amount of energy lost in each collision is a random event. Instead, a range distribution exists. In ion implantation, the total distance *R* traveled by an ion is not as important as the projection of *R* normal to the sample surface, commonly referred to as the projected range and denoted as R_p [Mah99, May90, Zie04]. The ion range distribution is Gaussian in nature [Mah99, Zie04]. The projected range distribution N(x) is represented as a 1-D Gaussian profile with a mean value of R_p , standard deviation ΔR_p from the mean, and maximum R_p concentration of N_{max} . These parameters are related by the mathematical equation [May90]

$$\frac{N(x)}{N_{\max}} = \exp\left[-\frac{1}{2}\left(\frac{x-R_p}{\Delta R_p}\right)^2\right]$$
(2-8)

For a Gaussian distribution, the full width Δx_p at half-maximum (FWHM) is given by the relation $\Delta x_p = 2(2\ln 2)^{\frac{1}{2}} \Delta R_p = 2.35 \Delta R_p$ and the accompanying integral [May90]

$$\int_{0}^{\infty} N(x) dx = N_{\max} (2\pi)^{\frac{1}{2}} \Delta R_{p} = Q_{I}$$
(2-9)

Figure 2-3 depicts a physical representation of the Gaussian range distribution for implanted ions [May90]. The concentration depth distribution $N_I(x)$ in atoms/cm³ is defined by [Mah99, May90]

$$N_I(x) = \frac{Q_I}{(2\pi)^{\frac{1}{2}} \Delta R_p} \exp\left[-\frac{1}{2} \left(\frac{x - R_p}{\Delta R_p}\right)^2\right]$$
(2-10)

As a rough approximation, the average dopant concentration $N_I(ave)$ can be calculated according to $N_I(ave) \cong \frac{Q_I}{\Delta x_p} \approx \frac{Q_I}{R_p}$ [May90]. For moderate mass ions, such as arsenic or phosphorus implanted into bulk silicon, $\Delta x_p \approx R_p$. Through ion implantation techniques, very high dopant concentrations can be achieved in near surface regions, ideal for the fabrication of integrated circuits [May90, Zie04]. Lighter ions exhibit greater penetration depths than heavier ions and ion ranges increase roughly linearly with implant energy [Mah99, May90]. Figure 2-4 illustrates the projected ranges of dopants as a function of implant energy, demonstrating the aforementioned dopant penetration trends [Mah99].

Implanted ions experience penetration fluctuations in both the vertical and lateral directions [Mah99, May90, Zie04]. Transverse or lateral straggle (ΔR_t) occurs in a direction perpendicular to the incident ion path. Lateral straggle is used to determine the level of ion penetration at mask edges into regions where ion implantation is not desired. Figure 2-5 shows the lateral distribution of ions implanted into silicon with straight-wall oxide masks. Straight edged masks demonstrate less transverse straggle than those with tapered or undercut edges [May90]. The concentration depth distribution calculation shown in Equation 2-9 does not incorporate the effects of lateral straggle, introducing error when determining ion concentrations near implant mask edges [Mah99].

For single crystal materials, such as bulk silicon, the orientation of the incident ion beam to the crystallographic substrate axis can also dramatically impact resultant ion profiles [May90, Zie04]. When the beam is aligned parallel to the substrate axis, a significant distribution of the incident ions can penetrate the sample to depths several times greater than the anticipated R_p . On the other hand, when the beam is oriented away from the substrate axis, at an angle of 7°, no ion channeling beyond the calculated R_p is observed [May90, Zie04]. Crystal orientation effects are generally referred to as channeling effects. Ions moving within the channels or open spaces between atomic planes do not experience collisions with lattice atoms and have lower rates of energy loss,

which correspond to greater penetration into the sample surface [Mah99, May90, Zie04]. Figure 2-6 portrays the "openness" of the (100) diamond cubic silicon lattice, as well as ion trajectories in an axial channel for different entrance angles. During channeling, ions lose energy and eventually come to rest due to Coulombic interactions [Mah99, Zie04].

The energy loss rate dE/dx of an energetic ion is determined by its collisions with substrate atoms and electrons. Two energy loss mechanisms can occur, namely nuclear and electronic [Mah99, May90, Zie04]. Nuclear loss arises from collisions with substrate atoms, while electronic loss occurs due to collisions with substrate electrons, whereby they are excited and ejected from their orbital. The energy loss rate can be defined as follows, where the subscripts *n* and *e* denote nuclear and electronic collisions, respectively [Mah99, May90]:

$$\frac{dE}{dx} = \frac{dE}{dx}_{n} + \frac{dE}{dx}_{e}$$
(2-11)

The energy losses of these mechanisms are presumed to be both independent and additive, as originally theorized by Lindhard, Scharff, and Schiott in 1963 [Mah99]. Nuclear collisions result in large discrete energy losses and small angular deflections in the trajectory of the incident ion [Mah99, May90, Zie04]. These collisions are responsible for the generation of lattice disorder by displacing substrate atoms from their lattice sites. Electronic collisions result in much smaller energy losses, large angular deflections, and no measurable lattice disordering [Mah99, May90, Zie04]. The magnitude of the contributions from these two separate mechanisms to the total energy loss rate depends on the incident energy and atomic number of the ion. As shown in Figure 2-7, the nuclear and electronic loss mechanisms contribute to the total energy loss to varying degrees based on the ion species and implant energy [Mah99]. Nuclear losses

dominate at low implant energies, while electronic losses are more prevalent at high energies. The crossover point between these two mechanisms is determined by the mass or weight of the implanted species. For example, when ¹¹B⁺, ³¹P⁺, and ⁷⁵As⁺ are implanted into bulk silicon, electronic losses become predominant at implantation energies of 10 keV, 130 keV, and 700 keV, respectively [Mah99]. Both of these energy loss mechanisms must be factored into ion range calculations. For light or low atomic number species, such as boron, electronic collisions are dominant over the entire ion trajectory. However, heavy elements, such as arsenic, have nuclear losses 10X greater than electronic losses [May90]. For implants where nuclear collisions dominate, the projected range may be alternately calculated by the following relationship [May90]:

$$R_{p} = \int_{E_{o}}^{0} \frac{1}{dE / dx} dE = \frac{E_{o}}{dE / dx_{n}}.$$
(2-12)

An implanted ion can generate a trail of damage through nuclear collisions that displace lattice atoms [Cha96b, Mah99, May90, Zie04]. A damage cascade is formed when energy is transferred from an incident ion to a lattice atom, displacing it and enabling it to displace additional lattice atoms, and so on. These collisions result in a range of defects, including point defects and amorphous regions [Mah99, May90, Zie04]. An interstitial point defect is described as an atom located in the space between lattice atoms, while a vacancy point defect represents an empty site within a crystal lattice. A Frenkel pair is defined as a vacancy-interstitial pair that is formed when an atom is displaced from a lattice site into an interstitial site. Each implanted ion can generate up to 100 point defects before coming to rest within the lattice [Cha96b]. Heavy ions, such as antimony, produce dense collision cascades and damage [May90]. Light ions, such as boron, participate in a limited number of nuclear collisions and result in dispersed areas of lattice damage, as shown in Figure 2-8 [Mah99]. During ion implantation, each ion creates a damage cascade. As more ions are introduced into the substrate, their respective cascades can overlap and produce an amorphous layer. Amorphous regions are defined as exhibiting no long-range crystallographic order. Nearest neighbors may still participate in covalent bonding, but their bond angles and lengths are distorted as compared to crystalline material. In order for a silicon atom to be displaced from its lattice site and create a vacancy, an energy barrier of 3.6 eV must be overcome for each Si-Si bond [Dan86]. Both light and heavy ions have the ability to amorphize substrate materials, under the appropriate implantation conditions. Depending upon the application at hand, the generation of an amorphous layer in semiconductor materials may not be desirable. Ion implantation is a highly effective technique for introducing dopant species into materials and may be tailored to fit the specific needs of a range of electronic devices.

Dopant Activation, Diffusion, and Transient Enhanced Diffusion (TED)

The high-purity silicon substrates used in conventional semiconductor manufacturing are highly resistive materials [Bra00]. The introduction of dopants can enable bulk silicon to become highly conductive and suitable for electronic applications. However, in order for dopant species to become electrically active, they must occupy substitutional lattice sites [Bra00, Fey88, May90]. Post ion-implantation, activation annealing techniques are commonly employed to facilitate the placement of dopant atoms onto lattice sites via diffusion and to remove lattice damage caused by the implantation process [Fey88]. Dopants are commonly non-isovalent, having fewer or more valence electrons than substrate atoms. This difference enables doping elements to contribute either holes to the valence band or electrons to the conduction band, respectively. An

increase in the electron or hole concentration can effectively increase the conductivity of a substrate material; very high doping levels are desirable in many electronic devices.

Diffusion in solids is described as the migration of atoms within a lattice. The rate of mass transfer is termed the diffusion flux *J* and is described as follows:

$$J = \frac{M}{At}$$
(2-13)

Where *M* represents the mass diffusing through and perpendicular to a unit cross section of area *A* per unit time *t* [Cal97]. If the diffusion flux does not change as a function of time, a steady-state condition exists. In this case, the diffusion flux is linearly related to the concentration gradient $\frac{dC}{dx}$ and diffusion coefficient *D* according to Fick's First Law [Cal97]. The diffusion flux is negative because atoms flow down a concentration gradient, moving from regions of higher to lower concentration [Cal97].

$$J = -D\frac{dC}{dx}$$
(2-14)

In most situations the diffusion flux and concentration gradient change as a function of time, denoting nonsteady-state conditions. In this case, Fick's second law applies, whereby a partial differential equation relates the diffusion coefficient and concentration C as functions of both time t and position x [Bra00, Cal97].

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \tag{2-15}$$

The magnitude of diffusion is influenced by the identity of the diffusing species and the solid matrix, as well as temperature [Bra00, Cal97]. The diffusion coefficient is commonly denoted as [Cal97, Nic89]

$$D = D_o e^{\left(\frac{-Q_D}{RT}\right)} \tag{2-16}$$

Where the parameters D_o , Q_D , R, and T represent the temperature-independent preexponential, activation energy for diffusion, universal gas constant, and absolute temperature, respectively.

During heat treatment, dopant species can diffuse within bulk substrate materials. Diffusion is defined as the migration of atoms from lattice site to lattice site [Cal97]. There are several well-established mechanisms by which atoms may diffuse within solid materials, such as silicon [Bra00, Cal97]. Atoms can theoretically diffuse through either direct or indirect mechanisms [Bra00]. The direct diffusion of elements occupying substitutional sites occurs by a direct exchange between elements and adjacent atoms. A ring mechanism depicting direct diffusion is illustrated in Figure 2-9 (a) [Bra00]. To date, no experimental evidence has been found to support this type of diffusion [Bra00, Nic89]. The diffusion of elements via indirect mechanisms is energetically more favorable. Elements can diffuse indirectly without the assistance of defects by utilizing interstitial lattice sites, as shown in Figure 2-9 (b) [Bra00]. Indirect diffusion mechanisms can also proceed in conjunction with intrinsic point defects, such as vacancies and interstitials. In these cases, elements behave as either vacancy or interstitialcy mediated, respectively. Isolated point defects and substitutional impurities form next-nearest AV (dopant-vacancy) and AI (dopant-interstitial) defect pairs due to Coulombic attractions that minimize local strain effects [Bra00]. Examples of these interactions are illustrated in Figure 2-9 (b) [Bra00]. Based upon lattice distortion effects, smaller dopant elements, such as boron, are likely to attract self-interstitials and repel vacancies [Azi97, Bra00]. The opposite is true for larger species, such as arsenic or phosphorus [Bra00]. During vacancy mediated diffusion, the AV pair partially dissociates. To complete the diffusion

step, the vacancy has to diffuse more than three nearest-neighbor lattice sites and return along a different path than that taken by the diffusing element. However, interstitial mediated diffusion can only occur if the AI pair does not dissociate during the diffusion process [Bra00].

Within crystalline material, dopants have been shown to exhibit anomalous enhanced diffusion during post-implant annealing. Diffusion enhancements exceeding conventional thermal diffusion by more than 100X have been observed. The duration of this phenomenon is highly temperature dependent, decreasing rapidly with increasing temperature [Eag94]. This diffusion enhancement is commonly referred to as transient enhanced diffusion (TED). All dopants undergo TED to a certain degree; however, interstitial diffusers experience the greatest diffusion enhancement. TED occurs as a result of an excess point defect population in the vicinity of implantation damage. A flux of interstitials moves outward during annealing, promoting dopant diffusion. The initial interstitial supersaturation is more than five orders of magnitude higher than the equilibrium value, drastically decreasing during the first second of annealing [Bon96].

In the initial stages of TED, some interstitials are lost by recombination of Frenkel pairs, diffusion to the surface, and migration towards the substrate where they form defect clusters [Cow99a, Cow99b, Cow00]. During annealing, stable clusters known as {311} defects are believed to nucleate and emit a portion of the interstitials that drive TED [Cow99a, Cow99b, Cow00, Eag94, Jon97]. Eaglesham et al. used transmission electron microscopy (TEM) to demonstrate that {311} defects are rod-like structures that precipitate on {311} planes as a single monolayer of hexagonal silicon and run in <110> directions [Eag94]. The densities of both {311} defects and dislocation loops decrease

rapidly as they grow in size [Eag94, Jon97]. They experience Ostwald ripening during annealing, dissolving through the release of interstitials [Eag94, Jon97]. During the coarsening process, most of the excess interstitials are stored within dislocation loops [Bon96]. The flow of interstitials between dislocation loops as they grow in size maintains a supersaturation of silicon self-interstitial atoms in the bulk, facilitating dopant diffusion [Bon96].

Short time diffusivity enhancements have been found to be independent of ion implantation dose, as defect clusters control the number of interstitials available to partake in TED [Cha96a]. Only the number of these defects, not their size, is determined by higher dose (i.e. $> 1 \times 10^{13}$ atoms/cm³) implant conditions [Cha96a]. Jones et al. demonstrated that as the implant temperature rises, the magnitude of interstitial backflow into the crystalline silicon decreases [Jon97]. This observation was correlated to a rise in the dislocation loop density, suggesting that loops act as barriers to interstitial backflow.

In the case of boron doping, subsequent annealing can also lead to the formation of boron interstitial clusters (BIC's) [Man01b, Sch00]. These clusters typically form at concentrations roughly one order of magnitude below the solid solubility level for boron in silicon and are electrically inactive, immobile structures [Man01b, Sto95]. BIC nucleation occurs in regions where implant damage coincides with the implanted boron profile [Man01b], requiring an activation energy of approximately 0.9 eV [Sch00]. In the peak region of the boron concentration profile, nearly all of the boron is clustered when the level of boron incorporation approaches the solid-solubility limit [Sch00]. BIC's can dissolve and release interstitials upon further annealing, exhibiting a rate dependence defined by the surrounding interstitial concentration [Man01b]. As-nucleated BIC's

prefer boron-rich configurations, however, during annealing an increase in the siliconinterstitial component increases BIC stability [Man01b]. Boron is not believed to occupy a unique site within BIC structures [Sch00]. The transition of boron atoms from clusters to substitutional lattice sites is believed to be the rate limiting step for both the production of silicon-interstitial-rich BIC's [Sch00] and the BIC dissolution process [Mir03]. Boron atoms are released with a mean activation energy of 2.3 eV and the diffusion of boron away from BIC's has not been shown to inhibit the further release of boron atoms from these clusters [Sch00].

Determination of Dopant Diffusion Mechanisms

Investigations of the diffusion mechanism and behavior of boron within silicon lead to the development of several novel processing and analysis techniques. Fahey et al. [Fah83, Fah85, Fah89a] were the first to utilize nitridation and oxynitridation reactions to investigate the influence of surface point defect populations upon dopant diffusion. Nitridation involves the exposure of bare silicon to an ambient of ammonia gas during high temperature annealing, resulting in the formation of silicon nitride. Oxynitridation, on the other hand, relates to the exposure of silicon dioxide to an ammonia gas ambient and the growth of an oxynitride material. During these reaction processes, point defects are injected into the surface regions of the silicon material. A supersaturation of vacancies was observed during nitridation, while interstitials were injected during oxynitridation in silicon.

Fahey et al. [Fah85, Fah89a] applied their knowledge of dopant interactions in the presence of point defects to determine the diffusion mechanisms of several common dopants in silicon. The fractional interstitial composition (F_i) is a measure of the degree of influence that interstitials have upon the diffusion of a given dopant species. For

example, a large F_i value designates that a particular species diffuses primarily by an interstitial-mediated mechanism, as opposed to a vacancy-mediated mechanism. If $F_i = 1$, then a dopant is shown to diffuse by a pure interstitial mechanism and a large interstitial defect population will lead to enhanced diffusion of the species. The fractional vacancy composition is designated as F_v , where $F_v = 1$ - F_i . The fractional interstitial and fractional vacancy compositions serve as benchmark values by which the diffusion characteristics of various dopants may be compared in a common substrate material in the same temperature range.

A groundbreaking technique for determining F_i values was also established by Fahey et al. [Fah85, Fah89a]. No initial assumptions were made regarding the generation rates of point defects, nor were relationships assumed to exist between the interstitial and vacancy concentrations. The fractional interstitial composition was defined as:

$$F_{iA} = \frac{\frac{\langle D_A \rangle}{D_A *} - \frac{\langle C_V \rangle}{C_V *}}{\frac{\langle C_i \rangle}{C_i *} - \frac{\langle C_V \rangle}{C_V *}}$$
(2-17)

Where C_i and C_v are the silicon interstitial and vacancy concentrations respectively, * denotes equilibrium conditions, <> designate time averaged quantities, and F_{iA} denotes the fractional interstitial composition of dopant A. A minimum value for F_{iA} is obtained when it is assumed that $\frac{\langle C_i \rangle}{C_i^*} = 0$ during direct nitridation and a maximum value is obtained when it is assumed that $\frac{\langle C_V \rangle}{C_V^*} = 0$ during oxynitridation. Equation 2-17 can be

rearranged to yield Equation 2-18.

$$\frac{D_A}{D_A*} = \frac{F_i C_i}{C_i*} + \frac{F_V C_V}{C_V*}$$
(2-18)

If the aforementioned assumptions are substituted into Equation 2-18, we yield the following under nitridation and oxynitridation processes, respectively:

$$\frac{D_A}{D_A*} = \frac{F_V C_V}{C_V*} \tag{2-19}$$

$$\frac{D_A}{D_A*} = \frac{F_i C_i}{C_i*} \tag{2-20}$$

By definition, F_i and F_v have a maximum value of one. Thus, the initial assumptions regarding defect generation during processing lead to the conservative estimate that during nitridation and oxynitridation annealing, respectively,

$$\frac{D_A}{D_A*} \le \frac{C_V}{C_V*} \qquad \text{and} \qquad \frac{D_A}{D_A*} \le \frac{C_i}{C_i*} \qquad (2-21, 2-22)$$

In the absence of direct measurements of the evolution of respective vacancy and interstitial populations, Fahey et al. [Fah85, Fah89a] simply made comparisons between different species examined under identical processing conditions.

By inputting diffusion data obtained for various anneal times at a given diffusion temperature, two ranges of values are obtained when all of the previously described assumptions are employed for the respective processing regimes. An overlap in F_{iA} ranges obtained during nitridation and oxynitridation is required to maintain selfconsistency within a given data set. The point of overlap is taken as the estimated F_{iA} value for the dopant species A for a given substrate material at a particular anneal temperature. Fahey et al. determined the fractional interstitial composition of arsenic in silicon to be between 0.3 and 0.4 at 1100°C [Fah85], which is in close agreement with subsequent calculations reported by Cowern where F_{iAs} is reported as 0.4 at 1100°C [Cow98]. These data indicate that arsenic is primarily a vacancy mediated diffuser, with a measurable interstitial dependence. Boron has been shown to be an interstitial mediated diffuser with a fractional interstitial composition approaching a value of one [Fan96a, Gos97, Ura99a]. The value of F_{iB} is considered constant for temperatures ranging from 800°C to 1200°C [Nic89] and suggests that boron has no measurable vacancy dependence in regards to diffusion. Recent studies have also found boron to exhibit similar F_{iB} values in silicon-rich SiGe alloys containing 0 to 20 at% germanium [Fan96a].

Features of the Amorphous Silicon Network

For the past thirty years, understanding and characterizing the nature of amorphous silicon has been a topic of profound interest. Radical distribution function (RDF) analysis was used as early as the 1950's to demonstrate that the diamond cubic structure of crystalline silicon and germanium is cursorily maintained in their amorphous counterparts [Gra70, Ric58, Weg96]. RDF data is obtained by x-ray diffraction analysis, providing information regarding the bond-angle deviation and average coordination number for a given sample [Izu04]. The second nearest neighbor peak is broadened and lacks sharpness for amorphous materials, as compared to crystalline specimens, indicating a range or distribution of distances between atoms. In addition, the third nearest neighbor peak is not well defined for amorphous samples, suggesting a loss of long range ordering, as expected for amorphous silicon [Gra70, Ric58, Weg96].

Amorphous silicon is not defined by one particular state, as it is highly dependent on the fabrication methodology employed [Ish02, Mer05]. For example, Laaziri et al. demonstrated that amorphous silicon generated via sputtering or vacuum evaporation can contain numerous defects and impurities, including voids [Laa99]. Materials formed by self-ion implantation techniques, on the other hand, were shown to have a more stable structure defined by dangling silicon bonds and an average coordination number of only 3.88 [Laa99]. Simulations of the amorphous silicon microstructure support these experimental results. Recent studies of cryo-ion implantation by Izumi et al. imply that dangling (3-fold coordinated rings) and floating bonds (5-fold coordinated rings) [Ish02], as well as 4 member rings permeate the amorphous state, representing the accumulation of implant damage [Izu04]. The calculated cohesive energy of amorphous silicon has been reported to be approximately 0.33 eV per atom lower than that of an ideal diamond structure, in agreement with the assertion that unpassivated bonds exist in amorphous materials [Uda87].

Amorphous silicon demonstrates short-range order (SRO), rather than the longrange order (LRO) definitive of crystalline material [Weg96, Zal83]. Figure 2-10 contains a ball and stick representation of amorphous and crystalline silicon, as constructed by the tight-bonding molecular dynamics model, illustrating the structural ordering of these two different materials [Kug04]. Graczyk et al. have reported bond angle fluctuations of 9% within the SRO of amorphous silicon [Gra70]. According to Van der Weg et al., the distribution of bond angles exhibits a spread of about 8° around the tetrahedral bond angle of 109° [Weg96]. For amorphous silicon formed via ion implantation, Sinke et al. have calculated the average energy needed to break highly strained bonds in as-implanted material to be only 0.5 eV [Sin88]. However, in order for a dangling bond to form in crystalline silicon, an energy barrier of 3.6 eV must be overcome [Dan86].

Despite the inherent structural differences between crystalline and amorphous silicon, their densities are very close in value with amorphous silicon reported to have a density 1.8% lower than crystalline silicon [Weg96]. The lower density of amorphous silicon has been attributed to the presence of bonding defects in the amorphous network,

including under-coordinated or dangling bonds [Laa99]. The microstructure of amorphous silicon is known to possess dangling, floating, and strained silicon bonds, as well as a relatively open structure. The level of openness and the number of nontetrahedrally coordinated or strained bonds depends on the fabrication method [Weg96].

Due to the nature of their structures, point defects are not defined in the same manner for amorphous and crystalline silicon. In crystalline materials, an interstitial point defect is described as an atom located in the space between lattice atoms, while a vacancy point defect represents an empty site within a crystal lattice. In amorphous silicon, 3-fold (T3) and 5-fold (T5) coordinated rings have been proposed as conjugate primitive defects [Pan86]. The T3 and T5 structures are termed dangling and floating bonds, respectively [Ish02, Pan86]. The canonical configuration of a T3 ring is a central atom with nearest neighbors at three of four possible tetrahedral directions. A T3 ring has three sp³ hybrids forming bonding and antibonding states with three out of the four linear combinations that can be constructed by use of the four s and p bonding orbitals of the central atom. The fourth linear combination remains unbonded, suggesting that a dangling bond can be considered a vacancy-like defect [Pan86]. The canonical configuration of a T5 ring is a central atom with nearest neighbors at each of the possible tetrahedral directions, plus a "fifth" neighbor at a site directly across from one of the other four nearest neighbors. A T5 ring has four s and p orbitals on the central atom forming bonding and antibonding states with four out of the five linear combinations that can be constructed by use of the 5 sp³ hybrids pointing towards the central atom; the fifth linear combination is unbonded forming an interstitial-like defect [Pan86].

A variety of defect pairs and configurations are believed to occur within the amorphous silicon network. For instance, a T3-T5 pair can be created by bond switching in the amorphous structure, enabling a T5 structure to move away from a T3 structure [Pan86]. A particular T5 site does not migrate through the network; instead it passes the extra bond from one silicon atom to another through small atomic movements [Pan87]. The activation energy for bond switching is smaller than the energy required for bond breaking [Pan86, Pan87]. Additionally, structures such as a T2 or a T3-T3 pair can be formed in the network, suggesting that atomic diffusion and doping processes in amorphous structures can be quite complicated [Pan86]. Numerous defect types are postulated to exist within amorphous silicon material. However, the precise structure of amorphous silicon remains widely uncharacterized.

Solid Phase Epitaxial Regrowth

At annealing temperatures well below the melting temperature of silicon, amorphous silicon reorders via solid phase epitaxial regrowth (SPER) [May90]. For SPER to occur, a layer or region of amorphous silicon must reside on a crystalline silicon substrate, forming a planar amorphous/crystalline (a/c) interface [Mah99]. During annealing, the a/c interface is maintained and moves toward the surface of the amorphous material. The orientation of the resulting crystalline region is replicated from the underlying crystalline substrate, which serves as a structural template [Mah99]. The thickness of the amorphous layer decreases linearly with annealing time, denoting a constant growth velocity for undoped (100) silicon [Cse78, May90]. The recrystallization velocity V_g is related to temperature through an Arrhenius relationship, where V_o is a preexponential factor, *Ea* is the activation energy for regrowth, *k* is Boltzmann's constant, and *T* is the temperature in degrees Kelvin [May90].

$$V_g = V_o e^{\left(\frac{-Ea}{kT}\right)}$$
(2-23)

The activation energy for SPER of silicon is approximately 2.3 eV [Cse75, Lic86, Sun82b]. During low temperature SPER, the substitutional impurity concentration increases with implant dose and can saturate at concentrations above the solid-solubility limits [Wil82]. SPER can be induced by a multitude of processes, including low temperature furnace annealing [Cse77, Mah99, May90, Sun84], laser annealing [Bean79, Gat78, Wil78], rapid thermal annealing [Ade88], and electron beams [McM80, Reg79]. The basic crystallization phenomena are similar, irrespective of the time and temperature ranges associated with these different heating methods [Wil83].

The SPER rate is highly dependent upon substrate orientation [Cse78] and the nature of impurity species [Ade88, Cse77, Ken77, Sun82a, Sun82b, Sun84, Wil83]. For example, silicon recrystallization is fastest in the <100> direction and slowest in the <111> direction [Cse78]. The presence of lattice impurities can dramatically impact the SPER process. Hydrogen, oxygen, carbon, nitrogen, and argon have been shown to inhibit the recrystallization of amorphous silicon [Ade88, Ken77, Rot90, Wil83]. Halogen species, including fluorine and chlorine, and noble gases such as neon, argon, and krypton also retard SPER [Ken77, Sun84]. Both fluorine and chlorine pile up at the a/c interface and impede its motion during SPER [Sun84]. Single implants of boron, arsenic, and phosphorus, present in low at% concentrations, increase the regrowth rate of silicon [Cse77, Ell98b, Sun82a, Sun82b, Wil83]. At high concentrations, the precipitation of arsenic into impurity clusters is attributed with limiting the silicon regrowth rate [Sun82a]. Suni et al. characterized the effects of multiple dopant species on SPER, demonstrating that shallow impurities of the same dopant type mutually enhance their

effect on regrowth rates, while impurities of opposite dopant types compensate their rate effects and behave similarly to intrinsic silicon [Sun84].

At present, two contrasting theories are attributed with explaining the observed impacts of dopant species on the SPER rate; namely stress relaxation and electronic impurity effects. Fundamental studies by Suni et al. have demonstrated that local stresses between impurity and lattice atoms can significantly affect regrowth rates at the a/c interface [Sun82b]. A stress relief mechanism is believed to account for the boron enhanced regrowth rates of bulk silicon, as recrystallization at the a/c interface occurs primarily through bond rearrangement [Sun82b]. Silicon regrowth velocities were similarly shown to increase exponentially with an applied environmental stress, impacting recrystallization kinetics [Lu91, Nyg85]. Lu et al. also demonstrated that defects residing at the a/c interface are responsible for governing the SPER processes of bulk silicon and germanium [Lu91]. Their detailed analysis determined that the various theories regarding the diffusion of interstitial and vacancy defects from the amorphous or crystalline phases to the a/c interface during SPER are not plausible regrowth mechanisms. Dangling bonds are believed to be the dominant defects involved in the recrystallization process [Lu91]. Adekoya et al. confirmed these assertions by illustrating the retardation affects of hydrogen upon SPER [Ade88]. Hydrogen atoms are known to passivate dangling silicon bonds [Bro79, Kap78] and are attributed with passivating a/c interfacial sites during annealing, resulting in lower regrowth rates. The ability of dangling bonds to serve as recombination centers may also contribute to a faster recrystallization process, if recombination occurs at the a/c interface, as proposed by Suski et al. [Sus79].

In contrast to these results, some authors attribute electronic Fermi energy level shifts with impacting the recrystallization rates of amorphous silicon [Ade88, Lic86, McC99, Par88a, Par88b, Sun82a, Wil83]. As the Fermi level in amorphous silicon is pinned near mid-gap, doping induced band bending and an electric field can attract charged defects to the a/c interface. According to the electronic impurity theory, SPER is controlled by the concentration of charged defects, such as vacancies, at the a/c interface [Sun82a]. Thus, an increase in the charged defect population will lead to faster recrystallization of silicon. Small concentrations of both donor and acceptor dopant species enhance the regrowth rate of amorphous silicon, suggesting that electronic processes may influence SPER kinetics [Wil83]. Despite their belief that stress relaxation is likely to govern the mechanism of SPER, Suni et al. acknowledge that this model cannot explain a portion of their experimental results [Sun82b]. For example, the stress relaxation model fails to fit their observations regarding compensated dopants [Sun84]. Regrowth rates were reduced for samples containing equal concentrations of boron and phosphorus or boron and arsenic; however, no compensation was exhibited when arsenic and phosphorus were co-implanted [Sun84]. These results indicate that simple stress relaxation effects do not govern SPER kinetics. With increasing doping, Suni et al. also observed a rise in regrowth rates and lowering of activation energies [Sun82a]. They attribute their results to a Fermi level shift away from the mid-gap and an increase in the concentration of charged vacancies, which in turn facilitates enhanced recrystallization. Park et al. observed a linear dependence of the normalized regrowth rate on the normalized boron concentration, suggesting that strain is not the dominant effect of dopant impurities upon the SPER process [Par88b]. Licoppe et al. showed that atomic

rearrangement at the a/c interface is sensitive to the Fermi level in the underlying crystal [Lic86]. The heavier the implantation dose, the lower the energy barrier for structural reordering.

Structural Relaxation

Roorda et al. demonstrated through differential scanning calorimetry (DCS) analysis that amorphous silicon can be structurally relaxed at temperatures below 600°C. without recrystallizing [Roo89, Roo90a, Roo91a]. Structural relaxation results in the annihilation of point defects and in a reduction of the dangling silicon bond density of amorphous silicon [Laa99, Roo90a, Roo90b, Roo91b, Roo99]. The low temperature heat releases observed during DSC of amorphous silicon are attributed to the removal of ion implantation induced damage and are not defined by a set activation energy [Roo90a, Roo91b]. The highest activation energy observed for structural relaxation was 2.2 eV, distinctively lower than the 2.7 eV barrier associated with SPER energy [Roo90a, Roo91b]. Relaxation inherently imparts short-range order and is accredited with a decrease in the average bond angle distortion of a continuous random network energy [Roo90a, Roo90b, Roo91b]. XRD analysis confirmed that relaxation involves reordering on an atomic level, denoting differences in the structure factors of amorphous and relaxed material [Laa99, Roo91b]. However, Custer et al. have shown that there is no measurable difference between the density of amorphous and relaxed silicon, initially formed via ion implantation [Cus94a].

Roorda et al. also investigated the effects of subsequent ion implantation upon relaxed silicon substrates using Raman spectroscopy [Roo90a, Roo90b, Roo91a, Roo91b]. When species are implanted at their amorphizing doses, such as Si^+ at $1x10^{15}$ atoms/cm², they completely de-relax the relaxed silicon material, similar to the manner in

which they would amorphize a crystalline substrate. Structural de-relaxation is attributed to nuclear collisions incurred during subsequent implantation [Roo90a, Roo90b, Roo91b]. Only one out of every twenty silicon atoms needs to be displaced by a nuclear collision to completely de-relax amorphous silicon [Roo91b]. It is important to note that amorphous material formed by silicon and germanium amorphizations were found to behave similarly in a relaxed state, in the absence of additional dopant species [Roo91b].

Rapid Thermal Annealing (RTA) and Flash Annealing

TED is a limiting factor regarding the formation of ultra-shallow junctions. To meet the requirements established for future technologies, dopant diffusion during activation annealing must be minimized. Several techniques have been developed over the years to meet this particular need, including rapid thermal annealing (RTA) and flash annealing. Studies have demonstrated that TED is a highly temperature dependent phenomena, decreasing rapidly with increasing temperature [Eag94]. At high temperatures, the activation energy barrier for TED to occur has been reported as being very small or even negative [Aga00a, Aga00b, Fio01, Raf96]. These results suggest that reaching anneal temperatures as quickly as possible, i.e. fast ramp-up rate, will reduce the contribution of TED to the total magnitude of dopant diffusion during annealing. By incorporating a high ramp rate, samples are exposed to a lower total thermal budget [Man01a]. Thus, activation techniques employing high ramp rates are advantageous for limiting diffusion.

The rapid thermal annealing technique is defined by ramp-up rates on the order of 200°C/s to 300°C/s, peak temperatures of approximately 1100°C, and ramp-down rates of only 80°C/s [Aga00a, Aga00b, Man01c]. Samples are heated by an array of incandescent lamps, providing both temperature uniformity and reproducibility [Fio01]. Tungsten-

halogen lamps are most commonly employed [Cam02, Gel02]. Sample temperatures are measured on the wafer back-side during processing by pyrometers [Fio01]. The duration spent at the anneal temperature before cool-down is often referred to as the soak time. Heating rates are dependent on the switching speed from heating to cooling, the intensity and wavelength of the infrared (IR) radiation source, and radiative or convective dissipation of heat during sample cool-down [Fio01]. Specimens are commonly cooled by simply turning off the heating lamps after the desired soak time [Fio01]. A "spike anneal" is known as an RTA cycle in which the soak time at the anneal temperature is minimized. Spike anneals are commonly on the order of roughly one second, reaching down to 0.3 seconds [Cam02]. The temperature profile of an RTA spike anneal is somewhat rounded, lacking sharpness. The large thermal mass of the tungsten lamps limits the speed at which the system may convert from a heating to cooling stage, resulting in a relatively non-uniform profile at the peak temperature [Cam02]. In order to achieve soak times less than 0.3 seconds, the sharpness of the temperature profile during processing must be improved.

For high implant energies, very fast RTA heating ramp rates have been shown to inadvertently retain a large population of silicon interstitial clusters, leading to substantial TED during the wafer cool-down stage [Cha00]. The benefits of a lower thermal budget are effectively overshadowed by the occurrence of TED at increasingly low temperatures. If the TED process is not completed during a fast ramp-up to the annealing temperature, then higher ramp-down rates are needed to inhibit dopant diffusion [Cha00]. It is important to note that low energy implants, i.e. less than1 keV, exhibit decreasing

junction depths with increasing heating ramp rates. These effects do not appear to saturate at elevated ramp rates, as observed for higher energy implants [Cha00].

Flash annealing techniques are an extension of conventional RTA methods [Cam02, Gel02, Ros02]. During processing, a continuous are lamp is used to heat the bulk of the wafer up to an intermediate temperature (*Ti*); then a high-energy flash lamp is employed to provide additional power to the top-side of the wafer through the arc lamp [Cam02, Gel02]. The effective duration of the flash annealing cycle is on the order of only 10^{-3} seconds [Cam02]. The entire sample is heated uniformly, increasing the processing speed of this technique, while reducing potential lateral thermal gradients that could result in residual defects [Gel02]. The back-side temperature of the sample is measured and monitored during heating by a radiometer operating at 1.45 µm. The front-side specimen temperature is calculated using the measured energy output of the lamp and the temperature rise measured on the sample back-side during the flash event. Due to the short flash time scale, it is impossible to directly measure the peak anneal temperature using current methods [Gel02].

Only a thin layer of the sample is actually heated during the flash portion of the temperature profile, facilitating rather high heating and cooling rates. During the flash portion of the process, typical heating and cooling rates of 10^{6} °C/s are achieved. By only heating a top portion of the sample, the bulk acts as a heat sink and removes heat from this top layer more efficiently than may be accomplished via bulk cooling [Cam02]. However, heating ramp rates from room temperature up to *Ti* are comparable to those of conventional RTA, reaching up to 400°C/s. Bulk cooling rates are roughly 150°C/s, resulting from radiative cooling effects [Cam02]. The flash portion of the temperature

profile is very sharp because the specimen is heated uniformly and the time constant of the flash is only about 1 ms. The thermal time constant of bulk silicon ranges from 10-20 ms, demonstrating the rapid nature of the flash annealing process [Cam02]. Figure 2-11 illustrates the time-temperature profile for samples receiving flash annealing [Cam02, Gel02]. The maximum achievable peak anneal temperature is approximately 1300°C, sufficiently below the melting temperature of conventional silicon wafers, eliminating potential integration and melting issues [Gel02]. Intermediate temperatures can range anywhere from 600°C to 1000°C, but *Ti* is believed to be responsible for controlling the magnitude of dopant diffusion via TED and the peak flash temperature determines the level of dopant activation [Gel02]. Thus, higher intermediate temperatures are more desirable. Flash annealing fills the gap in process times between conventional RTA and laser thermal processing (LTP), which occurs in approximately 10^{-9} seconds [Cam02].

Overview of Arsenic Behaviors in Bulk Materials

Many studies have characterized the behavior of arsenic in silicon over the last two decades [Fey88, Kri98, Kwo84, Mit03, Nob94, Pow81, Rou98, Sol98, Tsa81, Whe01, Yu93]. Arsenic has the propensity to form monoclinic SiAs clusters when the arsenic concentration exceeds a critical value of 3×10^{21} atoms/cm³ [Kri98, Nob94]. The transition between arsenic self-clustering and SiAs precipitation is not abrupt and these species may coexist [Kri98]. Dislocation loops have been observed to form at the peak of the arsenic implant profile, even though the arsenic concentration is well below the solid solubility limit. These structures are not believed to represent precipitates, but rather arsenic-vacancy complexes [Pen85, Sol98]. The fractional interstitial composition of arsenic in silicon is accepted as ranging from approximately 0.3 to 0.4, denoting a strong vacancy-mediated diffusion mechanism [Bra00, Fah85]. The sheet resistance of arsenic implanted structures commonly decreases with annealing time, as arsenic experiences an activation-deactivation cycle during annealing [Fey88, Rou98, Sei85]. To date, this cycle is not well understood.

Relatively few studies have addressed the diffusion behavior of dopants in pure germanium substrates. Hattangady et al. [Hat98] conducted preliminary investigations of arsenic diffusion in germanium. They determined that the percentage activation of arsenic is greater for lower dose implants and that diffusion characteristics during furnace annealing and rapid thermal annealing are dissimilar. Significant arsenic diffusion is observed during furnace annealing for temperatures above 575°C, while no motion is detected after rapid thermal annealing until temperatures exceed 650°C [Hat98]. These results raise the assertion that implanted arsenic may experience transient diffusion effects during annealing in germanium materials.

Overview of Boron Behaviors in Bulk Materials

Boron characteristics in bulk silicon material have been extensively studied over the years, as boron is the most common p-type dopant. Studies have demonstrated that boron can be electrically activated during the solid phase epitaxial regrowth process [Lin00, Tsa79b]. Lindfors et al. observed that the % boron activation decreases as the implant dose rises, due to increased interactions between the boron dopant and the a/c interface [Lin00]. For doses exceeding $5x10^{15}$ atoms/cm³, boron can actually inhibit the recrystallization process and degrade electrical properties [Lin00]. Boron may also deactivate during subsequent annealing via the formation of BIC's, as previously discussed [Man01b, Sch00]. The placement of boron atoms on substitutional lattice sites is crucial for enhancing the electrical properties of ultra high-purity silicon. The incorporation of fluorine has been shown to increase the level of boron activation after

both low temperature [Bea77, Mul71] and high temperature [Ohy90] annealing. As an interstitial diffuser [Fan96a, Gos97, Ura99a], boron is highly susceptible to TED [Bon96, Cow99a, Cow99b, Cow00, Eag94, Jon97, Man01b]. Fluorine co-implantation also serves to retard boron diffusion within crystalline silicon during annealing, decreasing the redistribution of boron with increasing fluorine dose [Imp05, Ohy90].

Minimal studies regarding boron diffusion and activation in bulk germanium have been conducted. Uppal et al. conducted preliminary studies in both (111) and (100) oriented germanium [Upp01a, Upp01b]. The observed boron diffusivities are on the order of 1.8×10^{-16} cm²/s and 1.3×10^{-16} cm²/s, respectively, at a temperature of 850°C. Boron solid-solubility values of approximately 4.5x10¹⁸ atoms/cm³ and 6.5x10¹⁸ atoms/cm³ at 850°C were also reported for (111) and (100) germanium. They question the common assertion that group III elements, including boron, diffuse through vacancy mediated mechanisms in germanium. Hattendorf et al. [Hat03] demonstrated that there is no measurable potential or binding force between boron and germanium strong enough to form Ge-B pairs or clusters in crystalline material at temperatures below 600°C. The probability of forming Ge-B complexes in materials containing less than 1 at% germanium is reported as being less than 0.05 [Hat03]. In addition, no diatomic bond enthalpy data pertaining to Ge-B can be found in the literature. Thus, the formation of Ge-B pairings in silicon-rich materials, such as germanium preamorphized silicon, is highly unlikely.



Figure 2-1: Schematic representation of ion implantation into a silicon wafer, where portions of the sample are masked by a SiO₂ layer whose thickness is greater than the penetrating ion range.



Figure 2-2: Diagram of a commercial ion implantation system. [May90]



Figure 2-3: Gaussian range distribution for implanted ions. [May90]



Figure 2-4: Projected range of various dopants as a function of implant energy, demonstrating that lighter elements exhibit greater sample penetration and that ranges vary linearly with implant energy. [Mah99]



Figure 2-5: Schematic of the lateral distribution of ions implanted into silicon with straight-wall oxide masks.


Figure 2-6: Schematic model of (a) the relative degree of "openness" of the (100) diamond cubic silicon lattice and (b) ion trajectories in an axial channel for different entrance angles.



Figure 2-7: Calculated values of *dE/dx* for various dopants at a range of implant energies. The individual nuclear (N) and electronic (E) energy loss components are shown. [Mah99]



Figure 2-8: Lattice damage due to (a) light and (b) heavy ions during ion implantation.



Figure 2-9: Schematic representation of (a) direct diffusion and (b) indirect diffusion of an element A in a solid. A_i, A_s, V and I denote interstitially and substitutionally dissolved foreign atoms, vacancies, and silicon selfinterstitials, respectively. AI and AV are defect pairs of the corresponding defects. [Bra00]



Figure 2-10: Ball and stick representation of amorphous (top) and crystalline (bottom) silicon, as constructed by the tight-bonding molecular dynamics model. [Kug04]



Figure 2-11: Schematic representation of the front-side time-temperature profile for the flash annealing process. [Cam02, Gel02]

CHAPTER 3 ANALYTICAL TECHNIQUES

The various analysis techniques used throughout these studies to characterize the physical properties of materials are detailed in this chapter. The techniques are ordered for ease of reference to subsequent chapters. A brief summary of each technique is provided, including the specific benefits and limitations pertaining to its use.

Secondary Ion Mass Spectrometry

Dynamic secondary ion mass spectrometry (SIMS) is commonly used to measure elemental concentration as a function of lateral depth [Bru92, Mah99]. SIMS systems can be used to detect and differentiate between elements ranging from hydrogen to uranium and all elemental isotopes [Bru92] with a detection limit on the order of 1x10¹⁶ atoms/cm³ [Bru92, Mah99]. SIMS is a destructive technique, incapable of providing chemical bonding information [Bru92]. Within the semiconductor industry, SIMS is utilized to characterize the distributions of both desired dopants and unwanted trace impurity species [Bru92, Mah99].

The detection limit of a given element is dependent on its ion yield or ionization potential [Bru92]. The greater the ion yield, the lower the detection limit. Three different types of primary ions can be used during dynamic SIMS analysis; namely oxygen, cesium, and argon [Bru92, Mah99]. An oxygen primary beam can increase the yield of positive ions, such as boron, while cesium increases the yield of negative ions, such as fluorine [Bru92]. An argon primary beam is not often used, as it does not enhance the total yield of sample ions [Bru92]. The use of an oxygen primary beam will also increase

the concentration of oxygen in the sample surface and persist at elevated levels throughout the analysis process. For obvious reasons, an oxygen primary beam is not used to analyze oxygen-containing materials.

SIMS analysis requires samples with smooth, clean surfaces in dimensions of less than 2.5 cm x 2.5 cm [Bru92]. Primary ions bombard the surface during analysis, sputtering atoms from the sample [Bru92, Mah99]. A mixing zone consisting of primary ions and displaced sample atoms is generated [Bru92, Mah99], as seen in Figure 3-1. Displaced sample atoms that have been ionized, either positively or negatively, are referred to as secondary ions [Bru92, Mah99]. The depth of the mixing zone defines the depth resolution during analysis and is a function of the sample matrix, primary ion species, primary beam energy, and angle of beam incidence [Bru92]. To ensure a depth resolution on the order of 2 nm, the primary ion beam is rastered over a given sampling area, creating flat-bottomed sputter craters [Bru92]. Secondary ions are only detected from the crater center, minimizing random contributions from the crater walls [Bru92], and are identified based on their mass-to-charge ratio [Mah99]. It should be noted that during sputtering, both monatomic and polyatomic sample particles, electrons, photons, and re-sputtered primary ions are generated and introduced into the mixing zone [Bru92]. Prior to mass analysis, the mixing zone constituents are filtered based on their energy, such that only ions with kinetic energies in a desired range are collected and analyzed. The desired energy range is defined based on the elemental species or isotope of interest. Systems primarily use quadrupole mass analyzers. However, a high specification time-offlight (TOF) analyzer can also be used to provide a greater mass range and higher sensitivity measurement.

SIMS profiles are typically collected as secondary ion counts per second versus sputtering time [Bru92]. They are then converted to a plot of elemental concentration verses sample depth, using comparisons to standards and the experimentally measured crater depth [Bru92, Mah99]. Figure 3-2 illustrates SIMS profiles for a silicon sample implanted with boron dopant (a) before and (b) after data after conversion [Bru92]. A separate instrument, known as a profilometer, is used to experimentally determine the crater depth. A profilometer stylus runs along the crater bottom and denotes vertical deflections or depths. The sputtering rate is defined as the rate the mixing zone penetrates into the sample and generally ranges from 0.5 to 5 nm/s [Bru92]. A lower sputter rate correlates to a better detection limit. The sample sputter yield relates the number of sputtered atoms to the number of incident primary ions, with ratios falling between 5 and 15. SIMS analysis is always performed under high vacuum conditions, with pressures less than 1×10^{-6} torr [Mah99], at both low and room temperature. To maintain uniform, low sputtering rates in bulk silicon samples, oxygen back-flooding can be employed. By continuously reacting with the silicon surface to form silicon dioxide, the oxygen ambient facilitates more accurate analysis of positively ionized species, such as boron. Dynamic SIMS analysis can be performed to depths of several microns in less than one hour [Bru92]. The SIMS depth profiling technique is used extensively throughout these studies to monitor dopant diffusion behaviors during SPER annealing. Species monitored include boron, germanium, fluorine, hydrogen, and silicon.

Transmission Electron Microscopy

Transmission electron microscopy (TEM) is a technique widely used for microstructural characterization [Bru92, Cul01, Wil96]. TEM is performed under high vacuum conditions at pressures less than 1×10^{-7} torr [Wil96]. During analysis, a finely

focused mono-energetic electron beam, with a spot size less than one micron, penetrates the sample [Bru92, Mah99]. To achieve electron transparency, samples must be less than 200 nm thick [Bru92, Cul01, Wi196]. As electrons exit the sample, two types of electron beams emerge, transmitted and diffracted [Bru92, May99, Wi196], as seen in Figure 3-3 [Wi196]. A direct or transmitted beam is comprised of electrons that pass through the sample without deflection. Electrons that have been scattered during their travel through the sample form the diffracted beam. Both types of electron signals can enter the detector, commonly a fluorescent screen, beneath the sample forming images [Bru92, Cul01, Wi196]. The relatively small wavelength of the incident electrons facilitate an image magnification range of 50 up to 1×10^6 , depending on the TEM system [Bru92, Cul01]. Commercial TEM machines have resolutions better than 0.2 nm, requiring acceleration voltages exceeding 200 kV [Bru92, Wi196].

During TEM analysis, two observation modes are possible [Bru92, Cul01, Wil96]. Diffraction patterns can be used to determine a material's atomic structure, while TEM micrographs are images that can aide in defect characterization and classification. A TEM diffraction pattern is equivalent to an x-ray diffraction pattern and electron scattering can induce the generation of characteristic x-rays [Bru92, Wil96], as shown previously in Figure 3-3 [Wil96]. Single crystal materials generate spot diffraction patterns, polycrystalline materials produce ring patterns, and amorphous materials induce a series of diffuse halos [Bru92, Wil96]. Examples of these three types of diffraction patterns are shown in Figure 3-4 parts (a), (b), and (c), respectively [Wil96]. Diffraction occurs when incident particles are deflected or scattered by atoms in the sample. The particles are scattered according to Bragg's Law [Cul01, Sma99, Wil96]

$$\lambda = 2d\sin\theta \tag{3-1}$$

Where λ is the wavelength of incident electrons, 2 θ is the diffraction angle, and *d* represents the atomic spacing. For a given angle θ , defined in this case as the angle formed between the incident electron beam and the lattice plane of interest, only certain atomic planes are able to satisfy Bragg's law and form a scattered beam. Amorphous materials are able to generate scattered beams due to incoherent scattering effects, while crystalline materials create coherent diffracted beams [Cul01]. The atomic spacing *d* of a cubic crystalline material is defined as follows [Sma99, Cal97]:

$$d = a/\sqrt{h^2 + k^2 + l^2}$$
(3-2)

Where *a* represents the lattice parameter of the material under analysis and the variables *h*, *k*, and *l* correspond to the Miller indices of the scattering atomic plane [Sma99, Cal97]. Diffraction patterns of crystalline materials can be used to ascertain the exact interplanar spacing *d* for a given sample [Wil96]. The atomic spacing *d* is related to the measured distance between the transmitted beam and the diffraction spot of interest R, the wavelength of the incident electron beam λ , and the camera length L according to

$$\mathbf{R}d = \lambda \mathbf{L} \tag{3-3}$$

The variables λ and L are determined by the operating parameters of the TEM instrument. The value of the product λ L is constant for a given diffraction pattern, such that the atomic spacing of neighboring lattice planes can be determined through the relation $R_1d_1 = R_2d_2$. TEM diffraction patterns can provide valuable information regarding sample orientation, phase distribution, and atomic arrangements.

TEM micrographs are images of the sample area illuminated by the electron beam [Bru92]. Image contrast is observed due to thickness variations, changes in diffraction

properties, mass or spatial differences, strain fields, and changes in phase [Bru92, Cul01, Wil96]. Several imaging modes are also possible: bright-field, dark-field, and highresolution electron microscopy phase [Bru92, Cul01, Mah99, Wil96]. During bright-field microscopy, only a transmitted beam is detected. Contrast within bright-field micrographs arises due to structural, thickness, or compositional variations phase [Bru92, Wil96]. Areas where significant electron scattering occur appear dark in a bright-field image. Dark-field microscopy, on the other hand, utilizes diffracted electron beams. Areas where significant electron scattering occur appear bright in a dark-field image. Finally, high-resolution electron microscopy incorporates a large-diameter aperture that allows only one transmitted beam and at least one diffracted beam to enter the detector [Bru92]. Using this mode, individual columns of atoms can be imaged and contrast is manifested as fringes that represent individual diffraction planes within the sample [Bru92, Mah99].

Traditionally, two types of TEM samples are analyzed, cross sectional (XTEM) and plane-view (PTEM). XTEM samples represent vertical slices of material and are used to determine the presence and depth location of a particular structure, such as a defect, and to calculate layer thicknesses. PTEM samples, on the other hand, are utilized in determining defect densities. They can also be used to quantify defect size, providing a means to monitor the growth or dissolution of a defect species. Figures 3-5 and 3-6 illustrate silicon XTEM and PTEM micrographs, respectively. Throughout these studies, XTEM analysis was used to monitor amorphous layer depth, or thickness, and to monitor the threading dislocation density. PTEM analysis was used to characterize the presence and evolution of {311} and dislocation loop defects.

Each of these sample types, PTEM and XTEM, requires a specific preparation methodology. PTEM samples are generated as follows. An ultrasonic coring machine is used to cut a 3 mm disk from the bulk sample. This disk is subsequently mounted onto a polishing tool, top-side down, with a crystal bond adhesive. The back-side of the disk is then hand polished until the disk is infinitely thin, i.e. barely discernable by the human touch. Once polishing is complete, the sample is removed from the polishing tool and subsequently mounted, top-side down, onto a hexagonal Teflon etching mount using wax as an adhesive. The front surface of the disk is coated with a thin layer of wax, while a small hole in the center of the back-side is not covered with wax. This exposed area will serve as the thinned region. The sample is then exposed to an etchant comprised of HF and HNO₃. The sample is slowly etched until a pinhole is created. Once etching is complete, the sample is removed from the Teflon mount and soaked overnight within heptane to remove any residual wax. After soaking, the sample is ready to image.

XTEM samples are generated with the assistance of a Focused Ion Beam (FIB) tool. The bulk sample is first adhered onto a FIB stage mount using carbon paint. It is then coated with a protective layer of either 60 nm of carbon or 50 nm of gold. According to Stopping and Range of Ions in Matter (SRIM) Simulations [Zie03], these thickness values represent the minimum plateau required to insulate the sample surface from the damaging ion beam at the operating acceleration voltage of 30 V. As the ion beam current is adjusted from 100 to 7000 pA the predicted penetration depth of the gallium ions will not increase beyond the protective films into the bulk sample. Next, the sample is loaded into the vacuum chamber of the FIB. Initially, a rectangular region of the sample surface, approximately 20 µm long and 1 µm wide, is coated with a 1 µm thick

protective platinum film. The platinum layer prevents the penetration of gallium ions into the sample during subsequent processing, where prolonged exposure to the ion beam leads to surface milling. The sample is then selectively milled in order to create a thin cross section. After milling is complete, the sample is removed from the FIB and loaded onto a micro-manipulator station. The micro-manipulator needle is used to extract the sample cross section and load it onto a carbon grid, completing the sample preparation process.

Variable Angle Spectroscopic Ellipsometry

Variable angle spectroscopic ellipsometry (VASE) is a nondestructive optical technique commonly used to determining layer thickness, optical constants, microstructure, and surface or interfacial roughness [Bru92, Hum93]. Clean, smooth samples with parallel interfaces, comprised of homogeneous materials, are required for analysis [Bru92]. Minimum sample dimensions vary from system to system, but typically exceed 1 cm x 1 cm and 1 mm in total thickness. For thin film analysis, a film thickness range from 1 nm to 1000 nm is optimal [Bru92]. Analysis can be performed under ambient conditions, vacuum, and in hostile or aqueous environments [Bru92].

During ellipsometry, a focused beam of polarized light penetrates the sample surface at a given incident angle and wavelength [Bru92, Hum93]. The incident light is reflected by the interfaces between the constituent layers, forming transmitted and reflected beams, as shown in Figure 3-7. The polarization of the reflected light is detected and analyzed by a second light polarizer. For each angle of incidence and wavelength of light, the reflected beam intensity and polarity are measured [Bru92, Hum93]. The quantity measured by the light polarizer is determined by the specific structure and dielectric constant(s) of the sample. It represents an amplitude reflection ratio between

the s-polarization and p-polarization, corresponding to the electric field perpendicular and parallel to the plane of incidence [Bru92, Hum93]. When the polarization components are exactly in phase, the projection onto a plane perpendicular to the reflected beam propagation direction is a straight line. However, when the polarization components are not in phase, an ellipse is projected, as illustrated in Figure 3-8 [Bru92]. The complete polarization state of light includes five separate components: [Bru92]

- 1. Azimuthal angle of the electric field vector α shown in Figure 3-8 (b)
- 2. Ellipticity e = b/a where b and a represent the minor and major axes of the projected ellipse shown in Figure 3-8 (b)
- 3. Handedness or rotation direction of the electric vector
- 4. Amplitude $A = (a^2 + b^2)^{2/3}$ where b and a represent the minor and major axes of the projected ellipse shown in Figure 3-8 (b)
- 5. Absolute phase of the vector components of the electric field

During ellipsometry, the first two components are always determined for the reflected beam. Based on the system, sometimes the handedness is also reported. The remaining polarization components are not required for the calculation of optical constants and are not measured during analysis, greatly simplifying the electronics of the analytical system.

During data acquisition, structural models are built to simulate sample structures and provide the desired ellipsometric parameters. A common structure assumed for ellipsometric analysis is shown in Figure 3-9. If the optical constants of the component materials are known, the individual layer thicknesses and interfacial roughness can be determined [Bru92]. Ellipsometry of silicon-germanium (SiGe) structures can become quite complex. Relaxed alloys require the incorporation of buffers that are often difficult to simulate. By restricting the VASE wavelengths to the spectral range of 240 nm to 500 nm, the beam penetration depth is limited to less than 1 µm [Sch05]. For structures comprised of SiGe layers thicker than this 1 µm threshold, only surface layers need to be modeled, simplifying the ellipsometric analysis. VASE is a rapid technique with monolayer resolution that can be performed in a matter of minutes [Bru92]. The optical VASE technique was used throughout these studies to determine amorphous layer thicknesses. Data was compared to TEM micrographs for verification.

Hall Effect

The Hall effect measures a sample's carrier concentration and mobility [Hum93, Mah99, May90, Plu00]. In doped silicon, carrier concentrations as low as 1×10^{12} carriers/cm³ can be detected [Hum93]. The Hall effect can be used to successfully monitor both electron and hole carriers [Hum93, Mah99, May90, Plu00]. Rectangular samples in excess of 1.0 cm x 1.0 cm, with a uniform thickness, are commonly required for accurate analysis [Mah99]. Prior to processing, ohmic contacts are created on the sample surface to provide a path for current flow through the sample. The contacts typically follow the Van der Pauw configuration, [Mah99] where the individual contacts are denoted as A, B, C, and D, as demonstrated in Figure 3-10. Indium is typically used to form contacts on silicon samples, where soft pellets of indium are pressed onto the sample corners. Care must be taken during indium application to ensure that native surface oxides are penetrated without damaging the silicon surface. Contacts formed with solid indium can be used for both room temperature and low temperature analysis, including vacuum conditions. Liquid metals, such as gallium-indium (GaIn), can also be used to form surface ohmic contacts. However, Hall effect measurements for GaIn contacts must be performed at room temperature under atmospheric conditions. Sample

measurements can be obtained in a matter of minutes, once the environmental conditions such as low temperature or vacuum have been achieved.

During Hall effect analysis, a magnetic field is applied in the z-direction normal to the applied current flow in the positive x-direction [Hum93, Mah99, May90, Plu00]. The magnetic field induces a force, known as the Lorentz force, that causes the carrier paths to curve as they flow through the sample. A schematic for a material, with electrons as the predominant carrier type, experiencing the Hall effect is shown in Figure 3-11 [Hum93]. The carriers and their associated charge accumulate on one face of the sample. The charge deficiency on the opposite face induces an electric field in the y-direction, denoted as the Hall field. An electric field must be generated in order to negate the Lorentz force and return the carriers to their original path. The creation of this electric field is referred to as the Hall effect. The associated voltage is the Hall voltage and the force is the Hall force. Measurement of the Hall voltage, for a known applied magnetic field and applied current, can be used to determine the carrier concentration [Hum93, Mah99, May90, Plu00]. Following the Van der Pauw configuration, R_{AB, CD} is defined as the resistance obtained by dividing the voltage applied between contacts C and D by the current that enters the sample at contact A and leaves through contact B (Figure 3-10) [Mah99]. The Van der Pauw method presumes that the resistance R_{BC, DA} can be defined in a similar fashion, such that

$$\rho = \frac{\pi d (R_{AB,CD} + R_{BC,DA}) f [R_{AB,CD} + R_{BC,DA}]}{2 \ln 2}$$
(3-4)

Where ρ is the resistivity and *d* is the sample thickness. The function f equals unity when $R_{AB, CD} = R_{BC, DA}$ [Mah99]. During Hall effect analysis, the applied current enters and leaves through diagonally opposite contacts, such as A and D in Figure 3-10, and the Hall

voltage forms between the remaining two contacts. The Hall voltage $V_{\rm H}$ is related to the Hall mobility $\mu_{\rm H}$, the applied current *I*, the resistivity ρ , the applied magnetic field *H*, and the thickness *d* as follows [Mah99]:

$$V_H = \frac{\mu_H I \rho H}{d} \tag{3-5}$$

The Hall mobility is calculated by measuring the change in $R_{BD, AC}$ induced by the applied magnetic field *H* where [Mah99]

$$\Delta R_{BD,AC} = \frac{V_{H}}{I} \tag{3-6}$$

All of the variables listed in Equations 3-5 and 3-6 are either known or measured experimentally, such that the carrier concentration c can be accurately calculated.

$$c = \frac{1}{\mu \mu \rho q} \tag{3-7}$$

Where the variable q represents the carrier charge [Mah99]. Through additional calculations, Hall effect data can also be used to ascertain a sample's sheet resistance [MMR95]. The sheet resistivity R_s is related to the resistivity ρ and sample thickness *d* according to the expression

$$R_s = \frac{\rho}{d} \tag{3-8}$$

The carrier concentration and sheet resistance are key factors regarding transistor performance for the semiconductor industry. Throughout these experiments, Hall effect measurements were used to characterize boron dopant activation as a function of implantation and annealing processes.

Four-Point Probe

The most common method for measuring wafer resistivity is with a four-point probe [Plu00, Smi58]. The sample sheet resistance can be directly measured by this method [May90, Plu00]. During analysis, four point contacts are made with the sample surface by the probe system. The probe system contains four thin collinear tungsten probes. Current is applied to the outer contacts and the voltage drop across the inner contacts is measured [May90, Plu00]. In practice, such measurements can be made with only two probes. However, the contact resistances of the probes themselves and the current spreading around the probes cannot be discounted during analysis [Plu00]. The use of four probes enables accurate measurement of the voltage drop by isolating the data collection to areas free of current spreading and extraneous resistances.

Flat samples with a uniform thickness are required for four-point probe analysis. In order for accurate electrical measurements of semiconductor materials, the active layer must be of opposite conductivity to the substrate. When they are of the same conductivity type, the active layer is not electrically insulated. During analysis, both the conductivity and resistivity of the substrate are measured, as the substrate provides an easier path for the applied current. No information regarding the active layer of interest is obtained. Any native surface oxides will need to be removed prior to analysis, such that good contact is made between the tungsten probes and the sample surface. Care must be taken to ensure that the tungsten probes are gently pressed to meet the sample surface and that sharp or rough tips are not used, as the sample can be punctured. Any damage to the sample surface can introduce leakage currents that artificially lower the measured resistivity.

For semiconductor dimensions presumed to be infinitely greater than the uniform probe spacing *s*, the material resistivity ρ is calculated according to [Plu00]

$$\rho = \frac{2\pi sV}{I} \tag{3-9}$$

Where *V* is the potential difference between the inner probes and *I* represents the current supplied to the outer two probes. If the probe spacing is equal to 1.588 mm, than the value of $2\pi s$ equals 1 cm and the resistivity calculation is fairly simple [Plu00]. In the case of implanted or doped semiconductors, the calculated resistivity ρ corresponds to the average resistivity of the doped region or junction. For these thin layers, the sheet resistance ρ_s is chosen as the figure of merit. The sheet resistance is mathematically defined as [May90, Plu00]

$$\rho_{s} = \frac{4.532V}{I} \tag{3-10}$$

Within many commercial systems, the required correction factors are built-in and the resistivity and sheet resistance are directly provided.

When the conducting layer dimension becomes comparable to the contact spacing, as for ultra-shallow semiconductor junctions, alternate geometrical correction factors are needed for accurate sheet resistance calculations [May90, Val54]. Figure 3-12 illustrates how the geometrical correction factor changes as a function of the thickness to probe spacing ratio (t/s) [Val54]. For t/s ratios greater than 0.5, no additional correction factors are required and Equations 3-9 and 3-10 are valid. In all other cases, the sample resistivity is defined as follows where the variable a represents the geometrical correction factor factor [Val54]:

$$\rho_o = \frac{a2\pi sV}{I} = a\rho \tag{3-11}$$

The correction factor for values of $t/s \le 0.5$ are estimated by [Val54]

$$a = \frac{0.72t}{s} \tag{3-12}$$

The corrected sheet resistance ρ_{so} for samples with $t/s \le 0.5$ is equivalent to

$$\rho_{so} = \frac{\rho_o}{t} \tag{3-13}$$

The four-point probe method was used during these studies for sheet resistance measurements. For all of the samples experimentally measured, the dimensions were sufficient to avoid the need for additional geometric correction factors.

High-Resolution X-ray Diffraction

High-resolution x-ray diffraction (HRXRD) techniques are used to identify crystalline phases and their respective structural properties [Bru92, Cul01, Sma99]. HRXRD can also be employed to determine strain states, orientation, crystallite size, and film thickness [Bru92, Cul01, Sma99]. For semiconductor applications HRXRD is used to quantify strain and defect populations, parameters that can impact electrical properties [Bru92]. HRXRD is a nondestructive technique commonly performed under ambient conditions [Bru92, Cul01]. During analysis, a collimated, monochromatic beam of x-rays penetrates the sample surface [Bru92, Cul01]. The incident beam is diffracted by crystalline phases in accordance with Bragg's law [Cul01, Sma99, Wil96], defined previously in Equation 3-1 [Wil96]. For a given wavelength and diffraction angle, only certain atomic planes can satisfy Equation 3-1 and create a diffracted beam [Cul01, Sma99]. The intensities of the diffracted beams are detected and recorded as a function of sample orientation and diffraction angle [Bru92, Cul01, Sma99]. The resultant diffraction pattern is used to ascertain structural properties. Elements with high atomic numbers are easier to detect, as they have larger diffraction intensities [Bru92]. However, analysis of

materials containing low atomic number elements requires a bigger sampling size, often exceeding 1 cm x 1 cm, reducing the resolution [Bru92].

Diffractometers are commonly employed in HRXRD systems to detect x-rays using photon counters [Bru92, Sma99]. Photon counters are more accurate than their photographic predecessors, providing superior angular resolution and signal-to-noise ratios [Bru92]. Advanced software programs are used to compare experimental data to patterns of known standards, assisting in phase and property identification [Cul01]. When beam intensity is plotted versus diffraction angle, the angular location of diffraction peaks facilitate the identification of differences in strain intensity and atomic spacing between samples [Bru92, Cul01]. For example, tensile strain increases atomic spacing and shifts the location of a given diffraction peak leftward to a lower diffraction angle [Cul01]. One of the primary types of scans performed for silicon and silicon-germanium material is a ω -2 θ scan. The angle formed between the incident x-ray beam and the sample surface is denoted as ω and 2θ is the angle formed between the incident beam and the detector, as shown in Figure 3-13 [Few89]. A ω -2 θ scan represents a one-dimensional measurement that probes planar spacings from a specific crystal orientation. The (004) reflection provides high intensity and is typically measured for silicon and silicon-based materials [Sch05]. In addition, the peak width, measured at half the maximum peak intensity, is indicative of the crystal thickness [Cul01]. A broader diffraction peak signifies a thinner crystal. Amorphous and liquid materials can also be detected via HRXRD techniques. However, their diffraction spectra simply show one or two broad peak maxima [Cul01]. Limited bonding and structural information is obtained.

Depending on the type of information desired and the range of diffraction angles scanned, HRXRD analysis can require anywhere from one hour to several hours to complete.

RsL Electrical Measurements

RsL is a novel technique for measuring the electrical properties of semiconductor junctions [Cur04, Fai04, Fai05]. By using photo-excitation, RsL alleviates potential issues of physical junction punch through and insensitivity to ultra-shallow junctions, commonly associated with 4-point probe [Cla02] and optical measurement techniques [Van03]. RsL is a non-contact technique that involves the measurement and modeling of photo-voltage signals [Cur04, Fai04, Fai05]. During analysis, the sample is exposed to a modulated beam of light, as seen in Figure 3-14, [Fai04] that excites electron-hole pairs in the junction and wafer substrate. For single junction samples, red LED light at a wavelength of 750 nm is modulated at 100 kHz during analysis. The generation and drift of these carriers is monitored in a spatially resolved manner using multiple transparent and non-transparent electrodes [Cur04, Fai04, Fai05].

RsL electrical measurements require extensive analysis of photo-voltage signals. The modulated light flux is defined as $\Phi(t) = \Phi_o(x, y)(1 - \cos(2\pi ft))$, where $\Phi_o(x, y)$ is the light flux distribution at the sample surface, *f* is the light modulating frequency, and x and y represent lateral coordinates [Fai94]. The surface photo-voltage distribution, denoted as $v(x,v,t) = v_o(x,v) * \cos(2\pi ft + \varphi(x,y))$, is highly dependent on the drift of carriers along the surface of the p-n junction [Cur04, Fai04, Fai05]. The surface voltage signals V₁ and V₂ (Figure 3-14) are determined by integrating $V(t) = Const \iint_{s} v(x,y,t) dxdy$. The

dynamics of photo-induced carrier creation, recombination, and diffusion are described by the following set of five Poisson and continuity equations:

$$\frac{\partial n}{\partial t} = g_n - r_n - \Delta j_n \tag{3-14}$$

$$\frac{\partial p}{\partial t} = g_p - r_p - \Delta j_p \tag{3-15}$$

$$j_n = \eta_n n \Delta \psi - D_n \Delta n \tag{3-16}$$

$$j_p = -\eta_p p \Delta \psi - D_p \Delta p \tag{3-17}$$

$$\Delta \psi = -\frac{q}{\varepsilon \varepsilon_0} (p - n + N) \tag{3-18}$$

The factors j_n and j_p represent the electron and hole fluxes. The concentration, charge, mobility, diffusion coefficient, and recombination rate for holes and electrons are denoted as p, μ_p , η_p , D_p , r_p , and n, μ_n , η_n , D_n , r_n , respectively. ψ is the electric potential, ε_0 is the permittivity of vacuum, ε is the permittivity of semiconductor material (i.e. silicon), and N is the total impurity concentration in the wafer substrate [Cur04, Fai04, Fai05]. Under monochromatic illumination, the generation rates for electrons (g_n) and holes (g_p) are determined by the relation $g_n = g_p = \alpha \Phi (1 - R) \exp^{(-\alpha z)}$, where α is the absorption coefficient, Φ is the light flux, R is the reflectivity coefficient, and z is the vertical spatial coordinate, as measured from the sample surface [Cur04, Fai04, Fai05]. RsL measurements are conducted in the regime of low excitation levels, such that the surface voltage is proportional to the absorbed light flux and the variation in width of the surface charge region induced by the illumination is negligible. By operating in the low light excitation regime, the dynamics of the photo-generated electron-hole pairs can be modeled with precise 2-D solutions to the aforementioned equations using spatially resolved capacitive sensors [Cur04, Fai04, Fai05].

For a 1-D solution, the voltage measured a distance *r* from the point of illumination is described as $V = Ae^{-\kappa r}$, where $\kappa = \sqrt{R_s G + i\omega R_s C_s}$. The term R_s represents the junction sheet resistance, *G* the junction conductivity, and Cs the junction capacitance. The parameter $\omega = 2\pi f$, where *f* is the light modulation frequency. The junction conductivity and leakage current density (I_o) are related according to $G = I_o(\frac{q}{kT})$, where q is the charge of an electron, k is Boltzmann's constant, and T is the absolute sample temperature given in Kelvin. The forward bias leakage current density (I) is subsequently calculated through the relation $I = I_o(e^{\frac{qV}{kT}} - 1)$, where V is the junction bias voltage [Cur04, Fai04, Fai05].

During RsL sample measurement, the amplitude and phase of the surface voltage signals are initially analyzed under high light modulation frequencies. Under these conditions, the harmonic term R_sC_s dominates the measured voltage and provides for direct determination of the junction sheet resistance [Cur04, Fai04, Fai05]. The *Rs* determination in this case is independent of both junction depth and leakage current effects. A second measurement, conducted at a lower modulation light frequency, enables the direct resolution of junction conductivity and leakage amplitude, as R_s is already known. In this case, the charge decay term R_sG is a dominant factor. Junction sheet resistance measurements vary by less than 0.2% between measurements for well-annealed samples with forward bias leakage currents less than 10⁻³ A/cm² [Cur04, Fai04, Fai05]. Samples exceeding 2.5 cm x 2.5 cm in dimension are required for RsL analysis. As a non-contact electrical measurement technique, sample surface preparation steps are

unnecessary. Thus, RsL measurements are an expeditious way to obtain accurate junction electrical data.

Differential Scanning Calorimetry

DSC is a thermal technique commonly used to characterize phase change temperatures, chemical reaction temperatures, melting points, or glass transition points. DSC yields peaks relating to endothermic and exothermic transitions and illustrates changes in heat capacity and heats of fusion [Ros93, Spe92]. During DSC, a sample of interest is compared to a reference material, such as powdered alumina, that does not have a transition in the temperature range of interest. Energy is supplied at a varying rate to the sample and the reference, so that the temperatures of the two remain equal as the sample is heated at a predetermined rate [Ros93, Spe92]. A DSC output plots the average temperature versus the energy supplied, enabling a direct correlation between peak areas and enthalpic changes [Spe92]. Differences in the DSC plots of the sample and the reference highlight any sample transitions in the temperature range examined.



Figure 3-1: Diagram of the SIMS sputtering process, illustrating the generation of a mixing zone.



Figure 3-2: SIMS profiles of a silicon sample containing a boron implant (a) before conversion (Secondary Ion Counts Vs. Time) and (b) after conversion (Boron Concentration Vs. Depth). [Bru92]



Figure 3-3: Types of signals generated when a high-energy beam of electrons interacts with a thin sample specimen. The directions shown for each signal do not always represent the physical direction of the signal; they designate where particular signals are of highest intensity and are commonly detected. [Wil96]



Figure 3-4: TEM diffraction patterns for (a) single crystalline aluminum, (b) polycrystalline gold, and (c) amorphous carbon. [Wil96]



Figure 3-5: XTEM bright field micrograph of a silicon sample implanted with 70 keV, 1x10¹⁵ atoms/cm² Si⁺ and 500 eV, 1x10¹⁵ atoms/cm² B⁺. The amorphous layer is buried less than 100 Å below the sample surface.



Figure 3-6: PTEM dark field micrograph of a silicon sample implanted with 70 keV, 1x10¹⁵ atoms/cm² Si⁺ and 500 eV, 1x10¹⁵ atoms/cm² B⁺. Furnace annealing was conducted at 750°C for 15 minutes. Dislocation loops and {311} defects are both present in the crystalline silicon specimen.



Figure 3-7: Planar structure commonly assumed for ellipsometric analysis. The variables n_0 and n_1 represent the complex index of refraction for the ambient medium and substrate medium, respectively. The angles of incidence and reflection are denoted as θ_0 .



Figure 3-8: Light polarization components for a linearly polarized beam in its x and y (or p and s) orthogonal component vectors. The projection plane is normal to the propagation direction of the beam. When these components are (a) exactly in phase they project a straight line, but (b) form an elliptical projection when they are not in phase. Variables *a* and *b* represent the major and minor axes of the ellipse, respectively. The angle α is the azimuthal angle relative to the x (or p) axis. [Bru92]



Figure 3-9: Experimental structure commonly assumed for ellipsometric data analysis. Where t_1 and t_3 are the thicknesses of the two deposited films, the interfacial roughness regions are denoted as t_2 and t_4 .



Figure 3-10: An electrical contact configuration for a sample prepared for Hall effect measurement using the Van der Pauw method. The dark triangles at the sample corners A, B, C, and D represent ohmic contacts.


Figure 3-11: Schematic for a material, with electrons as the predominant carrier type, experiencing the Hall effect. The applied magnetic field is denoted as B_{z} , while the Lorentz force causes electrons to curve along the y-axis, and the applied current flows along the x-axis. [Hum93]



Figure 3-12: Plot demonstrating how the geometrical correction factor *a* changes as a function of the sample thickness to probe spacing ratio *t/s*. For *t/s* ratios greater than 0.5, the correction factor *a* approaches unity. [Val54]



Figure 3-13: Schematic representation of a HRXRD experimental set-up. The two items ω and 2 θ designate the angle formed between the incident x-ray beam and the sample surface and the angle between the incident beam and the detector, respectively. [Few89]



Figure 3-14: Schematic of the photo-excitation and drift of carriers with a modulated light source and two capacitor electrodes for monitoring the induced surface photo-voltage in a spatially resolved manner. [Fai04]

CHAPTER 4 BORON DIFFUSION CHARACTERISTICS IN AMORPHOUS SILICON IN THE ABSENCE OF ANNEALING

Introduction

At present, germanium is the preamorphization species of choice over silicon, because it generates fewer defects and damage beyond the resultant amorphous/crystalline (a/c) interface and requires a much lower implant dose to amorphize silicon [Cla02, Jon87, Roo91a]. Previous works have utilized silicon and germanium preamorphizations relatively interchangeably when investigating boron diffusion characteristics, focusing on boron motion during annealing. This approach ignores the possibility that boron diffusion characteristics are highly dependent on the preamorphization species. As the semiconductor industry moves toward activation processes that inhibit additional dopant motion [Bae02, For02, Geb02, Hir99, Jua92a, Jua92b, Nap01b, Pri00], the characteristics of as-implanted dopant profiles will ultimately define junction depth. In this study, we characterize boron diffusion in germanium and silicon preamorphized silicon prior to activation annealing.

Experimental Design

Several (100) *n*-type Czochralski silicon wafers were commercially implanted at room temperature by Texas Instruments, Inc. (TI) and Axcelis Technologies. Wafers were preamorphized with either germanium ions at 60 keV or silicon ions at 70 keV at a uniform dose of 1×10^{15} atoms/cm². Cross-sectional transmission electron microscopy (XTEM) analysis and variable angle spectroscopic ellipsometry (VASE) confirmed

amorphous layer depths of approximately 930 Å and 1500 Å, respectively. The amorphized wafers were then implanted with 6 keV F^+ , 9 keV Si⁺, or 14 keV Ge⁺ at doses ranging from 1×10^{14} atoms/cm² to 5×10^{15} atoms/cm². Subsequent drift mode 500 eV, 1×10^{15} atoms/cm² ¹¹B⁺ co-implants were also performed. Fluorine, silicon, and germanium dopants were always implanted prior to the boron to eliminate any potential implant recoil effects [Jac02].

Secondary Ion Mass Spectrometry (SIMS) was performed at stage temperatures of both 25°C and -75°C. Boron SIMS profiles were obtained at room temperature (25°C) by TI and the Advanced Materials Processing and Analysis Center at the University of Central Florida (AMPAC). Samples were analyzed using a CAMECA IMS-6f tool with an O_2 + primary beam at a nominal current ranging from 50 nA to 70 nA. The beam was maintained 50° from the sample normal with a net impact energy of 800 eV. The primary beam was rastered over a 200 by 200 μ m² area, with ions collected from the center 15% of the area. A constant O_2 ambient was maintained with a sputter rate ranging from 0.08 nm/s to 0.1 nm/s. Fluorine counts were generated by TI and AMPAC at 25°C under Cs⁺ ion bombardment at an incident angle of 60°, current of 100 nA, and net impact energy of 1 keV. Secondary ions were obtained from the center 15% of the rastered area. Germanium counts were generated by AMPAC using a Cs⁺ primary beam with a current of 20 nA and energy of 3 kV.

Boron SIMS profiles were also generated by INFM-MATIS and Dipartimento di Fisica in Padova, Italy at low temperature (-75° C). A CAMECA IMS-4f tool was used with an O₂+ primary beam at a nominal current of 250 nA and net impact energy of 750 eV. A unique tilted sample holder, described previously by Napolitani et al. [Nap01a,

Nap04], enabled us to obtain a very low beam energy while maintaining a high extraction potential of 4.5 kV. The beam was rastered over a 250 by 250 μ m² area with sputtering rates of approximately 0.4 nm/s. Oxygen flooding was not incorporated during analysis at -75° C in order to reduce the probability of increased crater bottom roughening within the initial 20 nm of material, thereby compromising a sample region of primary interest. Within these measurements, increased roughening was only observed at depths greater than 50 nm.

Differential scanning calorimetry (DSC) was performed on a Seiko DSC 220, equipped with a liquid nitrogen cooling unit. Approximately 22 µg of amorphous silicon material was used for each DSC scan. A powdered alumina standard weighing 11.66 mg was used during analysis. Samples were held at room temperature for 5 minutes and then heated from 20°C to 400°C at a rate of 10°C/minute. The samples were then held at 400°C for three minutes before cooling to room temperature at a rate of 50°C/minute.

Fluorine Effects in Germanium-Amorphized Silicon

SIMS profiles for as-implanted boron and fluorine obtained under room temperature conditions are illustrated in Figure 4-1. The projected range of the 6 keV fluorine implants is approximately 160 Å [Zie03], corresponding to the tail region of the subsequent boron implants. In this figure we observe dramatic footing in the tail region of the boron profiles for those samples co-implanted with fluorine. Footing is a term used to describe profile shifts that are limited to the tail portion of dopant concentration profiles. The magnitude of anomalous deviation from the sample containing boron alone scales with increasing fluorine implant dose. When fluorine is co-implanted, boron profile footing appears to occur in as-implanted material up to a concentration of approximately 1×10^{19} atoms/cm³ (Figure 4-1). However, the SIMS measurement technique can have an estimated depth resolution ranging from approximately 10 Å to 20 Å due to the sputtering process, suggesting that the maximum footing concentration may only be as high as approximately 5×10^{18} atoms/cm³.

Figure 4-2 clearly shows the magnitude of boron profile footing prior to annealing, resulting from the presence of fluorine. The level of footing is represented as the difference in depth between a given co-implanted sample and the reference sample containing boron alone, at a particular boron concentration. For junctions defined at the boron concentration of 1×10^{18} atoms/cm³, as-implanted profiles can be up to nearly 90 Å (+/- 10 Å) deeper when co-implanted with fluorine at doses reaching 5×10^{15} atoms/cm². However, the fluorine dose for a 6 keV implant does not measurably influence the depth of as-implanted boron profiles for boron concentrations equal to or above approximately 5×10^{18} atoms/cm³.

Figure 4-1 indicates that the presence of highly concentrated fluorine increases the depth of boron profiles in germanium preamorphized material prior to annealing. To address the potential for contamination resulting from the SIMS analysis itself, the analysis was repeated at the much lower stage temperature of -75° C. During analysis, surface sputtering by the primary beam can lead to localized defect injection, thereby providing sufficient conditions for boron atoms to become mobile [Nap04]. The presence of fluorine could possibly exacerbate these effects by enhancing boron motion at room temperature. However, we observed no significant variation between boron profiles obtained at the different stage temperatures, under otherwise identical analysis parameters, for both high and low fluorine dose samples. Figure 4-3 shows as-implanted boron SIMS profiles for samples co-implanted with 6 keV, $5 \times 10^{15} \text{ atoms/cm}^2$ fluorine. There is no significant difference between the boron profiles obtained at the different temperatures, indicating a comparable level of profile footing. The two profiles illustrated were obtained under the same measurement parameters as previously outlined for the low temperature SIMS acquisition. This data is representative of fluorine doses at 6 keV ranging up to $5 \times 10^{15} \text{ atoms/cm}^2$ and demonstrates that the fluorine-enhanced boron diffusion observed in as-implanted samples is not an artifact of SIMS analysis.

Our experiments demonstrate fluorine enhanced boron concentration profile footing in germanium preamorphized silicon prior to activation annealing. When fluorine is implanted prior to boron at doses as low as $5x10^{14}$ atoms/cm², anomalous profile shifting is observed in comparison to conditions where boron is implanted alone. The depth of the boron tail region increases in magnitude as the fluorine dose increases. Anomalous boron profile footing has been observed in the presence of both germanium and fluorine co-implants. In order to understand the mechanism for this observed boron profile shifting, the individual roles of fluorine and germanium have been quantified. In addition, the effects of high dose ion implantation upon the structure of the amorphous silicon network are addressed.

Fluorine Effects in Self-Amorphized Silicon

Fluorine has been attributed with the ability to passivate dangling and strained silicon bonds within amorphous material [Ohy89, Fre95], suggesting that fluorine may be able to enhance boron motion by bonding with silicon. Fluorine-enhanced boron profile footing is observed in amorphous silicon formed through either germanium or silicon ion implantation. In this case, samples received a 70 keV, 1×10^{15} atoms/cm² Si⁺

preamorphization implant, creating a continuous surface amorphous layer approximately 1500 Å deep. Fluorine implantation was performed at an energy of 6 keV and doses ranging from 1×10^{15} atoms/cm² to 5×10^{15} atoms/cm², followed by boron implantation at an energy of 500 eV and dose of 1×10^{15} atoms/cm².

Figure 4-4 illustrates the as-implanted boron profiles for samples containing boron alone and co-implanted with fluorine. The fluorine profiles (not shown) are indistinguishable from those shown in Figure 4-1. At a boron concentration of 1×10^{18} atoms/cm³, the measured difference between the highest fluorine dose sample and the control is less than 20 Å and possibly within the SIMS measurement error. The magnitude of boron profile deviation at this concentration is approximately 80% lower in self-amorphized material containing fluorine, as compared to germanium amorphized material, indicative of less pronounced profile footing. At higher boron concentrations, the profiles shown in Figure 4-4 do not exhibit measurable deviation from the control sample. In addition, the depths of the as-implanted profiles do not sequentially increase with the fluorine dose, as samples co-implanted with 1×10^{15} atoms/cm² fluorine at 6 keV are identical.

Boron co-implanted with fluorine in germanium preamorphized samples exhibits more profile shifting than in self-amorphized material. In amorphous silicon formed via silicon implantation, profile footing does not scale in magnitude with the co-implanted fluorine dose. These results suggest that fluorine-silicon chemical interactions are possible, but are not solely responsible for the anomalous boron profile footing that occurs in germanium amorphized materials.

Germanium Effects in Self-Amorphized Silicon

Silicon-germanium interactions are also attributed with promoting the shifting of boron concentration profiles prior to annealing. As shown in Figure 4-5, co-implanted germanium doses exceeding 1×10^{14} atoms/cm² can influence the overall shape and depth of the boron SIMS profiles. Samples depicted here received a 70 keV, 1×10^{15} atoms/cm² Si⁺ preamorphization implant in conjunction with 14 keV Ge⁺ implants at doses ranging from 1×10^{14} atoms/cm² to 5×10^{15} atoms/cm². The projected range of the co-implanted germanium is approximately 160 Å [Zie03], corresponding to the tail region of the boron profiles. Boron was implanted at an energy of 500 eV and dose of 1×10^{15} atoms/cm².

Displacement of the boron profile tail region is observed in self-amorphized silicon and scales in magnitude with the increasing germanium dose. Minor profile shifts of approximately 10 Å occur at boron concentrations exceeding 1×10^{19} atoms/cm³, when coimplanted with germanium at doses exceeding 1×10^{14} atoms/cm². These small shifts are less than the SIMS measurement error. As such, the presence of germanium is attributed with enhancing profile footing at concentrations below approximately 5×10^{18} atoms/cm³.

Figure 4-6 illustrates the magnitude of boron profile footing in self-amorphized silicon resulting from the presence of germanium. At the boron concentration of 1×10^{18} atoms/cm³, as-implanted profiles are 65 Å (+/- 10 Å) deeper when co-implanted with germanium at a dose of 5×10^{15} atoms/cm². Comparisons between Figures 4-2 and 4-6 demonstrate that silicon-germanium interactions alone do not result in the anomalous profile shifts exhibited by germanium preamorphized samples.

Silicon Effects in Self-Amorphized Silicon

The extensive use of ion implantation raises the question of whether the boron profile footing observed in as-implanted samples is an implantation artifact. To address

this issue, additional samples receiving a 70 keV, $1x10^{15}$ atoms/cm² Si⁺ preamorphization implant and 9 keV Si⁺ implants at doses ranging from $1x10^{14}$ atoms/cm² to $5x10^{15}$ atoms/cm² were generated. The projected range of the silicon dopant implants is approximately 160 Å [Zie03], once again corresponding to the tail region of the boron co-implants. The purpose of an additional silicon implant was to study whether or not subsequent implantation and the further introduction of ions and damage affects the amorphous structure in a manner that might influence boron diffusion. By using silicon as the doping species, we can characterize the chemical dependence, if any, between the previously observed boron diffusion in as-implanted material and the co-dopant species.

Figure 4-7 shows the as-implanted boron profiles for samples co-implanted with 9 keV silicon. In all cases, the boron SIMS profiles are identical. No footing of the boron profiles is observed. The incorporation of additional implantation steps prior to boron implantation, even at high doses, does not inherently result in boron profile footing.

Differential scanning calorimetry was conducted in order to verify that there is no difference between the amorphous silicon structures due to silicon co-implantation. DSC analysis was performed on the control sample containing boron alone and the sample co-implanted with 9 keV silicon at the highest dose of 5×10^{15} atoms/cm². As will be discussed at length in Chapter 6, low temperature annealing of amorphous silicon is known to result in the annihilation of point defects and in a reduction of the dangling silicon bond density [Laa99a, Roo90a, Roo90b, Roo91b, Roo99, Uda87, Vol93]. If the DSC scans of the two samples of interest are identical, we can presume that there is no measurable difference in their defect populations or local structures within the sensitivity of the measurement.

Figure 4-8 illustrates the energy supplied as a function of heating temperature for as-implanted samples containing boron alone and co-implanted with 9 keV, $5x10^{15}$ atoms/cm² silicon. The energy differences in the DSC scans for these two samples are less than 200 micro-Watts for a given temperature and within the tool resolution. There is no measurable difference in the amorphous structure or defect population between samples with and without the preceding silicon implant. These results indicate that enhancement of boron motion in as-implanted samples is dependent upon both the element and dose of the co-implanted species. The effect is a result of the chemical nature of the implanted ion, rather than elastic collisions within the substrate lattice.

Discussion

The combination of a germanium preamorphization and a fluorine co-implant appears to facilitate the greatest magnitude of boron profile footing, implying that a complex chemical relationship may exist between germanium, fluorine, and silicon. Prior to activation annealing, both fluorine and germanium are believed to effectively enhance the boron mobility by binding with dangling and strained silicon bonds present within the amorphous network [Fre95, Hob95, Hob03, Ohy89].

Defect Density of Amorphous Silicon

In order to accurately describe the impact of germanium and fluorine co-doping on the shape and depth of as-implanted boron concentration profiles it also becomes necessary to quantify the defect population within ion implanted amorphous silicon. Preliminary studies of the amorphous silicon network were conducted using electron spin resonance (ESR) techniques. During ESR analysis, the measured spin density represents the estimated number of dangling silicon bonds. In as-implanted amorphous silicon formed via ion implantation the maximum spin density observed by ESR is $2x10^{19}$ spins/cm³, corresponding to a dangling bond density of approximately 0.04 at% [Spi83]. However, alternate analysis techniques suggest that ESR studies underestimate the total number of bonding defects in the amorphous structure [Bro79, Roo91b].

Using differential isothermal calorimetry (DIC) analysis, Roorda et al. calculated a defect density in amorphous silicon approaching 1×10^{20} sites/cm³. They demonstrated that when heated to 500°C for the first time, ion implanted amorphous silicon releases heat equal to approximately 5 kJ/mol, prior to the onset of recrystallization [Roo91b]. If the heat release observed by Roorda et al. is due solely to the complete annihilation of the dangling silicon bond population observed by Spitzer et al., then each dangling bond would contribute approximately 250 eV to the release. It is physically unlikely that each bond would contribute such a high energy, suggesting that low temperature annealing results in the removal of both dangling bonds and defects in amorphous silicon that are not detected by ESR methods [Roo91b]. By assuming that the formation enthalpy of a dangling bond in crystalline silicon (3.6 eV) is equivalent to the energy released during the annihilation event of a defect structure in amorphous silicon, defects are predicted to exist in as-implanted amorphous silicon formed through ion implantation on the order of approximately 1x10²⁰ defects/cm³ or 1 at% [Dan86, Roo91b]. A correlation between the enthalpy of dangling bond formation in crystalline silicon and the energy released during low temperature annealing of amorphous silicon, prior to recrystallization, presumes that all of the defect types in amorphous silicon can be annihilated under such conditions. This has not been definitively demonstrated. However, this simple relation can be used to provide a reasonable estimate of the order of magnitude in which defects may exist within amorphous silicon generated through ion implantation.

Hydrogen plasma exposure at elevated temperatures has been shown to completely eliminate the dangling silicon bond signal as detected by ESR [Kap78]. Infrared (IR) absorption spectral band analysis was used to confirm that hydrogenated films possess simple Si-H vibrations, demonstrating that the dangling bond density is decreased via hydrogen passivation [Kap78]. Thus, the level of hydrogen incorporation in amorphous silicon can also serve as a strong indication of the defect density for the material. Brodsky et al. demonstrated that amorphous silicon can be permeated with hydrogen concentrations up to 1×10^{20} atoms/cm³ [Bro79]. These results are in strong agreement with the aforementioned defect calculations of Roorda et al. established through DIC measurements [Roo91b]. Based upon these collective studies, it is reasonable to assume that the defect density of as-implanted amorphous silicon generated by ion implantation is in the range of approximately 1×10^{20} sites/cm³.

Defect Recombination

We observed boron profile footing in as-implanted, germanium-preamorphized silicon up to very high concentrations. At implant doses reaching $5x10^{15}$ atoms/cm², fluorine and germanium alone only partially eliminate the dangling bond population, primarily impacting the boron tail region. As shown previously in Figures 4-4 and 4-5, the incorporation of fluorine or germanium facilitates limited profile footing, which is confined to very low boron concentrations. However, it is proposed that a significant portion of these dangling bonds can be expunged when both germanium and fluorine atoms collectively bind with them, enabling boron to move at concentrations approaching $1x10^{19}$ atoms/cm³ (Figure 4-1). In these samples, the surface concentrations of the germanium and fluorine implants exceed $1x10^{18}$ atomc/cm³. At sample depths ranging from 100 Å to 500 Å, where boron profile footing is observed, germanium and fluorine

remain concentrated above 1×10^{19} atoms/cm³. Throughout the surface region, co-doping species are present in concentrations exceeding the maximum footing concentration.

The removal of defect and potential trapping sites in the near surface regions of implanted samples is believed to facilitate boron motion prior to annealing [Hob95, Hob03, Zie04]. Fundamental investigations of ion implantation have shown maximum lattice damage and defect generation to occur close to the substrate surface, where the distribution is generally Gaussian in nature [Zie04]. In Figure 4-9 the simulated damage profile for a 6 keV, 5×10^{15} atoms/cm² fluorine implant into amorphous silicon is shown [Zie03]. For reference, experimental boron and fluorine dopant concentration profiles are also included for samples implanted with boron alone and co-implanted with 5×10^{15} atoms/cm² fluorine. The damage profile is Gaussian in shape and representative of vacancy events that occur in the silicon substrate during the fluorine implant. As vacancies are created, dangling, strained, and weak silicon bonds are generated. The damage profile resulting from a 60 keV, 1×10^{15} atoms/cm² germanium preamorphization implant is greater in concentration than the fluorine damage profile shown in Figure 4-9 and extends beyond a depth of 1000 Å [Zie03]. The damage and collision profiles resulting from the germanium, fluorine, and boron implants exhibit substantial overlap in the near surface region.

Hobler et al. studied and developed process simulators that successfully model the effects of implantation damage in silicon [Hob95, Hob03]. They found that implantation collision cascades have the ability to stabilize existing defects through recombination, lowering the total defect population. The probability for defect recombination must be greater than that of survival in order for passivation to occur. Accurate probability

calculations require intense simulations of recoil cascades, suggesting the probabilities for recombination and survival are both system and species dependent [Hob03]. The shallower substrate regions have a greater propensity for defect trapping site passivation; thus allowing more mobile species. At greater depths, the implant damage cascades and the concentrations of incorporated species taper off [Zie04]. As a result, fewer trapping sites are removed and a smaller population of dopant atoms is mobilized beyond the surface region [Hob95, Hob03].

Our samples were sequentially implanted with germanium, fluorine, and then boron. The population of dangling silicon bonds and defect trapping sites is expected to decrease with each dopant implantation step. During the initial implantation step, germanium ions amorphize the silicon substrate, creating a dangling silicon bond population on the order of approximately 1×10^{20} sites/cm³. The damage profile of the fluorine doping implant overlaps with the existing defect population and stabilizes many of the dangling silicon bonds generated during the amorphization process via recombination with fluorine and germanium atoms. Boron is the second dopant introduced into the system and is exposed to fewer trapping sites, as a significant portion of the defect population was eliminated by the preceding fluorine damage cascade. Boron atoms are expected to diffuse in regions where the dangling silicon bond population is low. Experimentally, our specimens demonstrate boron motion in the profile tail region, corresponding to depths where the fluorine and germanium damage profiles exhibit the greatest overlap. The theory of defect and trapping site passivation applies well to our experimental observations, adequately modeling the overall shift of the boron concentration profiles and footing of the tail region [Hob95, Hob03, Zie04].

Local Bonding Arrangements

Recent works suggest that germanium interactions with surrounding boron or fluorine atoms are unlikely under the experimental conditions examined in our studies. Ajmera et al. [Ajm98] characterized a germanium effect, whereby boron implants completely contained within the amorphous layer exhibit decreasing motion during annealing with increasing germanium preamorphization dose. This effect is believed to be chemical in nature, involving Ge-B pairing or clustering. By interacting with constituent boron, germanium retards boron motion rather than enhancing it. In addition, Hattendorf et al. [Hat03] demonstrated that the binding forces between boron and germanium are not strong enough to promote Ge-B pair formation at temperatures below 600°C in silicon-rich SiGe material. While reactions with fluorine are indeed possible, Ge-F clusters or pairs have not been shown to subsequently mobilize boron. These results support the assertion that germanium and fluorine promote boron motion in as-implanted material by passivating the dangling silicon bond population.

Conventional analysis techniques of transmission fourier transform infrared spectroscopy (FTIR) and near edge x-ray absorption fine structure (NEXAFS) were used to characterize the local bonding arrangements of dopants within the amorphous silicon network. FTIR profiles were obtained on a Nicolet 560 system, while Grazing Angle FTIR (GATR) analysis was performed using Harrick GATR instrumentation. Fourier transform infrared spectroscopy is a non-destructive analysis technique that can provide information about the chemical bonds within a given material [Bru92]. FTIR monitors changes in the intensity of an incident beam of infrared radiation as a function of wavelength after it interacts with a given sample [Bru92]. Chemical bonds vary widely in their sensitivity to probing by infrared techniques and bond densities in excess of 10¹³

bonds/cm³ are required for detection of even the most intense signals [Bru92]. The specimens shown in Figure 4-1 were examined using FTIR, however, the system was unable to detect intensity changes indicative of Si-F bonding. The measurement profiles were identical for samples implanted with boron alone or co-implanted with fluorine at the highest dose of 5×10^{15} atoms/cm². If Si-F bonds are present in the material, they exist in concentrations below the detection limit of the FTIR analysis technique.

NEXAFS data was generated using the NIST-U7A synchrotron x-ray beamline at the National Synchrotron Light Source (NSLS) research facility. Near edge x-ray absorption fine structure is another non-destructive technique that can be used to determine chemical bonding information [Bru92]. Synchrotron sources are required to provide high intensity x-rays beam for sample analysis and can be used to measure constituent concentrations as low as approximately 1 at% [Bru92]. Resonances near the x-ray absorption edge of an element can indicate the type of bonding. Lighter elements, such as boron, are harder to analyze than heavier elements, such as gold, because their absorption edges occur at low photon energies that are difficult to produce [Bru92]. Low incident beam energies in the ultra-violet (UV) range were used to examine the fluorine-k and germanium-k absorption edges. The absorption edges of boron were not examined, as they are very low in energy and generally masked by the responses of other elements. The NEXAFS system was unable to detect the presence of either fluorine or germanium in the samples from Figure 4-1. No chemical bonding information for these species was obtained. The dopants under investigation were introduced into silicon in trace amounts and are below the detection limit of the NIST-U7A NEXAFS system. Collectively, these analysis results indicate that if Si-F and Si-Ge bonds are present within the amorphous

silicon networks examined, they exist in concentrations below approximately 1 at% and cannot be quantified by traditional analysis techniques.

Molecular Ion Implantation

Molecular ions represent a condition where simultaneous collision cascades partially overlap in both time and space [Zie04]. Crystal damage is enhanced, relative to the use of single ion implants, at low implantation temperatures [Zie04]. Energetic collisions result in the formation of collision cascades during implantation. These cascades form and collapse in less than approximately 10⁻¹² seconds and can lead to local heating [Zie04]. Figure 4-10 illustrates as-implanted boron concentration profiles for samples preamorphized with either 60 keV, 1x10¹⁵ atoms/cm² Ge⁺ or 58 keV, 1.5x10¹⁵ atoms/cm² GeF⁺. Samples were doped with 500 eV, 1x10¹⁵ atoms/cm² B⁺. For the GeF⁺ molecular implant, the equivalent germanium and fluorine implant energies are approximately 46 keV and 12 keV, respectively. The boron profiles are nearly identical, illustrating that the introduction of germanium and fluorine into silicon through molecular implantation does not lead to boron profile footing.

In the case of GeF⁺ implantation, both germanium and fluorine are introduced into crystalline silicon. The amorphous network is created during the implantation process, such that structural defects may not exist throughout the material at the time of dopant incorporation. Implantation of fluorine into preamorphized material also results in the overlap of collision cascades. However, when sequential amorphizing and doping implants are utilized additional cascades occur in regions containing preexisting lattice damage, differing from molecular implant conditions. Local heating effects from the collapse of subsequent damage cascades may facilitate the motion of dopants, such as germanium and fluorine, into structural defect sites thereby reducing the population of potential boron trapping sites.

Additionally, a GeF⁺ molecular implant could result in a greater number of structural defects in the amorphous network, as compared to equivalent singular Ge⁺ and F⁺ implants. Under these conditions, recombination events may still occur but not with enough frequency to passivate a significant number of trapping sites and enhance boron mobility. The absence of measurable profile footing following molecular GeF⁺ implantation demonstrates that the impact of recombination events during dopant implantation may be dependent upon the nature of the substrate material, as well as the manner in which dopant species are introduced into the system.

Background: Trap-Limited Boron Diffusion

Previously, Collart et al. demonstrated the room temperature migration and clustering of implanted boron in crystalline silicon [Col98]. A distinctive exponential decay in the tail of boron concentration profiles was observed. Mobile ¹¹B atoms were found to migrate until they became trapped by substitutional ¹⁰B. As the ¹⁰B background and trapping concentration was reduced, the boron profile footing became steeper and more pronounced. At room temperature, in the absence of trapping at imperfections or defects, interstitial boron atoms are believed to be free to perform a random walk in crystalline silicon [Col98]. Migration and trapping mechanisms were attributed with acting simultaneously, based on the visible exponential decay in the boron profiles. Without a trapping mechanism where no de-trapping or boron release occurs, room temperature migration would result in very low boron concentrations [Col98]. The ¹¹B diffusion length was shown to decrease as the ¹⁰B trapping site population increases.

For a simple model based on the interaction of a given species A and a trap T, there are two types of recombination reactions that can occur. A trap site is defined as an arbitrary defect or structure that can bind with and impede the mobility of a diffusing species. If a trap can continuously capture A with no change in efficiency, then the reaction is described by $A + T \leftrightarrow T$. This type of reaction results in a steady-state profile, as A is never released once trapped and the concentration of traps is never reduced [Gri87]. If trapping sites can be annihilated during the trapping process and subsequently release A, then the reaction is represented by $A + T \leftrightarrow AT$. At each point in time, only untrapped A is assumed to be mobile and contribute to the overall diffusion of A through the material. In this case, mobile species exhibit an effective diffusion coefficient with time [Gri87]. However, if the rate of release of A from AT is very low, then the reaction $A + T \leftrightarrow AT$ can be used to describe a perfect trap. Under perfect trapping conditions, essentially no A is released. The concentrations of mobile A and trapping sites steadily decrease with time, resulting in an exponential decay of the diffusion profile for species A.

Cowern has proposed two partial differential equations to describe the diffusion of silicon interstitials in the presence of immobile and saturable trapping sites [Cow94a]. It is important to note that the mathematical relationships subsequently discussed are not solely limited to the diffusion of silicon interstitials in bulk silicon. They can be applied to the diffusion of any dopant or defect species under trap-limited diffusion conditions in silicon. The partial differential equations presented by Cowern involve both the time and spatial evolution of the silicon interstitial concentration (C_I) and the intrinsic trapping site concentration (C_I), as shown below [Cow94a]. However, they do not include terms for

the introduction of additional silicon interstitials or the recombination of existing interstitials with vacancies at the sample surface during annealing [Mir02].

$$\frac{\partial C_I(x,t)}{\partial t} = \nabla (D_I \nabla C_I) - (4 \pi a_I D_I C_I C_t - G_I)$$
(4-1)

$$\frac{\partial C_t(x,t)}{\partial t} = -\frac{4\pi a_t D_l C_l C_t - G_t}{n}$$
(4-2)

The term D_I represents the diffusivity of silicon interstitials, a_t is the capture radius for the trapping reaction, and n is the mean number of interstitials required to eliminate one trap. The parameters G_I and G_T are the generation rates for the silicon interstitials and trapping sites, respectively, that depend on the nature of the traps [Cow94a]. The generation rate terms can also be interpreted as the probability of a reverse reaction, where a silicon interstitial is released from a trapping site, thus generating a mobile interstitial and a trap site [Mir02].

The expression $4\pi a_t D_t C_t C_t$ represents the interaction term between silicon interstitials and trapping sites, where $4\pi a_t D_t$ is the forward reaction rate constant for interstitial trapping [Cow94a, Gri87]. If the recombination rate constant is presumed to be diffusion limited, such that annihilation of the silicon interstitial population is limited only by the rate that they interact with trapping sites, then the recombination rate is defined as $4\pi a_t (D_t + D_t)$ [Aga95, Cow94a, Gri87, Mat89, Ric89, Vuo95]. Since the trapping sites are assumed to be immobile, D_t is equal to zero and the expression simplifies to $4\pi a_t D_t$. The recombination event is presumed to occur within a spherical reaction zone with a surface area equal to $4\pi r^2$. In order for silicon interstitials to bind with trapping sites, they must diffuse a distance *r* into the reaction zone. The radius of the reaction zone is synonymous with the effective capture radius a_t , leading to the expression $4\pi a_t$ within the interaction rate term and the forward reaction rate constant.

Authors commonly presume a reaction rate of the form $4\pi a_i D_A D_T$ for a diffusing species *A* combining with traps *T* in bulk silicon [Aga95, Cow94a, Gri87, Mat89, Ric89, Vuo95]. It is rather difficult to directly measure reaction rate constants and the mathematical derivations are rather complex, so simple kinetic approximations are routinely used. The effective capture radius is believed to follow an Arrhenius expression, where a_o is the temperature-independent exponential term in Angstroms, *k* is Boltzmann's constant (eV/K), *T* is the absolute temperature in Kelvin, and E_b is the energy barrier to the capture reaction (eV) [Col98, Cow94a]:

$$a_t = a_o \, e^{\left(\frac{-E_b}{kT}\right)} \tag{4-3}$$

When n = 1, a_o is of atomic dimensions, and a_t is on the order of the matrix or substrate lattice parameter [Cow94a].

For the case of silicon interstitials diffusing in the presence of immobile and saturable trapping sites in silicon, the total concentration of active silicon interstitials is equal to the sum of the concentration of mobile silicon interstitials (C_l) and the concentration of trapped silicon interstitials (C_l*n) [Cow94a]. If the concentration of active silicon interstitials is known and held constant, the calculated values for the concentration of mobile silicon interstitials and the concentration of trapped silicon interstitials are restricted by the imposed boundary condition, providing continuity to the diffusion process. Only the concentration of mobile or untrapped interstitials contributes

to the diffusion profile and this concentration changes with each point in time, resulting in an effective diffusion coefficient.

To ensure accurate calculations and predictions using Equations 4-1 and 4-2, values for several of the parameters must initially be assumed [Mir02]. For example, the number of interstitials required to passivate each trap site, the maximum concentration of trap sites, the equilibrium diffusivity of the silicon interstitial, and the generation rates for unbound silicon interstitials and trapping sites are parameters commonly assigned fixed values [Mir02]. The agreement between experimental and predicted diffusion profiles is highly dependent upon the initial assumptions.

Simulations: Trap-Limited Boron Diffusion

Our experimental results regarding boron diffusion in amorphous silicon at room temperature are comparable to the observations of Collart et al. for crystalline silicon [Col98]. These similarities suggest that boron diffusion in amorphous silicon may be limited by trapping at defect sites intrinsic to the amorphous structure. Diffusion simulations were conducted in order to investigate the role of immobile, saturable trapping sites in the diffusion mechanism for boron in amorphous silicon in the absence of annealing. Simulations were generated at room temperature (25°C) using the FLorida Object Oriented Process Simulator (FLOOPS).

Based on the work of Cowern [Cow94a], partial differential equations were developed to relate the concentrations of active, mobile, and trapped boron. The concentration of active boron is equal to the sum of the mobile and trapped boron concentrations. Active boron is defined as the population of boron atoms that are below the solubility limit for boron in amorphous silicon, which have the potential to diffuse. Mobile boron represents the group of boron atoms that are actually diffusing through the substrate. Trapped boron pertains to the population of boron atoms that have bonded with defects in the amorphous silicon structure and are no longer mobile.

The concentrations of mobile and trapped boron vary at each point in time, resulting in an effective diffusivity coefficient. The various diffusion parameters are related through our partial differential equations as follows:

$$\frac{\partial C_{TB}}{\partial t} = D_B \nabla (C_{AB} - C_{TT})$$

$$\frac{\partial C_{TT}}{\partial t} = kf 4 \pi a \left[\left[(C_{MT} - C_{TT}) (C_{AB} - C_{TT}) \right] - kr^* C_{TT} \right]$$
(4-4)
(4-5)

where C_{TB} is the total concentration of boron, ∇ represents the concentration gradient driving the diffusion of boron, C_{AB} is the active boron concentration, and C_{TT} is the trapped boron concentration. The maximum concentration of traps present in the substrate is C_{MT} . The parameter D_B represents the diffusivity of mobile boron, a is the effective capture radius for trapping, and kf and kr are forward and reverse interaction rate terms, respectively.

The total concentration of boron and the active boron concentration are related by the solubility limit for boron in amorphous silicon. At concentrations below the boron solubility limit $C_{TB} = C_{AB}$, while above the solubility limit C_{AB} simply equals the solubility limit. The total concentration of boron is known and fixed based upon experimental SIMS measurements, thus the concentration of active boron is also a known parameter. In these simulations it is assumed that one boron atom is required to eliminate one trapping site. For these simulations, the control sample containing boron alone was presumed to be the initial profile, establishing the concentrations of total and active boron. The asimplanted profiles for samples co-implanted with 6 keV fluorine at varying doses were presumed to be the diffused profiles (Figure 4-1), as boron is believed to diffuse at room temperature. The duration between boron implantation and SIMS measurement was several weeks, suggesting that the boron migration events at room temperature had already reached completion prior to analysis.

In order to obtain accurate agreement between the simulated and experimental profiles, several of the aforementioned parameters were assigned specific values. The asimplanted profile for samples co-implanted with 6 keV, $5x10^{14}$ atoms/cm² fluorine was used to establish preliminary parameter values, assuming a maximum trap concentration of $1x10^{20}$ traps/cm³ and an effective capture radius of 2.71 Å, equal to the lattice spacing of crystalline silicon. The parameter *kr* was set equal to $1x10^{-5}$ atoms/cm³, establishing a perfect trapping condition where boron atoms are not released once trapped. In order to simulate the exponential tail of the boron profiles, it was necessary to impose a solubility limit for boron in amorphous silicon. For these room temperature simulations, a boron solubility limit of approximately $2x10^{18}$ atoms/cm³ was assumed.

Collart et al. observed the migration events of a very small population of interstitial boron to reach completion within one hour at room temperature after boron implantation into crystalline silicon [Col98]. Their findings suggest that a time frame of several hours for completion of boron diffusion in amorphous silicon is reasonable. By setting D_B equal to 5×10^{-17} cm²/second and *kf* to 1×10^{-15} cm³/atoms-Å, strong agreement was obtained between the simulated and experimental profiles at 25°C. All of the

simulated trapping reactions were completed within less than nine hours after boron implantation. By predetermining the solubility limit, C_{TB} , C_{AB} , D_B , a, kf, and kr it was possible to extract the value for the maximum concentration of traps required to accurately simulate the behavior of the remaining SIMS diffusion profiles.

The experimental and simulated boron concentration profiles for samples implanted with boron alone and co-implanted with 6 keV fluorine at varying doses are illustrated in Figure 4-11. Diffusion was simulated at 25°C for a time of 1000 minutes, with no trapping events occurring after the first 540 minutes. The FLOOPS code used for these simulations is provided in Appendix A. The depth and concentration scales have been truncated in order to emphasize boron diffusion in the tail region of the boron profile. The simulated and experimental profiles exhibit strong agreement, differing by less than 1 nm across the entire profile range.

The simulated boron profiles demonstrate boron diffusion above the assumed solubility limit of approximately $2x10^{18}$ atoms/cm³ at room temperature. A rounding procedure for the solubility limit was used to ensure smooth simulation profiles, resulting in boron diffusion at higher concentrations. The simulated profiles enable boron diffusion up to concentrations of approximately $6x10^{18}$ atoms/cm³, three times greater than the defined solubility limit. The FLOOPS simulations were able to predict the shapes and relative features of the SIMS profiles, implying that boron diffusion in amorphous silicon at room temperature may be a trap-limited process where perfect trapping occurs.

Based on the FLOOPS simulations, the maximum concentration of trapping sites was found to change as a function of the co-implanted fluorine dose. The profiles from Figure 4-1 were used to calculate the dose of mobile boron as a function of the co-

implanted fluorine dose, assuming that only atoms below a concentration of 6×10^{18} atoms/cm³ are mobile. The mobile boron dose is representative of the difference in boron dose between a given co-implanted sample and the reference sample containing boron alone. As shown in Figure 4-12, the mobile dose of boron increases as the fluorine dose increases. However, the estimated trap concentration decreases as the fluorine dose increases. The mobile dose of boron (*BD_{Mobile}*) is related to the trapping site concentration (*T*) through a power law function with an R² value of 0.99.

$$BD_{Mobile} (atoms/cm^{3}) = \frac{5.97 \times 10^{21}}{T^{0.5}} (atoms/cm^{3})$$
(4-6)

Similarly, the dose of mobile boron and the trapping site concentration in amorphous silicon vary with the co-implanted fluorine dose according to power law functions. Comparable results were also obtained assuming a maximum mobile boron concentration of 1×10^{19} atoms/cm³, demonstrating the strength of the aforementioned correlations. These observations imply that the passivation of defect sites in the amorphous silicon structure, resulting from the overlap of successive implantation collision cascades, facilitates the diffusion of boron at room temperature. They also suggest that local defect structures are capable of serving as perfect trapping sites for boron atoms in amorphous silicon in the absence of annealing.

Summary and Conclusions

Boron can diffuse in amorphous silicon in the absence of annealing. Defects inherent to the structure of amorphous silicon can trap and immobilize boron atoms at room temperature. These trapping sites can be stabilized by recombination events during implantation, due to overlapping collision cascades. The probability for recombination is highly dependent on the choice of implanted species. Chemical reactions between silicon and fluorine, as well as silicon and germanium, are believed to result in the elimination of potential trapping sites. However, additional silicon-silicon interactions were not shown to alter the structure of amorphous silicon. The use of sequential germanium and fluorine implants results in greater boron motion, as compared to silicon and fluorine implants into silicon. Boron exhibits a solubility limit at room temperature in amorphous silicon generated via germanium implantation, with maximum mobile boron doses on the order of approximately 1×10^{12} atoms/cm².



Figure 4-1: Room temperature (25°C) dopant concentration profiles for as-implanted samples receiving 6 keV fluorine at doses ranging from 1x10¹⁵ atoms/cm² to 5x10¹⁵ atoms/cm², co-implanted with 500 eV, 1x10¹⁵ atoms/cm² boron. (60 keV, 1x10¹⁵ atoms/cm² Ge⁺ preamorphization)



Figure 4-2: Boron profile footing at concentrations ranging from 1×10^{18} atoms/cm³ to 1×10^{19} atoms/cm³ in as-implanted samples with 6 keV fluorine at varied doses. (60 keV, 1×10^{15} atoms/cm² Ge⁺ preamorphization)



Figure 4-3: Comparison of room temperature (25°C) and low temperature (-75°C) boron concentration profiles for as-implanted samples receiving 6 keV fluorine at a dose of 5x10¹⁵ atoms/cm² and co-implanted with 500 eV, 1x10¹⁵ atoms/cm² boron. (60 keV, 1x10¹⁵ atoms/cm² Ge⁺ preamorphization)



Figure 4-4: Room temperature (25°C) boron concentration profiles for as-implanted samples receiving 6 keV fluorine at doses ranging from 1x10¹⁵ atoms/cm² to 5x10¹⁵ atoms/cm², co-implanted with 500 eV, 1x10¹⁵ atoms/cm² boron. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 4-5: Room temperature (25°C) boron concentration profiles for as-implanted samples receiving 14 keV germanium at doses ranging from 1x10¹⁴ atoms/cm² to 5x10¹⁵ atoms/cm², co-implanted with 500 eV, 1x10¹⁵ atoms/cm² boron. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 4-6: Boron profile footing at concentrations ranging from 1×10^{18} atoms/cm³ to 1×10^{19} atoms/cm³ in as-implanted samples with varied dose 14 keV germanium. (70 keV, 1×10^{15} atoms/cm² Si⁺ preamorphization)


Figure 4-7: Room temperature (25°C) boron concentration profiles for as-implanted samples receiving 9 keV silicon at doses of 1x10¹⁴ atoms/cm² and 5x10¹⁵ atoms/cm², co-implanted with 500 eV, 1x10¹⁵ atoms/cm² boron. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 4-8: Differential scanning calorimetry (DSC) plot of the energy supplied as a function of heating temperature for as-implanted samples receiving 500 eV, $1x10^{15}$ atoms/cm² boron with and without co-implanted 9 keV, $5x10^{15}$ silicon. (70 keV, $1x10^{15}$ atoms/cm² Si⁺ preamorphization)



Figure 4-9: Simulated damage profile for a 6 keV, 5x10¹⁵ atoms/cm² fluorine implant [Zie03], shown with room temperature (25°C) dopant concentration profiles for as-implanted samples receiving 500 eV, 1x10¹⁵ atoms/cm² boron with and without co-implanted 6 keV, 5x10¹⁵ fluorine. (60 keV, 1x10¹⁵ atoms/cm² Ge⁺ preamorphization)



Figure 4-10: Room temperature (25°C) dopant concentration profiles for as-implanted samples receiving 500 eV, 1x10¹⁵ atoms/cm² boron implants. Samples were preamorphized with either 60 keV, 1x10¹⁵ atoms/cm² Ge⁺ or 58 keV, 1.5x10¹⁵ atoms/cm² GeF⁺ implants. No profile footing is observed when germanium and fluorine are incorporated via molecular implantation, versus successive singular implants.



Figure 4-11: Room temperature (25°C) dopant concentration profiles for samples receiving 6 keV fluorine at doses ranging from 1×10^{15} atoms/cm² to 5×10^{15} atoms/cm², co-implanted with 500 eV, 1×10^{15} atoms/cm² boron. Experimental and simulated boron diffusion profiles are shown after room temperature diffusion. (60 keV, 1×10^{15} atoms/cm² Ge⁺ preamorphization)



Figure 4-12: Calculated mobile boron dose as a function of the estimated trapping site concentration at room temperature. Samples received 6 keV fluorine at doses ranging from $5x10^{14}$ atoms/cm² to $5x10^{15}$ atoms/cm², co-implanted with 500 eV, $1x10^{15}$ atoms/cm² boron. Boron is presumed to be mobile at room temperature, varying in concentration with the fluorine dose. (60 keV, $1x10^{15}$ atoms/cm² Ge⁺ preamorphization)

CHAPTER 5 BORON DIFFUSION CHARACTERISTICS IN AMORPHOUS SILICON DURING THE SOLID PHASE EPITAXIAL REGROWTH PROCESS

Introduction

As the semiconductor industry moves toward activation processes that limit additional dopant motion [Bae02, For02, Geb02, Hir99, Jua92a, Jua92b, Nap01b, Pri00], the characteristics of as-implanted dopant profiles and dopant diffusion during the solid phase epitaxial regrowth (SPER) process will ultimately define transistor junction depth. At present, relatively few studies regarding dopant diffusion in ion implanted amorphous silicon have been conducted. Metallic dopants such as copper, gold, and silver have been shown to diffuse in both crystalline and amorphous silicon [Ell85, Pol90, Pri88]. Low temperature annealing can result in substantial diffusion of these species within amorphous silicon, such that if a dopant is a "fast diffuser" in crystalline silicon it will also exhibit a high diffusivity in amorphous silicon [Pri88, Ell85]. Metalloids and other metals have also demonstrated measurable diffusive behavior in amorphous silicon [Ell85]. However, arsenic, antimony, indium, and bismuth exhibit negligible diffusion at temperatures ranging from 500°C to 600°C when present in low concentrations [Ell85]. High concentrations on par with their solid solubility in crystalline silicon are required for measurable diffusion to occur during SPER [Ell85]. In addition to diffusion, precipitation of the aforementioned metallic and metalloid species also occurs in amorphous silicon during heating [Ell85, Pol90].

Preliminary studies have shown boron to diffuse within amorphous silicon during low temperature SPER annealing [Ell98a, Duf04, Jac05]. However, questions still remain regarding the activation energy for diffusion, the mechanism of diffusion, and the specific roles of germanium, fluorine, and hydrogen in regards to this enhanced boron diffusion. Within this study, boron diffusion phenomena in both germanium and silicon preamorphized silicon during SPER annealing are characterized. The influences of additional doping species upon boron diffusion in amorphous silicon and the SPER process are quantified.

Experimental Design

Several (100) n-type, 200 mm Czochralski wafers were commercially implanted at room temperature by Texas Instruments, Inc. (TI), Axcelis Technologies, International SEMATECH, and Varian Semiconductor Equipment Associates. Wafers were preamorphized with either germanium or silicon implants. Germanium ions were implanted at an energy of 60 keV and dose of 1×10^{15} atoms/cm². Silicon implants were conducted at energies of 15 keV and 70 keV, both at a dose of 1×10^{15} atoms/cm². To ensure the formation of continuous, surface amorphous layers, both 15 keV and 70 keV silicon implants were performed for self-amorphized samples, as silicon implants greater than 60 keV often generate buried amorphous layers. Variable angle spectroscopic ellipsometry (VASE) and cross-sectional transmission electron microscopy (TEM) analysis confirmed amorphous layer depths of approximately 930 Å and 1700 Å for germanium and self-amorphized material, respectively. VASE measurements were made at beam angles of 65°, 70°, and 75°.

The preamorphized wafers received a variety of subsequent doping implants at doses ranging from 1×10^{14} atoms/cm² to 5×10^{15} atoms/cm². Si⁺ implants were performed

at 9 keV, F^+ implants at 6 keV, and Ge^+ implants at an energy of 14 keV. Subsequent drift mode 500 eV, $1x10^{15}$ atoms/cm² ¹¹B⁺ co-implants were also performed for all wafers. In most cases, the silicon, fluorine, and germanium dopants were intentionally introduced prior to the boron to eliminate any potential implant recoil effects [Jac02]. The projected ranges of the silicon, fluorine, and germanium doping implants are approximately 160 Å, corresponding to the tail region of the subsequent boron implants [Zie03]. Ensuing sample annealing occurred at temperatures ranging from 500°C to 700°C under a flowing, inert N₂ ambient. Annealing at 500°C and 550°C was conducted in a quartz tube furnace, while annealing at 600°C and 700°C was performed in a rapid thermal annealing (RTA) system.

Secondary Ion Mass Spectrometry (SIMS) was performed at room temperature by TI, the Advanced Materials Processing and Analysis Center at the University of Central Florida, and International SEMATECH. Boron SIMS profiles were obtained using a CAMECA IMS-6f tool with an O_2 + primary beam at a nominal current ranging from 50 nA to 70 nA. The beam was maintained 50° from the sample normal with a net impact energy of 800 eV. The primary beam was rastered over a 200 by 200 μ m² area, with secondary ions collected from the center 15% of the area. A constant O_2 ambient was maintained with a sputter rate ranging from 0.08 nm/s to 0.1 nm/s. Fluorine counts were generated under Cs⁺ ion bombardment at an incident angle of 60°, current of 100 nA, and net impact energy of 1 keV. Germanium and hydrogen counts were also generated using a Cs⁺ primary beam with an energy of 3 kV. Nominal beam currents of 20 nA and 10 nA, respectively, were employed during analysis.

Boron Diffusion in Amorphous Silicon

Boron demonstrates significant diffusion in amorphous silicon during SPER annealing at 550°C in the absence of co-doping species. Figure 5-1 illustrates boron concentration profiles for self-amorphized samples containing boron alone. Wafers were preamorphized with both 15 keV and 70 keV Si^+ at a dose of 1×10^{15} atoms/cm², followed by B^+ implantation at an energy of 500 eV and dose of 1×10^{15} atoms/cm². Boron is clearly mobile at concentrations below approximately $2x10^{20}$ atoms/cm³, exhibiting a solubility limit in amorphous silicon. After annealing at 550°C for 15 minutes, some regrowth of the continuous, surface amorphous layer has occurred. However, the amorphous crystalline interface remains more than 500 Å deep and has not interacted with the boron concentration profiles. The profiles shown in Figure 5-1 are strictly representative of boron diffusion within amorphous silicon. Similar boron diffusion characteristics are observed for germanium amorphized silicon containing boron alone. In this case, samples were amorphized with 60 keV, 1×10^{15} atoms/cm² Ge⁺. As shown in Figure 5-2, boron diffusion profiles exhibit similar features in amorphous silicon formed via either silicon or germanium ion implantation.

Ion implantation generates concentration profiles that are Gaussian in nature [Zie04]. Gaussian distributions can be plotted via the mathematical expression [May90]:

$$P(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp^{\left(-\frac{(x-\bar{x})^2}{2\sigma^2}\right)}$$
(5-1)

Where σ is the standard deviation, σ^2 represents the variance, and *x* denotes the profile mean. By setting the mean equal to zero, a Half-Gaussian distribution can be obtained. Gaussian profiles are commonly described by their full width at half maximum (FWHM).

Changes to a given distribution that is originally Gaussian in shape, such as profile broadening, or comparisons between two separate Gaussian type distributions can be described by their difference in profile width at a fixed value. When monitoring the evolution of a given distribution, the half maximum value of the initial profile is commonly used as the reference point for reporting the profile width. This approach presumes that the profile remains Gaussian in nature throughout its evolution and can still be described by Equation 5-1. However, if a given distribution only changes below a fixed value then a modified-Gaussian distribution results. Under these conditions,

changes in the initial profile can be described by the profile width at $\frac{P(x)_M}{e}$, where $P(x)_M$ represents the maximum value at which a given profile deviates from the initial distribution. These practices can be extended directly to dopant concentration profiles implanted into amorphous silicon, as they generally follow Gaussian curves.

Within amorphous silicon, boron follows a modified-Gaussian distribution during the SPER annealing process. As-implanted boron concentration profiles are Gaussian in nature and boron is observed to diffuse at concentrations below a solubility limit on the order of approximately 1×10^{20} atoms/cm³. The diffusion length λ of a diffusing species corresponds to the change in profile width for a Half-Gaussian distribution. The diffusion length is routinely related to the diffusion coefficient *D* given in cm²/second and the annealing time *t* provided in seconds for a given annealing temperature according to the mathematical expression [May90]:

$$\lambda (\rm{cm}) = \sqrt{4Dt} (\rm{cm}) \tag{5-2}$$

In amorphous silicon at temperatures ranging from 550°C to 700°C, the boron diffusion length is calculated at a concentration of 3×10^{19} atoms/cm³ based on the relation

$$\frac{P(x)_M}{e} \cong \frac{1 \times 10^{20} \ atoms/cm^3}{e} \approx 3 \times 10^{19} \ atoms/cm^3 \tag{5-3}$$

By measuring the magnitude of boron diffusion at this concentration, the boron diffusivity for a Half-Gaussian distribution can be calculated. Throughout these annealing studies, the diffusion length and time-averaged boron diffusivity are reported at a uniform boron concentration of 3×10^{19} atoms/cm³.

Boron exhibits a stable time-averaged diffusivity in amorphous silicon. At a temperature of 550°C boron maintains a diffusivity of approximately $2x10^{-17}$ cm²/second throughout the annealing process. Diffusivities were calculated using a Half-Gaussian boron concentration of $3x10^{19}$ atoms/cm³. Boron diffusion during SPER annealing is not transient. Boron diffusion during the recrystallization process can be critical to transistor junction depths, as the time-averaged boron diffusivity in amorphous silicon is five orders of magnitude greater than the extrapolated value for boron diffusion in crystalline silicon [Law98]. These results are in close agreement with previous work by Elliman et al. for MBE samples annealed at 600°C [Ell98a], where boron exhibited a diffusivity of approximately $1x10^{-16}$ cm²/second; five orders of magnitude greater than values observed in crystalline silicon. Within amorphous silicon formed through ion implantation techniques, boron exhibits enhanced diffusion.

Non-Fickian Boron Diffusion

The diffusion coefficient is commonly denoted by the Arrhenius expression

$$D = D_o e^{\left(\frac{-Q_D}{RT}\right)}$$
(5-4)

Where D_o (cm²/second), Q_D (J/mol), and T (Kelvin) represent the temperatureindependent pre-exponential, activation energy for diffusion, and the absolute temperature, respectively [Cal97, Nic89]. The parameter R is the universal gas constant, equal to 8.314 J/K-mol [Hum93]. When the value of Q_D is provided in units of eV, the term R in Equation 5-4 is routinely replaced by Boltzmann's constant, denoted as either kor k_B , with a value of 8.617x10⁻⁵ eV/K [Hum93].

A partial differential equation is used to vary the diffusivity of a mobile species as a function of annealing time at a given temperature. Fick's second law represents the vector form of Fick's first law and is expressed as follows:

$$\frac{\partial C_A}{\partial t} = D_A \nabla(C_A) \tag{5-5}$$

Where $\frac{\partial C_A}{\partial t}$ represents the change in concentration of a given species A with time, D_A is the diffusivity or diffusion coefficient of A, ∇ is the concentration gradient driving the diffusion of A, and C_A is the concentration of species A [Gli00]. Equation 5-5 represents purely Fickian diffusion and assumes that all of the atoms of species A are mobile and free to diffuse during annealing. If the species A has a solubility limit in the diffusion matrix, only atoms below this limit are able to diffuse. Above the solubility limit, the diffusivity of species A is presumed to be very small. In this case, the mobile fraction of A can be represented as C_{MA} and the partial differential equation relating the diffusivity with time becomes

$$\frac{\partial C_A}{\partial t} = D_A \nabla(C_{MA}) \tag{5-6}$$

Equation 5-6 is based on Fick's second law and is representative of Fickian diffusion. Since boron exhibits a solubility limit within amorphous silicon, Equation 5-6 can be applied to ascertain whether or not boron diffusion is Fickian in nature.

A Fickian diffusion approach cannot be used to accurately predict the shape and features of boron diffusion profiles in amorphous silicon. FLOOPS was used to simulate boron diffusion in amorphous silicon at 550°C. Figures 5-3 and 5-4 illustrate the experimentally measured and simulated boron diffusion profiles for self and germanium amorphized materials, respectively, implanted with boron alone. In order to simulate the general shape of the experimental diffusion profiles it was necessary to apply a boron solubility limit in amorphous silicon. A solubility limit of 5×10^{20} atoms/cm³ was assumed for the profiles shown in Figures 5-3 and 5-4. Based on the experimentally calculated values for the time-averaged boron diffusivity, a value of 5.0×10^{-17} cm²/second was used for the boron diffusion coefficient. A single set of FLOOPS code was used to simulate Fickian boron diffusion, regardless of the preamorphization implant species. The related code for these samples is contained in Appendix B. For a given annealing time at 550°C, the experimental and simulated profiles do not demonstrate significant overlap (Figures 5-3 and 5-4). The magnitude of boron diffusion in the higher concentration regimes is not accurately predicted, suggesting that the boron diffusion coefficient may be dependent upon the boron concentration. The features of boron diffusion profiles in amorphous silicon during SPER are dictated by the initial boron concentration profile. These results illustrate that boron diffusion in amorphous silicon is non-Fickian.

Silicon and Germanium Effects upon Boron Diffusion

The presence of silicon and germanium co-dopants does not impact boron diffusion characteristics in amorphous silicon. Boron SIMS profiles for self-amorphized material

are illustrated in Figure 5-5. Samples containing boron alone and boron co-implanted with 9 keV, $5x10^{15}$ atoms/cm² silicon are shown as-implanted and after 15 minutes of annealing at 550°C. The purpose of the second silicon implant was to study whether or not subsequent implantation affects the amorphous structure in a manner that might influence boron diffusion. This annealing treatment results in approximately 700 Å of solid phase regrowth, such that boron resides in amorphous silicon throughout the diffusion process. The anneal times and temperatures subsequently discussed in this chapter were chosen in order to retain boron in amorphous silicon. The boron concentration profiles in Figure 5-5 are nearly identical, in both the presence and absence of annealing. Similar results were also observed for $1x10^{14}$ atoms/cm² and $1x10^{15}$ atoms/cm² dose 9 keV silicon co-implant conditions.

At a boron concentration of 1×10^{19} atoms/cm³, boron diffuses more than 30 Å after 15 minutes of SPER annealing at 550°C (Figure 5-5). Boron exhibits a relatively stable time-averaged diffusivity of approximately 2×10^{-17} cm²/second in amorphous silicon under these conditions. Within the experimental margin of error, the addition of the second silicon implant has no measurable impact on the boron diffusivity, as seen in Figure 5-6. Time-averaged boron diffusivity values were calculated for a Half-Gaussian boron concentration of 3×10^{19} atoms/cm³.

Similar experiments were conducted for self-amorphized samples co-implanted with 14 keV Ge⁺ at doses ranging up to 5×10^{15} atoms/cm². The preceding germanium implant exerts only a minor impact on the as-implanted and annealed boron concentration profiles, as shown in Figure 5-7 for a germanium dose of 5×10^{15} atoms/cm². The differences between the as-implanted profiles are less than 20 Å above a boron concentration of 3×10^{18} atoms/cm³ and within the estimated SIMS resolution. These differences are not observed after annealing. The time-averaged boron diffusivity within amorphous silicon at a temperature of 550°C was also found to be independent of the coimplanted germanium dose. Diffusivity values were calculated for a Half-Gaussian boron concentration of 3×10^{19} atoms/cm³. Figure 5-8 demonstrates that boron exhibits an intrinsic time-averaged diffusivity within amorphous silicon on the order of approximately 1×10^{-17} cm²/second at 550°C. The introduction of co-doping species prior to boron implantation does not inherently alter boron diffusion phenomena in amorphous silicon during the SPER process. The diffusion mechanism for boron appears to be independent of the presence of highly concentrated silicon and germanium, conventional preamorphization implant species.

Fluorine Effects upon Boron Diffusion

Fluorine has been attributed with the ability to passivate dangling and strained silicon bonds within amorphous material [Ohy89, Fre95], suggesting that fluorine may influence boron motion during SPER annealing by bonding with silicon. The role of fluorine has been thoroughly characterized in order to determine the level of participation, if any, of dangling silicon bonds in regards to the mechanism for boron diffusion in amorphous silicon. Fluorine and boron co-implantation was examined in both self and germanium amorphized silicon for a range of implantation conditions and SPER annealing temperatures.

Activation Energy for Boron Diffusion

When fluorine is co-implanted into self-amorphized silicon prior to boron, fluorine does not impact the as-implanted or annealed boron concentration profiles. Figure 5-9 portrays boron SIMS profiles for samples implanted with boron alone or co-implanted

with 6 keV, $2x10^{15}$ atoms/cm² F⁺. The boron concentration profiles are independent of the presence of fluorine. Similarly, the time-averaged boron diffusivity in amorphous silicon for a Half-Gaussian boron concentration of $3x10^{19}$ atoms/cm³ was found to be independent of the co-implanted fluorine dose. Figure 5-10 shows that within the experimental margin of error boron exhibits an intrinsic time-averaged diffusivity in amorphous silicon at 550°C of approximately $3x10^{-17}$ cm²/second.

Throughout the aforementioned study, boron diffusion was evident in the absence of implant recoil effects. By introducing the boron dopant after the co-implanted fluorine, as-implanted and annealed profiles are shallower. The order of co-implant steps, however, does not have a measurable impact on the magnitude of boron diffusion or the time-averaged boron diffusivity in amorphous material. Figure 5-11 depicts as-implanted and annealed boron concentration profiles for samples implanted with boron both prior and subsequent to a 6 keV, $2x10^{15}$ atoms/cm² fluorine co-implant. It is clear there is a recoil effect on the as-implanted profile when boron is implanted prior to fluorine. However, independent of the boron and fluorine implant order, boron diffuses approximately 110 Å after 6 hours of annealing at 500°C measured at a boron concentration of $1x10^{19}$ atoms/cm³.

The activation energy for boron diffusion in amorphous silicon formed through silicon ion implantation was calculated for these co-implanted samples. Specimens were annealed at temperatures of 500°C, 600°C, and 700°C, as shown in Figure 5-12. For specimens implanted with fluorine prior to boron, the time-averaged boron diffusivity is expressed as follows for a Half-Gaussian boron distribution with an R^2 of 0.99, where *T*

is the annealing temperature given in Kelvin and k is Boltzmann's constant, equal to 8.616x10⁻⁵ eV/K [Hum93]:

$$D(cm^{2}/_{sec ond}) = 0.19(cm^{2}/_{sec ond})e^{\frac{-2.5 eV}{k(eV/_{K})T(K)}}$$
(5-7)

When boron is implanted prior to the fluorine, the time-averaged boron diffusivity for a Half-Gaussian boron distribution can be calculated as follows with an R^2 of 0.98:

$$D(cm^{2}/_{sec ond}) = 0.32 \ (cm^{2}/_{sec ond}) \ e^{\frac{-2.5 \ eV}{k \ (eV/_{K}) \ T \ (K)}}$$
(5-8)

The boron diffusivity values were calculated for a Half-Gaussian boron concentration of $3x10^{19}$ atoms/cm³. The activation energy for boron diffusion in amorphous material during the SPER process was calculated to be approximately 2.5 eV.

The presence of silicon, germanium, and fluorine co-dopants, regardless of the implant order, has no measurable impact on the time-averaged boron diffusivity. As such, they do not influence the energy barrier for boron diffusion. The differences in the pre-exponential terms of Equations 5-7 and 5-8 are within the estimated calculation error of 25%, demonstrating that the entropy of the amorphous structure is not altered by the presence of co-dopant species. The annealing conditions were chosen such that the amorphous layer had only partially regrown and the amorphous/crystalline interface was significantly deeper than the tail of the boron concentration profile, as will be discussed. Boron diffuses in amorphous silicon with an activation energy of 2.5 eV, which is 30% lower than the activation energy of 3.75 eV required for boron diffusion in crystalline silicon [Had00]. Clearly, dopant diffusion within amorphous silicon during SPER can have a direct impact on the formation of advanced transistor junctions.

Silicon Recrystallization Rate

In many conventional applications boron is co-implanted with fluorine into germanium preamorphized silicon. Both singular and molecular implants can be performed, leading to a range of boron and fluorine implant energies and doses. Boron was monitored in the presence of both low and highly concentrated fluorine in order to address the impact of fluorine co-doping on boron diffusion characteristics.

Boron SIMS profiles for germanium-amorphized material are illustrated in Figures 5-13 and 5-14. Samples containing boron alone and boron co-implanted with preceding fluorine are shown for both as-implanted and annealed conditions. Fluorine was implanted at an energy of 6 keV and doses ranging from 1×10^{14} atoms/cm² to 5×10^{15} atoms/cm². The effect of fluorine on the as-implanted boron profile tails is apparent and was discussed previously in Chapter 4. At boron concentrations above approximately 1×10^{19} atoms/cm³, all of the as-implanted boron concentration profiles are nearly identical. After 10 minutes of annealing at 550°C, boron exhibits the same magnitude of diffusion, independent of the co-implanted fluorine dose (Figure 5-13). After 30 minutes of annealing at 550°C, on the other hand, the magnitude of boron diffusion during SPER begins to deviate as a function of the co-implanted fluorine dose, as seen in Figure 5-14. The higher the implanted fluorine dose the greater the magnitude of boron diffusion in amorphous silicon.

Figure 5-15 depicts the amorphous layer depths as a function of both annealing time at 550°C and the co-implanted fluorine dose, demonstrating the impact of fluorine on the recrystallization rate of silicon. Fluorine is known to retard the recrystallization rate of amorphous silicon, while boron greatly enhances it [Fau94, Sun82a, Sun82b, Sun84]. After 30 minutes of annealing, the SPER process has ended for the control

sample and samples co-implanted with fluorine at doses less than 5×10^{14} atoms/cm². Samples co-implanted with the higher fluorine doses exhibit greater levels of boron diffusion simply due to interactions between fluorine atoms and the advancing amorphous/crystalline (a/c) interface [Sun84]. These results are in agreement with the preliminary results of Duffy et al. regarding boron diffusion in germanium-amorphized material [Duf04]. Fluorine and silicon interactions at the a/c interface increase the time required to completely recrystallize the silicon substrate [Sun84], exposing boron to amorphous material at elevated temperatures for longer times.

At 550°C, fluorine exhibits a very low mobility and segregates at the moving a/c interface. Peaks in the fluorine concentration profiles are indicative of the position of the moving a/c interface [Tsa79b]. The inherent time-averaged boron diffusivity at 550°C, calculated for a Half-Gaussian boron concentration of $3x10^{19}$ atoms/cm³, is not measurably impacted by the co-implanted fluorine dose, as shown in Figure 5-16. The role of fluorine co-implants during the SPER process is simply to alter the silicon regrowth rate, thereby only indirectly influencing boron diffusion characteristics.

Of the co-implanted species investigated thus far, only fluorine alters the silicon recrystallization rate. Fluorine has a very low mobility in amorphous silicon at 550°C and only redistributes due to accumulation at the advancing a/c interface during the recrystallization process [Tsa79b]. The solid-solubility limit of fluorine in crystalline silicon is believed to be small compared to boron and is attributed with retrograde solid-solubility characteristics [Bea78, Nie86]. The solid-solubility limit of fluorine in crystalline in crystalline silicon increases with temperature, reaches a peak value, and then rapidly decreases with increasing temperature [Nie86]. This retrograde behavior can be observed

in terms of the formation of fluorine bubbles in highly doped silicon after recrystallization annealing at temperatures greater than 850°C, but not during annealing at lower temperatures [Che95, Nie86]. Silicon and germanium dopants, on the other hand, have no such solid-solubility limits because they are both completely miscible in crystalline silicon [Hir00].

Williams et al. have proposed a model for the regrowth of high-dose implanted (100) silicon when normal impurity diffusion is negligible [Wil82]. During bond breaking and atomic rearrangement at the advancing a/c interface, local bond distortions and interfacial strain are believed to occur as impurities are incorporated onto substitutional lattice sites, due to size differences between the impurity and silicon atoms. The level of interfacial strain is expected to increase with both the impurity concentration and the degree of covalent mismatch between the impurity atoms and silicon matrix atoms. High levels of strain at the a/c interface are attributed with impeding the silicon bond breaking and rearrangement process, thereby retarding the epitaxial regrowth rate. Excessive interfacial strain has been proposed as the driving force for the rejection of impurity atoms into the amorphous phase, rather than for their incorporation onto crystalline lattice sites. An impurity rejection process could also lower the local strain at the advancing a/c interface. An effective interfacial strain is attributed with controlling both the maximum local impurity concentration incorporated onto substitutional lattice sites and the rejection of excess impurity atoms into the amorphous phase ahead of the advancing regrowth front [Wil82].

Based on the diffusion and precipitation characteristics of fluorine during both low and high temperature regrowth annealing [Bea78, Che95, Nie86, Tsa79b], the

aforementioned recrystallization model is applicable to the case of fluorine dopant in silicon. It is also in agreement with the established observation that fluorine retards the silicon recrystallization rate [Duf04, Jac05, Mir05, Sun84]. The magnitude of reduction in the silicon regrowth rate scales with the fluorine implant dose, such that higher fluorine concentrations correlate with deeper transistor junctions.

When boron and fluorine are co-implanted within amorphous silicon, the overall magnitude of boron diffusion scales in conjunction with the fluorine dose. However, fluorine does not measurably impact the measured time-averaged boron diffusivity or the features of boron diffusion profiles. The boron diffusion process is not influenced by the presence of fluorine, irrespective of the co-implant order. The activation energy for boron diffusion in amorphous silicon was found to be 30% lower than that for diffusion in crystalline silicon and independent of the presence of co-dopant species, namely fluorine, silicon, and germanium. These preliminary investigations suggest that dangling silicon bonds may not play a primary role in the diffusion mechanism of boron in amorphous silicon during SPER annealing.

Discussion

Our results have demonstrated that boron diffuses in amorphous silicon during the SPER process. The presence of additional silicon, germanium, and fluorine implants does not impact the time-averaged boron diffusivity, irrespective of their implant dose or the implant order. Boron exhibits diffusivities in ion implanted amorphous silicon that are more than five orders of magnitude greater than extrapolated values for crystalline silicon [Ell98a]. In addition, the activation energy for boron diffusion in amorphous silicon is substantially lower than that of crystalline silicon [Had00]. However, boron diffusion phenomena may be dependent upon the preparation method for the amorphous silicon

matrix. For example, we will illustrate that hydrogen-retarded boron diffusion is observed within amorphous silicon generated through ion implantation, but not in glow-discharged deposited amorphous silicon. Collectively, these results indicate that the diffusion mechanism for boron in amorphous silicon may be rather complex.

At present, the diffusion mechanism for dopants in amorphous silicon during low temperature annealing is not clearly defined. Earlier, we demonstrated that a simple constant diffusivity does not adequately describe boron diffusion characteristics. Boron diffusion in amorphous silicon is non-Fickian, suggesting that more complex diffusion mechanisms need to be investigated. In order to cultivate a fundamental understanding of boron diffusion phenomena during SPER annealing, basic solid-state diffusion approaches and mechanisms previously established for dopant diffusion in crystalline silicon are applied to our experimental data. The applicability of charged species effects, boride enhanced diffusion, concentration dependent diffusion, and trap-mediated diffusion approaches are subsequently addressed at length.

In addition, diffusion behavior in alternate amorphous systems is utilized to provide insight into the boron diffusion process within ion implanted amorphous silicon. Constituent species, present in excess of 20 at%, are attributed with exhibiting a cooperative diffusion mechanism in bulk amorphous glass alloys [Gey95, Gey96, Oli99, Qiu96, Sch93, Sch97, Tei96, Tei97, Van97]. However, in our studies boron is present in relatively low atomic concentrations (less than approximately 3 at%) and is unlikely to participate in a cooperative hopping mechanism within ion implanted amorphous silicon. Additional information regarding this diffusion mechanism is available in Appendix C.

Charged Species Effects

In crystalline silicon, interactions between boron atoms and silicon interstitials are attributed with enhancing boron diffusion [Fai77]. The effective boron diffusivity is dependent on the hole concentration p and the intrinsic carrier concentration ni [Fai77]. Software packages, such as FLOOPS and TSUPREM, assign values to the term $\left(\frac{p}{ni}\right)$ based on the initial dopant profile and the diffusion temperature. They use data curves that relate temperature to the number of carriers in an intrinsic crystalline semiconductor.

FLOOPS simulations were used to characterize the role of charged species in the diffusion mechanism of boron in amorphous silicon. Gable conducted preliminary simulations of boron diffusion in amorphous silicon and reported that charged species effects are necessary to predict boron diffusion characteristics in germanium amorphized materials [Gab04]. However, the use of charged species effects did not result in accurate simulations of our experimental profile features. Manual adjustment of $\left(\frac{p}{m}\right)$ did not improve the agreement between simulated and experimental profiles. In crystalline silicon, p is synonymous with the concentration of active boron atoms. Hall effect analysis of amorphous silicon does not result in measurable active carrier concentrations, implying that p values and diffusion enhancements due to charged species are negligible in amorphous silicon. In addition, *ni* is based upon a point defect model for crystalline silicon that is not readily defined in the amorphous phase. Charged species diffusion terms commonly associated with crystalline silicon do not results in accurate simulations of boron diffusion behavior in amorphous silicon, suggesting that charged states do not influence the ability of boron to diffuse during SPER annealing.

Boride-Enhanced Diffusion (BED)

Recent studies have demonstrated boride-enhanced diffusion (BED) of boron in polycrystalline and crystalline silicon [Aga99a, Aga99b, Cow99c, Mon04, Sei02, Sha02]. BED involves (i) the formation of Si_nB_m and (ii) the release of interstitials [Aga99b]. The Si_nB_m layer generates boron and silicon interstitials, thereby facilitating boron diffusion through an interstitialcy mechanism [Aga99a, Aga99b, Cow99c, Mon04, Sha02]. Si_nB_m phases form in crystalline silicon when boron is incorporated above ~ 2 at% [Aga99a]. The solid-solubility limit of boron in crystalline silicon is exceeded during ultra-shallow junction formation via ion implantation into amorphous silicon, leading to nonequilibrium conditions [Sol90]. However, in contrast to BED conditions [Cow99c, Sha02], transient boron diffusion does not occur during SPER annealing of amorphous silicon implanted with 500 eV, $1x10^{15}$ atoms/cm² ¹¹B⁺.

At temperatures below 900°C, Si_nB_m phases are likely to be thermodynamically stable, however, the exact phase boundaries of the B-Si binary phase diagram are not known within this temperature range [Sie02]. It remains unclear if Si_nB_m precipitation occurs in amorphous silicon under SPER annealing conditions. It is worth noting that boron does not exhibit measurable diffusion at concentrations above approximately $1x10^{20}$ atoms/cm³ during heating of the amorphous phase. The source of this apparent immobility is presently unknown, however, it could be related to either a solid solubility limit of boron or formation of Si_nB_m phases in amorphous silicon. BED is dependent upon the formation of Si_nB_m phases and interactions between boron atoms and interstitial point defects, resulting in transient boron diffusion. Point defect models associated with crystalline silicon are not applicable to amorphous silicon, implying that boride-enhanced diffusion is an unlikely mechanism for boron diffusion in amorphous silicon.

Concentration Dependent Diffusion

As mentioned previously, boron exhibits concentration dependent diffusion behavior in amorphous silicon. The experimental data suggest that the diffusivity of boron in amorphous silicon is related to the concentration of boron dopant. To investigate this presumption, FLOOPS simulations were conducted comparing the applicability of concentration dependent diffusion parameters. Samples were preamorphized with either silicon or germanium implants and then implanted with boron alone or co-implanted with fluorine and boron. Annealing was conducted at temperatures ranging from 550°C to 700°C for times up to 90 minutes. Throughout the annealing process, boron was retained in amorphous silicon.

Concentration dependent diffusion terms can be used to simulate boron concentration profiles during diffusion in amorphous silicon. The diffusion coefficient for boron diffusion is modified as follows to incorporate concentration dependence:

$$D_C = D_F + (D_B * B_A) \tag{5-9}$$

Where Dc is the concentration dependent diffusion coefficient, D_F represents the diffusivity due to Fickian diffusion, and D_B is the diffusivity term due to the boron concentration profile. The parameter B_A denotes the population of boron atoms that are active and able to diffuse. The term B_A is dictated by the initial boron concentration profile and the assumed solubility limit of boron in amorphous silicon. An example of the FLOOPS code used to simulate boron diffusion in self and germanium-amorphized material via concentration dependent diffusion is contained in Appendix D.

Experimentally measured and simulated boron concentration profiles for amorphous specimens containing boron alone are shown in Figures 5-17 and 5-18.

FLOOPS simulations of self-amorphized material at 550°C assumed a D_F of 5x10⁻¹⁷ cm²/second and boron solubility limit of $1.5x10^{20}$ atoms/cm³ (Figure 5-17). The extracted value of D_B was $2.5x10^{-36}$ cm⁵/atoms-second. At high boron concentrations, such as $5x10^{19}$ atoms/cm³, the diffusivity due to the boron concentration profile will dominate the diffusion of boron during annealing and result in a broadening of the diffusion profile below the solubility limit. The simulated and experimental profiles in self-amorphized material demonstrate strong agreement for the entire profile range, differing by less than 1 nm, when concentration dependent diffusion terms are utilized.

Simulations of germanium-amorphized material at 550°C employed a D_F of 2×10^{-17} cm^2 /second and boron solubility limit of 1.5×10^{20} atoms/cm³ (Figure 5-18). The extracted value of D_B for these simulations was 2.0×10^{-36} cm⁵/atoms-second. Within germanium amorphized material, significant alignment of the experimental and simulated boron diffusion profiles (i.e. within 1 nm) occurs at boron concentrations below approximately 1×10^{20} atoms/cm³. The significant dip in the boron profile after 20 minutes of annealing, observed above the shoulder of the boron SIMS profiles at depths ranging from 40 Å to 80 Å, is not accurately simulated. However, it is important to note that the differences between the as-implanted and experimentally diffused profiles in this region are within the estimated SIMS resolution of approximately 10 Å. The values assumed for the Fickian diffusion coefficient were different for silicon and germanium amorphized samples, but within the estimated measurement error of the time-averaged boron diffusivity, upon which they were based. The fluctuation in the values extracted for the diffusivity due to the boron profile is very small, suggesting that the concentration dependent nature of boron is independent of the preamorphization implant species.

Concentration dependent diffusion terms can be used to successfully simulate boron diffusion behavior in amorphous silicon, in both the presence and absence of fluorine. Co-implanted samples were preamorphized with silicon and subsequently implanted with both boron and fluorine. The order of the doping implants was alternated, providing two types of samples. Specimens were annealed at temperatures of 550°C, 600° C, and 700° C for times up to 90 minutes. The aforementioned parameters D_F , D_B , and the boron solubility limit (*SL*) can all be represented by Arrhenius relationships. The concentration dependent simulation code for co-implanted samples incorporated the following equations for D_F and D_B :

$$DF(\operatorname{cm}^{2}/\operatorname{second}) = 0.0009 \operatorname{cm}^{2}/\operatorname{second} e^{\left(\frac{-2.273 \operatorname{eV}}{k(eV_{K}) T(K)}\right)}$$
(5-10)
$$DB\left(\frac{\operatorname{cm}^{5}}{\operatorname{atoms} \cdot \operatorname{second}}\right) = 4.387 \times 10^{-11} \frac{\operatorname{cm}^{5}}{\operatorname{atoms} \cdot \operatorname{second}} e^{\left(\frac{-4.18 \operatorname{eV}}{k(eV_{K}) T(K)}\right)}$$
(5-11)

The solubility limit for samples implanted with boron prior to fluorine was held constant at 1.9×10^{20} atom/cm³, while the solubility limit for samples implanted with fluorine prior to boron was presumed to change in accordance with the following Arrhenius equation:

$$SL(\underset{cm^{3}}{atoms}) = 1.5256 \times 10^{21} \underset{cm^{3}}{atoms} e^{\left(\frac{-0.167 \text{ eV}}{k(eV_{K}) T(K)}\right)}$$
(5-12)

Other than the difference in presumed solubility limit values, the simulation code used for co-implanted samples was independent of the boron and fluorine implant order. One set of code was used to simulate boron diffusion within amorphous silicon in the temperature range of 550°C to 700°C. The concentration dependent simulation code used for co-implanted material is contained in Appendix E. Table 5-1 summarizes the specific values

assumed for D_F and extracted for D_B at the annealing temperatures of 550°C, 600°C, and 700°C (Equations 5-10 and 5-11). The solubility limit values used for samples coimplanted with fluorine prior to boron are also included (Equation 5-12). As mentioned previously, in the high boron concentration regime the diffusivity due to the boron concentration profiles dominates the effective diffusivity of boron during annealing, resulting in a shouldering effect below the boron solubility limit.

The experimental and simulated boron diffusion profiles for samples implanted with fluorine prior to boron are portrayed in Figures 5-19, 5-20, and 5-21. For each of the annealing times shown the advancing amorphous/crystalline (a/c) interface has not reached the boron concentration profiles. At 550°C, the difference between the experimentally annealed and simulated profiles is less than 3 nm for a given boron concentration (Figure 5-19). For the longer annealing times of 70 minutes and 90 minutes, boron profiles differ by less than 1 nm and demonstrate strong agreement. Similar results were also observed at the higher annealing temperatures. After annealing at 600°C (Figure 5-20) and 700°C (Figure 5-21), the simulated and experimental profiles deviate by less than approximately 1 nm throughout the profile range.

Boron diffusion profiles for self-amorphized specimens co-implanted with boron prior to fluorine are shown in Figures 5-22, 5-23, and 5-24. When fluorine is introduced into the material subsequent to boron, the drop in the boron concentration, in facilitation of profile shouldering is less pronounced than when fluorine implantation precedes that of boron. This difference is best observed in the behavior of the imposed boron solubility limit, which was held constant at 1.9×10^{20} atoms/cm² for these samples. At temperatures of 550°C (Figure 5-22), 600°C (Figure 5-23), and 700°C (Figure 5-24) the simulated and experimental boron profiles are nearly identical, differing by less than 1 nm throughout the profile range. The single set of FLOOPS code developed for self-amorphized samples co-implanted with boron and fluorine appears to more closely match specimens implanted with boron prior to fluorine. However, these differences are within the margin of error for the SIMS analysis technique.

The general shape and behavior of the experimental boron diffusion profiles was successfully duplicated by the FLOOPS simulations, indicating that boron exhibits concentration dependent diffusion in both the presence and absence of co-implanted fluorine. These simulations coincide with our experimental observations of boron diffusion characteristics within amorphous material, but provide no indication of the precise mechanism by which boron diffuses under these conditions.

Trap-Moderated Diffusion

Several investigations regarding dopant diffusion in amorphous silicon pertain to transition metal species, focusing on the diffusion characteristics of palladium, copper, and gold [Cof91a, Cof91b, Cof92, Fra96, Pol90]. Structural defects intrinsic to amorphous silicon have been attributed with the ability to interact with and trap impurity or dopant species, thereby decreasing their effective diffusivity [Cof91a, Cof91b, Cof92, Fra96, Kem93, Pol90]. Under trap-moderated diffusion conditions, a dopant will diffuse until it finds an unoccupied trap site in amorphous silicon, enabling additional atoms to diffuse freely through a trap-saturated region [Cus94b]. Diffusion across a sample results from hopping between adjacent trapping sites, where traps are presumed to form a random substitutional sub-lattice [Kem93].

In amorphous silicon, transition metals are believed to diffuse via an interstitial-like mechanism [Cof91a, Cof91b, Cof92, Fra96]. Frank et al. and Coffa et al. have suggested

that these dopants diffuse through a direct mechanism involving immobile trapping sites, such as vacancy-like defects [Cof92, Fra96]. As the transition metal concentration increases and becomes comparable to the trap site concentration, the dopant diffusivity also increases during annealing in amorphous silicon [Cof92, Fra96]. Above the amorphization threshold, the amount of impurity trapping does not increase with the dose of a self-amorphization implant, as the silicon lattice damage saturates at a level of approximately 1×10^{21} atoms/cm³ [Cof91a]. Structural defects in amorphous silicon are believed to include broken or strained silicon bonds, as well as strained silicon-silicon bonds [Cof91b]. Ion implantation induced point defect species have not been clearly defined in amorphous silicon [Cof92]. However, it is not unreasonable to presume that more than one type of defect structure exists in amorphous silicon that is capable of interacting with mobile dopant species.

Diffusion simulations were conducted in order to investigate the role of immobile, saturable trapping sites in the diffusion mechanism for boron in amorphous silicon during SPER annealing. FLOOPS simulations were generated for annealing temperatures ranging from 550°C to 700°C and times up to 90 minutes. The basic equations and relationships involved in trap-mediated diffusion simulations were discussed at length in Chapter 4. Only the partial differential equations used to simulated boron diffusion through a trap-mediated mechanism are reviewed here. Two partial differential equations were developed to relate the concentrations of active, mobile, and trapped boron.

$$\frac{\partial C_{TB}}{\partial t} = D_B \nabla (C_{AB} - C_{TT})$$
(5-13)

$$\frac{\partial C_{TT}}{\partial t} = kf 4 \pi a \left[\left[(C_{MT} - C_{TT}) (C_{AB} - C_{TT}) \right] - kr^* C_{TT} \right]$$
(5-14)

Where C_{TB} is the total concentration of boron, ∇ represents the concentration gradient driving the diffusion of boron, C_{AB} is the active boron concentration, and C_{TT} is the trapped boron concentration. The maximum concentration of traps present in the substrate is C_{MT} . The parameter D_B represents the diffusivity of mobile boron, a is the effective capture radius for trapping, and kf and kr are forward and reverse interaction rate terms, respectively.

The concentration of active boron is equal to the sum of the mobile and trapped boron concentrations. Active boron is defined as the population of boron atoms that are below the solubility limit for boron in amorphous silicon, which have the potential to diffuse. Mobile boron represents the group of boron atoms that are actually diffusing through the substrate. Trapped boron pertains to the population of boron atoms that have bonded with defects in the amorphous silicon structure and are no longer mobile. The total concentration of boron and the active boron concentration are related by the solubility limit for boron in amorphous silicon. At concentrations below the boron solubility limit $C_{TB} = C_{AB}$, while above the solubility limit C_{AB} simply equals the solubility limit. The total concentration of boron is known and fixed based on experimental SIMS measurements, thus the concentration of active boron is also a known parameter. The concentrations of mobile and trapped boron vary at each point in time, resulting in an effective diffusivity coefficient.

In order to obtain accurate agreement between the simulated and experimental profiles, several of the aforementioned parameters were assigned specific values. The maximum number of traps was held constant at a value of 5×10^{19} sites/cm³; in line with prior studies that have suggested the defect density in amorphous silicon is in the range of

approximately 1×10^{19} sites/cm³ to 1×10^{20} sites/cm³ [Bro79, Roo91b, Spi83]. The effective capture radius for a trapping reaction was assumed to be 2.71 Å, equal to the lattice spacing of crystalline silicon. In these simulations it is assumed that one boron atom is required to eliminate one trapping site.

The diffusivity of mobile boron in the absence of trapping sites (D_B) was assumed to be approximately one order of magnitude greater than the measured time-averaged boron diffusivity during SPER. For self-amorphized and germanium amorphized samples containing boron alone, D_B was assumed to be 2.1×10^{-16} cm²/second and 1.0×10^{-16} cm²/second, respectively. In simulations of co-implanted material, the diffusivity values of mobile boron were established according to the following Arrhenius expression:

$$DB (\text{cm}^{2}/\text{second}) = 3.27 \times 10^{8} \text{ cm}^{2}/\text{second} e^{\left(\frac{-3.99 \text{ eV}}{k(eV/_{K}) T(K)}\right)}$$
(5-15)

Boron diffusivities in the absence of traps were assumed to be 1.20×10^{-16} cm²/second at 550°C, 3.02×10^{-15} cm²/second at 600°C, and 7.05×10^{-13} cm²/second at 700°C for samples implanted with both boron and fluorine.

In order to simulate the shouldering observed in diffused boron profiles, a boron solubility limit in amorphous silicon was required. In samples containing boron alone, the solubility limit was held constant at a value of 2.0×10^{20} atoms/cm³ during annealing at 550°C. However, the boron solubility limit was observed to fluctuate with temperature in samples co-implanted with boron and fluorine. These fluctuations were observed to follow an Arrhenius expression:

$$SL(atoms/_{cm^3}) = 5.793 \times 10^{21} atoms/_{cm^3} e^{\left(\frac{-0.254 \text{ eV}}{k(eV/_K) T(K)}\right)}$$
(5-16)

At annealing temperatures of 550°C, 600°C, and 700°C boron exhibits a solubility limit in amorphous silicon of approximately 1.613×10^{20} atoms/cm³, 2.12×10^{20} atoms/cm³, and 2.80×10^{20} atoms/cm³, respectively.

By establishing these preliminary values, it was possible to obtain strong agreement between the simulated and experimental boron concentration profiles. Based on Equation 5-14, in order for de-trapping of boron to occur during annealing the term $(kr*C_{TT})$ must be sufficiently large enough to impact the value of the term $(C_{MT}-C_{TT})(C_{AB}-C_{TT})$. Below kr values of approximately $7x10^{18}$ atoms/cm³, no de-trapping of boron occurs under the experimental conditions investigated. To ensure that perfect trapping conditions did not arise during annealing, the parameter kr was held constant at $9x10^{18}$ atoms/cm³ for all of the trap-mediated simulations.

The values of the final parameter *kf* were determined based upon the boron concentration profile abruptness. They were observed to change with annealing temperature according to the following Arrhenius expression:

$$kf(cm^{3}/_{atoms-\AA}) = 4.43 \times 10^{9} (cm^{3}/_{atoms-\AA}) e^{\left(\frac{-4.01 \text{ eV}}{k(eV/_{K}) T(K)}\right)}$$
(5-17)

For the annealing temperatures of 550°C, 600°C, and 700°C forward interaction rate term values of 1.22×10^{-15} cm³/atoms-Å, 3.12×10^{-14} cm³/atoms-Å, and 7.46×10^{-12} cm³/atoms-Å, respectively, were used. The aforementioned *kf* values were used for samples with and without fluorine co-doping. Based on Equation 5-14, the value of *kf* must be sufficiently small enough to offset the value of the term $(C_{MT}-C_{TT})(C_{AB}-C_{TT})$ and ensure that the calculated concentration of trapped boron does not meet or exceed the concentration of

active boron for any given point in time. The FLOOPS code used to simulate boron diffusion under trap-moderated conditions is provided in Appendix F.

Equation 5-14 also provides information regarding the forward (*rf*) and (*rr*) reverse trapping reaction rates. The ratio of *rf/rr* can be represented as follows, where numerical values have been substituted for *kr* and C_{MT} (Equation 5-14):

$$\frac{rf}{rr} = \frac{(5x10^{19} - C_{TT})(C_{AB} - C_{TT})}{9x10^{18}C_{TT}}$$
(5-18)

Equation 5-18 indicates that trapping is more likely to occur in regions where C_{TT} is low, as the ratio of *rf/rr* will be greater than one. Conversely, de-trapping is more likely to occur in regions where C_{TT} is high, as the ratio of *rf/rr* will be less than one. In addition, by assuming a maximum concentration of trapping sites that is less than the concentration of active boron, as determined by the boron solubility limit, the effective diffusivity of boron will always be maximized in the peak region of the boron profile (Equation 5-13). In the tail region of the profile, however, the value of the term (C_{AB} - C_{TT}) approaches zero, resulting in a very small effective diffusivity. These combined effects can lead to the generation of trap-mediated boron diffusion profiles that are very similar to those resulting from concentration dependent diffusion behavior. However, at very long annealing times trap-mediated and concentration dependent diffusion behavior result in measurably different diffusion profiles, where dopants exhibit greater diffusion under concentration dependent diffusions.

The simulated and experimental boron concentration profiles for samples implanted with boron alone are illustrated in Figures 5-25 and 5-26. The experimental and simulated profiles are nearly identical for self-amorphized specimens (Figure 5-25). Profiles for the germanium amorphized samples exhibit strong agreement in the concentration range of 1×10^{18} atoms/cm³ to 1×10^{20} atoms/cm³ (Figure 5-26), but the simulations do not capture the apparent dip in the experimental profiles at depths ranging from 40 Å to 80 Å. However, it is important to note that the differences between the asimplanted and experimentally diffused profiles in this region are within the estimated SIMS resolution of approximately 10 Å. Overall, the application of trap-moderated diffusion terms leads to accurate simulations of boron diffusion characteristics in amorphous silicon during the SPER process.

Trap-moderated diffusion can also be used to successfully simulate boron diffusion in amorphous silicon in the presence of fluorine. Figures 5-27, 5-28 and 5-29 portray experimental and simulated diffusion profiles for samples implanted with fluorine prior to boron. At a temperature of 550°C (Figure 5-27), the profiles demonstrate good alignment, differing by less than approximately 1 nm throughout the profile range. At temperatures of 600°C (Figure 5-28) and 700°C (Figure 5-29), however, the profiles are nearly identical, showing excellent agreement.

Similar results were obtained for samples co-implanted with boron prior to fluorine. For the range of annealing temperatures and times examined, the simulated and experimental profiles are nearly identical. They differ by less than 0.5 nm (Figure 5-30, Figure 5-31, Figure 5-32). Utilizing the initial conditions and assumptions employed for these simulations, trap-mediated diffusion terms can be used to accurately predict boron diffusion characteristics in amorphous silicon.

These results demonstrate that trap-mediated diffusion is also a potential mechanism by which boron diffuses in amorphous silicon during the SPER process. The diffusivity of boron in amorphous silicon is clearly related to the concentration of boron
dopant, as demonstrated by the successful use of both trap-mediated and concentration dependent simulations to predict the diffusion behavior of boron at temperatures ranging from 550°C to 700°C. Unfortunately, the successful application of these basic diffusion approaches provides no clear indication of the precise mechanism by which boron diffuses. The specific structural defects that may act as boron trapping sites in the amorphous silicon network remain unknown. However, our experimental results indicate that the manner in which boron atoms are potentially trapped and de-trapped during annealing is not measurably affected by the presence of fluorine dopant or the use of a germanium preamorphization implant.

Hydrogen Effects upon Boron Diffusion

Several authors have implied that fluorine enhances boron diffusion by bonding with dangling silicon bonds [Fre95, Ohy89]. However, recent investigations have shown that fluorine affects boron diffusion in amorphous silicon only by slowing down the recrystallization rate (Figures 5-14 and 5-15). On the other hand, electron spin resonance (ESR) analysis has shown that exposure to a hydrogen plasma at elevated temperatures can completely eliminate the dangling silicon bond signal [Kap78]. Infrared (IR) absorption spectral band analysis was used to confirm that hydrogenated films possess simple Si-H vibrations, demonstrating that the dangling bond density was decreased via hydrogen passivation [Kap78].

Studies have definitively illustrated the ability of hydrogen to passivate dangling and strained silicon bonds [Ade88, Bro79, Kap78, Hir96, Pan86, Ste79, Ste80, Tsu87]. Jackson et al. also demonstrated that hydrogen termination of these bonds, resulting in the formation of Si-H, does not impact the bond angle variation of the amorphous matrix [Jac91]. Hydrogen is commonly associated with passivating dangling silicon bonds,

however, hydrogen can react with both T3 and T5 defect structures [Pan86]. Thus, boron diffusion characteristics under hydrogen incorporation are expected to serve as a better indicator of the role of bonding defects in regards to boron diffusion in amorphous silicon through a trap-mediated diffusion mechanism, as opposed to fluorine co-implantation.

Silicon Recrystallization Rate

Initially, the effects of hydrogen co-doping upon the silicon recrystallization process are discussed. As addressed previously for the case of fluorine co-implantation, changes in the regrowth rate can indirectly influence the observed boron diffusion characteristics in amorphous silicon. In this study samples were preamorphized with 70 keV, $1x10^{15}$ atoms/cm² Si⁺ prior to exposure to a hydrogen plasma at a dose of $1x10^{16}$ atoms/cm² and temperature of 250°C for 1 hour. Boron dopant was subsequently implanted at an energy of 500 eV and dose of $1x10^{15}$ atoms/cm². SPER annealing was conducted at 550°C for times ranging up to 30 minutes.

Hydrogen significantly lowers the silicon regrowth rate, as seen in Figure 5-33. Under these processing conditions, hydrogen increases the time required for complete recrystallization by approximately 40%. These results are in agreement with prior studies that have demonstrated a decreasing silicon recrystallization rate with an increasing level of hydrogen doping [Acc96, Ade88, Obe87, Ols94]. The solubility of hydrogen is presumably lower in crystalline silicon versus amorphous silicon, as hydrogen atoms are prevented from diffusing through the advancing a/c interface into crystalline material during SPER annealing [Ols94]. Hydrogen is also well known to passivate dangling and floating bonds in amorphous silicon [Ade88, Bro79, Kap78, Hir96, Pan86, Ste79, Ste80, Tsu87]. By passivating interfacial sites at the a/c interface hydrogen disrupts the bond rearrangement process, thus slowing down the regrowth rate [Ade88]. The solubility difference for hydrogen in crystalline and amorphous silicon may also lead to hydrogen accumulation at the interface and blocking of its movement, due to the rejection of hydrogen atoms from the crystalline phase [Ade88, Ols94]. The silicon recrystallization rate is not dramatically reduced during the first 10 minutes of annealing at 550°C, suggesting that hydrogen requires time to accumulate at the a/c interface and hinder its movement. These results imply that the solubility limit of hydrogen in crystalline silicon is not substantially lower than that of amorphous silicon, as hydrogen does not immediately segregate at the advancing interface in a quantity large enough to measurably impact the silicon regrowth process.

Hydrogen Diffusion Characteristics

During hydrogen plasma exposure, hydrogen was incorporated at a dose of approximately 1×10^{16} atoms/cm². The resultant hydrogen concentration profiles are portrayed in Figure 5-34 for both as-implanted and annealed conditions. Throughout the annealing process, hydrogen remains concentrated at or above 1×10^{19} atoms/cm³, despite substantial out-diffusion. It is interesting to note that hydrogen remains highly concentrated near the sample surface after SPER annealing at 550°C.

Recent studies by Kuroi et al. support our observations regarding the evolution of hydrogen concentration profiles during annealing [Kur05]. Crystalline silicon samples were implanted with 10 keV $B_{18}H_8^+$, resulting in near-surface hydrogen concentrations exceeding 1×10^{21} atoms/cm³. At depths greater than 300 Å, the hydrogen concentration was uniform at approximately 1×10^{20} atoms/cm³. The molecular $B_{18}H_8^+$ implant also resulted in the formation of a 700 Å deep continuous, surface amorphous layer. During high temperature annealing, hydrogen atoms diffused out of the samples as they recrystallized, but remained concentrated at 1×10^{20} atoms/cm³ [Kur05]. The difference in

the final hydrogen concentration within these two studies may be related to their preparation methods, as hydrogen is not incorporated into preamorphized silicon during $B_{18}H_8^+$ molecular implantation.

During annealing at temperatures above 200°C, hydrogen can be released from the amorphous silicon network and become mobile [Acc96, Tsa79c]. However, upon thermal treatment hydrogen can also remain stably bonded to defect sites present within the amorphous silicon network [Acc96]. As discussed previously in Chapter 4, the total density of structural defects in as-implanted amorphous silicon formed via ion implantation is in the range of approximately 1×10^{20} sites/cm³. ESR measurements have shown the dangling silicon bond density in amorphous silicon formed by ion implanted to be on the order of 1×10^{19} sites/cm³ [Kap78]. These observations suggest that within our specimens, hydrogen adequately passivates a majority of the dangling silicon bond population and possibly other types of network defects in the amorphous silicon matrix.

Chemical Hydrogen Interactions

Hydrogen incorporation severely retards boron diffusion in amorphous silicon. Figure 5-35 shows boron concentration profiles for samples with and without hydrogen co-doping. For a Half-Gaussian boron concentration of $3x10^{19}$ atoms/cm³, boron exhibits a time-averaged diffusivity of approximately $1.7x10^{-18}$ cm²/second in the presence of hydrogen. At a concentration of $1x10^{19}$ atoms/cm³, boron diffuses less than 15 Å during annealing for times up to 30 minutes. These results are in stark contrast to conditions where boron is incorporated alone (Figure 5-35). At a concentration of $1x10^{19}$ atoms/cm³, boron diffuses approximately 35 Å after annealing for 20 minutes at 550°C in the absence of hydrogen, exhibiting a time-average diffusivity on the order of $1x10^{-17}$ cm²/second. During low temperature annealing, hydrogen reduces the boron mobility and decreases the time-averaged boron diffusivity at 550°C by one order of magnitude.

Hydrogen exhibits the unique ability of inhibiting boron diffusion during SPER in amorphous silicon generated via self-amorphization. In many respects, hydrogen and fluorine behave similarly in amorphous silicon. They passivate dangling silicon bonds, out-diffuse, and retard the recrystallization rate [Acc96, Ade88, Bro79, Duf04, Fre95, Kap78, Hir96, Jac05, Kur05, Mir05, Obe87, Ohy89, Ols94, Pan86, Ste79, Ste80, Sun84, Tsa79b, Tsu87]. However, only hydrogen is highly mobile and impedes the diffusion of boron in amorphous material during SPER annealing.

One possible explanation is that bonding defects in the amorphous structure facilitate boron diffusion in amorphous silicon. Hydrogen can dramatically reduce the number of diffusion pathways available to the boron atoms by passivating a majority of these defects. By incorporating hydrogen at a plasma temperature of 250°C, a majority of the dangling silicon bond population in the near surface region should be passivated through terminal S-H bonds prior to boron incorporation. The subsequent boron implant could remove a number of these bonds through recoil reactions. However, hydrogen exhibits a high mobility at 550°C and is free to diffuse throughout the amorphous network binding with any remaining dangling silicon bonds [Acc96, Tsa79c].

Hydrogen is effective at binding with dangling, strained, and weak silicon bonds throughout the amorphous phase [Bro79]. The Si-H bonds in amorphous silicon can remain stable during heat treatment [Acc96], as evidenced by the hydrogen concentration profiles shown in Figure 5-34. The release of hydrogen into the matrix during annealing can also result in the reconstruction of potential dangling silicon bonds left behind through the formation of Si-Si bonds [Tsa79c]. However, if reconstruction is incomplete new defect sites in the form of dangling bonds can be introduced into the amorphous matrix [Tsa79c]. Pantelides has proposed a mechanism for hydrogen diffusion in amorphous silicon that may be applicable to other dopants [Pan87]. When a migrating floating bond is passed to a silicon atom that is already bonded to three other silicon atoms and one hydrogen atom forming a standard Si-H bond, the hydrogen atom is no longer needed for tetrahedral coordination of the silicon atom and is subsequently released into the amorphous network [Pan87]. This mechanism presumes a low activation energy for dopant diffusion, on the order of approximately 1.5 eV [Pan87]. The diffusion and passivation characteristics of hydrogen in amorphous silicon suggest that boron diffusion may be related to the presence of bonding defects.

Another possibility is that boron diffusion during SPER is hindered by the formation of B-H pairings, as defined by chemical interactions during the annealing process. The diatomic bond strength of a B-H bond (389 kJ/mol) has been reported to be 20% greater than that of a Si-H bond (318 kJ/mol), implying that if B-H pairings do occur they will be more stable than Si-H interactions [Cot58, Dar70, Tsa79c]. To date, characterization of the properties of boron-doped hydrogenated amorphous silicon films has only been conducted for films doped during the growth or deposition process. Under such conditions, boron atoms are completely incorporated into the amorphous silicon structure. However, the manner in which boron is integrated into the amorphous network can provide insight into the likelihood of the formation of B-H bonds in ion implanted amorphous silicon during annealing at 550°C, as hydrogen is known to diffuse at temperatures as low as 200°C [Acc96, Tsa79c].

Tsai used IR spectroscopy to examine boron-doped hydrogenated amorphous silicon films deposited via glow-discharged plasma techniques at 270° C [Tsa79c]. As the boron concentration in the films was increased, the number of H-B bonds increased in proportion to the decrease in the H-Si bond population [Tsa79c]. The films were shown to possess B-Si bonds in the form of SiB₄ and SiB₆, however, the intensity of these peaks in the IR transmission spectra were weak [Tsa79c]. Hydrogen was shown to bind with boron in the form of either terminal (H-B) or bridging (B-H-B) bonds. Bridging bonds were proposed to exist with different bond strengths in amorphous silicon due to angular constraints imposed by the structure of the amorphous network [Tsa79c]. Terminal hydrogen bonds, on the other hand, were not limited by steric hindrances.

In the case of boron-doped (0.5 at%) hydrogenated amorphous silicon films deposited at 230°C, Boyce and Ready demonstrated that approximately 40% of the constituent boron existed in the form of B-H bonds [Boy88]. However, no measurable populations of B-H and P-H bonds were observed in compensated hydrogenated amorphous silicon films doped with 2 at% boron and 2 at% phosphorus [Boy88]. The chemical affinity of hydrogen for boron may be altered when both boron and phosphorus are present, such that B_mP_n clusters impact the bonding of hydrogen [Boy88]. These results suggest that hydrogen migration and preferential bonding may occur during amorphous film deposition at temperatures of 230°C and 270°C. Boyce and Ready also proposed that the network structure, and possibly the behavior, of hydrogenated amorphous silicon doped with boron might be similar to that of hydrogen-passivated crystalline silicon doped with boron [Boy88].

In boron-doped crystalline silicon, the diffusion of hydrogen proceeds via a traplimited process [Zun92]. During annealing at temperatures below 140°C, B-H complexes are formed due to the large Coulombic interaction between H^+ and B^- species. In the temperature regime examined, the hydrogen diffusion process was controlled entirely by the trapping and release of hydrogen by boron atoms [Zun92]. As the boron concentration increased, the effective diffusivity of hydrogen decreased. The dissociation energy of a B-H complex in crystalline silicon was estimated to be approximately 1.3 eV [Zun89], which is high enough to temporarily impede the diffusion of hydrogen during annealing. If H-B bonds are also continuously formed and dissociated during annealing in hydrogenated amorphous silicon implanted with boron, this process would account for the fact that hydrogen remains highly concentrated near the sample surface during annealing at 550°C (Figure 5-34). Post annealing, hydrogen overlaps a majority of the boron concentration profiles. Hydrogen demonstrates significant out-diffusion throughout the annealing process, but is prevented from completely exiting the sample surface. Boron is present at concentrations exceeding 4×10^{20} atoms/cm³ in the initial 50 Å of material, suggesting that hydrogen would spend the majority of its time within this region in a B-H complex, as it doesn't have to diffuse far before encountering another boron atom. Similarly, when the boron atoms are involved in B-H complexes they are also prevented from diffusing freely into the substrate.

Boron exhibits measurable diffusion during annealing in amorphous silicon, but the effective time-averaged boron diffusivity is approximately one order of magnitude lower when hydrogen is present. The nanovoid free and compact structure of amorphous silicon generated through ion implantation may also contribute to the apparent immobility of

boron during annealing, as B-H complexes may be unable to diffuse through the network unobstructed. For example, the range of bond angles present in the amorphous structure, in combination with an absence of nanovoids, could stericly hinder the motion of bridging bonds formed between the hydrogen and boron atoms [Tsa79c]. Boron has been shown to preferentially bond with hydrogen during the low temperature deposition of amorphous films, implying that boron may also react with hydrogen during SPER annealing of hydrogenated layers implanted with boron.

The boron mobility in amorphous silicon is greatly hindered during SPER annealing by hydrogen co-doping. Within self-amorphized silicon, hydrogen lowers the measured time-averaged boron diffusivity by approximately one order of magnitude at a temperature of 550°C. Hydrogen may retard boron motion by either passivating silicon bonding defects or binding with mobile boron atoms. The strength of H-B bonds exceeds that of H-Si bonds [Cot58, Dar70, Tsa79c], implying that hydrogen is more likely to interrupt the boron diffusion process in amorphous silicon by forming immobile H-B pairs during low temperature recrystallization annealing.

Amorphous Silicon Microstructure

Matsumura et al. used the nuclear reaction ${}^{10}B(n,\alpha)^7Li$ to demonstrate that the boron diffusivity within glow-discharged boron-doped hydrogenated amorphous silicon substantially exceeds that of crystalline silicon [Mat83]. During annealing at 330°C, the boron diffusivity was calculated to be approximately $2x10^{-16}$ cm²/second; twelve orders of magnitude higher than values extrapolated for crystalline material [Mat83]. The error in their estimation of the boron diffusivity was approximately 70%, based on errors inherent to the profile measurement process and subsequent conversion from an alpha particle energy to sample depth scale [Mat83].

Matsumura et al. repeated this study at annealing temperatures of 200°C and 400°C, enabling them to determine the activation energy for boron diffusion in hydrogenated glow-discharge deposited films (1.5 eV) [Mat83]. The reported value is 2.2 eV lower than the energy barrier in crystalline silicon [Had00] and similar to the calculated activation energy for hydrogen diffusion in amorphous silicon at 330°C (1.5 eV) [Car78], as well as the dissociation energy for a B-H complex in crystalline silicon (1.3 eV) [Zun89]. Matsumura et al. speculate that there may be a strong correlation between the diffusion of boron and hydrogen in glow-discharged hydrogenated amorphous silicon, but do not propose a specific diffusion mechanism [Mat83]. It remains unclear if boron diffuses in the form of a mobile B-H complex, participates in a trap and release process with hydrogen, or if boron is released from its network bonds and diffuses on its own in a mechanism similar to that of hydrogen.

Unfortunately, Matsumura et al. made no mention of the estimated hydrogen and boron contents of their films [Mat83]. Beyer et al. showed that glow-discharged films containing more than 20 at% hydrogen have relatively open and void-rich structures that are heterogeneous in nature, whereas films with less hydrogen are homogeneous and more compact [Bey83]. The distinct differences between our findings and those of Matsumura et al. result primarily from the fact that very different forms of amorphous silicon were used in the examination of boron diffusion characteristics. Amorphous silicon formed through ion implantation has not been shown to contain nanovoids, whereas deposited or sputtered films are known to possess substantial void populations and more open structures [Acc96, Bey83, Weg96]. The microstructures and bonding arrangements of these two types of material differ significantly.

Boron diffuses in ion implanted amorphous silicon with a measured time-averaged diffusivity five orders of magnitude higher than crystalline silicon and an activation energy 30% lower. When hydrogen is present the measured diffusivity decreases by approximately one order of magnitude. In deposited hydrogenated amorphous silicon, on the other hand, boron exhibits a diffusivity twelve orders of magnitude higher than crystalline silicon and an activation energy 60% lower [Had00, Mat83]. The main difference between these forms of silicon, namely ion implanted amorphous silicon, deposited amorphous silicon, and crystalline silicon, is their void concentration [Weg96]. The more open the structure, the lower the energy barrier for boron diffusion to occur and the greater the measured time-averaged diffusivity during low temperature annealing.

Matsumura et al. have suggested that boron diffuses by completely different mechanisms in amorphous and crystalline silicon [Mat83]. Our results assert that boron diffuses in amorphous material by utilizing random open spaces to move through the microstructure. Amorphous silicon provides a multitude of pathways for dopants to diffuse, whereas crystalline silicon contains repeating channels of a set width. In crystalline material, boron requires the assistance of silicon interstitials to diffuse [Fan96a, Gos97, Nic89, Ura99a]. The precise mechanism for boron diffusion in amorphous silicon remains unknown, however, the participation of vacancy-like or interstitial-like defects cannot be excluded.

The distribution of bond angles in amorphous diamond-cubic material is believed to facilitate the large-scale motion of dopants and is not limited to assisting small species,

such as boron. The large metallic species of gold, silver, copper, arsenic, antimony, and indium have also been shown to diffuse rapidly in amorphous substrates [Ell85, Pol90, Pri88]. The diffusion of these metals in crystalline material is often mediated by gettering at defects sites, [Pol90] following a separate diffusion mechanism from that displayed in amorphous material [Ell85, Pol90, Pri88]. The aforementioned studies collectively demonstrate that dopants can diffuse in amorphous silicon during annealing at both low and high temperatures. For the range of dopant species investigated at this time, the void population in the sample microstructure appears to determine the magnitude of diffusion enhancement in amorphous material, as compared to crystalline silicon. Co-implanted species may influence the diffusion behavior of one another by blocking or altering diffusion pathways, eliminating or creating trapping sites, or by forming a range of complexes that require a given degree of open space to diffuse during annealing.

Summary and Conclusions

Boron diffuses significantly faster in amorphous silicon during SPER annealing than in crystalline silicon. The presence of silicon, germanium, and fluorine co-implants has no measurable impact on the measured time-averaged boron diffusivity, regardless of their co-implant ordering or implant dose. The activation energy for boron diffusion in amorphous silicon was calculated to be approximately 2.5 eV; 30% lower than the enthalpy barrier for boron diffusion in crystalline silicon. Both fluorine and hydrogen hinder the silicon recrystallization process, increasing the time boron is exposed to amorphous material at elevated temperatures. In the case of fluorine, this results in a greater boron diffusion length. However, the mere presence of hydrogen drastically retards boron diffusion.

Hydrogen has been proposed to hinder the mobility of boron in amorphous silicon in two possible ways [Ade88, Boy88, Bro79, Cot58, Dar70, Hir96, Jac91, Kap78, Pan86, Ste79, Ste80, Tsa79c, Tsu87, Zun89, Zun92]. In the first, hydrogen is attributed with passivating dangling silicon bonds throughout the amorphous network, thereby hindering the ability of boron to diffuse freely. In this instance, the impact of dangling bond passivation would contradict the effect of fluorine co-implantation within as-implanted amorphous silicon, as discussed in Chapter 4. This case is based on the assumption that bonding defects facilitate boron diffusion. The second case presumes the formation of H-B pairings that are immobile in the nanovoid free and compact structure of ion implanted amorphous silicon. The precise manner in which hydrogen impacts boron diffusion remains unknown, however, the diatomic bond strength of H-B bonds is 20% stronger than that of H-Si bonds, suggesting that there is a higher driving force for the formation of H-B bonds.

The random, open structure of amorphous silicon appears to facilitate enhanced boron diffusion. The activation energies for boron diffusion in amorphous material are dependent on the material microstructure, remaining substantially lower than the energy barrier for diffusion in crystalline silicon. The resultant time-averaged boron diffusivity values appear to scale in magnitude with the void density in amorphous silicon. These results are in strong agreement with the reported diffusion behavior of beryllium atoms in bulk amorphous glass alloys [Gey96, Qui96].

Simple simulations of boron diffusion in amorphous silicon have also provided insight into the potential diffusion mechanism. Charged species effects were unable to predict experimental profile behavior for multiple annealing times in the temperature

range of 550°C to 700°C, suggesting that charged states do not influence the ability of boron to diffuse in amorphous silicon during the SPER process. Concentration dependent and trap-mediated diffusion approaches were both able to accurately predict boron diffusion characteristics for the processing conditions examined. These results demonstrate that the effective diffusivity of boron is dependent upon the concentration of boron dopant in amorphous silicon. However, the precise manner in which boron may diffuse in either the presence or absence of trapping sites remains uncertain.



Figure 5-1: Room temperature boron diffusion profiles after annealing at 550°C for 10 minutes and 15 minutes. Samples were preamorphized with 15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ and implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺.



Figure 5-2: Room temperature boron diffusion profiles after annealing at 550°C for 10 minutes and 15 minutes. Samples were preamorphized with 60 keV, 1x10¹⁵ atoms/cm² Ge⁺ and implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺.



Figure 5-3: Experimental and simulated boron diffusion profiles after annealing at 550°C for 10 minutes and 15 minutes. Samples were preamorphized with 15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ and implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using Fickian diffusion parameters.



Figure 5-4: Experimental and simulated boron diffusion profiles after annealing at 550°C for 10 minutes and 20 minutes. Samples were preamorphized with 60 keV, 1x10¹⁵ atoms/cm² Ge⁺ and implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using Fickian diffusion parameters.



Figure 5-5: Boron concentration profiles for samples containing boron alone and boron co-implanted with preceding 9 keV, 5x10¹⁵ atoms/cm² silicon. Boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². As-implanted and 550°C, 15 minute annealing conditions are shown.
(15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure 5-6: Time-averaged boron diffusivity as a function of annealing time at 550°C for samples co-implanted with 9 keV silicon at doses ranging from 1×10^{14} atoms/cm² to 5×10^{15} atoms/cm² and 500eV, 1×10^{15} atoms/cm² boron. Boron diffusivity values were calculated for a Half-Gaussian boron concentration of 3×10^{19} atoms/cm³. (15 keV and 70 keV, 1×10^{15} atoms/cm² Si⁺ PAI)



Figure 5-7: Boron concentration profiles for samples containing boron alone and boron co-implanted with germanium. Samples were preamorphized with 15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ implants. Germanium was implanted at an energy of 14 keV and dose of 5x10¹⁵ atoms/cm², followed by 500 eV, 1x10¹⁵ atoms/cm² boron. As-implanted and 550°C, 15 minute annealing conditions are shown.



Figure 5-8: Time-averaged boron diffusivity as a function of annealing time at 550°C for samples co-implanted with 14 keV germanium at doses ranging from 1x10¹⁴ atoms/cm² to 5x10¹⁵ atoms/cm² and 500eV, 1x10¹⁵ atoms/cm² boron. Boron diffusivity values were calculated for a Half-Gaussian boron concentration of 3x10¹⁹ atoms/cm³. (15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure 5-9: Boron concentration profiles for samples containing boron alone and boron co-implanted with fluorine. Samples were preamorphized with 15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ implants. Fluorine was implanted at an energy of 6 keV and dose of 2x10¹⁵ atoms/cm², followed by 500 eV, 1x10¹⁵ atoms/cm² boron. As-implanted and 550°C, 15 minute annealing conditions are shown.



Figure 5-10: Time-averaged boron diffusivity as a function of annealing time at 550°C for samples co-implanted with 6 keV fluorine at doses of 1x10¹⁵ atoms/cm² and 5x10¹⁵ atoms/cm² and 500eV, 1x10¹⁵ atoms/cm² boron. Boron diffusivity values were calculated for a Half-Gaussian boron concentration of 3x10¹⁹ atoms/cm³. (15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure 5-11: Boron concentration profiles for samples co-implanted with 6 keV, 2x10¹⁵ atoms/cm² fluorine and 500 eV, 1x10¹⁵ atoms/cm² boron, in alternating implant orders. As-implanted and 500°C, 6 hour annealing conditions are shown. (15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure 5-12: Time-averaged boron diffusivity as a function of annealing temperature for samples co-implanted in alternating orders with 500eV, 1x10¹⁵ atoms/cm² boron and 6 keV, 2x10¹⁵ atoms/cm² fluorine. Boron diffusivity values were calculated for a Half-Gaussian boron concentration of 3x10¹⁹ atoms/cm³ at temperatures ranging from 500°C to 700°C. (15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure 5-13: Boron concentration profiles for samples containing boron alone and boron co-implanted with preceding 6 keV fluorine at doses ranging from 5x10¹⁴ atoms/cm² to 2x10¹⁵ atoms/cm². Boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². As-implanted and 550°C, 10 minute annealing conditions are shown. (60 keV, 1x10¹⁵ atoms/cm² Ge⁺ PAI)



Figure 5-14: Boron concentration profiles for samples containing boron alone and boron co-implanted with preceding 6 keV fluorine at doses ranging from 5x10¹⁴ atoms/cm² to 2x10¹⁵ atoms/cm². Boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². As-implanted and 550°C, 30 minute annealing conditions are shown. (60 keV, 1x10¹⁵ atoms/cm² Ge⁺ PAI)



Figure 5-15: Amorphous layer depth as a function of annealing time at 550°C and the coimplanted fluorine dose. Samples were implanted with 6 keV fluorine at doses ranging from 5x10¹⁴ atoms/cm² to 5x10¹⁵ atoms/cm² and 500 eV, 1x10¹⁵ atoms/cm² boron. (60 keV, 1x10¹⁵ atoms/cm² Ge⁺ PAI)



Figure 5-16: Time-averaged boron diffusivity as a function of annealing time at 550° C for samples co-implanted with 6 keV fluorine at doses ranging from $1x10^{15}$ atoms/cm² to $5x10^{15}$ atoms/cm² and 500eV, $1x10^{15}$ atoms/cm² boron. The boron diffusivity values were calculated for a Half-Gaussian boron concentration of $3x10^{19}$ atoms/cm³. (60 keV, $1x10^{15}$ atoms/cm² Ge⁺ PAI)



Figure 5-17: Experimental and simulated boron diffusion profiles after annealing at 550°C for 10 minutes and 15 minutes. Samples were preamorphized with 15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ and implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using concentration dependent diffusion terms.



Figure 5-18: Experimental and simulated boron diffusion profiles after annealing at 550°C for 10 minutes and 20 minutes. Samples were preamorphized with 60 keV, 1x10¹⁵ atoms/cm² Ge⁺ and implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using concentration dependent diffusion terms.

Table 5-1: Simulation parameters for boron diffusion in self-amorphized material containing both boron and fluorine dopants. The D_F and D_B values are representative of boron diffusion in amorphous silicon irrespective of the implant ordering, i.e. B+F or F+B. However, the solubility limit values only apply to the case of F+B, as the solubility limit of B+F samples was held constant at 1.9×10^{20} atoms/cm³.

Annealing	$D_{\rm F}$	D _B	Solubility Limit
Temperature (°C)	(cm ² /second)	(cm ⁵ /atoms-second)	(atoms/cm ³) [F+B]
550	1.08×10^{-17}	1.11×10^{-36}	1.448×10^{20}
600	6.80x10 ⁻¹⁷	3.25x10 ⁻³⁵	1.657×10^{20}
700	1.52×10^{-15}	9.80x10 ⁻³³	2.082×10^{20}



Figure 5-19: Experimental and simulated boron diffusion profiles after annealing at 550°C for varying times up to 90 minutes. Samples were implanted with 6 keV, 2x10¹⁵ atoms/cm² F⁺ and 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using concentration dependent diffusion terms. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 5-20: Experimental and simulated boron diffusion profiles after annealing at 600°C for one minute. Samples were implanted with 6 keV, 2x10¹⁵ atoms/cm² F⁺ and 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using concentration dependent diffusion terms. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 5-21: Experimental and simulated boron diffusion profiles after annealing at 700°C for three seconds. Samples were implanted with 6 keV, 2x10¹⁵ atoms/cm² F⁺ and 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using concentration dependent diffusion terms. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)


Figure 5-22: Experimental and simulated boron diffusion profiles after annealing at 550°C for varying times up to 30 minutes. Samples were implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺ and 6 keV, 2x10¹⁵ atoms/cm² F⁺. Profiles were simulated using concentration dependent diffusion terms. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)











Figure 5-25: Experimental and simulated boron diffusion profiles after annealing at 550°C for 10 minutes and 15 minutes. Samples were preamorphized with 15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ and implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using trap-mediated diffusion terms.



Figure 5-26: Experimental and simulated boron diffusion profiles after annealing at 550°C for 10 minutes and 20 minutes. Samples were preamorphized with 60 keV, 1x10¹⁵ atoms/cm² Ge⁺ and implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using trap-mediated diffusion terms.



Figure 5-27: Experimental and simulated boron diffusion profiles after annealing at 550°C for varying times up to 90 minutes. Samples were implanted with 6 keV, 2x10¹⁵ atoms/cm² F⁺ and 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using trap-moderated diffusion terms. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 5-28: Experimental and simulated boron diffusion profiles after annealing at 600°C for one minute. Samples were implanted with 6 keV, 2x10¹⁵ atoms/cm² F⁺ and 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using trapmoderated diffusion terms. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 5-29: Experimental and simulated boron diffusion profiles after annealing at 700°C for three seconds. Samples were implanted with 6 keV, 2x10¹⁵ atoms/cm² F⁺ and 500 eV, 1x10¹⁵ atoms/cm² B⁺. Profiles were simulated using trap-moderated diffusion terms. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 5-30: Experimental and simulated boron diffusion profiles after annealing at 550°C for varying times up to 30 minutes. Samples were implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺ and 6 keV, 2x10¹⁵ atoms/cm² F⁺. Profiles were simulated using trap-moderated diffusion terms. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 5-31: Experimental and simulated boron diffusion profiles after annealing at 600°C for one minute. Samples were implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺ and 6 keV, 2x10¹⁵ atoms/cm² F⁺. Profiles were simulated using trap-moderated diffusion terms. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 5-32: Experimental and simulated boron diffusion profiles after annealing at 700°C for three seconds. Samples were implanted with 500 eV, 1x10¹⁵ atoms/cm² B⁺ and 6 keV, 2x10¹⁵ atoms/cm² F⁺. Profiles were simulated using trap-moderated diffusion terms. (70 keV, 1x10¹⁵ atoms/cm² Si⁺ preamorphization)



Figure 5-33: Amorphous layer depths for samples containing boron alone and boron with hydrogen during SPER annealing at 550°C. Samples were exposed to a hydrogen plasma at a dose of 1x10¹⁶ atoms/cm² and temperature of 250°C for 1 hour prior to boron implantation at an energy of 500eV and dose of 1x10¹⁵ atoms/cm². (70 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure 5-34: Hydrogen concentration profiles for samples containing boron dopant. Samples were preamorphized with 70 keV, $1x10^{15}$ atoms/cm² Si⁺ prior to exposure to a hydrogen plasma at a dose of $1x10^{16}$ atoms/cm² and temperature of 250°C for 1 hour. Boron was subsequently implanted at an energy of 500eV and dose of $1x10^{15}$ atoms/cm². SPER annealing was conducted at 550°C for times ranging from 10 minutes to 30 minutes.



Figure 5-35: Boron concentration profiles for samples with and without hydrogen doping. Samples were preamorphized with 70 keV, $1x10^{15}$ atoms/cm² Si⁺ prior to exposure to a hydrogen plasma at a dose of $1x10^{16}$ atoms/cm² and temperature of 250°C for 1 hour. Boron was subsequently implanted at an energy of 500eV and dose of $1x10^{15}$ atoms/cm². SPER annealing was conducted at 550°C for times ranging up to 30 minutes.

CHAPTER 6 BORON DIFFUSION CHARACTERISTICS IN RELAXED SILICON DURING THE SOLID PHASE EPITAXIAL REGROWTH PROCESS

Introduction

Structural relaxation is an irreversible transition pertaining to changes in the short range order (SRO) of amorphous silicon prior to crystallization [Ish02]. Differential scanning calorimetry (DCS) analysis has shown that amorphous silicon can be structurally relaxed at temperatures below 600°C for varying anneal times, without recrystallizing [Roo89, Roo90a, Roo91a]. The structural changes in amorphous silicon as a function of relaxation annealing have been characterized extensively through Raman spectroscopy. With low temperature annealing, the transverse optic (TO) peak shifts to higher wavenumbers and becomes narrower, signifying a decrease in the distribution of bond angles [Roo90a, Roo90b, Roo91b, Roo99, Sin88, Tsu84, Tsu85]. Raman analysis has demonstrated that the level of structural relaxation initially increases logarithmically with annealing time and then saturates for longer times [Sin88]. The relaxation process corresponds to a lowering of the free energy state for amorphous silicon and can be delayed if the anneal temperature decreases during processing [Ish02, Roo91a]. Shifts in the Raman TO peak demonstrate that long range order (LRO) becomes pronounced with continued annealing and subsequent recrystallization [Ish02].

Structural relaxation results in the annihilation of point defects and in a reduction of the dangling silicon bond density of amorphous silicon [Laa99a, Roo90a, Roo90b, Roo91b, Roo99, Uda87, Vol93]. As the degree of structural relaxation rises, so does the

level of chemical bonding and SRO [For88, Sha89, Uda87]. The low temperature heat releases observed by DSC during annealing of amorphous silicon are attributed to the removal of ion implantation induced damage and are not defined by a set activation energy [Roo90a, Roo91a, Roo91b]. The density of unrelaxed amorphous silicon remains unchanged by the structural relaxation process, suggesting that defect annihilation during relaxation is limited to the removal of both low and high density defects within the amorphous network [Cus94a, Roo91b]. In amorphous silicon formed through ion implantation, the onset temperature of a DSC heat release increases linearly with the temperature at which the amorphization implant was conducted [Mer05]. However, the magnitude of a DSC heat release, provided in mW, is independent of the amorphization implant temperature for low fluence implants [Mer05]. The energy stored in the amorphous silicon network due to bond angle distortions can be as high as 40 kJ/mol for as-implanted material [Sin88]. The highest activation energy observed for structural relaxation was 2.2 eV, distinctively lower than the 2.7 eV barrier associated with the SPER process [Roo90a, Roo91b].

Studies by Volkert have reported that annealing at temperatures ranging from 250°C to 500°C leads to atomic rearrangements in amorphous silicon [Vol93]. The thermal expansion coefficient of amorphous silicon has been reported to be approximately 6.5% lower than that of crystalline silicon and independent of the degree of structural relaxation [Vol93]. The disordered nature of amorphous silicon is attributed with restricting local expansion during heating, resulting in a lower thermal expansion coefficient [Vol93]. The annihilation of point defects as a result of structural relaxation is believed to mediate the flow of amorphous silicon, leading to an increase in the viscosity

[Vol93]. Viscosity has been shown to increase linearly with annealing time during structural relaxation [Vol93].

Structural relaxation inherently imparts SRO and is accredited with a decrease in the average bond angle distortion of a continuous random network [Roo90a, Roo90b, Roo91b, Tsu84, Tsu85]. XRD analysis confirmed that relaxation involves reordering on an atomic level, denoting differences in the structure factors of amorphous and relaxed material [Laa99a, Roo91b]. Despite the inherent structural differences between crystalline and amorphous silicon, their densities are very close in value with amorphous silicon reported to have a density approximately 1.8% lower than crystalline silicon [Cus94a, Weg96]. Roorda et al. also investigated the effects of subsequent ion implantation upon relaxed silicon substrates using Raman spectroscopy [Roo90a, Roo90b, Roo91a, Roo91b]. When species are implanted at their amorphizing doses, such as Si^+ at 1×10^{15} atoms/cm², they completely de-relax the relaxed silicon material, similar to the manner in which they would amorphize a crystalline substrate. Structural derelaxation is attributed to nuclear collisions incurred during subsequent implantation [Roo90a, Roo90b, Roo91b]. Only one out of every twenty silicon atoms needs to be displaced by a nuclear collision to completely de-relax amorphous silicon [Roo91b]. It is important to note that amorphous material formed by amorphizing silicon and germanium implants were found to behave similarly in a relaxed state, in the absence of additional dopant species [Roo91b].

In this study, the role of structural relaxation on boron diffusion in silicon and germanium preamorphized silicon during SPER activation annealing is characterized. Boron diffusion phenomena are monitored in both the presence and absence of co-

implanted fluorine. A range of structural relaxation conditions is explored, including relaxation annealing prior and subsequent to dopant incorporation. The effects of structural relaxation upon silicon recrystallization rates, boron diffusivities, boron activation, and junction depth are addressed at length.

Experimental Design

Several (100) n-type, 200 mm Czochralski wafers were commercially implanted at room temperature by Texas Instruments, Inc. (TI) and Axcelis Technologies (AT). Wafers were preamorphized with either silicon or germanium implants. Silicon implants were performed at energies of 15 keV and 70 keV at a uniform dose of 1×10^{15} atoms/cm². To ensure the formation of continuous, surface amorphous layers, both 15 keV and 70 keV silicon implants were used for self-amorphized samples. Germanium ions were implanted at an energy of 80 keV and dose of 1×10^{15} atoms/cm². Cross-sectional TEM (XTEM) and variable angle spectroscopic ellipsometry (VASE) analysis confirmed amorphous layer depths of approximately 1500 Å and 1100 Å, respectively. VASE measurements were performed at beam angles of 65° , 70° , and 75° .

Co-implanted samples were subsequently implanted with 12 keV, 1.5×10^{15} atoms/cm² fluorine. Some specimens then received structural relaxation annealing at 400°C for 30 minutes, 475°C for 15 minutes, or 475°C for 30 minutes. Structural relaxation anneals conducted prior to boron incorporation were performed in commercial annealing systems under a flowing dry N₂ ambient by TI and AT. The fluorine dose utilized throughout these studies can successfully amorphize crystalline silicon and return a structurally relaxed amorphous layer to an unrelaxed amorphous state [Roo91a]. Therefore, co-implanted samples were always implanted with fluorine prior to the structural relaxation process, maintaining a relaxed state during further processing steps. Amorphous samples also received fluorine implants prior to boron co-implantation in order to eliminate any potential implant recoil effects [Jac02].

All wafers were then implanted with drift mode 500 eV, 1x10¹⁵ atoms/cm² boron dopant. Structural relaxation anneals performed subsequent to boron incorporation are referred to as pre-anneals throughout these experiments. Some samples received preanneals at 475°C for times ranging from 10 minutes to 120 minutes. Pre-anneals were performed in a quartz tube furnace under an inert flowing nitrogen environment. SPER annealing at lower temperatures was conducted in a quartz tube furnace in an inert nitrogen environment at 500°C, 550°C, or 600°C for varying times. SPER annealing at higher temperatures was performed in a rapid thermal annealing (RTA) system at temperatures of 650°C or 700°C for a range of times in a flowing inert nitrogen ambient. RsL techniques were used by Frontier Semiconductor to obtain junction sheet resistance data. Sheet resistance data are reported with a 15% margin of error, as 1.0 in. by 1.0 in. samples were measured rather than full sized 200 mm or 300 mm wafers.

Secondary Ion Mass Spectrometry (SIMS) was performed at room temperature by TI. Boron SIMS profiles were obtained using a CAMECA IMS-6f tool with an O_2^+ primary beam at a nominal current ranging from 50 nA to 70 nA. The beam was maintained 50° from the sample normal with a net impact energy of 800 eV. The primary beam was rastered over a 200 µm by 200 µm area, with ions collected from the center 15% of the area. A constant O_2 ambient was maintained with a sputter rate ranging from 0.08 nm/s to 0.1 nm/s. Fluorine counts were generated under Cs⁺ ion bombardment at an incident angle of 60°, current of 100 nA, and net impact energy of 1 keV. Secondary ions were obtained from the center 15% of the rastered area. Comparisons are made throughout these studies between amorphous and relaxed material formed via silicon and germanium preamorphizations. Specimens containing boron alone were processed as follows: (i) PAI Implant + Boron Implant, (ii) PAI Implant + Structural Relaxation Anneal + Boron Implant, or (iii) PAI Implant + Boron Implant + Pre-Anneal. SPER annealing followed at temperatures ranging from 500°C to 700°C for varying times. The co-implanted samples received the following processing steps prior to recrystallization annealing: (i) PAI Implant + Fluorine Implant + Boron Implant or (ii) PAI Implant + Fluorine Implant + Structural Relaxation Anneal + Boron Implant. For ease of reference, wafers processed according to case (i) are referred to as amorphous or unrelaxed, case (ii) as relaxed, and case (iii) as pre-annealed throughout these studies.

Silicon Preamorphized Silicon

Boron Alone

In self-amorphized silicon substrates, structural relaxation does not impact boron diffusion when boron is implanted alone. Figure 6-1 shows boron concentration profiles for amorphous and relaxed samples under their as-implanted and annealed conditions. Samples were relaxed at 475°C for 30 minutes. The amorphous and relaxed profiles are nearly identical both before and after 30 minutes of annealing at 550°C. Structural relaxation does not measurably influence the boron diffusion process under these processing conditions.

The time-averaged boron diffusivity is independent of structural relaxation in selfamorphized material containing boron alone, as seen in Figure 6-2. In both amorphous and relaxed material, boron maintains a stable time-averaged diffusivity of approximately $4x10^{-17}$ cm²/second during the SPER process at 550°C. Diffusivity values were

determined for a Half Gaussian boron concentration of 3×10^{19} atoms/cm³. The silicon recrystallization rate, level of boron activation, and final junction depth are also independent of structural relaxation.

Junction characteristics are plotted in Figure 6-3 for boron concentrations of both $1x10^{18}$ atoms/cm³ and $1x10^{19}$ atoms/cm³. Final junction depths differ by less than 4 Å for amorphous and relaxed samples, which is below the SIMS resolution. Sheet resistances are less than 5% lower in relaxed specimens and are also within the inherent resolution of the electrical measurement process. Collectively, these results indicate that structural relaxation has no measurable impact on the junction characteristics of self-amorphized substrates implanted with boron alone.

Boron Co-Implanted with Fluorine

Structural relaxation does not measurably influence boron diffusion characteristics when both fluorine and boron are co-implanted within self-amorphized silicon substrates. Figure 6-4 illustrates dopant SIMS profiles during annealing at 550°C for relaxed samples containing both fluorine and boron. Samples were relaxed at 475°C for 30 minutes. Boron exhibits a stable time-averaged diffusivity of approximately 4x10⁻¹⁷ cm²/second during SPER annealing at 550°C, as calculated for a Half Gaussian boron concentration of 3x10¹⁹ atoms/cm³. The same diffusion characteristics were observed for amorphous silicon, as seen previously in Figures 5-9 and 5-12. The boron and fluorine concentration profiles for relaxed samples are nearly identical to those of amorphous specimens (not shown). Fluorine dopant exhibits out-diffusion and dose loss during annealing, but remains concentrated above the boron. The peaks in the fluorine SIMS profiles correspond to the changing position of the a/c interface with annealing time in both amorphous and relaxed material, as fluorine is known to segregate and pile up at the

advancing a/c interface [Tsa79b]. As demonstrated previously for self-amorphized substrates containing boron alone, the time-averaged boron diffusivity, junction parameters, and recrystallization rate are all independent of structural relaxation when both fluorine and boron dopants are present. These results are supported by the work of Roorda et al., which demonstrated that the recrystallization rate of self-amorphized silicon is not measurably impacted by the structural relaxation process [Roo91b].

Figure 6-5 portrays junction characteristics for boron concentrations of both 1×10^{18} atoms/cm³ and 1×10^{19} atoms/cm³. Final junction depths differ by less than 5 Å for amorphous and relaxed samples, which is below the SIMS resolution. Sheet resistance values are approximately 25% lower in relaxed specimens. However, these differences are not believed to be statistically significant, as the respective error bars exhibit measurable overlap (Figure 6-5). The electrical measurement values are reported with a margin of error of 15% based on a sample size of 1 inch². The accuracy of the RsL measurement technique improves as the sample size increases. Structural relaxation does not measurably influence junctions formed in self-amorphized materials via boron implantation, in the presence or absence of co-implanted fluorine.

Germanium Preamorphized Silicon

Boron Alone

The incorporation of structural relaxation has a marked effect on germanium amorphized material containing boron alone. Figures 6-6 and 6-7 depict boron concentration profiles for amorphous and relaxed samples, respectively, containing boron alone under as-implanted and annealed conditions. Samples were relaxed at 475°C for 30 minutes. Clearly, the magnitude of boron diffusion during annealing at 550°C is lower in structurally relaxed material, as compared to amorphous conditions. For a boron

concentration of 1×10^{19} atoms/cm³, boron diffuses approximately 40% less in relaxed material during the SPER process. It is important to mention that during the first seven minutes of annealing amorphous and relaxed specimens exhibit nearly identical diffusion characteristics, as seen in Figure 6-8. Only in the latter portion of the recrystallization process is the diffusion of relaxed samples retarded, as compared to amorphous material.

Differences between the amorphous and relaxed SIMS profiles may be due partially to changes in the time-averaged boron diffusivity, as demonstrated in Figure 6-9. Boron diffusivities were calculated for a Half Gaussian boron concentration of $3x10^{19}$ atoms/cm³. Within the experimental margin of error, boron exhibits a stable timeaveraged diffusivity of approximately $3x10^{-17}$ cm²/second in amorphous germanium amorphized silicon, well in agreement with self-amorphized conditions. However, relaxed germanium amorphized specimens demonstrate a slightly lower boron diffusivity of approximately $2x10^{-17}$ cm²/second. These apparent differences are within the estimated margin of error. A decrease in the calculated time-averaged boron diffusivity in the final minutes of annealing is not uncommon, as boron is known to accelerate the recrystallization process once it encounters the advancing a/c interface [Sun82a, Sun82b].

Figure 6-10 illustrates the resultant junction characteristics for these samples at boron concentrations of 1×10^{18} atoms/cm³ and 1×10^{19} atoms/cm³. The sheet resistance of relaxed material is 8% lower than crystalline material and junctions are approximately 10% shallower. Differences of only 8% in the level of boron activation are within the 15% error of the electrical measurement technique. For germanium amorphized material containing boron alone, structural relaxation annealing can lead to shallower junctions, without impacting the level of boron activation.

The primary factor influencing the magnitude of boron diffusion during SPER appears to be the silicon recrystallization rate. As illustrated in Figure 6-11, amorphous samples require more than 20 minutes of annealing at 550°C to complete the regrowth process, whereas relaxed specimens are regrown after only 15 minutes of annealing. Relaxed specimens recrystallize 40% faster at 550°C, corresponding well with the observed 40% reduction in the magnitude of boron diffusion at boron concentrations ranging from 1×10^{18} atoms/cm³ to 1×10^{19} atoms/cm³. Structural relaxation reduces the length of time that boron is exposed to non-crystalline material and able to diffuse, rather than altering the effective boron diffusivity.

The activation energy for silicon recrystallization was calculated for amorphous and relaxed samples containing boron alone at annealing temperatures of 500°C, 550°C, 600° C, 650° C, and 700° C. Amorphous and relaxed samples were annealed for the same times at each temperature. The a/c interface had not interacted with the boron concentration profile for each calculated data point. For amorphous material, the silicon regrowth rate is expressed as follows with an R² of 0.99, where *k* is Boltzmann's constant and *T* is the annealing temperature in Kelvin [Hum93]:

$$R(^{A}_{s}) = 6.57 \times 10^{18} (^{A}_{s}) e^{\frac{-3.1 \text{ eV}}{k(^{eV}_{K}) T(K)}}$$
(6-1)

For structurally relaxed material, the recrystallization rate can be calculated with an R^2 of 0.99 according to the Arrhenius relation

$$R(\mathring{A}_{s}) = 1.15 \times 10^{18} (\mathring{A}_{s}) e^{\frac{-2.9 \text{ eV}}{\overline{k(eV_{K}) T(K)}}}$$
(6-2)

Relaxation annealing at 475°C for 30 minutes reduces the SPER activation energy from 3.1 eV to 2.9 eV, a change of approximately 7%. The structural relaxation process lowers the energy barrier for solid phase epitaxial regrowth for germanium amorphized silicon.

The pre-exponential term for relaxed material is approximately 6X lower than that of amorphous material (Equations 6-1 and 6-2). Based upon the change in Gibbs free energy, the Arrhenius expression for the recrystallization rate can also be written as follows, where ΔS represents the configurational entropy and ΔH is the configurational enthalpy, commonly referred to as the activation energy [DeH93]:

$$R\left(\overset{\text{a}}{/_{s}}\right) = e^{\frac{\Delta S\left(\text{eV/K}\right)}{k\left(\text{eV/K}\right)}} e^{\frac{-\Delta H\left(\text{eV}\right)}{k\left(\text{eV/K}\right) T\left(K\right)}} \left(\overset{\text{a}}{/_{s}}\right)$$
(6-3)

The Arrhenius pre-exponential term is equivalent to the expression $e^{\frac{\Delta S(eV/K)}{k(°/k)}}$, facilitating the extraction of the configurational entropy for a given material. The entropy values for the aforementioned relaxed and amorphous materials are 3.58 meV and 3.73 meV, respectively. The calculated difference of 0.15 meV corresponds to an entropy reduction of 4% for samples receiving relaxation annealing at 475°C for 30 minutes, suggesting that the relaxed material may be in a more ordered state as compared to unrelaxed amorphous silicon. Thus, the acceleration in the SPER velocity from structural relaxation is the result of a reduced activation energy that overcomes a slowing of the regrowth rate due to the decrease in entropy. In germanium amorphized material containing boron alone, structural relaxation has a dramatic impact on the silicon recrystallization rate, indirectly contributing to the observed boron diffusion characteristics.

The level of acceleration in the silicon regrowth rate and magnitude of boron diffusion appear to be determined by the degree of structural relaxation. Boron

concentration profiles for germanium amorphized materials implanted with boron alone are presented in Figures 6-12 and 6-13. Specimens were relaxed at 400°C for 30 minutes, 475°C for 15 minutes, or 475°C for 30 minutes. The control sample represents amorphous material that did not receive a structural relaxation anneal. As-implanted and annealed conditions at 550°C for 15 minutes and 45 minutes, respectively, are shown. During the initial 15 minutes of annealing (Figure 6-12), all of the boron SIMS profiles are nearly identical, regardless of their degree of structural relaxation. Only the sample relaxed at 475°C for 30 minutes has completed the recrystallization process. After 45 minutes of SPER annealing (Figure 6-13), all of the samples have completed the regrowth process. The boron concentration profiles have deviated from one another. During the additional 30 minutes of annealing in crystalline material, boron did not exhibit measurable TED in the sample relaxed at 475°C for 30 minutes. It is interesting to note that the amorphous or control samples behave similarly to specimens relaxed at 400°C for 30 minutes. The more relaxed the material, the shallower the final profile depth.

The recrystallization rates for the aforementioned sample types are depicted in Figure 6-14 as a function of both annealing time at 550°C and the structural relaxation condition or degree of relaxation. The fastest silicon regrowth rates are exhibited by samples relaxed at 475°C for 30 minutes, implying that these samples are indeed the most relaxed. The recrystallization rates steadily decrease as the relaxation time at 475°C is reduced and the relaxation anneal temperature declines. Samples relaxed at 475°C for 15 minutes and 30 minutes recrystallize 18% and 40% faster than amorphous material, respectively. Once again, amorphous samples behave almost identically to those relaxed at 400°C for only 30 minutes. These results suggest that after 30 minutes of annealing at

400°C, minimal structural relaxation has occurred. Longer anneal times at 400°C are presumably required for measurable relaxation to take place. Structural relaxation impacts boron diffusion by controlling the recrystallization rate and the time boron is exposed to amorphous material. The amount of regrowth rate acceleration appears to scale with the degree of structural relaxation, resulting in increasingly shallower junctions.

The process of structural relaxation was observed to alter the silicon recrystallization rate for germanium amorphized samples containing boron alone only when relaxation annealing occurred prior to dopant incorporation. The recrystallization rates for amorphous and pre-annealed samples are illustrated in Figure 6-15 as a function of both SPER annealing time at 550°C and pre-anneal time. Samples were pre-annealed at 475°C for times of 10, 30, 60, and 120 minutes after boron implantation and just prior to SPER annealing. For clarity, only pre-anneal times of 10 minutes and 120 minutes are shown. Within the experimental margin of error, there is no measurable change in the recrystallization rate due to pre-annealing. Relaxation annealing at 475°C for 30 minutes is sufficient to reduce the time required for complete recrystallization by 40%, however, pre-annealing for 120 minutes at this temperature does not appreciably alter the silicon recrystallization process. Similar results were observed for germanium amorphized material in the absence of dopants. No measurable change in the silicon recrystallization rate was observed in samples relaxed at 475°C and then annealed at 550°C to induce the SPER process, as compared to unrelaxed material.

The delay period between boron implantation and recrystallization annealing for the samples discussed in Figures 6-6 through 6-14 was several weeks. To investigate

potential effects of this delay period, additional annealing was performed using germanium amorphized silicon with and without boron. Samples without boron were processed as follows one year after amorphization: 475°C relaxation anneal for 30 minutes, 325°C anneal for 30 minutes, and SPER annealing at 550°C. Samples were annealed at 325°C to simulate room temperature exposure for a period of several weeks. Samples with boron were relaxed at 475°C prior to boron implantation and annealed at 550°C one year later. The recrystallization rates of these two sets of samples were not impacted by the delay period between relaxation and SPER annealing. These results confirm that low temperature annealing only accelerates the silicon recrystallization process for germanium amorphized samples containing boron alone when annealing occurs prior to dopant incorporation.

Boron Co-Implanted with Fluorine

When fluorine and boron are co-implanted in germanium amorphized material, structural relaxation has no measurable impact on either boron diffusion or junction characteristics. Figure 6-16 shows boron concentration profiles for amorphous and relaxed samples containing both fluorine and boron. Samples were relaxed at 475° C for either 15 minutes or 30 minutes. Irrespective of the degree of structural relaxation, all three of these samples possess nearly identical as-implanted and annealed boron SIMS profiles. The fluorine concentration profiles (not shown) behave similarly in both self and germanium amorphized materials, under otherwise identical processing conditions. As observed previously for self-amorphized material, boron maintains a stable time-averaged boron diffusivity of approximately $4x10^{-17}$ cm²/second throughout the SPER process at 550° C. Boron diffusivities were calculated for a Half Gaussian boron concentration of $3x10^{19}$ atoms/cm³.

Germanium amorphized samples relaxed at 475°C for times of 0 minutes, 15 minutes, and 30 minutes recrystallize at similar rates during annealing at 550°C. The Si-F diatomic bond strength of 553 kJ/mol [Far78] at 298 K is greater than that of Si-Si (327 kJ/mol) [Cha75], Si-Ge (301 kJ/mol) [Gay68], or Si-B (288 kJ/mol) [Ver64] bonds. No chemical bonding data is currently available for Ge-B bonds. The significant differences between these diatomic bond energies suggest that there is a driving force for dangling bonds in amorphous silicon to preferentially bond with fluorine over themselves, germanium, or boron.

When fluorine is co-implanted with boron, the accelerating effects of structural relaxation on the recrystallization process may be outweighed by interactions between fluorine atoms and dangling bonds at the a/c interface, retarding its advancement. Fluorine has a very low mobility in amorphous silicon at 550°C and only redistributes due to accumulation at the advancing a/c interface during recrystallization resulting from a small solid-solubility limit for fluorine in crystalline silicon [Bea78, Tsa79b]. In addition, fluorine also has the potential to form very strong bonds with boron, limiting boron's interaction with dangling bonds at the moving interface during SPER. Lau et al. have reported a F-B diatomic bond strength of 757 kJ/mol [Lau80], representing the most stable bonding structure in our system. These data coincide with our observations that germanium amorphized material co-implanted with fluorine and boron does not experience a change in recrystallization kinetics resulting from structural relaxation annealing. The ability of fluorine to retard the silicon regrowth rate dominates over the observed accelerating effects of relaxation in conjunction with the presence of boron during SPER annealing.

The junction characteristics for these samples are shown in Figure 6-17 for boron concentrations of both 1×10^{18} atoms/cm³ and 1×10^{19} atoms/cm³. Final junction depths differ by less than 10 Å for these processing conditions, which is below the SIMS resolution. Sheet resistances are less than 4% lower in specimens relaxed at 475°C for 30 minutes and only 6% higher in samples relaxed at 475°C for 15 minutes, as compared to amorphous material. These fluctuations are contained in the experimental margin of error of the measurement technique. Structural relaxation does not influence p-type transistors formed in germanium amorphized materials via fluorine and boron co-implantation.

Discussion

These studies have characterized the effects of the structural relaxation process upon silicon recrystallization, boron diffusion, and junction parameters for both self and germanium amorphized materials. The impacts of these effects were addressed for samples containing boron in the presence and absence of fluorine during the SPER process. Self-amorphized materials are not measurably influenced by structural relaxation. The time-averaged boron diffusivity, junction depth, sheet resistance, and recrystallization rates of samples containing boron alone or fluorine co-implanted with boron are independent of the degree of structural relaxation. Similar results were observed for germanium amorphized substrates implanted with both boron and fluorine dopants. The time-averaged boron diffusivity during SPER at 550°C remains stable on the order of approximately $4x10^{-17}$ cm²/second, irrespective of the preamorphization species, degree of structural relaxation, or the presence of fluorine.

As previously discussed, the recrystallization rates of germanium amorphized material containing boron alone were shown to scale with the degree of structural relaxation when the low temperature anneal is performed prior to boron implantation. The regrowth rates of germanium amorphized specimens were verified to be identical, whether unrelaxed or relaxed, in the absence of dopants, supporting the fundamental findings of Lu et al. [Lu91]. Likewise, the recrystallization rate of unrelaxed amorphous silicon was observed to be independent of the preamorphization species, silicon verses germanium, when boron is implanted alone. The structural relaxation process exerts the most profound influence on the recrystallization rates of germanium amorphized material containing boron alone. By controlling the length of the SPER process and the amount of time that boron is able to diffuse in non-crystalline silicon, structural relaxation indirectly determines the magnitude of boron diffusion and the resultant junction depth.

Stress Effects on Silicon Recrystallization

Fundamental studies by Suni et al. have demonstrated that local stresses between lattice atoms and impurity or dopant species can significantly affect recrystallization rates at the advancing a/c interface [Sun82b]. A stress relief mechanism is believed to account for the boron enhanced regrowth rates of bulk silicon, as recrystallization at the a/c interface occurs primarily through a bond rearrangement process [Sun82b]. Silicon regrowth velocities were similarly shown to increase exponentially with an applied environmental stress, altering recrystallization kinetics [Lu91, Nyg85]. Lu et al. also demonstrated that defects residing at the a/c interface are responsible for governing the SPER processes of bulk silicon and germanium [Lu91]. Their detailed analysis determined that the various theories regarding the diffusion of interstitial and vacancy defects from the amorphous or crystalline phases to the a/c interface during SPER are not plausible regrowth mechanisms.

Dangling bonds are believed to be the dominant defects involved in the recrystallization process of silicon and germanium [Lu91]. Prior studies have

demonstrated a decreasing silicon recrystallization rate with an increasing level of hydrogen doping [Acc96, Ade88, Obe87, Ols94]. Hydrogen is well known to passivate dangling and floating bonds in amorphous silicon [Ade88, Bro79, Kap78, Hir96, Pan86, Ste79, Ste80, Tsu87]. By passivating interfacial sites at the a/c interface hydrogen disrupts the bond rearrangement process, thus slowing down the regrowth rate [Ade88]. Hydrogen atoms must be released from their Si-H bonds before the silicon bond rearrangement process may proceed at the a/c interface. Additionally, the solubility of hydrogen is presumably lower in crystalline silicon versus amorphous silicon, as hydrogen atoms are prevented from diffusing through the advancing a/c interface into crystalline material during SPER annealing [Ols94]. The solubility difference for hydrogen in crystalline and amorphous silicon can lead to hydrogen accumulation at the interface and blocking of its movement, due to the rejection of hydrogen atoms from the crystalline phase [Ade88, Ols94]. Suski et al. have also proposed that the ability of dangling bonds to serve as recombination centers may also contribute to a faster recrystallization process, if recombination occurs at the a/c interface [Sus79].

Structural relaxation does not promote accelerated SPER by supplementing a stress relief process. The recrystallization rate of relaxed germanium amorphized material containing boron dopant was observed to accelerate, in comparison to unrelaxed material, at sample depths far removed from the boron concentration profile (Figure 6-11). During the initial ten minutes of annealing, the a/c interface remains more than 400 Å deep and has not yet encountered the boron dopant. In this region, relaxed samples with and without boron dopant should behavior similarly. However, samples implanted with boron demonstrate accelerated recrystallization at sample depths ranging from 400 Å to 1100 Å.

Similar amorphous layer depths were measured for samples annealed either several weeks or one year after boron implantation, demonstrating that these results are reproducible and independent of the time duration between dopant implantation and SPER annealing.

Structural relaxation annealing performed prior to boron implantation was conducted in a commercial furnace system, rather than the quartz tube furnace and RTA systems used for the remaining sample anneals. However, no contaminant species were found to exist within these samples, suggesting that the observed recrystallization rates are independent of the annealing system. The mechanism by which the silicon regrowth process is impacted by structural relaxation annealing in germanium amorphized silicon containing boron dopant remains unknown. At present, there is no clear explanation for these experimental results.

Electronic Effects on Silicon Recrystallization

Several authors attribute electronic Fermi energy level shifts with impacting the silicon recrystallization rate [Ade88, Lic86, McC99, Par88a, Par88b, Sun82a, Wil83], rather than a stress relaxation mechanism. In amorphous silicon the Fermi level is pinned near mid-gap, such that doping is believed to induce band bending and an electric field that attracts charged defects to the a/c interface. According to the electronic impurity theory, SPER is controlled by the concentration of charged defects, such as vacancies or dangling bonds, at the a/c interface [Sun82a]. An increase in the charged defect population is presumed to lead to faster recrystallization of amorphous silicon. Williams et al. demonstrated that small concentrations of both donor and acceptor dopant species can enhance the regrowth rate of silicon, suggesting that electronic processes may influence SPER kinetics [Wil83]. Licoppe et al. [Lic86] showed that atomic

rearrangement at the a/c interface is sensitive to the Fermi level in the underlying crystal. Park et al. [Par88b] observed a linear dependence of the normalized silicon regrowth rate on the normalized boron concentration, implying that strain is not the primary effect of dopant impurities on the SPER process.

As mentioned previously, the structural relaxation process inherently results in the annihilation of point defects and in a reduction of the dangling silicon bond density of amorphous silicon [Laa99a, Roo90a, Roo90b, Roo91b, Roo99, Uda87, Vol93]. The density of unrelaxed amorphous silicon remains unchanged by the structural relaxation process, suggesting that defect annihilation during relaxation is limited to the removal of both low and high density defects within the amorphous network [Cus94a, Roo91b]. Dangling silicon bonds can exist in three separate states: neutral, positively charged, and negatively charged [Kni99]. By reducing the dangling silicon bond population, structural relaxation in effect also reduces the number of charged dangling bonds at the advancing a/c interface and in the amorphous region. According to the electronic impurity theory, a reduction in the concentration of charged defects at the a/c interface and in the immediate vicinity of the regrowth front will result in a decrease in the silicon recrystallization rate. Recrystallization rates were not experimentally observed to change in self-amorphized structurally relaxed material containing boron alone, suggesting that an enhancement from the boron Fermi energy level shift dominates over potential dangling bond effects.

Role of Dangling Silicon Bonds in the Boron Diffusion Process

The structural relaxation process does not measurably impact the mechanism for boron diffusion in amorphous silicon. For each of the cases examined, boron exhibited time-averaged diffusivity values on the order of approximately 1×10^{17} cm²/second at a temperature of 550°C. The diffusion characteristics and profile features of boron appear

to be identical in relaxed and unrelaxed amorphous silicon during SPER annealing, independent of the preamorphization species. These results suggest that dangling silicon bonds are unlikely to participate in the boron diffusion mechanism. However, the events associated with structural relaxation do not negate the possibility of a trap-mediated boron diffusion mechanism in amorphous silicon.

Relaxation is well known to result in the annihilation of structural defects and a decrease in the bond angle variation within amorphous silicon. A large fraction of the energy associated with structural defects is thought to be stored in the distorted bonds surrounding them and the heat release that accompanies relaxation is attributed to the changing network structure around collapsing defects [Roo91b]. The densities of relaxed and unrelaxed amorphous silicon are not measurably different [Cus94a, Roo91b], illustrating that all of the defects inherent to the amorphous network are not removed during the relaxation process. The specific structural defects that may act as boron trapping sites in the amorphous silicon network remain unknown. However, the defect population immune to annihilation during low temperature annealing may influence the ability of boron to diffuse in non-crystalline material.

Summary and Conclusions

The structural relaxation process has no measurable impact on silicon recrystallization rates, boron diffusion, or boron activation for self-amorphized material. Samples implanted with either boron alone or fluorine and boron co-implants behave similarly. Boron was found to inherently diffuse in non-crystalline silicon at a stable time-averaged diffusivity on the order of 1×10^{-17} cm²/second during SPER annealing at 550°C. Germanium amorphized samples co-implanted with fluorine and boron are not influenced by structural relaxation, behaving similarly to self-amorphized material.

The incorporation of structural relaxation annealing in germanium amorphized material impacts boron diffusion phenomena by altering the recrystallization rates of specimens containing boron alone. Exposure time to non-crystalline material is directly related to the magnitude of boron diffusion and the final junction depth. The mechanism by which structural relaxation accelerates SPER in boron-doped germanium amorphized material remains unknown. The activation energy for silicon recrystallization decreases as the degree of structural relaxation increases for germanium amorphized material implanted with boron alone. Pre-annealing does not affect the regrowth process and the regrowth rates of germanium amorphized specimens are identical, whether amorphous or relaxed, in the absence of dopants. The time-averaged diffusivity of boron during annealing is independent of the relaxation process.

Structural relaxation does not influence boron diffusion characteristics. The shapes and features of boron concentration profiles are nearly identical for amorphous and relaxed materials. Dangling silicon bonds are not believed to impact the mobility of boron in amorphous silicon. Defect structures in the amorphous network that remain stable during low temperature annealing may facilitate a trap-mediated boron diffusion mechanism during the solid phase epitaxial regrowth process.


Figure 6-1: Boron concentration profiles for amorphous and relaxed samples containing boron alone. Structural relaxation annealing was conducted at 475°C for 30 minutes and boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². As-implanted and 550°C, 30 minute annealing conditions are shown. (15 keV and 70 keV, 1x10¹⁵ atoms/cm³ Si⁺ PAI)



Figure 6-2: Time-averaged boron diffusivity as a function of annealing time at 550°C for amorphous and relaxed samples containing boron alone. Structural relaxation annealing was conducted at 475°C for 30 minutes and boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². Boron diffusivity values were calculated for a Half-Gaussian boron concentration of 3x10¹⁹ atoms/cm³. (15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure 6-3: Sheet resistance verses junction depth (Xj) data for amorphous and relaxed samples containing boron alone. Structural relaxation annealing was conducted at 475°C for 30 minutes and boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². Junction depth measurements for boron concentrations of 1x10¹⁸ atoms/cm³ and 1x10¹⁹ atoms/cm³ are shown. (15 keV and 70 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure 6-4: Boron concentration profiles for relaxed samples containing both fluorine and boron. Fluorine was incorporated at an energy of 12 keV and dose of 1.5×10^{15} atoms/cm². Structural relaxation annealing was conducted at 475°C for 30 minutes and boron was implanted at 500 eV, 1×10^{15} atoms/cm². As-implanted and annealing conditions at 550°C for times up to 130 minutes are shown. (15 keV and 70 keV, 1×10^{15} atoms/cm³ Si⁺ PAI)



Figure 6-5: Sheet resistance verses junction depth (Xj) data for amorphous and relaxed samples containing both fluorine and boron. Fluorine was incorporated at an energy of 12 keV and dose of 1.5×10^{15} atoms/cm². Structural relaxation annealing was conducted at 475°C for 30 minutes and boron was implanted at 500 eV, 1×10^{15} atoms/cm². Junction depth measurements for boron concentrations of 1×10^{18} atoms/cm³ and 1×10^{19} atoms/cm³ are shown. (15 keV and 70 keV, 1×10^{15} atoms/cm² Si⁺ PAI)



Figure 6-6: Boron concentration profiles for amorphous samples containing boron alone. Boron was implanted at 500 eV, $1x10^{15}$ atoms/cm². As-implanted and annealing conditions at 550°C for times up to 30 minutes are shown. (80 keV, $1x10^{15}$ atoms/cm³ Ge⁺ PAI)



Figure 6-7: Boron concentration profiles for relaxed samples containing boron alone. Structural relaxation annealing was conducted at 475°C for 30 minutes and boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². As-implanted and annealing conditions at 550°C for times up to 15 minutes are shown. (80 keV, 1x10¹⁵ atoms/cm³ Ge⁺ PAI)



Figure 6-8: Boron concentration profiles for amorphous and relaxed samples containing boron alone. Structural relaxation annealing was conducted at 475°C for 30 minutes and boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². As-implanted and annealing conditions at 550°C for times up to 7 minutes are shown. (80 keV, 1x10¹⁵ atoms/cm³ Ge⁺ PAI)



Figure 6-9: Time-averaged boron diffusivity as a function of annealing time at 550°C for amorphous and relaxed samples containing boron alone. Structural relaxation annealing was conducted at 475°C for 30 minutes and boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². Boron diffusivity values were calculated for a Half-Gaussian boron concentration of 3x10¹⁹ atoms/cm³. (80 keV, 1x10¹⁵ atoms/cm² Ge⁺ PAI)



Figure 6-10: Sheet resistance verses junction depth (Xj) data for amorphous and relaxed samples containing boron alone. Structural relaxation annealing was conducted at 475°C for 30 minutes and boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². Junction depth measurements for boron concentrations of 1x10¹⁸ atoms/cm³ and 1x10¹⁹ atoms/cm³ are shown. (80 keV, 1x10¹⁵ atoms/cm² Ge⁺ PAI)



Figure 6-11: Recrystallization rates as a function of annealing time at 550°C for amorphous and relaxed samples containing boron alone. Structural relaxation annealing was conducted at 475°C for 30 minutes and boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². (80 keV, 1x10¹⁵ atoms/cm² Ge⁺ PAI)



Figure 6-12: Boron concentration profiles for amorphous (control) and relaxed samples containing boron alone. Structural relaxation annealing was conducted at 400°C for 30 minutes, 475°C for 15 minutes, or 475°C for 30 minutes. Boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². As-implanted and 550°C, 15 minute annealing conditions are shown. (80 keV, 1x10¹⁵ atoms/cm³ Ge⁺ PAI)



Figure 6-13: Boron concentration profiles for amorphous (control) and relaxed samples containing boron alone. Structural relaxation annealing was conducted at 400°C for 30 minutes, 475°C for 15 minutes, or 475°C for 30 minutes. Boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². As-implanted and 550°C, 45 minute annealing conditions are shown. (80 keV, 1x10¹⁵ atoms/cm³ Ge⁺ PAI)



Figure 6-14: Recrystallization rates as a function of both annealing time at 550°C and the degree of structural relaxation for amorphous and relaxed samples containing boron alone. Structural relaxation annealing was conducted at 400°C for 30 minutes, 475°C for 15 minutes, or 475°C for 30 minutes. Boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². (80 keV, 1x10¹⁵ atoms/cm² Ge⁺ PAI)



Figure 6-15: Recrystallization rates as a function of both annealing time at 550°C and pre-anneal time for amorphous and pre-annealed samples containing boron alone. Boron was implanted at 500 eV, 1x10¹⁵ atoms/cm². Pre-annealing was conducted at 475°C for times of 10 minutes and 120 minutes after boron implantation. In this case, the low temperature anneal does not measurably affect the regrowth velocity. (80 keV, 1x10¹⁵ atoms/cm² Ge⁺ PAI)



Figure 6-16: Boron concentration profiles for amorphous and relaxed samples containing both fluorine and boron. Fluorine was incorporated at an energy of 12 keV and dose of 1.5×10^{15} atoms/cm². Structural relaxation annealing was conducted at 475°C for either 15 minutes or 30 minutes. Boron was implanted at 500 eV, 1×10^{15} atoms/cm². As-implanted and 550°C, 260 minute annealing conditions are shown. (80 keV, 1×10^{15} atoms/cm³ Ge⁺ PAI)



Figure 6-17: Sheet resistance verses junction depth (Xj) data for amorphous and relaxed samples containing both fluorine and boron. Fluorine was incorporated at an energy of 12 keV and dose of 1.5×10^{15} atoms/cm². Structural relaxation annealing was conducted at 475°C for either 15 minutes or 30 minutes. Boron was implanted at 500 eV, 1×10^{15} atoms/cm². Junction depth measurements for boron concentrations of 1×10^{18} atoms/cm³ and 1×10^{19} atoms/cm³ are shown. (80 keV, 1×10^{15} atoms/cm² Ge⁺ PAI)

CHAPTER 7 EXPERIMENTAL SUMMARY

As complimentary metal-oxide-semiconductor (CMOS) devices continue to be aggressively scaled in dimension, the drive to form highly activated and ultra-shallow transistor junctions becomes more pressing. Semiconductor devices are scaled as small as possible in order to decrease carrier travel distances and improve switching speeds. The switching speed is determined by how fast charge carriers traverse the distance between source and drain extensions within the channel region [May90]. Faster switching speeds correlate to improved data processing capabilities and lower power consumption. In addition, scaling maximizes the expensive real estate of semiconductor substrates by increasing the device packing factor. Decreasing the depth of the source and drain extensions, commonly referred to as the junction depth, is difficult to achieve due to dopant diffusion during post-implantation processing at elevated temperatures.

Novel activation processes have illustrated that our shallowest transistor junctions will be determined by as-implanted dopant concentration profiles and their diffusion during the solid phase epitaxial regrowth (SPER) process [Bae02, For02, Gab05, Geb02, Hir99, Jua92a, Jua92b, Nap01b, Pri00]. Germanium is currently the preamorphization species of choice over silicon [Cla02, Jon87, Roo91a] and authors have utilized silicon and germanium preamorphizations relatively interchangeably when investigating boron diffusion characteristics, focusing on boron motion during high temperature annealing. However, this approach ignores the possibility that boron diffusion characteristics may be dependent on the preamorphization species.

An investigation of boron diffusion characteristics in amorphous silicon material has been conducted in order to cultivate a knowledge base for the formation of ultrashallow p-type transistors via conventional processing techniques. Boron diffusion phenomena were monitored in self and germanium amorphized silicon in both the presence and absence of several co-dopant species. The impacts of a range of processing conditions on the boron diffusivity, silicon recrystallization rates, level of boron activation, and junction depth are discussed. Questions pertaining to the activation energy for diffusion, the mechanism of diffusion, and the specific roles of germanium, fluorine, and hydrogen in regards to boron diffusion in amorphous silicon are addressed, providing insight into the challenges facing future devices in regards to continued device scaling.

Boron has been shown to diffuse in amorphous silicon in the absence of annealing, resulting in concentration profiles with exponential tails. Defects inherent to the structure of amorphous silicon have been shown to effectively trap and immobilize boron atoms at room temperature. The precise nature of these trapping sites remains unknown, however, they can be stabilized by recombination events during the implantation process due to overlapping collision or damage cascades. The probability for recombination and defect annihilation is highly dependent on the dose and choice of implanted species.

Chemical reactions between silicon and fluorine, as well as silicon and germanium, are believed to result in the elimination of potential trapping sites. However, additional silicon-silicon interactions were not shown to alter the structure of amorphous silicon and impact the trapping site population. The use of sequential germanium and fluorine implants results in greater boron motion, as compared to silicon and fluorine implants into silicon. At a concentration of 1×10^{18} atoms/cm³, boron diffuses approximately 90 Å

in germanium amorphized silicon implanted with 6 keV, $5x10^{15}$ atoms/cm² fluorine and less than 20 Å in self-amorphized silicon receiving the same fluorine and boron implants. These observations emphasize the dependence of the probability for recombination on the species present in the amorphous system.

Boron exhibits an apparent solubility limit at room temperature in amorphous silicon generated via germanium implantation, with maximum mobile boron doses on the order of approximately 1×10^{12} atoms/cm². The mobile boron dose can be related to the trapping site concentration and the co-implanted fluorine dose through strong power law functions. As the fluorine dose increases, the density of trapping sites decreases and the dose of mobile boron increases. The observed room temperature boron diffusion can be avoided by minimizing the number of sequential implants, i.e. utilizing molecular implants such as BF₂⁺ and GeF⁺ to co-implant species, and by keeping implant doses low. These actions reduce the probability for a recombination event to occur by minimizing the overlap of individual implant collision cascades and by reducing the number of collision events during the implant process that can lead to defect annihilation and facilitate boron diffusion.

Boron diffuses significantly faster in amorphous silicon during SPER annealing. The presence of silicon, germanium, and fluorine co-implants has no measurable impact on the measured time-averaged boron diffusivity, regardless of their co-implant ordering or implant dose. The activation energy for boron diffusion in amorphous silicon was calculated to be approximately 2.5 eV; 30% lower than the energy barrier for boron diffusion in crystalline silicon (3.75 eV). Both fluorine and hydrogen hinder the silicon recrystallization process, increasing the time boron is exposed to amorphous material at elevated temperatures. In the case of fluorine, this results in a greater boron diffusion length. However, the mere presence of hydrogen drastically retards boron diffusion.

Hydrogen has been proposed to hinder the mobility of boron in amorphous silicon in two possible ways. In the first, hydrogen is attributed with passivating dangling silicon bonds throughout the amorphous network, thereby hindering the ability of boron to diffuse freely. This case is based on the assumption that dangling silicon bonds facilitate boron diffusion. The second case presumes the formation of H-B pairings that are immobile in the nanovoid free and compact structure of ion implanted amorphous silicon. The precise manner in which hydrogen impacts boron diffusion remains unknown, however, the diatomic bond strength of H-B bonds is 20% stronger than that of H-Si bonds, suggesting that there is a higher driving force for the formation of H-B bonds.

The random, open structure of amorphous silicon appears to facilitate boron diffusion. The activation energies for boron diffusion in amorphous material are dependent on the material microstructure, remaining substantially lower than the energy barrier for diffusion in crystalline silicon. The resultant time-averaged boron diffusivity values appear to scale in magnitude with the void density in amorphous silicon and are in agreement with the reported diffusion behavior of beryllium atoms in bulk amorphous glass alloys. The level of boron activation is not measurably impacted by the choice of preamorphization species, silicon or germanium. However, fluorine co-implantation leads to more active junctions in self-amorphized silicon, as compared to germanium amorphized material.

Simple simulations of boron diffusion in amorphous silicon have also provided insight into the potential diffusion mechanism. Charged species effects were unable to

predict experimental profile behavior for multiple annealing times in the temperature range of 550°C to 700°C, suggesting that charged states do not influence the ability of boron to diffuse in amorphous silicon during the SPER process. Concentration dependent and trap-mediated diffusion approaches were both able to accurately predict boron diffusion characteristics for the processing conditions examined. These results demonstrate that the effective diffusivity of boron is dependent upon the concentration of boron dopant in amorphous silicon. However, the precise manner in which boron may diffuse in either the presence or absence of trapping sites during the recrystallization process remains uncertain.

The structural relaxation process has no measurable impact on silicon recrystallization rates, boron diffusion, or the degree of boron activation for selfamorphized material. Samples implanted with either boron alone or fluorine and boron co-implants behave similarly. Boron was found to inherently diffuse in non-crystalline silicon at a stable time-averaged diffusivity on the order of 1×10^{-17} cm²/second during SPER annealing at 550°C.

The incorporation of structural relaxation annealing in germanium amorphized material impacts boron diffusion phenomena by altering the recrystallization rates of specimens containing boron alone. Exposure time to non-crystalline material is directly related to the magnitude of boron diffusion and the final junction depth. The mechanism by which structural relaxation accelerates SPER in boron-doped germanium amorphized material remains unknown. The activation energy for silicon recrystallization decreases as the degree of structural relaxation increases for germanium amorphized material implanted with boron alone. Pre-annealing does not affect the regrowth process and the

regrowth rates of germanium amorphized specimens are identical, whether amorphous or relaxed, in the absence of dopants.

The time-averaged diffusivity of boron during annealing is independent of the relaxation process. Germanium amorphized samples co-implanted with fluorine and boron are not influenced by structural relaxation, behaving similarly to self-amorphized material. At present, the use of structural relaxation does not appear to be beneficial, or detrimental, to the generation of highly active, ultra-shallow junctions. The manner in which relaxation annealing impacts the recrystallization rate of germanium amorphized material implanted with boron alone requires clarification and further verification before the technique can be attributed with improving achievable junction depths.

The final junction depth is determined by the magnitude of boron diffusion during the activation process. Boron diffusion in amorphous silicon can be minimized in a number of ways. For example, the use of either co-dopants that accelerate the silicon regrowth rate or high annealing temperatures will reduce the time duration that boron is exposed to amorphous material and able to diffuse. Hydrogen co-implantation in the form of molecular implants, such as $B_{18}H_8^+$, can also be employed to restrict the mobility of boron in amorphous silicon. Knowledge of boron diffusion characteristics in amorphous material enables the optimization of implantation and activation processes, supporting the formation of ultra-shallow p-type junctions using conventional processing techniques.

CHAPTER 8 FUTURE WORK – SIGE ALLOY MATERIAL

SiGe Background & Introduction

As microelectronic devices continue to scale in accordance with Moore's Law [Moo65], the ability to form ultra shallow junctions and predict dopant diffusion characteristics become paramount. In recent years, interest within Silicon-Germanium (SiGe) alloys has steadily increased as a potential alternative to conventional CMOS silicon based structures. By incorporating compatible SiGe alloys within traditional transistor structures, the performance capabilities and applicability of many silicon devices can be extended to additional advanced technology nodes. Current applications include bipolar and complimentary metal oxide semiconductor field effect transistors (MOSFETs), superlattice detectors, modulation doped field effect transistors (MODFETs), heterojunction bipolar transistors (HBTs), and mixed tunneling transistors [Ari92, Jai91, Kam89, Kin89, Mac91, Mye90, Nay91, Pat90].

Researchers are currently investigating the characteristics of both strained and relaxed silicon-germanium (SiGe) alloys. Silicon and germanium are completely miscible elements, as seen in Figure 8-1, with lattice parameters differing by approximately 4% [Hir00]. The lattice mismatch between silicon and SiGe alloys can be substantial and lead to internal stresses and strain during the epitaxial growth process. The germanium content and SiGe lattice constant follow a nearly linear relationship, more closely resembling the Pauling limit than Vegard's law [Fit02, Yon01]. Chemical vapor deposition (CVD) techniques are commonly employed to generate SiGe structures, rather than molecular

beam epitaxy (MBE) [Cha03, Mah99]. CVD is a conformal process capable of growing and depositing layers upon multiple wafers simultaneously. The equipment is relatively simple and has a high wafer throughput, making it the logical growth method for potential integration into a large-scale manufacturing environment [Cha03, Mah99]. In spite of the abrupt interfaces and ability to conduct in-situ monitoring of the growth process, MBE remains a very slow growth, single wafer technique and serves more strongly as a research tool [Mah99].

During the initial growth stages, SiGe films biaxially strain in order to accommodate the level of lattice mismatch with the silicon substrate. As the SiGe film thickness increases, the level of internal strain increases and surface roughening can occur [Sta98]. If a SiGe film exceeds a concentration-dependent critical thickness, the layer will structurally relax the growth related strains by generating misfit dislocations [Sta98]. The critical film thickness decreases with increasing germanium content [Peo86]. However, a SiGe material that is pseudomorphically grown on a silicon substrate below the critical thickness specified by its atomic germanium content is referred to as strained and free of misfit dislocations. Thus, the internal stresses incurred during growth remain.

Relaxed SiGe layers, on the other hand, are grown using compositionally graded buffer layers [Cha03]. Utilizing standard (100) silicon substrate wafers, a silicon buffer layer 1.0 µm thick is initially deposited [Lar94]. The silicon buffer layer serves to introduce an atomically smooth and clean surface for subsequent layer growth, consuming any initial surface particulates. Samples grown without this initial buffer layer exhibit higher dislocation densities in the subsequent relaxed SiGe layers [LeG92]. The

graded SiGe buffer layer is grown next. During the growth process, the germanium content within the SiGe alloy layer coherently grown upon the silicon substrate is slowly increased until the desired alloy composition is reached; this portion of the structure is denoted as the buffer layer. Two types of graded SiGe buffer layers can be used, continuous and step graded. A continuous graded buffer layer incorporates germanium at a gradually increasing flow rate, until the desired composition is achieved. The resulting structure is shown in Figure 8-2 (a). The coloration represents the germanium content. Clearly, there are no distinct concentration regimes and one heterogeneous layer results. The step graded buffer layer, on the other hand, utilizes individual sub-layers of uniform composition, as shown within Figure 8-2 (b), to reach the desired relaxed SiGe composition [LeG92]. Within the buffer layer, dislocations form and relieve the internal stresses until the desired germanium content is achieved. This compositional grading gradually relaxes the structure, thereby minimizing the dislocation density. An XTEM micrograph illustrates the segregation of misfit locations to the buffer layer in Figure 8-3 for a relaxed Si_{0.65}Ge_{0.35} alloy. It has been proposed by LeGoues et al. that a modified Frank-Read source governs the introduction and growth of dislocations within relaxed SiGe structures [LeG92]. Half-loops and whole loops are generated during layer growth by Frank-Read sources, illustrated in Figure 8-4 [LeG92]. These defects structurally relax the material when they intersect surfaces and enable dislocations to form and relieve misfit strain. These results imply that a greater number of interfaces within the overall graded SiGe layer will lead to a relaxed film with a lower dislocation density, thus a step graded buffer layer is theoretically more advantageous than a continuous graded buffer layer. Conventional growth techniques incorporate continuous graded SiGe buffer layers

with grading rates of 10% germanium per micron of relaxed SiGe growth [Cha03, Lar94]. The thickness of the graded buffer layer will vary according to the desired alloy composition in the relaxed SiGe layers; the higher the germanium content the thicker the buffer layer. The SiGe layer grown above the buffer layer has a uniform elemental composition and is referred to as a relaxed structure. Dislocation densities can decrease by as much as seven orders of magnitude in relaxed SiGe materials when buffer layers are incorporated, as compared to relaxed alloys of the same germanium content without the buffer layers [Lar94].

Once the relaxed SiGe material is grown, an encapsulating layer is commonly added to the structure. The native oxide of germanium is a highly soluble material, whereupon anodic oxidation results in a heterogeneous, easily penetrable film [Cha03, Coo00, Fit02, Hat87, Hat98]. These attributes make the use of native germanium and SiGe oxides undesirable, leading to the widespread use of strained silicon capping layers. These layers are commonly 20 nm thick, minimizing inherent CVD batch processing variability [Cha03]. The use of strained silicon is also advantageous due to an increase in electron mobility, as compared to bulk silicon [Car94, Fit02, Ish04]. However, the effectiveness of the strained silicon channel can be reduced as a result of germanium indiffusion and film outgassing or densification [Coo00, Cur01]. The encapsulation layer must also remain below its critical thickness, as dislocations can form during subsequent high temperature exposure and degrade device performance [Cur01].

Electron and hole carrier mobilities are highly dependent upon SiGe material properties. In relaxed SiGe, low germanium contents result in tensile stresses that increase electron mobilities above that of bulk silicon, while high contents impart

compressive stresses that raise hole mobility values [Car94, Fit02, Man93]. Strained SiGe alloys also exhibit enhanced carrier mobilities. Electron mobility values saturate at the germanium composition of 20 at%; enhanced nearly 2X over bulk silicon [Cur01, Fit02]. The effective Hall carrier mobility decreases with increasing germanium content due to escalating alloy scattering effects [Ber96, Car94, Iri02]. As the level of film strain increases, hole mobilities are continuously enhanced at compositions exceeding 40 at% germanium [Car94, Cur01, Man93]. High carrier mobilities are desirable for faster switching speed devices [Man93].

SiGe alloys are indirect bandgap materials [Blo94]. Valence band alignment is a function of both strain and composition [Blo94, Peo86]. In relaxed Si_{1-x}Ge_x alloys, the bandgap decreases slowly with increasing germanium content, dropping off as x reaches 0.85 [Blo94]. On the other hand, strained materials exhibit an immediate bandgap lowering with germanium incorporation [Blo94]. Alloys containing 60 at% germanium have lower bandgaps than pure germanium due to extensive valence band bending [Blo94]. Conduction bands, however, are similar for bulk silicon and SiGe alloys containing less than 85 at% germanium [Peo86]. Lower bandgap values make SiGe materials viable for long wavelength applications, such as high-speed photodetectors and optoelectronic devices [Man93, Peo86].

In addition to potentially high dislocation densities, SiGe alloys exhibit several potentially undesirable characteristics. Strained SiGe alloys induce both chemical and strain effects upon dopants that are not easily separated, presenting a significant challenge for dopant diffusion studies. In both strained and relaxed SiGe materials, clustering with dopants has been observed, resulting in electrically inactive complexes

such as GeB, SiAs, and GeAs [Fan95, Fan96b, Tis96, Zou98, Zou00]. The majority of deleterious attributes of SiGe alloys pertain to conditions under arsenic incorporation. Strained SiGe layers experience a different relaxation mechanism when implanted with arsenic. The process by which arsenic influences the relaxation mechanism of SiGe is not well understood, but may be related to the formation of GeAs precipitates, as lower peak concentrations of arsenic are required for precipitation in SiGe than in silicon [Tis96, Zou98, Zou00]. The solid solubility and maximum active concentration of arsenic decrease as the germanium content is increased, reaching values almost one order of magnitude below those reported in bulk silicon [Zou97].

By far, the dominant negative characteristic of SiGe alloys is the observed diffusion enhancement of arsenic. As the germanium content increases, the diffusivity of arsenic drastically increases [Egu02, Egu04, Zou97]. Eguchi et al. observed the effective diffusivity of arsenic in relaxed Si_{0.8}Ge_{0.2} to be 7X that of arsenic in silicon at temperatures ranging from 900°C to 1050°C [Egu02]. Clearly, forming shallow junctions via arsenic implantation in SiGe alloys poses a formidable challenge. Questions regarding the influence of internal strain, germanium chemical effects, arsenic interactions with point defects, and activation annealing parameters remain unanswered.

Boron diffusion in SiGe alloys, on the other hand, is greatly suppressed during annealing. In strained alloys, the magnitude of boron diffusion suppression scales with germanium content [Kuo93, Kuo95a, Leo93, Lev98, Mor93, Raj01, Zan03]. For Si_{0.83}Ge_{0.17} alloys, the boron diffusivity is one order of magnitude lower than that exhibited in bulk silicon [Kuo93]. These differences become more pronounced as the boron concentration increases as well [Kuo93]. Boron diffusion also decreases with

increasing material strain, exhibiting a linear activation energy dependence with strain [Cow94b]. The increase in activation energy for boron diffusivity is attributed to Ge-B pairing [Kol01, Zan03]. Local interactions between germanium and boron atoms are believed to occur due to their opposite types of strain, such that the energy barrier for boron mobility increases as boron is surrounded by more germanium nearest neighbors [Kol01]. Similar results were observed for relaxed SiGe alloys, while their suppression of boron diffusion is less pronounced [Lev98, Zan03].

Preliminary diffusion studies within SiGe materials have been derived directly from of our knowledge base encompassing silicon systems. Due to a much lower melting temperature and effective bond strength, vacancies are more likely to form within bulk germanium than in silicon [Hir00, Pak02, Zan01]. SiGe materials are substitutionally disordered, such that no preferential ordering of germanium-germanium bonds occurs and the vicinity of vacancies is not uniquely determined [Ven02, Yon01]. In order to form a vacancy with four germanium nearest neighbors, it is necessary to overcome an energy barrier of approximately 2 eV. However, an energy barrier of 3 eV limits the creation of a vacancy with four silicon atoms as nearest neighbors [Ven02]. Clearly, as the germanium content rises above 50 at%, vacancies surrounded by germanium atoms will dominate. As the SiGe composition varies, the lengths and angles of germaniumgermanium, silicon-silicon, and possibly germanium-silicon bonds are also distorted [Yon01]. The mere presence of germanium is attributed with promoting higher vacancy and interstitial concentrations, such that dopants are expected to diffuse faster in relaxed SiGe materials [Pak02]. Due to the apparent bond distortions within SiGe alloys [Yon01], it is difficult to predict the annealing conditions and alloy compositions necessary for

immobile precipitates, such as GeB, SiAs, or GeAs [Fan95, Fan96b, Tis96, Zou98, Zou00], to form and evolve in localized regions under dynamic conditions.

Very few researchers have conducted fractional interstitial compositional calculations for SiGe materials. Fang et al. reported the fractional interstitial composition of boron in strained Si_{0.8}Ge_{0.2} to be approximately 0.8, reaching as high as 0.99 if vacancy and interstitial interactions are relaxed [Fan96a]. The equilibrium diffusion mechanism of boron in strained $Si_{0.8}Ge_{0.2}$ is similar to bulk silicon [Bon01]. Within Fang's studies, boron marker layers were grown, rather than implanted, within strained Si_{0.8}Ge_{0.2} and silicon layers thereby avoiding residual damage effects [Fan96a]. The surface silicon layers underwent nitridation in a pure ammonia gas ambient at 850°C to inject vacancies, oxidation in a dry oxygen ambient at 850°C to inject interstitials, or annealing within an inert nitrogen gas ambient at 850°C. These studies neglect the use of transmission electron microscopy (TEM) to verify the injection of interstitials and vacancies [Fan96a]. However, Kuo et al. demonstrated previously that strained SiGe alloys with less than 30 at% germanium content do not serve as sinks for interstitials injected during silicon oxidation [Kuo95b]. These results imply that interstitials are not absorbed by the SiGe layer and can travel freely throughout the structure during annealing at 850°C. Boron is believed to remain an interstitial mediated diffuser in SiGe alloy materials [Bon01, Fan96a].

Eguchi et al. reported on the diffusion characteristics of arsenic in relaxed $Si_{0.8}Ge_{0.2}$ structures during rapid thermal processing [Egu04]. They utilized techniques previously established by Fahey et al. and Kuo et al. regarding the use of nitridation and oxidation to influence surface point defect populations for diffusion studies [Fah85, Fah89a, Kuo95b].

Preliminary results suggest that arsenic diffusion within relaxed SiGe structures is strongly vacancy-mediated in nature in the temperature range from 950° C to 1050° C [Egu04]. However, as with many experiments pertaining to arsenic in SiGe alloys [Fan95, Fan96b, Gai98], Eguchi et al. implanted arsenic at very high doses, generating peak concentrations greater than $1x10^{21}$ atoms/cm³ [Eug04]. The damage resulting from ion implantation, coupled with arsenic concentrations well within the clustering regime [Tis96, Zou00], add significant variability to the observed dopant interactions with point defects and host atoms. These studies also neglect the use of TEM to verify the injection of point defects. The aforementioned results are indeed promising, but must be verified through fractional interstitial composition calculations under carefully controlled experimental conditions.

The self-diffusion characteristics of silicon and germanium in SiGe alloys provide support for the assertions that arsenic and boron remain vacancy and interstitial diffusers, respectively. In the bulk, germanium self-diffuses by a purely vacancy mediated mechanism [Wer85]. In silicon, on the other hand, germanium demonstrates both interstitial and vacancy mediated diffusion components [Fah89b]. Within germaniumrich materials, germanium atoms prefer diffusion paths with germanium nearest neighbors and diffuse as if they were in bulk germanium. In silicon-rich SiGe alloys, however, germanium atoms demonstrate more complex diffusion paths with no apparent preferences [Ven02]. As the germanium alloy content is increased, germanium atoms exhibit an enhanced diffusivity in SiGe [Zan01]. Silicon self-diffusion exhibits mixed behaviors depending upon temperature. Below 1080°C silicon atoms self-diffuse by a vacancy mediated mechanism, however, above this temperature silicon atoms behave as interstitial diffusers [See69, Tan97, Ura99b]. For all temperatures, the diffusivity of silicon vacancies was also observed to exceed the diffusivity of silicon interstitials [Tan97]. Recently, researchers in Finland and Germany reported novel findings regarding the self-diffusion mechanisms of germanium and silicon in SiGe [Lai02, Str02]. At temperatures ranging from 653°C to 1263°C, transitions in the self-diffusion mechanisms were observed. Strohm et al. illustrated a mechanism shift to occur at 35 at% germanium content [Str02]. Above this concentration level, both silicon and germanium were observed to diffuse via a vacancy mediated mechanism. Within alloys containing less than 35 at% germanium, both constituents exhibit an interstitial dominated self-diffusion mechanism. The self-diffusivities were also observed to increase as the germanium content increases [Str02]. Laitinen et al. illustrated a similar shift that occurs at 25 at% germanium [Lai02]. Clearly, these works indicate that diffusion mechanisms within relaxed SiGe materials are complex and non-uniform across the compositional range of these alloys. The fractional vacancy component for dopants generally increases as the size of the diffuser increases, i.e. arsenic would be expected to demonstrate a larger Fv in SiGe than boron, germanium, or silicon [Zan01].

Relaxed and strained SiGe alloys possess many material properties that differ from bulk silicon and germanium, making their use more desirable for high-speed and optoelectronic applications. Carrier mobility and bandgap values are improved in both relaxed and strained alloy structures, denoting optimal processing regimes. Boron diffusion is inhibited, while arsenic diffusion is drastically enhanced. Dopant diffusion mechanisms appear to be a function of both alloy composition and strain. Clearly, SiGe alloys have a strong potential for integration into conventional CMOS applications, expanding into the realm of compound semiconductors as well.

Fractional Interstitial Calculations in Relaxed SiGe Alloy Material

If the precise diffusion mechanisms of common transistor dopants in SiGe alloy materials are known, processing parameters may be optimized so that junctions with a desired set of characteristics may be formed. Studies are needed to systematically characterize the diffusion behavior of arsenic within relaxed SiGe alloys under strict experimental conditions, in order to extract fractional interstitial composition values for arsenic as a function of allov composition and annealing temperature. By utilizing relaxed SiGe alloy layers, the effects of lattice strain upon arsenic dopant diffusion can be effectively eliminated, enabling studies to focus upon potential germanium chemical effects. The germanium contents suggested for this type of study range as follows: 0 at%, 5 at%, 15 at%, 25 at%, 35 at%, and 50 at%. The incorporation of different alloy compositions will facilitate (i) the determination of arsenic diffusion behavior as a function of germanium content and (ii) the evaluation of compositional influences on the diffusion mechanism of arsenic. The majority of studies regarding arsenic diffusion in SiGe alloys pertain to structures with less than 30 at% germanium [Egu04, Fan95, Fan96b, Gai98, Im96, Tis96, Zou97, Zou98, Zou00] and limited work has evaluated arsenic diffusion within bulk germanium [Hat98]. It is crucial to determine whether or not arsenic changes from a primarily vacancy-mediated diffusion mechanism to an interstitial-mediated mechanism within a given SiGe alloy composition range. The relative diffusion behavior of arsenic has a direct correlation to acceptable processing parameters for the generation of ultra shallow and abrupt junctions within SiGe materials.

A proposed experimental structure is illustrated within Figure 8-5, utilizing standard 200 mm, (100) Czochralski silicon substrate wafers. Initially, a silicon buffer layer 1.0 µm thick is grown [Lar94]. It is recommended that conventional relaxed SiGe growth techniques be followed, such that continuous graded SiGe buffer layers are incorporated with a grading rate of 10 at% germanium per micron of growth [Cha03]. Once the continuous graded SiGe buffer layer is complete, approximately one micron of relaxed SiGe material of the desired composition is incorporated within the experimental structure (Figure 8-5). A 20 nm thick arsenic spike with a peak chemical composition of $2x10^{19}$ atoms/cm³ is included in the middle of the relaxed SiGe layer. The peak concentration of arsenic in this spike is well below the minimum calculated solid solubility limit and clustering composition of 9×10^{20} atoms/cm³ [Tis96, Zou00]. The arsenic concentration required for precipitation in SiGe alloys, with less than 30 at% germanium content, is approximately one order of magnitude lower than that in bulk silicon [Kri98, Nob94, Tis96, Zou00]. Based upon the germanium-arsenic phase diagram, approximately 49 at% arsenic is required for the precipitation of GeAs [Hir00]. Thus, a peak concentration of 2×10^{19} atoms/cm³ is predicted to avoid the precipitation of both GeAs and SiAs as the SiGe alloy composition is varied throughout these studies. The selected thicknesses of 0.5 µm and 20 nm for the undoped and arsenic doped layers, respectively, allow for substantial arsenic diffusion (i) before the arsenic concentration drops into the noise level of secondary ion mass spectrometry (SIMS) detection at a concentration of approximately 1×10^{16} atoms/cm³ [Bru92] and (ii) the arsenic diffuses through the homogeneous relaxed SiGe layers into surrounding material. By growing the arsenic dopant into the experimental structure, rather than using ion implantation,

residual damage effects and potential interfacial effects are removed as experimental variables and all changes in point defect populations will be the direct result of subsequent annealing conditions.

The first encapsulating layer grown upon these structures is a strained silicon cap. The silicon layer was chosen to be approximately 20 nm thick in order to minimize inherent CVD batch processing variability [Cha03]. The next layer is comprised of a deposited silicon dioxide region 35 nm thick and the final capping material is an 80 nm thick deposited layer of silicon nitride (Figure 8-5). The incorporation of these encapsulating layers permits the generation of three separate annealing environments via basic photolithography and etching techniques, as demonstrated previously by Fahey et al. [Fah83]. As illustrated in Figure 8-5, exposure of bare silicon to an ammonia ambient results in a nitridation reaction, while annealing of the silicon dioxide layer under such conditions leads to oxynitridation. Finally, annealing of the surface silicon nitride layer in ammonia simulates an inert environment. The previously outlined structure provides an environment suitable for the characterization of arsenic diffusion behavior solely as a function of SiGe alloy composition, arsenic interactions with point defects, and activation annealing parameters.

Traditionally, fractional interstitial compositions are determined in bulk silicon at anneal temperatures exceeding 1000° C [Fah83, Fah85, Fah89b, Hay82, Miz83]. To ensure equilibrium diffusion conditions in ion implanted samples, anneal times range from one to four hours. The melting temperature of silicon is approximately 1400° C, greatly exceeding that of pure germanium at ~ 940° C [Hir00]. As germanium is added to silicon forming a solid solution, the melting temperature drops, reaching ~ 1200° C at 50
at% germanium [Hir00]. Using Vegard's Law [Tho99, Veg21], an anneal temperature of 1000°C in silicon corresponds to approximately 860°C in Si_{0.5}Ge_{0.5}. Thus, we can infer that Fi studies of SiGe alloys containing less than 50 at% germanium should commence at temperatures above 850°C to maintain continuity between substrates. Nitridation of native silicon films and oxynitridation of silicon dioxide occur at substrate temperatures exceeding 800°C [Cla05, Egu04, Fah83, Fah85, Fah89b, Fan96a, Gos97, Hay82, Miz83]. Arsenic has been observed to diffuse in SiGe alloys with compositions ranging from 0 at% to 43 at% germanium at temperatures greater than 800°C [Egu02, Egu04, Fan95, Fan96b, Mit03, Zou97]. Based upon these considerations, experimental samples will be furnace annealed in an ammonia ambient at temperatures between 900°C and 1100°C. As the annealing temperature approaches the melting temperature of the SiGe alloy, dopant diffusion enhancements increase. Thus, various anneal times will be employed accordingly at each temperature for the respective alloy compositions.

In order to approximate appropriate annealing times, diffusion simulations were developed using the Florida Object Oriented Process Simulator (FLOOPS) [FLO02]. Based upon the work of Eguchi et al. [Egu02], a script was generated that approximates the diffusion enhancement of arsenic within bulk SiGe as a function of germanium content. Utilizing a linear extrapolation, the anticipated diffusion enhancement is related according to Equation 8-1.

$$D_{SiGe} = D_{Si} \left[1 + \frac{(at\% \ Ge*6.0)}{20} \right]$$
(8-1)

Clearly, the largest germanium content material will exhibit the greatest diffusion enhancement during high temperature annealing. Figure 8-6 illustrates the simulated diffusion behavior of arsenic during annealing at 1000°C for 60 minutes in an oxidizing ambient. As anticipated, the magnitude of arsenic diffusion increases with germanium concentration. Figure 8-7 demonstrates the diffusion behavior of arsenic in bulk silicon at 900°C, according to internal FLOOPS parameters [FLO02]. Using the accepted fractional interstitial component of arsenic in silicon as 0.4 [Bra00, Fah85] results in an observable diffusion enhancement in an oxidizing ambient. Due to the absence of a nitridation ambient available within FLOOPS, subjective approximations are generated based upon oxidation diffusion profiles and the initial assumption that arsenic remains a vacancy diffuser within SiGe structures [FLO02].

The FLOOPS simulations provide a strong indication of the presumed diffusion behavior of arsenic within SiGe alloys under inert and oxidizing conditions. If the diffusion enhancement of arsenic in SiGe alloys scales linearly with the value of 7X at a 20 at% germanium content, as assumed, then we can expect to observe significant diffusivities during these studies. SIMS detection experiences a lower bound of 1×10^{16} atoms/cm³ [Bru92], thus diffusion profiles must remain above this plateau and exhibit motion exceeding resolution thresholds between selected annealing times. Figure 8-8 portrays the simulated behavior of arsenic within a SiGe alloy containing 25 at% germanium at 1000°C during oxidation. Under these annealing conditions, arsenic exhibits significant diffusion within five minutes of annealing. If arsenic is truly a vacancy-mediated diffusion species in SiGe structures, then these anneal times are further limited by additional diffusion enhancements not accounted for by these simulations. Approximated furnace annealing parameters were derived based upon a multitude of process simulations and the aforementioned analysis restrictions. Table 8-1 summarizes the individual simulations performed, as well as the extrapolated sample annealing time

frames. The precise annealing conditions employed will be determined during the experimental process once the initial assumptions have been verified.

Prior to sample annealing and analysis, the silicon dioxide and silicon nitride capping layers will need to be selectively removed. To preferentially etch silicon, silicon dioxide, and silicon nitride a multitude of techniques are available [Bac99, Bac00, Cla05, Lam99, McK00, Skr99]. Bulk silicon material can be etched with a variety of acid solutions. However, etch rates can range from less than 2 Å/min to several μ m/min [Bac99, Bac00, Cla05, McK00]. Silicon is generally isotropically etched with HNA (hydrofluoric acid, nitric acid, acetic acid) [Bac00]. HNA is comprised of 160 mL acetic acid (C₂H₄O₂), 60 mL nitric acid (HNO₃), and 20 mL of hydrofluoric acid (HF). Etch rates of 1-3 µm/min result, based upon the lifetime of the etchant [Bac00]. To anisotropically wet etch silicon, potassium hydroxide (KOH) is often chosen [Bac99]. KOH preferentially etches silicon along the (100) plane. Potassium hydroxide (30 wt%) is generated by mixing 70 g of commercially available KOH pellets with 190 mL of deionized (DI) water. The initial mixture is warmed until all of the KOH has dissolved, then 40 mL of isopropyl alcohol is added to the solution. An etch rate of 1 μ m/min is achieved at room temperature [Bac99].

Buffered hydrofluoric acid is the standard for wet etching silicon dioxide (SiO₂) [Lam99, Skr99]. Buffered HF is comprised of one part HF for each part ammonium fluoride (NH₄F). At room temperature, this solution will etch thermally grown SiO₂ at a rate of 700 Å/min and deposited SiO₂ at approximately 900 Å/min [Lam99, Skr99]. After substantial high temperature annealing the deposited silicon dioxide densifies and assumes the etch rate of a thermally deposited material. All etch rates will steadily decrease with time as the solution deteriorates [Lam99]. Hot phosphoric acid (H₃PO₄) is commonly used to etch silicon nitride (Si₃N₄) [Cla05, McK00]. The respective etch rates are dependent upon the temperature and concentration of the acid. The maximum concentration at which phosphoric acid is commercially available is approximately 85 wt%, with a boiling point of 154°C. By heating the acid to 160°C, a concentration of approximately 87 wt% H₃PO₄ results [Cla05]. At this temperature, silicon nitride is preferentially etched at approximately 50 Å/min. Silicon and silicon dioxide are both etched at less than 2 Å/min under these conditions [McK00]. Based upon this data, it is important to ensure that silicon nitride is indeed the surface layer. Initially, samples are dipped into an HF etch solution to remove possible silicon dioxide or SiO_xN_y surface films. HF is selective to oxides over nitrides by a factor of 30:1 [McK00].

The methodology for determining the fractional interstitial composition of arsenic within relaxed SiGe films contains many facets. The approach for these studies are based upon fundamental studies conducted by Fahey et al. [Fah83, Fah85, Fah89a]. Initially, basic assumptions must be made. During oxidation it is presumed that the quantity of $\frac{C_V}{C_V*}$ is greater than zero and less than or equal to one. Accordingly, the value of $\frac{C_i}{C_i*}$ is also bound in the same manner during nitridation annealing. No initial inferences regarding the relationships between respective interstitial and vacancy concentrations or the generation rates of these defects are made.

The injection of point defects during annealing is commonly monitored through plane-view transmission electron microscopy (PTEM) techniques. Implanted SiGe samples will be utilized as a control medium for the purpose of defect tracking. Portions of the wafers are implanted with Si⁺ at a dose of 1×10^{15} atoms/cm² and energies of 15 and

70 keV, creating a layer of dislocation loops approximately 160 nm below the structure surface, i.e. 25 nm into the top SiGe layer. Two separate implants are utilized in order to ensure the formation of a continuous, surface amorphous region and a distinct region of damage and defects. The net growth or dissolution of dislocation loops during annealing under the various conditions is clearly discernable using TEM. Visible defects such as interstitially comprised dislocation loops and stacking faults grow during oxidation or oxynitridation and dissolve during nitridation reactions [Hay82, Miz83]. TEM images will be used to approximate values for C_i and C_v , however, no information is available in regards to the values of C_i^* and C_v^* . The loop evolution will simply serve as a means to verify either a supersaturation of vacancies or the injection of interstitials. The values obtained through such calculations are not directly integrated into the final Fi calculations.

Fahey et al. [Fah83, Fah85, Fah89b] determined the fractional interstitial compositions of dopants within silicon substrates through comparative studies. In the case of arsenic, antimony was used as a benchmarking species. Antimony was observed to exhibit a higher diffusivity during nitridation annealing and a lower diffusivity under oxynitridation conditions, as compared to arsenic. These results implied that antimony has a lower Fi value in silicon than arsenic, being very close to zero. Data pertaining to phosphorus, a strong interstitial-mediated diffusion species, supported the above assertion and aided in the modification of the initial experimental assumptions [Fah85]. Clearly, the inclusion of multiple species, presumed to be representative of vacancy and interstitial-mediated diffusion mechanisms, is necessary for the determination of fractional interstitial values. In order to minimize errors incurred on the basis of the

preliminary assumptions, boron and antimony dopant species are subsequently incorporated into the experimental plan. The additional experimental structures are extensions of Figure 8-5, where the arsenic doped layer is simply substituted with either boron or antimony doped regions. The solid solubility of antimony is greater in relaxed SiGe alloys than in either strained SiGe alloys or bulk silicon [Hon93]. Thus, a peak chemical concentration of $2x10^{19}$ atoms/cm³ is not anticipated to result in the precipitation of antimony based complexes. In the case of boron, such a concentration level is also below the maximum achievable concentration of $8x10^{19}$ atoms/cm³ observed in strained SiGe [Mor93]. One can safely assume that the trends in solid solubility for arsenic can be extended to boron dopant atoms as well. The relative diffusion behaviors of the three dopants, namely arsenic, boron, and antimony, will be used to adequately evaluate and alter the various experimental assumptions.

SIMS concentration profiles serve as a direct means for extracting dopant diffusivities during annealing. In the course of these studies, Gaussian FLOOPS diffusion simulations will be created and compared to the raw SIMS data. The experimental dopant diffusion profiles are Gaussian in nature, as a result of the experimental structure. The simulated profiles are adjusted accordingly until the raw and calculated diffusion profiles align, whereupon the dopant diffusivities are extracted. Diffusivity data created through exposure to nitridation and oxynitridation conditions correspond to respective $\langle D_A \rangle$ values, while measurements generated within an inert environment provide D_A^* quantities. Subsequently, the ratio of $\frac{\langle D_A \rangle}{\langle D_A \rangle^*}$ can be obtained and provide relative diffusivity enhancement or retardation data for the different dopant species under various

annealing conditions. The incorporation of SIMS techniques facilitates the determination of experimental and evaluation of the preliminary theoretical assumptions.

Arsenic, in contrast to boron, is the defining dopant for junction fabrication in CMOS SiGe alloys. Prior studies have demonstrated the propensity for enhanced arsenic diffusion [Egu02, Egu04, Zou97] and allude to the dominant diffusion mechanism [Egu02, Egu04]. However, fractional interstitial composition values as a function of germanium content are presently unavailable. In order to accurately predict and model arsenic diffusion behavior in relaxed SiGe, germanium chemical effects must be quantified. Based upon the current literature, arsenic is believed to exhibit a primarily vacancy mediated diffusion mechanism in all silicon and germanium solid solutions. The experiments outlined here will characterize the diffusion mechanisms of arsenic, antimony, and boron within relaxed SiGe.

Boron Diffusion in Amorphous Relaxed SiGe Alloy Material

Authors have recently reported the ability of boron to inherently diffuse within amorphous silicon material during solid phase epitaxial regrowth (SPER) annealing [Ell98a, Duf04, Jac05]. Our experiments demonstrated boron diffusion in amorphous silicon material to be independent of the preamorphization species. The time-averaged boron diffusivites were shown to be approximately five orders of magnitude greater than the equilibrium values extrapolated for crystalline silicon [Ell98a, Jac05, Law98]. The presence of additional fluorine, germanium, or silicon doping implants in sub-atomic concentrations does not impact the boron diffusivity, irrespective of their co-implanted dose or the implant ordering. As mentioned previously, boron diffusion is hindered within both strained and relaxed crystalline SiGe material during annealing, as compared to bulk silicon or germanium [Ku093, Ku095a, Le093, Lev98, Mor93, Raj01, Zan03]. Some authors attribute chemical Ge-B interactions with raising the activation energy required for boron diffusion in crystalline SiGe [Kol01, Zan03], suggesting that increasing germanium content facilitates the retardation of boron diffusion. At present, however, the role of germanium in regards to boron diffusion in amorphous SiGe alloy material remains unknown.

By characterizing boron diffusion phenomena in relaxed SiGe material, potential effects from lattice strain during the recrystallization process from strained SiGe material are minimized. Si_{1-x}Ge_x alloys with x values of 0.0, 0.05, 0.10, 0.15, 0.20, and 1.0 represent a diverse range of alloy compositions. Alloys with germanium contents ranging from approximately 25 at% to nearly 100 at% are not commonly utilized within the semiconductor industry due to increasing defect densities associated with rising germanium concentrations [Cha03]. Experimental structures comprised of a 1.0 µm thick silicon buffer layer, a continuous graded SiGe buffer layer, and a 1.0 µm thick relaxed SiGe layer are recommended, both with and without a 20 nm strained silicon capping layer. The use of a strained silicon cap facilitates the study of local surface strain effects upon boron diffusion in relaxed SiGe material. By preamorphizing wafers with both silicon and germanium implants prior to boron dopant incorporation, questions regarding the influence of amorphizing species upon boron diffusion may be addressed. Annealing of amorphous, relaxed SiGe samples in the presence and absence of strained silicon capping layers provides a means by which boron diffusion phenomena may be studied during the recrystallization process. In corollary, changes in the recrystallization rate and epitaxial nature of the regrowth process for relaxed SiGe alloy material as a function of germanium content may also be determined.



Figure 8-1:Binary phase diagram for germanium and silicon. These elements are completely miscible at all alloy compositions. [Hir00]



Figure 8-2:Graded buffer layers (a) continuous graded and (b) step graded. The shade of coloration corresponds to a particular germanium content, with the darker shades signifying a higher content.



Figure 8-3:XTEM micrograph denoting the segregation of misfit dislocation to the buffer layer, for a $Si_{0.65}Ge_{0.35}$ alloy.



Figure 8-4:Simplified representation of the Frank-Read Mechanism. [LeG92]



Figure 8-5: Experimental annealing structure for fractional interstitial composition determination.



Figure 8-6: FLOOPS simulated boron diffusion profiles for a range of SiGe alloys exposed to an oxidizing ambient at 1000°C for 60 minutes.



Figure 8-7: FLOOPS simulated boron diffusion profiles for bulk silicon exposed to both inert and oxidizing ambient conditions at 900°C for varying anneal times.



Figure 8-8: FLOOPS simulated boron diffusion profiles for a Si_{0.75}Ge_{0.25} alloy exposed to an oxidizing ambient at 1000°C for a range of anneal times.

% Si	% Ge	Temperature	Model Times (Ox) (min)	Proposed Anneal Times (min)
100	0	900 C	60, 120, 180, 300	60, 120, 180, 240
95	5	900 C	60, 120, 180, 300	60, 120, 180, 240
85	15	900 C	60, 120, 180, 240	60, 120, 180, 240
75	25	900 C	60, 120, 180, 240	60, 120, 180, 240
65	35	900 C	60, 120, 180, 240	60, 120, 180, 240
50	50	900 C	60, 120, 180, 240	60, 120, 180, 240
100	0	1000 C	60, 90, 180, 240	60, 120, 180, 240
95	5	1000 C	60, 90, 180, 240	60, 90, 120, 180
85	15	1000 C	30, 60, 90, 120	20, 45, 70, 90
75	25	1000 C	5, 10, 15, 20, 30, 60, 90, 120	15, 30, 45, 60
65	35	1000 C	30, 60, 90, 120	15, 30, 45, 60
50	50	1000 C	30, 60, 90, 120	15, 30, 45, 60
100	0	1100 C	10, 30, 60, 90	15, 30, 45, 60
95	5	1100 C	10, 30, 60, 90	15, 30, 45, 60
85	15	1100 C	10, 20, 30, 40, 60, 90	10, 20, 30, 40
75	25	1100 C	5, 10, 15, 20, 40, 60	5, 10, 15, 20
65	35	1100 C	5, 10, 30, 60	5, 10, 15, 20
50	50	1100 C	5, 10, 30, 60	5, 10, 15, 20

Table 8-1: Summary of FLOOPS simulated and proposed annealing parameters.

APPENDIX A TRAP-LIMITED DIFFUSION FLOOPS CODE FOR GERMANIUM AMORPHIZED MATERIAL CONTAINING FLUORINE AND BORON

math diffuse dim=1 umf none col !scale

solution add name=Test solve !negative solution add name=TestTrap solve !negative pdbSetDouble Silicon Test Abs.Error 1.0e5 pdbSetDouble Silicon TestRel.Error 1.0e-2 pdbSetDouble Silicon TestTrap Abs.Error 1.0e5 pdbSetDouble Silicon TestTrap Rel.Error 1.0e-2

#Create a Simple Grid line x loc=0.0 spac=0.001 tag=top line x loc=0.2 spac=0.001 tag=bot region silicon xlo=top xhi=bot

init

#Initialize the Test Concentration (Boron Alone) profile inf = No_F.tcl name=Test

#Initialize the TestTrap Concentration sel z=1.0e5 name=TestTrap

#Solubility Limit for Amorphous Silicon at 25C
term name = TestActive add silicon eqn = {(2.0e18 * Test)/(2.0e18 + Test)}

#Trapping Parameters
set DB {5.0e-17}
set MaxTrap 5.5e19
set Kf {1.0e-19 * 400.0 * 3.14159 * [pdbGetDouble Si LatticeSpacing]}
set Kr [expr \$Kf * 1.0e-5]

#Fickian Diffusion Equation pdbSetString Silicon Test Equation "ddt(Test) - \$DB * grad(TestActive-TestTrap)"

#Trap Limiting Equation
pdbSetString Silicon TestTrap Equation "ddt(TestTrap) - \$Kf * (\$MaxTrap - TestTrap) *
(TestActive - TestTrap) + \$Kr * TestTrap"

#Plot the Initial Test Concentration (As-implanted Profile)
sel z=log10(Test)
plot.1d label=As-Implanted

```
#Plot the Initial Concentration of Trapped Boron on the Existing Graph
#sel z=log10(TestTrap)
#plot.1d !cle label=Trap1
```

```
#Movie to Watch Profiles Evolve During Anneal
#diffuse time = 120000.0 temp=25 init=1.0e-3 movie = {
    sel z=log10(Test)
    # plot.1d !cle label=Simulated
    # sel z=log10(TestTrap)
    # plot.1d !cle label=Trap2
#}
diffuse time = 1000.0 temp=25 init=1.0e-3
#Plot the Simulated Profile on the Existing Graph
    sel z=log10(Test)
    plot.1d !cle label=Simulated
#Plot the Final Concentration of Trapped Boron on the Existing Graph
    sel z=log10(TestTrap)
    plot.1d !cle label=Trap2
```

#File Name for the Experimental Diffused Profile profile inf = 1e15FDose.tcl name=Final

#Plot the Experimental Diffused Profile on the Existing Graph
sel z=log10(Final)
plot.1d !cle label=Annealed

APPENDIX B FICKIAN DIFFUSION FLOOPS CODE FOR SILICON AMORPHIZED MATERIAL CONTAINING BORON ALONE

math diffuse dim=1 umf none col !scale

solution add name=Test solve !negative

pdbSetDouble Silicon Test Abs.Error 1.0e-8 pdbSetDouble Silicon Test Rel.Error 1.0e-2

#Create a Simple Grid line x loc=0.0 spac=0.0002 tag=Top line x loc=0.2 spac=0.001 tag=Bottom

region silicon xlo=Top xhi=Bottom

init

#File Name for the As-Implanted Concentration Profile profile inf = Si As-Imp um.tcl name=Test

#Plot the As-Implanted Concentration Profile sel z=log10(Test) plot.1d label=As-Implanted

#Diffusivity Terms
term name = TestDiff add silicon eqn = {[Arrhenius 2.809e-47 -4.94]}

#Solubility Limit Terms
term name = TestActive add silicon eqn = {("5.0e20" * Test)/("5.0e20" + Test)}

#Fickian Diffusion Equation pdbSetString Silicon Test Equation "ddt(Test) - TestDiff * grad(TestActive)"

diffuse time = 10.0 temp=550 init=1.0e-1

#Plot the Final Simulated Profile on the Existing Graph sel z=log10(Test) plot.1d !cle label=Simulated

#File Name for the Experimental Diffused Concentration Profile

profile inf = Si_10min_um.tcl name=Final

#Plot the Experimental Diffused Concentration Profile on the Existing Graph
sel z=log10(Final)
plot.1d !cle label=Annealed

APPENDIX C COOPERATIVE DIFFUSION

To date, the most widely studied amorphous systems are those of bulk metallic glass (BMG) alloys. Metallic glass materials are representative of amorphous metals that have been produced directly from the liquid state during cooling. BMG alloys are disordered on an atomic scale, exhibiting only short-range order. They do not possess many of the defect types commonly associated with crystalline materials, such as dislocations. A substantial number of diffusion studies have been conducted in BMG alloys for a wide range of species. The similarities in microstructure between amorphous silicon and bulk metallic glass alloys imply that boron may diffuse in amorphous silicon through a mechanism comparable to cooperative diffusion.

Molecular dynamics simulations of amorphous bulk metallic glass alloys assert that diffusion proceeds through a collective hopping mechanism involving more than ten atoms [Oli99, Sch93, Sch97, Tei96, Tei97, Van97]. Diffusion is suggested to occur by bursts of mutually triggering chain transitions, rather than by statistically independent events. A primary diffusion mechanism in metallic glasses is the migration of atoms by the thermally activated local displacement of chains or rings [Oli99, Sch97, Tei97, Van97]. The mode-coupling theory states that the cage formed by the neighboring atoms of a given atom freezes in at a critical temperature due to an increase in density. Liquidlike viscous flow through atomic collisions cannot take place in a solid environment below the critical temperature and atomic transport or diffusion proceeds exclusively via local hopping processes [Ehm98, Gey95, Got91]. It has been suggested that the diffusion

of dopants and constituents in metallic glass materials occurs due to the excess free volume in the system, favoring a spread-out diffusion mechanism [Hor88, Spa77]. Atomic jumps are initiated by fluctuations in the free volume created by strong displacements of surrounding atoms opposite to the jump direction [Fau90, Fra94, Gey96]. Diffusion in metallic glasses does not exhibit pressure dependence, implying that diffusion is not mediated by thermal quasi-vacancies [Fau90, Fau03].

Isotope measurements were used extensively to demonstrate the collective hopping diffusion mechanism in amorphous BMG's. Isotope effects are commonly used to discriminate between different diffusion mechanisms based on mass dependence [Sch58, Ehm99]. The isotope effect parameter *E* is unit-less and related to the diffusivity *D* (cm²/second) and mass *m* (grams) of an isotope pair α and β according to the mathematical relation [Sch58]

$$E_{\alpha,\beta} = \frac{D_{\alpha}/D_{\beta}-1}{\sqrt{\frac{m_{\beta}}{m_{\alpha}}-1}}$$
(C-1)

For an ideal single-jump diffusion mechanism E equals unity due to the m^{-1/2} dependence of the jump frequency [Meh90, Mul61]. When the value of E is small, the mass of the diffusing species does not have an appreciable effect on the diffusion mechanism. Small isotope effect parameters are asserted as being indicative of cooperative motion [Ehm99, Fau03, Hee00, Mul61, Zum01].

A highly collective hopping process involving a large number of atoms is expected to cause a very small isotope effect due to the dilution of the mass effect by the participation of other atoms in the jump process [Cla66, Hee95, Mul61]. A simplified quantitative description of this dilution effect, presented in terms of an effective mass (m+M) in grams of all the atoms participating in the collective hopping process, is provided by the following approach where Df (grams^{-1/2}) is the dilution factor for the isotope effect parameter [Cla66, Mul61]:

$$Df \propto \frac{1}{\sqrt{m+M}}$$
 (C-2)

Low isotope effect parameter values have been recorded for as-quenched and relaxed amorphous glass materials, suggesting collective diffusion mechanisms in both states [Hee01, Zol00]. The collective nature of the diffusion mechanism was not observed to change at the caloric glass transition temperature, demonstrating that long-range diffusion in a deeply super-cooled BMG melt is also dictated by a cooperative diffusion process [Ehm98, Ehm99]. A small isotope effect has been attributed with excluding the possibility of thermal and non-thermal defects participating as diffusion carriers, leading to a direct diffusion mechanism [Fau90].

The cooperative diffusion mechanism of amorphous BMG materials has been reported to involve more than ten atoms in the atomic jump process [Ehm98, Ehm99, Qiu96, Rat96, Sch93, Zol02]. Neighbor atoms are believed to facilitate diffusion by increasing the frequency of free volume fluctuations in a given substrate material [Gey96]. The diffusion coefficient D (cm²/second) in amorphous glasses can be expressed through a modified Arrhenius equation as follows [Gey95, Gey96]:

$$D = D_o \exp\left(\frac{N}{N_A} \frac{\Delta S(T)}{k_B}\right) \exp\left(\frac{-\Delta Hm}{k_B T}\right)$$
(C-3)

where D_o is the temperature-independent pre-exponential given in cm²/second, N is the number of nearest neighbors that influence the jump of a given atom given in atoms, and N_A is Avagadro's number, equal to 6.022×10^{23} atoms/mole. The parameter $\Delta S(T)$ is the configuration entropy expressed in eV/K-mol, *T* is the absolute temperature in Kelvin, ΔHm is the configuration enthalpy in eV, and k_B represents Boltzmann's constant, equal to 8.616x10⁻⁵ eV/K [Hum93]. The configuration entropy parameter incorporates changes due to the glass transition temperature of the material. The effects of atomic movement can similarly be represented according to the modified Arrhenius relation [Gey95]

$$D = D_o \exp\left(2.9N \frac{T - Tg}{Tg}\right) \exp\left(\frac{-\Delta Hm}{k_B T}\right)$$
(C-4)

Where the term Tg is the glass transition temperature in Kelvin. Equations C-3 and C-4 describe cooperative diffusion by incorporating an intrinsic, or Fickian, diffusion term in conjunction with a temperature dependent atomic jump term. The atomic jump term takes into consideration changes in the local structure, including the creation of free volume.

The manner in which species diffuse in amorphous material is not believed to be consistent with vacancy or interstitial mediated processes, suggesting that diffusion down a concentration gradient may be related to structural free volume. The jumping or hopping rate Ω (jumps/second) of a diffusing atom in an amorphous metallic glass is assumed to be spatially homogenous. It can be related to the parameters *Z* (atoms) and v_o (jumps/second/site) by the modified Arrhenius expression [Tan98]

$$\Omega = Zv_o \exp\left(\frac{\Delta S(T)}{k_B}\right) \exp\left(\frac{-\Delta Hm}{k_B T}\right)$$
(C-5)

Where Z is the number of nearest neighbor sites that influence diffusion and v_o is a temperature-independent exponential. The number of nearest neighbor sites that influence dopant diffusion in amorphous BMG materials is specific to a particular constituent, meaning that only neighboring atoms of the same species can participate in the collective

jump process. For instance, if aluminum is the diffusing species in $Ni_{23}Zr_{62}Al_{15}$ bulk glass, only neighboring aluminum atoms participate in the diffusion process.

Many of the studies regarding the collective hopping mechanism of BMG materials pertain to beryllium diffusion in Zr-Ti-Cu-Ni-Be metallic glasses [Gey95, Gey96, Qiu96, Tan98]. Beryllium was selected as the diffusing component because it is the smallest and presumably fastest species in the glass, enabling more accurate diffusion measurements for a given anneal temperature. Beryllium does not have an easily obtainable isotope, requiring the use of deposited beryllium surface layers. A diffusion couple was formed between a bulk glass and a beryllium thin film and monitored during annealing.

Beryllium was a primary constituent of the metallic glasses investigated, present in excess of 20 at% [Gey95, Gey96, Qiu96, Tan98]. The diffusion of beryllium atoms was observed to be approximately 10X faster in the alloy $Zr_{46.7}Ti_{8.3}Cu_{7.5}Ni_{10}Be_{27.5}$ for a given heat treatment below the glass transition temperature, as compared to the alloy $Zr_{41.2}Ti_{13.8}Cu_{12.5}Ni_{10}Be_{22.5}$ [Gey96, Qiu96]. Plots of the measured diffusivity versus 1/Temperature were used to extract values for the parameter ΔHm and the expression

$$D_o \exp\left(\frac{N}{N_A} \frac{\Delta S(T)}{k_B}\right) = D_o \exp\left(2.9N \frac{T - Tg}{Tg}\right)$$
(C-6)

The activation energy for beryllium diffusion was reported to be approximately 1.0 eV for each of the alloys examined [Gey96, Qiu96].

In each case the glass transition temperature was assumed to be 625° C, establishing equivalent configuration entropy values for the two alloys, based on the correlation between Equations C-3 and C-4 [Gey96, Qiu96]. Thus, any differences in the measured beryllium diffusivity are manifested in the parameters D_o and N (Equations C-3 and C-4). However, it remains unclear how the value of the diffusion term shown in Equation C-6 was separated and attributed to specific values for the parameters D_o and N. The number of nearest neighbor atoms influencing the jump of a given beryllium atom was reported to be 13 in the alloy containing 27.5 at% beryllium [Gey96] and 22 in the alloy containing 22.5 at% beryllium [Qiu96]. The critical free volume fluctuation required for the motion of beryllium atoms was achieved by the cooperative rearrangement of fewer atoms in the BMG alloy with the higher beryllium content, suggesting that the value of N is simply representative of the fraction of free volume in a given alloy [Gey96]. Where a larger value of N corresponds to a lower fraction of free volume. If the free volumes and densities of these two alloys are known to be different, the presumption that they exhibit identical glass transition temperatures and the same configuration entropy value is invalid. Thus, the reported diffusion parameters for beryllium atoms in these alloys do not provide an accurate portrayal of beryllium diffusion characteristics.

The approach and calculations provided by Guyer et al. and Qiu et al. do not clearly substantiate a collective hopping mechanism, where constituent beryllium atoms generate local fluctuations in the free volume of the amorphous structure that facilitate the hopping of beryllium dopant atoms through the glass during annealing. However, their observations do support the assertion that the void population and open space in a given sample microstructure determines the magnitude of diffusion enhancement in an amorphous material [Gey96, Qiu96].

APPENDIX D CONCENTRATION DEPENDENT FLOOPS CODE FOR GERMANIUM AMORPHIZED MATERIAL CONTAINING BORON ALONE

math diffuse dim=1 umf none col !scale

solution add name=Test solve !negative

pdbSetDouble Silicon Test Abs.Error 1.0e-8 pdbSetDouble Silicon Test Rel.Error 1.0e-2

#Create a Simple Grid line x loc=0.0 spac=0.0002 tag=Top line x loc=0.2 spac=0.001 tag=Bottom

region silicon xlo=Top xhi=Bottom

init

#File Name for the As-Implanted Concentration Profile profile inf = Ge_As-Imp_um.tcl name=Test

#Plot the As-Implanted Concentration Profile sel z=log10(Test) plot.1d label=As-Implanted

#Solubility Limit Terms
#term name = TestActive add silicon eqn = {("1.5e+20" * Test)/("1.5e+20" + Test)}
term name = TestActive add silicon eqn = "(Test>2.3e20)?2.3e20:Test"

#Concentration Dependent Diffusion Step
set D { "3.0e-17" + "3.0e-37" * TestActive}
term name = TestDiff add silicon eqn = \${D}
pdbSetString Silicon Test Equation "ddt(Test) - TestDiff * grad(TestActive)"

diffuse time = 10.0 temp=550 init=1.0e-1

#Plot the Final Simulated Profile on the Existing Graph
sel z=log10(Test)
plot.1d !cle label=Simulated

#File Name for the Experimental Diffused Concentration Profile profile inf = Ge_10min_um.tcl name=Final

#Plot the Experimental Diffused Concentration Profile on the Existing Graph sel z=log10(Final) plot.1d !cle label=Annealed

APPENDIX E CONCENTRATION DEPENDENT FLOOPS CODE FOR SELF AMORPHIZED MATERIAL CONTAINING BORON AND FLUORINE

math diffuse dim=1 umf none col !scale solution add name=Test solve !negative

pdbSetDouble Silicon Test Abs.Error 1.0e-8 pdbSetDouble Silicon Test Rel.Error 1.0e-2

#Create a Simple Grid line x loc=0.0 spac=0.0002 tag=Top line x loc=0.2 spac=0.001 tag=Bottom

region silicon xlo=Top xhi=Bottom

init

#File Name for the As-implanted Concentration Profile profile inf = F+B_550C_As-Imp.tcl name=Test

#Plot the As-implanted Concentration Profile sel z=log10(Test) plot.1d label=As-Implanted

#Solubility Limit Terms
term name = TestActive add silicon eqn = "(Test>1.9e20)?1.9e20:Test"
#term name = TestActive add silicon eqn = {([Arrhenius 9.14e20 .11] * Test)/([Arrhenius
9.14e20 .11] + Test)}

#Concentration Dependent Diffusion Step
set D { [Arrhenius 0.0009 2.273] + [Arrhenius 4.387e-11 4.18] * TestActive}
term name = TestDiff add silicon eqn = \${D}
pdbSetString Silicon Test Equation "ddt(Test) - TestDiff * grad(TestActive)"

diffuse time = 30.0 temp=550 init=1.0e-1

#Plot the Final Diffused Concentration Profile on the Existing Graph sel z=log10(Test) plot.1d !cle label=Simulated #File Name for the Experimental Diffused Concentration Profile profile inf = $F+B_50C_30m.tcl$ name=Final

#Plot the Experimental Diffused Concentration Profile on the Existing Graph sel z=log10(Final) plot.1d !cle label=Annealed

#Display the Si Potential Equation in the Terminal Window #pdbGetString Si Potential Equation

APPENDIX F TRAP-MODERATED FLOOPS CODE FOR SELF AMORPHIZED MATERIAL CONTAINING BORON AND FLUORINE

math diffuse dim=1 umf none col !scale

solution add name=Test solve !negative solution add name=TestTrap solve !negative pdbSetDouble Silicon Test Abs.Error 1.0e5 pdbSetDouble Silicon TestRel.Error 1.0e-2 pdbSetDouble Silicon TestTrap Abs.Error 1.0e5 pdbSetDouble Silicon TestTrap Rel.Error 1.0e-2

#Create A Simple Grid line x loc=0.0 spac=0.001 tag=top line x loc=0.2 spac=0.001 tag=bot region silicon xlo=top xhi=bot

init

#Initialize the Test Concentration (As-Implanted Boron Profile) profile inf = F+B 550C As-Imp.tcl name=Test

#Initialize the TestTrap Concentration sel z=1.0e5 name=TestTrap

#Solubility Limit Terms
term name=TestActive eqn=(Test>1.613e20)?(1.613e20):Test
#term name = TestActive add silicon eqn = {([Arrhenius 5.793e21 0.254] *
Test)/([Arrhenius 5.793e21 0.254] + Test)}

```
#Trapping Parameters
set DB {[Arrhenius 3.27e8 3.99]}
set MaxTrap 5.0e19
set Kf [expr 1.22e-17 * 400.0 * 3.14159 * [pdbGetDouble Si LatticeSpacing]]
#set Kf {[Arrhenius 44260943.85 4.010525] * 400.0 * 3.14159 * [pdbGetDouble Si
LatticeSpacing]}
set Kr [expr $Kf * 9.0e18]
```

#Fickian Diffusion Equation pdbSetString Silicon Test Equation "ddt(Test) - \$DB * grad(TestActive-TestTrap)" #Trap Moderating Equation
pdbSetString Silicon TestTrap Equation "ddt(TestTrap) - \$Kf * (\$MaxTrap - TestTrap) *
(TestActive - TestTrap) + \$Kr * TestTrap"

#Plot the Initial Test Concentration (As-implanted Profile) sel z=log10(Test) plot.1d label=As-Implanted

#Plot the Initial Concentration of Trapped Boron on the Existing Graph sel z=log10(TestTrap) plot.1d !cle label=Trap1

```
#Movie to Watch Profiles Evolve During Anneal
#diffuse time = 90.0 temp=550 init=1.0e-3 movie = {
# sel z=log10(Test)
# plot.1d !cle label=Simulated
# sel z=log10(TestTrap)
# plot.1d !cle label=Trap2
#}
diffuse time = 45.0 temp=550 init=1.0e-3
#Plot the Final Simulated Concentration Profile on the Existing Graph
sel z=log10(Test)
plot.1d !cle label=Simulated
```

#Plot the Final Concentration of Trapped Boron on the Existing Graph #sel z=log10(TestTrap) #plot.1d !cle label=Trap2

#File Name for the Experimental Diffused Concentration Profile profile inf = F+B_550C_45m.tcl name=Final

#Plot the Experimental Diffused Concentration Profile on the Existing Graph sel z=log10(Final) plot.1d !cle label=Annealed

APPENDIX G BORON DIFFUSION CHARACTERISTICS IN SILICON MATERIAL DURING HIGH TEMPERATURE ACTIVATION ANNEALING

Introduction

As silicon-based devices within the CMOS semiconductor industry continue to miniaturize, the challenges and boundaries to achieving shallower junction depths, while maintaining low sheet resistances, become paramount. Presently, ion implantation is the standard method utilized for dopant incorporation into silicon substrates. This technique is advantageous due to the strict control it provides over the resultant dopant concentration profiles and electrical attributes [Mah99, May90, Zie04]. Ion implantation, however, can generate significant damage in the silicon lattice, leading to the formation of various defect structures, including point defects [Mah99, May90, Zie04]. The most critical of these defects are silicon self-interstitials that occur due to momentum transfer and atom displacements as the substrate is bombarded with in-coming high energy ions [Zie04]. At sufficient implant energies and doses, implant species can be amorphizing, generating a continuous surface amorphous region within the substrate [Zie04]. Channeling tails in the concentration profiles of subsequently implanted dopants, such as boron, can be drastically reduced within preamorphized material, thereby providing a means for more abrupt junctions [Liu83].

Post-implant annealing is conducted in order to repair ion implantation induced lattice damage and to electrically activate dopant atoms by placing them on substitutional lattice sites [Bra00, Fey88, May90]. Once dynamic recombination has commenced

between silicon interstitials and vacancies resulting from the implantation process, a region of excess interstitials resides near the projected range of the implanted species [Chu02]. During annealing, these silicon interstitials react with dopant atoms that diffuse via an interstitialcy mechanism, such as boron [Fan96a, Gos97, Ura99a], and temporarily enhance their diffusivity by orders of magnitude above their thermal equilibrium values [Bon96, Cow99a, Cow99b, Cow00, Eag94, Jon97, Man01b, Sto97]. The exhibited transient enhanced diffusion (TED) phenomenon is known to be a limiting factor in the formation of ultra-shallow junctions [Geb02, Zie04]. In order to minimize the increase in junction depth incurred during activation annealing, the overall thermal budget of the process must be decreased [Eag94]. Traditional rapid thermal processing (RTP) systems incorporate relatively short annealing times, when compared to techniques such as furnace annealing, with the use of high temperatures [Aga00a, Aga00b, Man01c]. Prior studies have demonstrated a correlation between the level of diffusion and ramp rate, namely that both thermal diffusion and TED effects are alleviated by a high heating rate [Aga00a, Aga00b, Fio01, Raf96]. By reducing the amount of time spent at any particular temperature during the activation process, improved trade-offs between the sheet resistance and junction depth can be achieved [Mey01]. One of the most prominent RTP techniques is currently that of Spike Rapid Thermal Annealing (Spike RTA). Ramp rates scaling up to 250°C/s, soak times of less than one second, and peak process temperatures in the range of 1100°C are commonly employed [Aga00a, Aga00b, Man01c]. The quest to achieve increasingly shallower and more active junctions, with minimal integration challenges, has lead to the development of flash processing techniques. The incorporation of higher ramp rates and peak temperatures of up to 1350°C has contributed to the near

complete suppression of TED and improved dopant activation during flash processing [Geb02]. During processing, a continuous arc lamp is used to heat the wafer bulk up to an intermediate temperature (Ti) at rates up to 400° C/s, whereupon high intensity flash lamps quickly flash anneal the surface of the wafer up to the desired peak temperature [Cam02, Geb02, Gel02, Ros02]. By utilizing novel light flashes, effective flash anneal times range from only 100 µs to 10 ms. Wafers are heated from Ti to the peak temperature at an estimated rate of 10^{6} °C/s during the flash portion of the process [Cam02, Geb02]. These attributes enable flash annealing techniques to access the processing regime that currently separates traditional RTP and laser thermal processing (LTP) [Cam02, Gel02].

Over the years there has been increasing interest within the co-implantation of fluorine and boron for the formation of ultra shallow p-type junctions [Col04, Duf04, Dus02, Gra04, Jac02, Jac03, Jac04, Jac05, Mub05, Ohn00]. Prior studies have collaboratively demonstrated the unique ability of fluorine to reduce boron TED, while simultaneously increasing the boron solubility limit during high temperature annealing [Dow98, Ohy89, Phy90, Rob01]. These effects are theorized to originate from the ability of fluorine to bind with the excess silicon interstitials and therefore reduce subsequent boron interstitial cluster formation. Recent studies have demonstrated the inherent ability of boron to diffuse within amorphous silicon during the Solid Phase Epitaxial Regrowth (SPER) process [Ell98a, Duf04, Jac05]. In our studies, boron diffusion was shown to be independent of the preamorphization species employed. The time-averaged diffusivities of boron in amorphous silicon are five orders of magnitude higher than equilibrium values extrapolated for identical conditions in crystalline silicon [Ell98a, Jac05, Law98].
The presence of fluorine, germanium, and silicon doping species has no measurable impact on boron diffusion characteristics in amorphous silicon. Boron diffusion during SPER imposes critical limits on our ability to form ultra-shallow transistor junctions. The culmination of relationships between the atomic species and defects present within the system during both ion implantation and activation annealing further stress the importance of process optimization. Within these studies, a variety of experiments were conducted in order to cultivate a knowledge base for the role of fluorine co-implantation within current rapid thermal processing methodologies for p-type junction activation. The applicability of high fluorine concentrations is addressed as post-implant annealing techniques incorporate higher peak temperatures at shorter durations and higher ramp rates, thereby decreasing the time for SPER and defect evolution to occur.

Experimental Design

Several 200 mm, (100) n-type Czochralski silicon wafers were commercially implanted by Advanced Micro Devices using a VARIAN VIISTA80 Implanter. All implants were conducted at room temperature with wafers twisted at an angle of 30° . Ion beam currents ranged from 1.0 mA to 1.9 mA. Certain wafers were preamorphized with silicon ions at an energy of 2.5 keV and dose of 1×10^{15} atoms/cm². Select wafers were also implanted with 3 keV, 2×10^{15} atoms/cm² fluorine. Cross-sectional TEM (XTEM) and variable angle spectroscopic ellipsometry (VASE) analysis confirmed amorphous layer depths of approximately 180 Å and 100 Å, respectively, for amorphized specimens processed with and without the singular fluorine implant. VASE measurements were performed at beam angles of 65° , 70° , and 75° . Co-implanted samples were subsequently implanted with either drift mode 250 eV, 1×10^{15} atoms/cm² ¹¹B⁺ or 1.1 keV BF₂⁺ at a dose of 1×10^{15} atoms/cm². Samples received singular fluorine implants prior to boron or BF_2^+ co-implantation in order to eliminate any potential implant recoil effects [Jac02]. Post-implant activation annealing was conducted by Advanced Micro Devices and Vortek Advanced Semiconductor RTP within commercial RTA and flash annealing systems, respectively, under a flowing, inert N₂ ambient. Samples receiving spike RTA or spike annealing were exposed to a peak temperature of 1110°C with no substantial soak period. A ramp rate of 250°C/s was used to heat wafers up to the peak temperature, while wafers were cooled at approximately 80°C/s. Specimens processed within a flash annealing system were ramped up to a Ti of 800°C, before being immediately heated to a flash temperature of 1300°C. Ramp rates of 200°C/s and 150°C/s, respectively, were used during heating to and cooling from the Ti temperature. Heating and cooling rates of 10^6 °C/s were estimated during the flash portion of the flash annealing process. The duration of the flash process was approximately three milliseconds. Hall effect electrical measurements were made by Vortek Advanced Semiconductor RTP using a Keithley Lakeshore RMC temperature dependent Hall system with a temperature range of 10K to 400K. Four-point probe measurements were also used to verify the Hall effect data.

SIMS profiles were obtained by Advanced Micro Devices on a Physical Electronics ADEPT-1010 quadruple SIMS instrument. The counts of $^{11}B^+$ were generated using an O_2^+ beam with a net impact energy of 650 eV and beam current of 180 nA. At an angle of 45°, the beam was rastered over a 400 µm x 400 µm square area, with a detectable area of 70 µm x 70 µm. Samples were processed under a constant O_2 ambient of approximately $6x10^{-7}$ torr in order to provide complete oxidation of the silicon surface during analysis, maintaining sputter rates ranging from 0.08 nm/s to 0.1 nm/s. The fluorine counts were obtained under Cs⁺ bombardment at an impact energy of 1 keV and

incident angle of 60°. The secondary ions were subsequently collected from the center 5% of the rastered area.

Results

The incorporation of fluorine co-implants is beneficial to the formation of p-type junctions activated via spike annealing. Figures G-1 and G-2 illustrate boron concentration profiles for annealed samples processed with and without both preamorphization implants and preceding fluorine co-implants. When boron is singularly implanted (Figure G-1) or molecularly implanted in the form of BF_2^+ (Figure G-2), a preceding fluorine implant induces shallower junctions and more abrupt SIMS profiles. The use of preamorphization implants is beneficial in reducing implant channeling [Liu83], but does not always correlate to shallower profiles post-annealing. In the majority of cases investigated here, preamorphized conditions exhibit deeper concentration profiles. Significant fluorine redistribution occurs during annealing (not shown) and high concentrations of fluorine remain in the surface material for samples coimplanted with F⁺. The junction characteristics for these samples are shown in Figure G-3 at a boron concentration of 1×10^{19} atoms/cm³. The inclusion of a preamorphization implant leads to increased boron activation, irrespective of the presence of co-implanted fluorine or the manner of boron incorporation (i.e. B^+ or BF_2^+). The most dramatic impact occurs when BF_2^+ is implanted alone. The sheet resistance is reduced by 15% when BF_2^+ is implanted into amorphous material. In the remaining cases, boron activation is improved by less than 6% due to preamorphization. The residual fluorine does not appear to influence boron activation under these conditions except in the case of BF_2^+ implanted into amorphous material. Additional fluorine leads to a 10% rise in the sheet resistance. The degradation in dopant activation is counterbalanced by a 25% decrease in the

junction depth. The best junction achieved by spike annealing occurs when amorphous material is co-implanted with F^+ and BF_2^{+} . However, the measured characteristics only satisfy junction characteristics as outlined for 65 nm node transistors (Figure G-3) [SIA03].

The boron concentration versus depth profiles for preamorphized samples implanted with boron alone are depicted in Figure G-4. Flash and spike annealing conditions are shown. The superiority of the flash annealing generated junction depth over that formed via spike annealing is apparent. The as-implanted and flash annealed profiles demonstrate extensive channeling effects manifested as tail footing. The continuous, surface amorphous layer was initially 100 Å deep, placing the majority of the boron profile into crystalline silicon. The spike annealed profile exhibits minimal footing and superior profile abruptness. Similar results are obtained in B⁺ and F⁺ co-implanted samples. The additional fluorine implant serves to shift the amorphous layer depth farther into the substrate to approximately 180 Å. The addition of a fluorine co-implant improves profile depths following spike annealing, as previously discussed, but does not exert a measurable impact on flash annealed profiles. Fluorine redistributes during activation annealing (not shown), as expected [Jen92], with more residual fluorine present near the surface in flash annealed samples.

Figure G-5 illustrates boron and fluorine SIMS profiles for samples containing only molecular BF_2^+ dopant implants. The flash annealing process induces a limited shift in the junction depth of less than 20%, whereas the spike annealed profile exhibits a junction shift of approximately 180% from the as-implanted profile. These results are consistent with prior high temperature studies [Gel02, Ros02]. Flash annealed profiles

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have an abruptness of approximately 10 nm/decade, inferior to the 8 nm/decade of the spike annealed samples. The chemical structure of the BF₂ molecule generates an inherent 2:1 fluorine to boron dose ratio, with only 22% of the implant energy being transferred to the boron atoms. The resultant projected range of the fluorine atoms is only 25 Å [Zie03], thus limiting the overall population of fluorine atoms in the vicinity of the boron concentration tail. As seen within Figure G-5, the as-implanted fluorine profile only marginally exceeds that of the boron. Significant fluorine redistribution is demonstrated during processing. After both flash and spike annealing, the retained dose of the fluorine drastically decreases below that of the boron and moves towards the surface. Minimal concentrations of fluorine remain in the near surface region.

Samples receiving both singular F^+ and molecular BF_2^+ implants exhibit increasingly complex characteristics. The fluorine precursor implant raises the overall fluorine concentration and also displaces the total fluorine profile so that it overlaps the boron tail region, thereby maximizing the previously reported fluorine enhancement effects [Dow98, Ohy89, Ohy90, Rob01]. The preceding singular fluorine implant, however, induced negligible effects upon the as-implanted boron profile, as seen in Figures G-5 and G-6. After flash annealing, the junction increase is limited to only 10%, whereas spike annealing results in a 120% shift. Flash annealed profiles have an abruptness of approximately 4 nm/decade, superior to the 6 nm/decade of the spike annealed samples. The incorporation of additional fluorine induces a minor gain in junction depth and a 2.5x improvement in profile abruptness for samples containing BF_2^+ after flash annealing. The fluorine redistribution, in comparison with the exhibited boron motion, is also illustrated for samples receiving both F^+ and BF_2^+ implants. Before any

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activation annealing occurs, the fluorine SIMS profile greatly exceeds that of the boron throughout the material. The fluorine concentration remains marginally higher than the boron profile after flash annealing, while conversely dropping below that of the boron following spike annealing. Fluorine peaks appear at approximately 160 Å after annealing. These are attributed to fluorine interactions with end-of-range (EOR) defects, resulting in fluorine segregation near remaining silicon interstitial dislocation loops. These effects arise due to the close proximity of fluorine atoms to the EOR damage, at the original amorphous-crystalline interface, as they migrate towards the surface during high temperature processing [Chu93, Kaa96b, Tsa79b, Wal92].

The corresponding sheet resistance versus junction depth data for the aforementioned samples are collectively displayed within Figure G-7. Preamorphized specimens implanted with boron or BF_2^+ , with and without a preceding fluorine implant, are shown. It is evident that the incredible gains in junction depth achieved through flash annealing are offset by an increase in the sheet resistance for these particular implant conditions; whereas the less desirable junction depths created through spike annealing are compensated for by very low sheet resistances. The focus of these studies is to characterize the applicability of fluorine co-implants under different high temperature processing methodologies. Spike annealing is clearly more successful at forming shallow junctions when fluorine is co-implanted. At best, however, spike annealing can generate junctions that satisfy the requirements for 45 nm node technologies (Figure G-7) [SIA03]. After flash annealing, additional fluorine leads to a 90% decrease in boron activation with a minimal change in junction depth when singular boron implants are used. On the other hand, junction characteristics are very similar after flash processing

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when BF_2^+ is implanted alone or incorporated with additional fluorine. The use of BF_2^+ alone is more advantageous as fewer processing steps are required, BF_2^+ does not require mass separation like F^+ or B^+ [Nar85], and no fluorine segregates below the junctions. In addition, less overall fluorine is present in the system, potentially aiding in subsequent degenerative boron penetration of the gate oxide [Bro01, Kim97, Min97, Tse92]. Flash annealing techniques lead to the formation of p-type junctions that satisfy the depth and activation requirements of the 28 nm technology node (Figure G-7) [SIA03].

Discussion

Flash annealing is a superior rapid thermal activation annealing technique, as compared to spike annealing, resulting in ultra-shallow junctions with relatively low sheet resistances [Geb02]. The durations allowed for defect migration and interactions afforded during the RTP processes, in conjunction with the migrating fluorine concentration, drastically influence the physical and electrical junction characteristics. Spike annealing exposes samples to temperatures above 800°C for times at least two orders of magnitude greater than that of flash annealing [Aga00a, Aga00b, Cam02, Geb02, Gel02, Man01c]. By residing within high temperature conditions for a longer period of time, spike annealing enables more dopant and defect diffusion and interactions to occur, as compared to flash annealing. As seen previously within Figures G-5 and G-6, both the boron and fluorine dopants demonstrate drastic motion during the spike annealing process. The fluorine in the spike anneal system is further enabled to preferentially migrate towards the surface and to potentially react with the silicon interstitial population. Authors have speculated that fluorine interacts with silicon interstitials, thereby reducing the boron clustering and diffusion processes [Dow98, Kaa96a, Mey01, Ohy89, Par99, Phy90, Rob01]. The dramatic junction depth reduction

observed after spike annealing when additional fluorine is incorporated, as seen within Figures G-1 and G-2, supports this assertion. To further optimize the p-type boron junctions activated via spike annealing, higher doses of co-implanted fluorine may be advantageous for the achievement of shallower junctions. However, there is a limit to the benefits of additional fluorine in regards to boron activation. Authors have demonstrated that excessive fluorine implant doses, such as $4x10^{15}$ atoms/cm², can lead to higher sheet and contact resistances following RTA annealing [Lee02, Ohy89]. Subsequent characterization regarding the proper fluorine to boron dose ratio and projected range are required for continued process improvements.

Conversely, during flash annealing the inclusion of additional fluorine does not lead to significant changes in the overall magnitude of boron motion. Fluorine surface migration during annealing is a strongly temperature-dependent, thermally activated process [Jen92]. Previous studies have demonstrated that one pulse during flash processing induces no significant boron dopant redistribution, while after two flash pulses samples demonstrate significant boron diffusion and an increased level of boron activation [Geb02]. Cowern et al. have recently reported that short RTA processing times result in higher sheet resistances for samples co-implanted with boron and fluorine, while longer durations correlate to increased boron activation [Cow05]. Strong B-F chemical interactions [Mok02] are attributed with hindering the placement of boron atoms onto active lattice sites [Cow95, Nak97], while mobile fluorine atoms are believed capable of blocking silicon interstitials from binding with boron atoms and deactivating them [Cow05, Tsa79b]. Clearly, the lower effective processing time constants during flash annealing drastically retard the ability of boron and fluorine dopants, as well as defects such as silicon interstitials, to experience thermally induced phenomena, resulting in minimal junction motion and relatively high sheet resistances. A significant fraction of the boron population may already be electrical active after solid phase epitaxial regrowth of the amorphous layer [Lin00, Tsa79a], prior to the flash anneal portion of the process. A "short" thermal process dramatically reduces the ability of fluorine to influence boron diffusion or activation [Jen92] and lead to superior junction characteristics [Rob01], but is substantial enough to induce competing process regarding fluorine-enhanced boron activation and deactivation. The % decrease in junction sheet resistance is proportional to the % increase in the magnitude of fluorine diffusion during annealing [Sri03], supporting our observation that spike annealing results in deeper, more active junctions than flash annealing. Thus, the role of fluorine for USJ formation via conventional flash annealing is presently limited.

Summary and Conclusions

The applicability of additional fluorine for the advancement of ultra shallow junctions is strongly dependent upon the high temperature activation method employed. If spike annealing is utilized, the addition of fluorine yields more desirable junctions than those formed through implantation of either B^+ or BF_2^+ alone. The more fluorine contained within the system, the better the overall junction characteristics, until excessive fluorine doses are reached. On the other hand, when flash annealing is selected for use the addition of fluorine has only marginal affects on the implant and annealed conditions studied. The advantages of not using an additional fluorine implant include fewer processing steps, higher throughput, no fluorine segregation below the junctions, and less inherent fluorine-assisted boron diffusion into the gate oxide. These factors may override the rather slight decrease in junction depth gained through its use. Based upon current industry trends [SIA03], the addition of fluorine atoms can result in boron activation levels that are undesirable after the flash annealing process. The incorporation of fluorine within ultra shallow junctions will be dictated by the prevailing high temperature activation methodology embraced by the semiconductor community. As the effective processing time scales decrease, so do the benefits of fluorine for the formation of boron, p-type transistor junctions.



Figure G-1: Boron concentration profiles for samples containing boron with and without both preamorphization and fluorine implants. Fluorine was implanted at 3 keV, 2x10¹⁵ atoms/cm² and boron was implanted at 250 eV, 1x10¹⁵ atoms/cm². Samples were spike annealed at 1110°C. (2.5 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure G-2: Boron concentration profiles for samples containing BF₂⁺ with and without both preamorphization and fluorine implants. Fluorine was implanted at 3 keV, 2x10¹⁵ atoms/cm² and BF₂⁺ was implanted at 1.1 keV, 1x10¹⁵ atoms/cm². Samples were spike annealed at 1110°C. (2.5 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure G-3: Sheet resistance versus junction depth (Xj) for samples containing boron or BF₂⁺ with and without both preamorphization and fluorine implants. Fluorine was implanted at 3 keV, 2x10¹⁵ atoms/cm², boron was implanted at 250 eV, 1x10¹⁵ atoms/cm², and BF₂⁺ was implanted at 1.1 keV, 1x10¹⁵ atoms/cm². Samples were spike annealed at 1110°C. (2.5 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure G-4: Boron concentration profiles for samples containing boron alone. Asimplanted, spike, and flash annealed profiles are shown. Boron was implanted at 250 eV, 1x10¹⁵ atoms/cm². Samples were either spike annealed at 1110°C or flash annealed at a Ti of 800°C and peak temperature of 1300°C. (2.5 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure G-5: Dopant concentration profiles for samples containing BF₂⁺ alone. Asimplanted, spike, and flash annealed profiles are shown. BF₂⁺ was implanted at 1.1 keV, 1x10¹⁵ atoms/cm². Samples were either spike annealed at 1110°C or flash annealed at a Ti of 800°C and peak temperature of 1300°C. (2.5 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure G-6: Dopant concentration profiles for samples containing F⁺ and BF₂⁺ coimplants. As-implanted, spike, and flash annealed profiles are shown. Fluorine was implanted at 3 keV, 2x10¹⁵ atoms/cm² and BF₂⁺ was implanted at 1.1 keV, 1x10¹⁵ atoms/cm². Samples were either spike annealed at 1110°C or flash annealed at a Ti of 800°C and peak temperature of 1300°C. (2.5 keV, 1x10¹⁵ atoms/cm² Si⁺ PAI)



Figure G-7: Sheet resistance versus junction depth (Xj) for samples containing boron or BF_2^+ with and without preceding fluorine co-implants. Fluorine was implanted at 3 keV, $2x10^{15}$ atoms/cm², boron was implanted at 250 eV, $1x10^{15}$ atoms/cm², and BF_2^+ was implanted at 1.1 keV, $1x10^{15}$ atoms/cm². Samples were spike annealed at 1110°C or flash annealed with a Ti of 800°C and peak temperature of 1300°C. (2.5 keV, $1x10^{15}$ atoms/cm² Si⁺ PAI)

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BIOGRAPHICAL SKETCH

Jeannette Michelle Jacques was born in Brooklyn, New York, on the 9th day of December 1978. She was raised in Tallahassee, Florida, by her parents Lani and Damian Pieschacon, along with her younger brother Jeffrey Jacques. After graduating as her class salutatorian from James S. Rickards High School in May of 1997, Jeannette enrolled as a freshman at the University of Florida in Gainesville, Florida. Jeannette worked as an undergraduate laboratory assistant for the SWAMP Research Center and served as the inaugural Chairman of the University of Florida Engineering Student Advisory Council (Gainesville, Florida). During her college career, Jeannette completed six semesters of internships with Texas Instruments, Inc. (Dallas, Texas) and a summer internship with Advanced Micro Devices (Sunnyvale, California), where she was honored as its Intern of the Year for 2002. Jeannette earned her B.S., M.S., and Ph.D. degrees in materials science and engineering from the University of Florida in May 2002, December 2003, and December 2005, respectively, with specializations in polymers and electronic materials. She was recognized in 2002 as the inaugural Outstanding Gator Engineer, Four-Year Scholar for the College of Engineering and received a USA TODAY All-USA College Academic Team Honorable Mention. Jeannette completed her graduate studies as both an IBM/Semiconductor Research Corporation and National Science Foundation Graduate Fellow. She will join the Silicon Technology Development Group (SiTD) at Texas Instruments, Inc., after completing her doctoral studies in December of 2005. Her research interests include advanced materials and process development.

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